Electronic Supporting Information

to

Understanding Structure and Dynamics of Cationic Surfactants from Studies of Pure Solid Phases

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Additional Experimental Details

1. Sample Preparation

Octadecyltrimethylammonium bromide (C_{18}TAB, CAS No. 1120-02-1, MW = 392.50, Aldrich, Cat. No. 359246, 98%) was recrystallized from water; with a single-crystal obtained by further recrystallization from an acetone/water mixture in a fridge. Hexadecyltrimethyl-ammonium bromide (C_{16}TAB, CAS No. 57-09-0, MW = 364.45, Fluka, Cat. No. 52365, $\geq$ 99%) was recrystallized from an acetone/ethanol mixture, with a single-crystal obtained by further recrystallization in water. Tetradecyltrimethylammonium bromide (C_{14}TAB, CAS No. 1119-97-7, MW = 336.40, Sigma, Cat. No. T4762, $\geq$ 99%) was used as received. Dodecyltrimethylammonium bromide (C_{12}TAB, CAS No. 1119-94-4, MW = 308.34, Sigma, Cat. No. D5047, ~99%) was used as received and a single-crystal was grown from a cold acetone/ethanol mixture. Decyltrimethylammonium bromide (C_{10}TAB, CAS No. 2082-84-0, MW = 280.29, Aldrich Cat. No. 30725, $\geq$ 98%) was used as received and a single-crystal was grown from cold acetone. Alkyl chain deuterated tetradecyltrimethylammonium bromide (C_{14}TAB-D_{29}, MW = 365.57, Oxford Deuteration Laboratory) was recrystallized by Dr Peixun Li from an acetone/ethanol mixture and used as supplied. Tetramethylammonium bromide (C_1TAB, CAS No. 64-20-0, MW = 154.05, Sigma-Aldrich, 426296) was used as supplied. When not in use, the surfactants were stored long term at about 2 °C.

2. TGA Measurements and Analysis

Thermogravimetric analysis (TGA) was performed with a PerkinElmer Pyris 1 TGA instrument using a N_2 gas flow of 30 L min^{-1}. The samples were initially held at 30 °C and then heated at 10 °C min^{-1} up to 350 °C or until the mass reached zero. A few mg of sample were used in each experiment. The data, shown in Fig. S1, demonstrate sample stability to around 200 °C for all C_nTAB investigated. The results further show the absence of any hydrate phase within the samples. With the sole exception of C_{16}TAB which decomposed at about 325 °C, possibly due to a much larger crystallite size; the other C_nTAB samples all decomposed below 300 °C. A sample of C_{14}TAB recrystallized from water showed no hydrate phase but some mass loss that is consistent with loosely-bound water on the surface of the crystallites.

3. DSC Measurements and Analysis

DSC experiments were performed with a PerkinElmer DSC8000 calorimeter equipped with an Intracooler 2. With the exception of C_{12}TAB which was a fine powder and so used as supplied, samples were gently ground to a fine powder before sealing in crimped aluminium sample pans. Approximately 10 mg of each sample were weighed out using a PerkinElmer AD6000 6 digit microbalance. Samples of C_nTAB were held at base temperature, and then heated at 10 °C min^{-1} to an upper temperature, held for 1 min, and then cooled back to base temperature at the same rate. In addition, some preliminary DSC measurements were made on C_{12}TAB using heating / cooling rates of 40 °C min^{-1} and the measurement on C_{10}TAB was repeated to check for reproducibility of weak peaks seen in the first scan. Details for the temperature ranges used for each sample are given in the figure captions to Figs. S2-S6. Transition temperatures and enthalpy changes were determined using the thermal analysis software Pyris, version 11.1.1.0492, from PerkinElmer.

4. PXRD Measurements and Analysis

4.1. PXRD Measurements

Laboratory X-ray powder diffraction data were collected for C_nTAB samples held in a spinning 0.7 mm capillary using a Stoe Stadi-P® diffractometer equipped with a Cu anode ($K\alpha_1$ λ = 1.54056 Å), Ge<111> monochromator, a restricted-height collimator to reduce axial divergence, a Dectris Mythen 1K® detector, and an Oxford Instruments CryojetHT® (90-500 K) with an in-house modified sample set-up (see Fig. S59). For the final data sets presented here, the detector was scanned in 2θ from 0° to 65° in steps of 0.5° at 10 s per step, a complete scan lasting approx. 30 min. Initially, variable temperature scans were performed manually as control software was still under development at the time of the data collection; later measurements were made under computer control using software developed by Dr R. E. Ghosh. A typical temperature ramp took about 10 min and the sample was equilibrated for a further 5 min between scans. Once samples had been heated into the plastic phase, they were not reused, particularly given concerns regarding sample degradation when subjected to the highest temperature for a prolonged period of time (see Fig. S60). For each compound, a room temperature scan was made after cooling from high temperature as shown in Fig. S12-S16. Structural changes associated with phase transitions were identified by PXRD and correlated well with the DSC results given in Table 1. These measurements were used to determine the nominal temperatures for the single-crystal X-ray experiments.

A sample of C_{18}TAB was measured from 27 to 227 °C in 10 °C steps, and the PXRD data are shown in Fig. S7. A sample of C_{16}TAB was measured at 27, 47, 87, 127, 167, and 207 °C; a second new sample was then measured at 27, 37, 57, 72, 77, 82, 92, 97, 102, 107, 117, 137, 157, 177, 197, and 217. The data, in 10 °C steps only, is shown in Fig. S8. A sample of C_{14}TAB was measured at 27, 57, 67, 77, 87, and then from 117 to 227 °C in 10 °C steps; to fill in the gaps in temperature, a second sample was measured at 7, 17, 37, 47, 97, and 107 °C. The data is shown in Fig. S9. A sample of C_{12}TAB was measured from −3 to 67 °C in 10 °C steps, and from 72 to 107 °C in 5 °C steps, and from 117 to 167 °C in 10 °C steps. In addition, a few scans were made on cooling from −13 to −43 °C in 10 °C steps. The data, in 10 °C steps only, is shown in Fig. S10. A sample of C_{10}TAB was measured at −123 °C for comparison with the single-crystal data at the same nominal temperature, from −93 to 197 °C in 10 °C steps, and following the observation of an anomaly at 57 °C, additional scans at 52 and 62 °C were made. The data, without the two additional scans, is shown in Fig. S11.

For C_{18}TAB, C_{16}TAB, and C_{14}TAB, the three solid phases III, II, and I were observed. For C_{12}TAB, four solid phases designated III, II, IIa, and I were observed, where phase IIa is an additional incommensurate phase with similarities to phase II. However, for C_{10}TAB, a total of five solid phases were found that are designated III, II, Ib, and I, where Ib is an additional plastic phase similar to phase I. The fifth phase, designated phase IV as being the lowest symmetry phase, was found in a very limited range of temperature within the temperature boundaries of phase II. Since crystals of C_nTAB do not survive the transition to the high-temperature phase I for single-crystal X-ray diffraction, repeated measurements at a fixed temperature were made on each material in phase I to provide data of good statistical accuracy. For C_{10}TAB, this was necessary for both phases Ib and I. These data are shown as indexed PXRD patterns in Figs. S44-S49.

To investigate more thoroughly the re-entrant behaviour of phase IV of C_{10}TAB in which peak splitting was observed (see Fig. S11), new samples were measured, both from the original sample and also from a new sample from a different supplier. The transition to phase IV was only observed on the first heating of a fresh sample. It was not observed on cooling or on re-heating so care had to be taken to take small temperature steps on heating over a suitable temperature range. The transition was observed more clearly when a sample was taken from deep within a fresh bottle than when taken from the surface of an old previously opened container. These results suggest that perhaps the hygroscopic properties of C_{10}TAB influence this transition. Crushing or grinding the sample appeared to have little effect on the observation of this transition suggesting that it is not driven by crystallite size. Multiple measurements clearly showed that the observation was reproducible. PXRD data were obtained from 47 to 67 °C in 1 °C steps, with multiple scans being measured for good statistics at 57 °C. These variable temperature PXRD data are shown in Fig. S54.

Finally, variable temperature PXRD data were obtained on C_1TAB from −153 to 207 °C in 10 °C steps. No phase transitions were observed over this range of temperature: thus the single-crystal structure determined in this work at −123 °C (see Section 5) matches that reported earlier at room temperature.

4.2. PXRD Analysis

The primary purpose of the PXRD analysis was the determination of lattice parameters as a function of temperature as the data are not of sufficient statistical quality for analysis using the Rietveld method. Le Bail whole pattern fitting[1] using the program Rietica[2] (version 1.7.7) was used to refine the cell parameters from the data. Values for the unit-cell parameters and molecular volume (obtained by dividing the unit-cell volume by the number of molecules per cell, Z) are given in Tables S19-S24 and the results are plotted in Figs. S36-S43.

For phase I, the repeated data sets at a fixed temperature were merged to a single pattern so that the position of weak peaks could be determined accurately. The peak positions for C_{16}TAB were used as input to the pattern indexing software suite Crysfire.[3] Both the Dicvol and the Lzon programs within the Crysfire suite produced an indexed tetragonal solution with small values of $a \approx b \approx 6.5$ Å and a large value of $c \approx 31.3$ Å consistent with a crystal structure containing a long-chain amphiphile. Accurate unit cell parameters were then obtained from the indexed pattern using Refcel.[4] From an analysis of the observed peaks, the sole reflection condition appeared to be $hk0$: $h + k = 2n$, indicative of space groups $P4/n$ or $P4/nmm$. Phase I was evidently a plastic phase due to the drastic reduction in intensity with increasing scattering angle; such phases are also typified by high symmetry due to extensive motional disorder. This suggests strongly that the space group for phase I is $P4/nmm$. It is interesting to note that the space-group symmetry of C_1TAB determined from SXD measurements is also $P4/nmm$. However, there are distinct differences in the arrangement of cations and anions in C_1TAB versus phase I of C_nTAB (see Fig. S52). In the former, the cations lie on a site of $\bar{4}m2$ symmetry with the bromide on $4mm$. By contrast, both cations

[1] A. Le Bail, *Powder Diffr.*, 2005, **20**, 316–326.
[2] *http://www.ccp14.ac.uk/tutorial/lhpm-rietica/index.html* ; *http://www.rietica.org/* .
[3] J. Bergmann, A. Le Bail, R. Shirley and V. Zlokazov, *Z. Kristallogr.*, 2004, **219**, 783–790.
[4] *http://pd.chem.ucl.ac.uk/www/pdpl/pdpl.htm#refcel* .

and anions must have 4*mm* symmetry in phase I of C_nTAB due to the packing requirement of 2 molecules per unit cell as seen in the schematic structure envisaged in Fig. 6. One consequence of the different arrangements is that the lattice parameter *a* for phase I of C_nTAB is much smaller than that of C_1TAB and is approximately constant with chain length *n*.

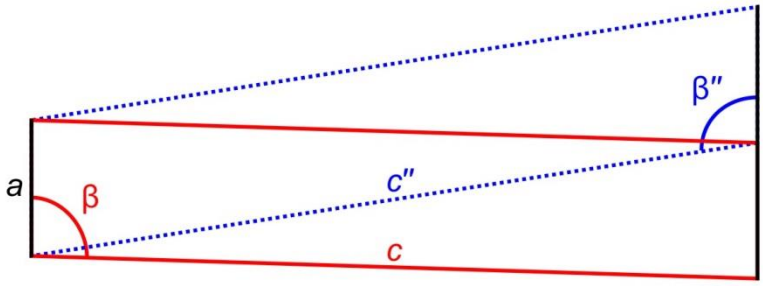
Phase Ib of C_{10}TAB is very similar to that of phase I with a similar pattern and intensity of 00*l* reflections. However, weaker peaks observed at 13.8°, 14.9°, and 16.9° in 2θ can only be indexed as 101, 103, and 105, respectively, with a doubled-length unit cell along *c*. With this cell, all of the indexed peaks satisfy the body-centred reflection condition *hkl*: $h + k + l = 2n$. No additional reflection conditions were identified. Moreover, given that the Br^- anions and trimethylammonium head groups must be arranged in a broadly similar way to phase I because of the corresponding peak positions and intensities in the PXRD patterns, the space-group symmetry of phase Ib is limited to either $I\bar{4}$ or $I\bar{4}2m$. In contrast to phase I, phase Ib cannot be centrosymmetric so higher symmetry tetragonal space groups are excluded. Space group $I\bar{4}2m$ is more likely given disorder of the alkyl chains about a mirror plane.

Obtaining unit-cell parameters using whole-pattern fitting methods is fraught with pitfalls for the less-experienced researcher for monoclinic systems with a long *c*-axis. From single-crystal X-ray data, unit cells were known for C_nTAB at −123 °C and 22 °C (see discussion in Section 4 below). Therefore, some researchers might be tempted to use an automatic sequential refinement approach where the output for one whole-pattern fit is used as the input file for the fit to the next temperature data set. We explain below why this approach is likely to fail with C_nTAB (and possibly other systems).

The first problem relates to the fact that the monoclinic angle β can change as a function of temperature from bigger than 90° to smaller than 90°. In contrast to Rietveld refinement of a crystal structure, whole-pattern fitting methods for PXRD cannot distinguish between unit cells with $\beta > 90°$ and $\beta' < 90°$ where $\beta' = 180° - \beta$ since both cells have the same shape (as shown below) and metric tensor.

An automatic sequential refinement approach starting with $\beta > 90°$ will maintain this condition incorrectly even when, in reality, the monoclinic angle goes below 90°.

The second problem is that as β approaches 90°, the lattice tends towards orthorhombic symmetry resulting in unstable refinements of monoclinic unit-cell parameters. It is therefore advisable to monitor each whole pattern fit in turn and to plot the results as they are obtained, in contrast to the automatic fitting approach where the results would be plotted at the end of the refinement sequence. Only a careful approach enables correct and comparative β values to be obtained as shown in Fig. S43. The third problem is particularly relevant to the unit cells of C_nTAB which have a large value for the *c*-axis due to the long alkyl-chain length. For lattices with monoclinic symmetry, an infinite number of choices are possible with β values getting progressively further away from 90°. Two such adjacent unit cells are shown below:



As the value of β increases, the value of β″ decreases and a point will be reached at which the value of β″ will approach 90°. This will lead to unstable refinements using whole-pattern fitting due to the orthorhombic symmetry of the lattice, which is not obvious when the value of β is not close to 90°. This situation may be less problematic for some structures since the space group symmetry of adjacent unit cells of this type alternate between $P2_1/c$ and $P2_1/n$ symmetry, which have different reflection conditions. For lattices with monoclinic symmetry, a huge number of unit cells are possible with β values getting progressively further away from 90° as *c* increases. This is demonstrated using the equivalent unit cells listed below (where β′ = 180° − β, *i.e.* the complimentary value of β) for C_{18}TAB at −123 °C:

a	*c*	β	β′	S.G.
5.5924	63.2603	117.36	62.64	$P2_1/c$
5.5924	60.8933	112.68	67.32	$P2_1/n$
5.5924	58.9634	107.66	72.34	$P2_1/c$
5.5924	57.5144	102.34	77.66	$P2_1/n$
5.5924	56.5835	96.80	83.20	$P2_1/c$
5.5924	56.1963	91.13	88.87	$P2_1/n$
5.5924	56.3641	85.44	94.56	$P2_1/c$
5.5924	57.0819	79.83	100.17	$P2_1/n$
5.5924	58.3294	74.42	105.58	$P2_1/c$
5.5924	60.0738	69.27	110.73	$P2_1/n$
5.5924	62.2731	64.45	115.55	$P2_1/c$

The values highlighted in blue are the ones reported in our single-crystal analysis of C_{18}TAB at −123 °C. Note that the equivalent cell highlighted in red has similar parameters plus it has the same setting of space group no. 14. At some particular temperature, these two cells will be indistinguishable when β equals its complementary value β′ in terms of cell metric (though not equal in terms of crystal structure), again leading to problems with an automatic sequential refinement approach to whole-pattern fitting. As an aside, it should be noted that automatic data processing of single-crystal data will choose the monoclinic cell with β′ = 91.13° and space-group symmetry $P2_1/n$ as this cell minimises correlations during least-squares refinement of atomic coordinates although this cell is a poor choice for comparing different C_nTAB structures as discussed in Section 5.

All of these issues have the potential to lead to false minima in fitting data and so great care has to be taken to obtain values for the comparative lattice parameters that are listed as a function of temperature in Tables S19-S23. The final point to note regarding whole-pattern fitting is that the difference in the PXRD patterns of the doubled-length unit cell of phase III and the single-length unit cell of phase II is very small. Therefore, a choice is required with

respect to using 2*c* and space group $P2_1/c$ (for phase III) or *c* and space group $P2_1/m$ (for phase II). The decision on this was made on the basis of the change in slope of the lattice parameters and unit-cell volume at the temperature of transition from phase III to II.

For phase IIa of C_{12}TAB, incommensurate behaviour was suspected from the additional low-angle reflection that appears in the PXRD data on heating phase II to just below the transition temperature to the plastic phase I. In contrast to other reflections, the *d*-spacing value of this peak is strongly temperature dependent, a characteristic of many incommensurate systems. Incommensurate behaviour was confirmed by SXD measurements on C_{12}TAB (see Figs. S56 and S57).

Phase IV of C_{10}TAB was strongly suspected of being a triclinic distortion of phase II given the observed peak splitting in the PXRD data (see Fig. S54). This was confirmed by a LeBail fit to the data obtained from the summation of the multiple scans measured on C_{10}TAB at 57 °C (see Fig. S55). The triclinic angle α refined away from 90° in marked contrast to γ which stayed close to 90° (see Table S23) indicating a shear of the monoclinic cell parallel to the ionic plane. Rietveld refinement provides no additional information on the structure of phase IV given the huge number of geometric restraints required, the anisotropic motion of the atoms, and possible sample granularity effects with respect to the PXRD data.

5. SXD Measurements and Analysis

X-ray diffraction data on single crystals of C_nTAB, as shown in Fig. S61, were obtained using an Agilent Oxford Diffraction SuperNova equipped with a microfocus Cu Kα X-ray source and an Atlas CCD detector. Full spheres of data were collected to 0.84 Å resolution with each 1° scan frame in ω collected twice. Total collection time varied depending on size and quality of crystal, and sample temperature. The Cryojet5® used for these measurement is the original prototype device developed by Oxford Instruments and the Pt-resistance sensor is located in the copper-block heat exchanger and not in the nozzle of the instrument close to the sample (in contrast to the CryojetHT® used in the PXRD experiments). Thus the temperatures quoted in these SXD experiments should be treated as nominal (despite stability to much better than 0.1 °C). Data were collected on C_{18}TAB at −123 °C, 22 °C, and 117 °C; on C_{16}TAB at −123 °C, 22 °C, and 117 °C; on C_{14}TAB at −123 °C, 22 °C, and 107 °C; on C_{14}TAB-D_{29} at −123 °C; on C_{12}TAB at −123 °C, 22 °C, and 97 °C; and on C_{10}TAB at −173 °C, −123 °C, −23 °C, 22 °C, and 102 °C. To enable comparisons with phase I of C_nTAB, SXD data were collected on C_1TAB at −123 °C. Attempts to measure single-crystal data of the plastic phases always resulted in severe damage to the single-crystals as they passed through the transition temperature from the more ordered phase.

Automatic data reduction for phase III of C_nTAB using the CrysAlis^{Pro} software package from Oxford Diffraction, versions 1.171.37.35 (Agilent) and 1.171.38.43 (Rigaku)[5], generally resulted in an incorrect sub-cell being chosen, followed by an incorrect space group (*i.e.* $P2_1$) and wrong structure determination. This explains, to some extent, errors in the crystal structures of some C_nTABs reported previously using automated diffractometers (see Section 6). It is noteworthy that one of the earliest crystallographic studies on C_{16}TAB using photographic X-ray film with a Weissenberg camera and visual inspection did not make this

[5] *https://www.rigaku.com/en/products/smc/crysalis* .

sub-cell error.[6] In order to make a comparison between the structures of C_nTAB at −123 °C, several manual steps are required. After visual examination of frames of data (see Fig. S22), the default unit cell was doubled in length along *c* to account for weak *hkl* reflections with *l* odd and the structure was solved and refined by least-squares within the Olex2 program suite[7] using the older structure-solution program ShelXS[8] and the 2014 version of the refinement program ShelXL.[9]

Once the crystal structures were solved, the unit cell for each C_nTAB was transformed using the user matrix option within CrysAlis^{Pro} to obtain a consistent choice of unit cell. C_{14}TAB was chosen as the comparative "standard" since its crystallographic unit cell for phase III has a β value just above 90° when the standard space-group setting of $P2_1/c$ is used. With this cell, the β values for each C_nTAB at −123 °C are 85.5°, 89.3°, 92.3°, 94.8°, and 96.8° for n = 10, 12, 14, 16, and 18, respectively; note that a non-standard value of β, i.e. one with a value < 90°, is required for n = 10 and 12. The raw X-ray data were then reprocessed with the new choice of unit cell within CrysAlis^{Pro}. The bromide anion was then positioned manually within the new unit cell to the same equivalent position in each structure and the remaining atom positions including those of hydrogen were determined by difference Fourier methods within ShelXL. To ensure that the alkyl chains twisted in the same sense for each C_nTAB structure, the coordinates were manually adjusted for model consistency before starting the least-squares refinement. The positions of all atoms were refined freely, with isotropic displacement parameters for the H atoms constrained to be the same for H atoms attached to the same C atom and with anisotropic displacement parameters for the remaining atoms. Crystal structures are illustrated with the program Mercury from CCDC with thermal ellipsoids (including H atoms) shown at 50% probability.[10]

For the refinements of the structure of phase II, the positions of the hydrogens were constrained using a combination of the ShelXL instructions DFIX and SADI with isotropic temperature values constrained using a riding model. As for the structure of phase III, the bromide anion was positioned at the same position in the unit cell for each C_nTAB so as to generate comparative crystal structures. Further details on phases II and III of the C_nTAB structures determined in this study are provided in the tables below (Tables S1a-f to S17a-f). The calculation of bond (and torsion angles) for phase II of C_nTAB involves the use of atoms related by the mirror plane at x, ¼, z that bisects the amphiphile cation: these symmetry-related atoms are noted with a numbered superscript and a note of the symmetry operator used (x, ½−y, z) is given at the end of each relevant table.

In order to obtain possible insight into the behaviour of the cationic head group in phase I of C_nTAB, the structure of C_1TAB (which has no alkyl tail group) was measured at −123 °C and variable temperature PXRD measurements were made over a wide range of temperature as

[6] J. Chojnacki, J. Grochowski, E. Hoffman-Zaborowska, M. Kruczek and T. Wojtasik, *Rocz. Chem.*, 1971, **45**, 1997–1998; J. M. Grochowski, Abstract for IUCr Congress XII in *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 1981, **37**, C74.

[7] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Crystallogr.*, 2009, **42**, 339–341.

[8] G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Adv.*, 2008, **64**, 112–122.

[9] G. M. Sheldrick, *Acta Crystallogr.*, *Sect. C: Struct. Chem.*, 2015, **71**, 3–8.

[10] C. F. Macrae, I. J. Bruno, J. A. Chisholm, P. R. Edgington, P. McCabe, E. Pidcock, L. Rodriguez-Monge, R. Taylor, J. van de Streek, P. A. Wood, *J. Appl. Crystallogr.*, 2008, **41**, 466–470.

discussed earlier. The single-crystal structure determined in this work at −123 °C (see Section 5) matches the room temperature structure reported nearly a century ago by Wyckoff[11] and re-determined in the 1990s.[12] However, given the different packing of the ions as discussed in Section 4 (and shown in Fig. S52), the comparison with C_nTAB gave less insight than hoped for.

6. Literature on the Crystal Structures of C_nTAB with Comments

Listed below are known papers that make reference to the solid-state structure of C_nTAB (with journal references given as footnotes). The lack of any systematic study of this series of surfactants is clear from the list, as is the total absence of information for n = 10 and 18.

C_nTAB	Author(s)	Ref.	Title of Paper
C_1	R. W. G. Wyckoff	[11]	The crystal structure of the tetramethyl ammonium halides.
C_1	D. J. Evans & D. L. Hughes	[12]	Structure of tetramethylammonium bromide: a redetermination.
C_{12}	K. Szulzewsky *et al*.	[13]	The crystal-structure of dodecyltrimethylammonium bromide.
C_{12}	S. Kamitori *et al*.	[14]	Molecular and crystal structures of dodecyltrimethyl-ammonium bromide and its complex with *p*-phenylphenol.
C_{14}	W. Pimtong *et al*.	[15]	Tetradecyltrimethylammonium bromide molecular aggregation.
C_{14}	M. Ramos Silva *et al*.	[16]	Pseudosymmetry in tetradecyltrimethylammonium bromide.
C_{14}, C_{16}	A. Norbert *et al*.	[17]	Crystallographic constants of tetradecyltrimethyl-ammonium bromide and hexadecyltrimethyl-ammonium bromide.
C_{16}	J. Chojnacki *et al*.	[6]	Preliminary structural investigations of hexadecyl trimethyl-ammonium halides.
C_{16}	J. M. Grochowski	[6]	The crystal structure of antimicrobial products: hexadecyltrimethyl ammonium bromide and iodide.
C_{16}	A. R. Campanelli and L. Scaramuzza	[18]	Hexadecyltrimethylammonium bromide.
C_{16}	H. H. Paradies & S. F. Clancy	[19]	Crystalline polymorphism of cetyltrimethylammonium bromide and distearyldimethylammonium (DSDMA) compounds. A comparison of the hydrated DSDMA...
C_{16}	Z. Wei *et al*.	[20]	Ionic liquid crystals of quaternary ammonium salts with a 2-hydroxypropoxy insertion group

[11] R. W. G. Wyckoff, *Z. Kristallogr.*, *Kristallgeom.*, *Kristallphys.*, *Kristallchem.*, 1928, **67**, 91–105.
[12] D. J. Evans and D. L. Hughes, *Acta Crystallogr.*, *Sect. C: Cryst. Struct. Commun.*, 1990, **46**, 1452–1454.
[13] K. Szulzewsky, B. Schulz and D. Vollhardt, *Cryst. Res. Technol.,* 1983, **18**, 1003–1008.
[14] S. Kamitori, Y. Sumimoto, K. Vongbupnimit, K. Noguchi and K. Okuyama, *Mol. Cryst. Liq. Cryst. Sci. Technol., Sect. A*, 1997, **300**, 31–43.
[15] W. Pimtong, O. Rangsiman, K. Vongbupnimit and K. Tashiro, in "*Computer Modelling and Simulation of Materials II*", Proc. CIMTEC 2002, eds. P. Vincenzini and A. Lami, *Adv. Sci. Technol*., 2003, **36**, 129–136.
[16] M. Ramos Silva, A. Matos Beja and J. A. Paixão, *Acta Crystallogr., Sect. E: Struct. Rep. Online*, 2003, **59**, o1151–o1152; plus Abstract for ECM 22, *Acta Crystallogr., Sect. A: Found. Crystallogr*., 2004, **60**, s271.
[17] A. Norbert, B. Brun and Chan-Dara, *Bull. Soc. Fr. Mineral. Cristallogr.*, 1975, **98**, 111–112.
[18] A. R. Campanelli and L. Scaramuzza, *Acta Cryst. C* 1986, **42**, 1380–1383.
[19] H. H. Paradies and S. F. Clancy, *Rigaku J*., 2000, **17**, 20–34.
[20] Z. Wei, X. Wei, X. Wang, Z. Wang and J. Liu, *J. Mater. Chem*., 2011, **21**, 6875–6882.

In addition, there are no comprehensive diffraction studies made as a function of temperature as seen from this second list, which is a summary of the crystallographic information gleaned from the listed papers:

C_nTAB	Ref.	Space Group	*a* / Å	*b* / Å	*c* / Å	β / °	*Z*	*T* / °C
C_1	[11]	4 *Di* – 7 [21]	7.76	= *a*	5.53	N/A	2	(RT) [22]
C_1	[12]	*P*4/*nmm*	7.708(1)	= *a*	5.498(1)	N/A	2	20
C_{12}	[13]	$P2_1/m$	5.636(2)	7.261(3)	21.603(9) [23]	86.85(2)	2	(RT)
C_{12}	[14]	$P2_1$	5.638(2)	7.244(1)	21.554(2)	93.06(2)	2	(RT)
C_{14}	[15]	$P2_1$	5.67(5)	7.33(5)	23.72(5)	91.4(2)	2	25
C_{14}	[16]	$P2_1/c$	5.6323(13)	7.240(2)	47.3900(15)	91.170(11)	4	20
C_{14}	[17]	$P2_1$/c	5.645(4)	7.286(8)	47.46(4)	91.23(15)	4	(RT)
C_{16}	[6]	$P2_1/c$	5.66(1)	7.26(1)	51.9(1)	94	4	(RT)
C_{16}	[17]	$P2_1/c$	5.637(2)	7.270(5)	52.08(5)	93.81(10)	4	(RT)
C_{16}	[18]	$P2_1/c$	5.638(1)	7.260(2)	52.072(7)	93.78(1)	4	25
C_{16} (I)	[19]	$P2_1$	5.596(5)	7.162(4)	25.899(3)	96.64(3)	2	−120
C_{16} (II)	[19]	$P2_1/n$	5.631(4)	7.259(5)	51.956(4)	92.40(4)	4	20
C_{16} (III)	[19]	$P2_1$	5.634(2)	7.254(1)	26.01(2)	93.78(4)	2	23
C_{16}	[20]	$P2_1$	5.6382(6)	7.2724(7)	26.007(2)	93.778(2)	2	(RT)

The 1981 conference abstract by Grochowski[6] gives some information about the packing of alkyl chains in C_{16}TAB but not a complete structure; there is mention of Grochowski's dissertation from Krakow (1975) as containing a preliminary interpretation, but this is probably the same information as that published earlier.[6] Paradies and Clancy[19] describe different structures of C_{16}TAB as polymorphs although 'polymorph I' is measured at a much lower temperature, *i.e.* at −120 °C. The argument for polymorphs was that the solvents for crystallisation and morphology of the crystals were different. However, Paradies and Clancy appear to be unaware of some of the pitfalls associated with monoclinic cells, which are given in Section 4. An alternative cell for so-called 'polymorph II' is one with c = 52.0253 Å and β = 93.81°, space group setting $P2_1/c$, which happens to have exactly twice the value of c of the cell used for 'polymorph III' and with the same β angle. As with Pimtong *et al.*[15] and Wei *et al.*,[20] Paradies and Clancy have almost certainly used the wrong unit cell, *i.e.* the sub cell, for 'polymorph III' due to an over reliance on automated diffractometer software. The reported structure of 'polymorph I' is clearly wrong: their Table 4 reports some very large C–C–C alkyl-chain angles in excess of 120° and the cell volume does not match the lattice parameters. There was probably a transcription error in the value of β at some stage in their data processing, which based on *a*, *b*, *c* and *V* quoted in their Table 2 should be 94.4°; this would match the β angle in our study (see Table S4a). Also, the 'kink' in the middle of the alkyl chain in their structure is probably due to the use of a sub-cell combined with the wrong space group. Likewise, Kamitori *et al.*[14] have used the wrong space group in contrast to the earlier work by Szulzewsky *et al.*[13] Data from several authors are described in the paper by Alonso *et al.*[24] but the only new X-ray work is some SAXS measurements of 00*l* peaks. The

[21] Old notation cited, but it is equivalent to *P*4/*nmm*.

[22] The designation (RT) refers to measurements either described as made at room temperature without further definition or assumed to be so when the measurement temperature is not reported.

[23] Original paper has *a* and *c* values swapped with respect to those cited here to aid the comparison with the other cell parameters shown in the list.

[24] B. Alonso, D. Massiot, P. Florian, H. H. Paradies, P. Gaveau and T. Mineva, *J. Phys. Chem. B*, 2009, **113**, 11906–11920.

paper has some typographical errors, *e.g*. the value for the lattice parameter *c* of C_{12}TAB is misquoted as '21.06 Å' from the paper by Szulzewsky *et al*.[13] The supplementary information published by Alonso *et al*.[24] contains the data for the crystal structure of 'polymorph III' of Paradies and Clancy but with some small typographical differences.

Table S1a. Crystal data and structure refinement for C_{18}TAB phase III at −123 °C.

Identification code	exp_791
Empirical formula	$C_{21}H_{46}BrN$
Formula weight	392.50
Temperature / K	150
Crystal system	monoclinic
Space group	$P2_1/c$
a / Å	5.59242(10)
b / Å	7.15259(9)
c / Å	56.5835(8)
α / °	90
β / °	96.8007(14)
γ / °	90
Volume / Å^3	2247.43(6)
Z	4
ρ_{calc} / g cm^{-3}	1.160
μ / mm^{-1}	2.472
F(000)	856.0
Crystal size / mm^3	0.4073 × 0.0793 × 0.0167
Radiation	Cu Kα (λ = 1.54184 Å)
2θ range for data collection / °	9.444 to 153.058
Index ranges	−6 ≤ h ≤ 6, −8 ≤ k ≤ 8, −70 ≤ l ≤ 70
Reflections collected	37501
Independent reflections	4675 [R_{int} = 0.0481, R_{sigma} = 0.0235]
Data/restraints/parameters	4675/0/365
Goodness-of-fit on F^2	1.036
Final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0384, wR_2 = 0.1026
Final R indexes [all data]	R_1 = 0.0498, wR_2 = 0.1130
Largest diff. peak/hole / e Å^{-3}	0.81/−0.52

Table S1b. Fractional atomic coordinates and equivalent isotropic displacement parameters for C_{18}TAB phase III at −123 °C. U_{eq} is defined as ⅓ of the trace of the orthogonalised U_{ij} tensor.

Atom	*x*	*y*	*z*	*U*(eq) / Å^2
C(1)	0.8474(3)	0.2540(2)	0.05443(3)	0.0180(3)
C(2)	0.9485(4)	0.2219(3)	0.08027(3)	0.0240(4)
C(3)	0.7563(4)	0.2775(3)	0.09593(3)	0.0265(4)
C(4)	0.8130(4)	0.2219(3)	0.12205(3)	0.0240(4)
C(5)	0.6297(4)	0.2996(3)	0.13731(3)	0.0237(4)
C(6)	0.6613(4)	0.2255(3)	0.16278(3)	0.0231(4)
C(7)	0.4778(4)	0.3071(3)	0.17797(3)	0.0225(4)
C(8)	0.5000(4)	0.2263(3)	0.20316(3)	0.0222(4)
C(9)	0.3182(4)	0.3088(3)	0.21827(3)	0.0222(4)
C(10)	0.3375(4)	0.2261(3)	0.24339(3)	0.0219(4)
C(11)	0.1559(4)	0.3089(3)	0.25858(3)	0.0225(4)
C(12)	0.1768(4)	0.2264(3)	0.28361(3)	0.0225(4)
C(13)	−0.0035(4)	0.3088(3)	0.29897(3)	0.0234(4)
C(14)	0.0170(4)	0.2255(3)	0.32396(3)	0.0229(4)
C(15)	−0.1607(4)	0.3100(3)	0.33952(3)	0.0246(4)
C(16)	−0.1393(4)	0.2256(3)	0.36450(3)	0.0253(4)
C(17)	−0.3148(5)	0.3097(3)	0.38021(4)	0.0305(5)
C(18)	−0.2923(6)	0.2225(4)	0.40498(4)	0.0415(6)
C(19)	0.8847(4)	0.2563(3)	0.01231(3)	0.0234(4)
C(20)	1.1895(4)	0.4176(3)	0.03918(3)	0.0216(4)
C(21)	1.1778(4)	0.0761(3)	0.03862(3)	0.0225(4)
N(1)	1.0273(3)	0.2501(2)	0.03648(3)	0.0171(3)
Br(1)	0.64585(3)	0.75210(3)	0.03329(2)	0.02774(11)
H(1A)	0.770(5)	0.366(4)	0.0517(4)	0.022(4)
H(1B)	0.738(5)	0.157(4)	0.0494(4)	0.022(4)
H(2A)	1.095(5)	0.301(4)	0.0843(5)	0.030(5)
H(2B)	0.993(5)	0.087(4)	0.0826(5)	0.030(5)
H(3A)	0.740(6)	0.416(4)	0.0952(5)	0.038(5)
H(3B)	0.611(6)	0.228(4)	0.0899(6)	0.038(5)
H(4A)	0.974(6)	0.266(4)	0.1282(5)	0.030(5)
H(4B)	0.814(5)	0.081(4)	0.1232(5)	0.030(5)
H(5A)	0.638(5)	0.437(4)	0.1376(5)	0.032(5)
H(5B)	0.475(6)	0.270(4)	0.1304(5)	0.032(5)
H(6A)	0.823(5)	0.253(3)	0.1703(5)	0.029(5)
H(6B)	0.647(5)	0.085(4)	0.1628(5)	0.029(5)
H(7A)	0.498(5)	0.439(4)	0.1789(5)	0.034(5)
H(7B)	0.314(6)	0.283(4)	0.1700(5)	0.034(5)
H(8A)	0.666(6)	0.252(4)	0.2112(5)	0.030(5)

H(8B)	0.479(5)	0.094(4)	0.2026(5)	0.030(5)
H(9A)	0.344(4)	0.443(4)	0.2191(4)	0.024(4)
H(9B)	0.149(5)	0.287(4)	0.2103(4)	0.024(4)
H(10A)	0.496(6)	0.244(3)	0.2511(5)	0.028(5)
H(10B)	0.313(5)	0.087(4)	0.2422(5)	0.028(5)
H(11A)	0.181(5)	0.441(4)	0.2597(5)	0.029(4)
H(11B)	−0.009(6)	0.289(4)	0.2507(5)	0.029(4)
H(12A)	0.332(6)	0.253(3)	0.2916(5)	0.028(5)
H(12B)	0.159(5)	0.098(5)	0.2830(4)	0.028(5)
H(13A)	0.025(5)	0.442(4)	0.3003(5)	0.032(5)
H(13B)	−0.164(6)	0.289(4)	0.2917(5)	0.032(5)
H(14A)	0.180(6)	0.246(4)	0.3318(5)	0.031(5)
H(14B)	−0.007(5)	0.095(4)	0.3232(5)	0.031(5)
H(15A)	−0.129(5)	0.443(4)	0.3408(5)	0.033(5)
H(15B)	−0.339(6)	0.295(4)	0.3304(5)	0.033(5)
H(16A)	0.029(5)	0.241(3)	0.3724(5)	0.027(5)
H(16B)	−0.160(5)	0.093(4)	0.3632(5)	0.027(5)
H(17A)	−0.287(6)	0.446(4)	0.3817(5)	0.038(5)
H(17B)	−0.476(6)	0.293(4)	0.3725(5)	0.038(5)
H(18A)	−0.143(8)	0.242(5)	0.4130(7)	0.058(6)
H(18B)	−0.339(7)	0.091(6)	0.4035(6)	0.058(6)
H(18C)	−0.422(7)	0.289(5)	0.4151(7)	0.058(6)
H(19A)	0.778(5)	0.369(4)	0.0111(4)	0.024(2)
H(19B)	0.790(5)	0.153(4)	0.0108(4)	0.024(2)
H(19C)	0.993(5)	0.263(3)	0.0007(5)	0.024(2)
H(20A)	1.286(5)	0.408(4)	0.0542(5)	0.024(2)
H(20B)	1.095(5)	0.519(4)	0.0380(4)	0.024(2)
H(20C)	1.292(5)	0.414(4)	0.0271(4)	0.024(2)
H(21A)	1.079(5)	−0.024(4)	0.0379(4)	0.024(2)
H(21B)	1.286(5)	0.077(3)	0.0535(4)	0.024(2)
H(21C)	1.277(5)	0.075(4)	0.0262(4)	0.024(2)

Table S1c. Anisotropic displacement parameters for C_{18}TAB phase III at −123 °C. The anisotropic displacement factor exponent has the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11} / Å^2	U_{22} / Å^2	U_{33} / Å^2	U_{23} / Å^2	U_{13} / Å^2	U_{12} / Å^2
C(1)	0.0139(8)	0.0233(9)	0.0176(7)	0.0000(6)	0.0051(6)	0.0030(7)
C(2)	0.0228(10)	0.0301(10)	0.0194(8)	0.0031(7)	0.0037(7)	0.0040(8)
C(3)	0.0246(11)	0.0371(11)	0.0187(8)	0.0022(7)	0.0063(7)	0.0066(9)
C(4)	0.0225(10)	0.0310(10)	0.0191(8)	0.0020(7)	0.0054(7)	0.0043(8)
C(5)	0.0246(11)	0.0269(9)	0.0208(8)	0.0011(7)	0.0069(7)	0.0032(8)
C(6)	0.0228(10)	0.0275(10)	0.0199(8)	0.0008(7)	0.0064(7)	0.0025(8)
C(7)	0.0237(11)	0.0256(9)	0.0192(8)	0.0013(7)	0.0071(7)	0.0021(7)
C(8)	0.0238(10)	0.0240(9)	0.0196(8)	0.0016(6)	0.0058(7)	0.0020(7)
C(9)	0.0241(10)	0.0235(10)	0.0198(8)	0.0007(6)	0.0058(7)	0.0015(7)
C(10)	0.0228(10)	0.0242(9)	0.0196(8)	0.0013(7)	0.0058(7)	0.0023(7)
C(11)	0.0238(11)	0.0237(9)	0.0205(8)	−0.0004(7)	0.0050(7)	0.0013(7)
C(12)	0.0229(10)	0.0251(11)	0.0205(9)	0.0014(6)	0.0066(7)	0.0006(7)
C(13)	0.0252(11)	0.0238(9)	0.0221(8)	0.0010(7)	0.0065(7)	0.0002(7)
C(14)	0.0237(11)	0.0243(9)	0.0220(8)	0.0008(7)	0.0076(7)	0.0011(8)
C(15)	0.0270(11)	0.0252(10)	0.0227(9)	0.0010(7)	0.0073(7)	−0.0002(8)
C(16)	0.0297(12)	0.0250(10)	0.0221(9)	0.0008(7)	0.0073(8)	0.0005(8)
C(17)	0.0358(13)	0.0309(11)	0.0266(10)	−0.0023(8)	0.0119(9)	−0.0013(9)
C(18)	0.0582(18)	0.0417(13)	0.0269(10)	−0.0002(9)	0.0150(11)	−0.0114(12)
C(19)	0.0203(10)	0.0350(11)	0.0150(7)	−0.0004(6)	0.0019(7)	−0.0013(8)
C(20)	0.0181(10)	0.0198(9)	0.0277(9)	0.0005(7)	0.0059(7)	−0.0032(7)
C(21)	0.0206(10)	0.0205(9)	0.0279(9)	−0.0018(7)	0.0082(7)	0.0008(7)
N(1)	0.0150(7)	0.0202(7)	0.0165(6)	−0.0011(5)	0.0040(5)	0.0003(6)
Br(1)	0.01901(16)	0.02011(15)	0.04511(16)	0.00076(8)	0.00795(10)	0.00051(8)

Table S1d. Selected bond lengths for C_{18}TAB phase III at −123 °C.

Atom — Atom	Length / Å	Atom — Atom	Length / Å
N(1) — C(1)	1.512(2)	C(11) — C(12)	1.526(2)
C(1) — C(2)	1.521(2)	C(12) — C(13)	1.525(3)
C(2) — C(3)	1.525(3)	C(13) — C(14)	1.526(3)
C(3) — C(4)	1.527(2)	C(14) — C(15)	1.529(3)
C(4) — C(5)	1.521(3)	C(15) — C(16)	1.528(3)
C(5) — C(6)	1.526(2)	C(16) — C(17)	1.524(3)
C(6) — C(7)	1.530(3)	C(17) — C(18)	1.526(3)
C(7) — C(8)	1.529(2)	C(19) — N(1)	1.500(2)
C(8) — C(9)	1.523(3)	C(20) — N(1)	1.500(2)
C(9) — C(10)	1.532(2)	C(21) — N(1)	1.499(2)
C(10) — C(11)	1.525(3)		

Table S1e. Selected bond angles for C_{18}TAB phase III at −123 °C.

Atom — Atom — Atom	Angle / ˚	Atom — Atom — Atom	Angle / ˚
N(1) — C(1) — C(2)	116.21(15)	C(12) — C(13) — C(14)	113.23(17)
C(1) — C(2) — C(3)	108.17(16)	C(13) — C(14) — C(15)	113.37(17)
C(2) — C(3) — C(4)	114.49(17)	C(16) — C(15) — C(14)	113.05(18)
C(5) — C(4) — C(3)	112.18(16)	C(17) — C(16) — C(15)	113.48(18)
C(4) — C(5) — C(6)	113.52(17)	C(16) — C(17) — C(18)	112.7(2)
C(5) — C(6) — C(7)	112.83(17)	C(19) — N(1) — C(1)	106.73(14)
C(8) — C(7) — C(6)	113.15(17)	C(20) — N(1) — C(1)	111.06(14)
C(9) — C(8) — C(7)	112.98(17)	C(20) — N(1) — C(19)	108.60(14)
C(8) — C(9) — C(10)	113.16(17)	C(21) — N(1) — C(1)	111.90(14)
C(11) — C(10) — C(9)	113.25(17)	C(21) — N(1) — C(19)	109.34(14)
C(10) — C(11) — C(12)	112.95(17)	C(21) — N(1) — C(20)	109.12(15)
C(13) — C(12) — C(11)	113.34(18)		

Table S1f. Selected torsion angles for C_{18}TAB phase III at −123 °C.

Atom — Atom — Atom — Atom	Angle / ˚	Atom — Atom — Atom — Atom	Angle / ˚
N(1) — C(1) — C(2) — C(3)	166.36(16)	C(10) — C(11) — C(12) — C(13)	179.78(18)
C(1) — C(2) — C(3) — C(4)	169.86(18)	C(11) — C(12) — C(13) — C(14)	179.76(17)
C(2) — C(3) — C(4) — C(5)	173.61(19)	C(12) — C(13) — C(14) — C(15)	179.09(18)
C(3) — C(4) — C(5) — C(6)	172.25(18)	C(13) — C(14) — C(15) — C(16)	179.91(18)
C(4) — C(5) — C(6) — C(7)	179.18(18)	C(14) — C(15) — C(16) — C(17)	179.68(19)
C(5) — C(6) — C(7) — C(8)	177.11(18)	C(15) — C(16) — C(17) — C(18)	179.5(2)
C(6) — C(7) — C(8) — C(9)	179.62(18)	C(2) — C(1) — N(1) — C(19)	171.88(16)
C(7) — C(8) — C(9) — C(10)	179.17(17)	C(2) — C(1) — N(1) — C(20)	−69.91(19)
C(8) — C(9) — C(10) — C(11)	179.89(18)	C(2) — C(1) — N(1) — C(21)	52.3(2)
C(9) — C(10) — C(11) — C(12)	−179.80(18)		

Table S2a. Crystal data and structure refinement for C_{18}TAB phase III at 22 °C.

Identification code	exp_798
Empirical formula	$C_{21}H_{46}BrN$
Formula weight	392.5
Temperature / K	295
Crystal system	monoclinic
Space group	$P2_1/c$
a / Å	5.63143(14)
b / Å	7.27158(15)
c / Å	56.7610(14)
α / °	90
β / °	95.805(2)
γ / °	90
Volume / Å^3	2312.41(10)
Z	4
ρ_{calc} / g cm^{-3}	1.127
μ / mm^{-1}	2.403
F(000)	856
Crystal size / mm^3	0.4526 × 0.089 × 0.0135
Radiation	Cu Kα (λ = 1.54184 Å)
2θ range for data collection / °	9.396 to 147.284
Index ranges	$-6 \le h \le 6$, $-8 \le k \le 8$, $-70 \le l \le 69$
Reflections collected	33203
Independent reflections	4531 [R_{int} = 0.0531, R_{sigma} = 0.0297]
Data/restraints/parameters	4531/0/365
Goodness-of-fit on F^2	1.264
Final R indexes [$I \ge 2\sigma(I)$]	R_1 = 0.0634, wR_2 = 0.0942
Final R indexes [all data]	R_1 = 0.0881, wR_2 = 0.1015
Largest diff. peak/hole / e Å^{-3}	0.65/−0.58

Table S2b. Fractional atomic coordinates and equivalent isotropic displacement parameters for C_{18}TAB phase III at 22 °C. U_{eq} is defined as ⅓ of the trace of the orthogonalised U_{ij} tensor.

Atom	$-x$	y	z	U(eq) / Å^2
C(1)	0.8435(5)	0.2530(7)	0.0544(5)	0.039(6)
C(2)	0.9406(7)	0.2201(5)	0.0799(6)	0.041(8)
C(3)	0.7509(8)	0.2767(7)	0.0958(6)	0.054(11)
C(4)	0.8069(7)	0.2287(7)	0.1216(6)	0.054(10)
C(5)	0.6255(7)	0.2983(5)	0.1373(6)	0.049(10)
C(6)	0.6583(7)	0.2296(7)	0.1626(6)	0.049(9)
C(7)	0.4770(8)	0.3062(5)	0.1780(6)	0.048(9)
C(8)	0.4997(7)	0.2324(7)	0.2031(6)	0.050(9)
C(9)	0.3182(7)	0.3085(5)	0.2185(6)	0.048(9)
C(10)	0.3371(7)	0.2297(6)	0.2433(6)	0.048(8)
C(11)	0.1579(7)	0.3093(5)	0.2588(6)	0.048(9)
C(12)	0.1759(7)	0.2293(7)	0.2836(6)	0.049(9)
C(13)	−0.0023(7)	0.3091(5)	0.2992(6)	0.048(9)
C(14)	0.0175(7)	0.2291(7)	0.3240(6)	0.050(9)
C(15)	−0.1572(8)	0.3091(6)	0.3399(7)	0.051(9)
C(16)	−0.1385(8)	0.2290(7)	0.3646(6)	0.053(9)
C(17)	−0.3096(9)	0.3083(6)	0.3806(8)	0.063(12)
C(18)	−0.2880(12)	0.2267(10)	0.4052(8)	0.088(17)
C(19)	0.8813(6)	0.2575(8)	0.0125(5)	0.050(8)
C(20)	1.1831(9)	0.4154(5)	0.0387(8)	0.047(10)
C(21)	1.1697(8)	0.0798(6)	0.0382(8)	0.047(10)
N(1)	1.0224(4)	0.2529(5)	0.0363(4)	0.035(5)
Br(1)	0.6430(6)	0.7515(7)	0.0333(2)	0.057(13)
H(1A)	0.765(6)	0.374(5)	0.0530(6)	0.041(6)
H(1B)	0.738(7)	0.159(5)	0.0493(6)	0.041(6)
H(2A)	1.076(6)	0.310(5)	0.0836(6)	0.043(7)
H(2B)	0.990(6)	0.095(5)	0.0823(6)	0.043(7)
H(3A)	0.716(7)	0.406(6)	0.0947(7)	0.059(8)
H(3B)	0.606(7)	0.214(6)	0.0901(6)	0.059(8)
H(4B)	0.835(7)	0.097(6)	0.1235(7)	0.063(8)
H(4A)	0.964(7)	0.268(6)	0.1274(6)	0.063(8)
H(5A)	0.635(7)	0.437(6)	0.1371(7)	0.057(8)
H(5B)	0.472(7)	0.263(6)	0.1305(6)	0.057(8)
H(6A)	0.817(7)	0.254(6)	0.1695(6)	0.055(7)
H(6B)	0.650(7)	0.094(6)	0.1624(6)	0.055(7)
H(7A)	0.492(7)	0.450(6)	0.1785(7)	0.063(8)
H(7B)	0.319(7)	0.277(6)	0.1706(6)	0.063(8)
H(8A)	0.662(7)	0.253(7)	0.2106(6)	0.058(8)
H(8B)	0.480(7)	0.098(6)	0.2017(7)	0.058(8)

H(9A)	0.334(7)	0.444(6)	0.2192(7)	0.056(8)
H(9B)	0.162(7)	0.287(5)	0.2111(6)	0.056(8)
H(10A)	0.498(7)	0.249(6)	0.2509(6)	0.053(7)
H(10B)	0.318(7)	0.092(5)	0.2425(6)	0.053(7)
H(11A)	0.182(7)	0.440(6)	0.2596(7)	0.057(8)
H(11B)	0.003(7)	0.290(5)	0.2515(6)	0.057(8)
H(12A)	0.335(6)	0.253(6)	0.2913(6)	0.054(7)
H(12B)	0.152(7)	0.095(6)	0.2829(7)	0.054(7)
H(13A)	0.020(7)	0.444(6)	0.2998(6)	0.056(8)
H(13B)	−0.157(7)	0.286(5)	0.2921(6)	0.056(8)
H(14A)	0.180(6)	0.268(6)	0.3316(6)	0.052(7)
H(14B)	−0.004(7)	0.100(5)	0.3228(6)	0.052(7)
H(15A)	−0.138(7)	0.444(6)	0.3406(7)	0.061(9)
H(15B)	−0.321(7)	0.295(5)	0.3326(6)	0.061(9)
H(16A)	0.023(7)	0.235(6)	0.3722(6)	0.054(7)
H(16B)	−0.168(7)	0.099(6)	0.3637(7)	0.054(7)
H(17A)	−0.304(8)	0.447(6)	0.3808(8)	0.076(10)
H(17B)	−0.478(8)	0.296(6)	0.3729(7)	0.076(10)
H(18A)	−0.125(8)	0.244(8)	0.4129(8)	0.089(9)
H(18B)	−0.324(9)	0.092(7)	0.4032(8)	0.089(9)
H(18C)	−0.414(8)	0.300(6)	0.4148(8)	0.089(9)
H(19A)	0.782(7)	0.374(6)	0.0121(7)	0.054(3)
H(19C)	0.994(6)	0.266(6)	0.0006(6)	0.054(3)
H(19B)	0.775(8)	0.159(6)	0.0113(7)	0.054(3)
H(20A)	1.275(7)	0.410(5)	0.0550(7)	0.054(3)
H(20B)	1.085(8)	0.529(5)	0.0389(7)	0.054(3)
H(20C)	1.280(8)	0.424(5)	0.0265(7)	0.054(3)
H(21A)	1.068(8)	−0.016(6)	0.0364(7)	0.054(3)
H(21B)	1.267(8)	0.079(5)	0.0525(7)	0.054(3)
H(21C)	1.272(7)	0.092(5)	0.0247(7)	0.054(3)

Table S2c. Anisotropic displacement parameters for C_{18}TAB phase III at 22 °C. The anisotropic displacement factor exponent has the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11} / Å^2	U_{22} / Å^2	U_{33} / Å^2	U_{23} / Å^2	U_{13} / Å^2	U_{12} / Å^2
C(1)	0.0324(16)	0.0478(17)	0.0383(14)	−0.0015(18)	0.0093(12)	0.012(2)
C(2)	0.046(2)	0.036(2)	0.0422(16)	0.0025(14)	0.0108(14)	0.0086(16)
C(3)	0.053(2)	0.071(3)	0.0415(17)	0.0012(19)	0.0134(15)	0.013(2)
C(4)	0.051(2)	0.071(3)	0.0408(17)	0.006(2)	0.0111(15)	0.014(2)
C(5)	0.051(2)	0.055(3)	0.0424(18)	0.0013(15)	0.0107(16)	0.0056(17)
C(6)	0.050(2)	0.055(2)	0.0423(17)	0.0039(18)	0.0132(15)	0.008(2)
C(7)	0.052(2)	0.052(2)	0.0418(18)	0.0003(14)	0.0129(16)	0.0034(17)
C(8)	0.053(2)	0.056(2)	0.0408(16)	−0.0019(19)	0.0132(15)	0.003(2)
C(9)	0.050(2)	0.053(2)	0.0420(18)	0.0009(15)	0.0119(16)	0.0028(16)
C(10)	0.054(2)	0.049(2)	0.0424(16)	0.0024(18)	0.0128(15)	0.003(2)
C(11)	0.049(2)	0.052(2)	0.0443(19)	−0.0001(15)	0.0122(16)	0.0019(16)
C(12)	0.054(2)	0.050(2)	0.0441(16)	0.0015(18)	0.0137(15)	0.003(2)
C(13)	0.048(2)	0.052(2)	0.0449(19)	−0.0004(15)	0.0117(16)	0.0011(16)
C(14)	0.054(2)	0.049(2)	0.0469(17)	0.0008(18)	0.0126(15)	0.000(2)
C(15)	0.053(2)	0.054(2)	0.047(2)	−0.0018(15)	0.014(17)	0.0002(17)
C(16)	0.062(2)	0.051(2)	0.0488(18)	0.0025(19)	0.0146(16)	−0.001(2)
C(17)	0.071(3)	0.061(3)	0.059(2)	−0.0042(18)	0.024(2)	−0.003(2)
C(18)	0.123(4)	0.091(4)	0.056(2)	−0.007(3)	0.036(3)	−0.030(4)
C(19)	0.046(2)	0.068(2)	0.0354(15)	−0.002(2)	0.0045(13)	0.004(3)
C(20)	0.049(3)	0.038(2)	0.056(3)	0.0003(17)	0.011(2)	−0.0039(19)
C(21)	0.034(3)	0.045(2)	0.061(3)	−0.0053(18)	0.010(2)	0.0096(18)
N(1)	0.0313(12)	0.0388(12)	0.0369(11)	0.0019(13)	0.0078(9)	0.0123(16)
Br(1)	0.0423(2)	0.04314(19)	0.0859(3)	0.0017(2)	0.01377(16)	0.0056(3)

Table S2d. Selected bond lengths for C_{18}TAB phase III at 22 °C.

Atom — Atom	Length / Å	Atom — Atom	Length / Å
N(1) — C(1)	1.510(3)	C(11) — C(12)	1.518(5)
C(1) — C(2)	1.513(4)	C(12) — C(13)	1.520(5)
C(2) — C(3)	1.524(5)	C(13) — C(14)	1.516(5)
C(3) — C(4)	1.508(5)	C(14) — C(15)	1.513(5)
C(4) — C(5)	1.508(5)	C(15) — C(16)	1.512(5)
C(5) — C(6)	1.514(5)	C(16) — C(17)	1.508(6)
C(6) — C(7)	1.516(5)	C(17) — C(18)	1.506(7)
C(7) — C(8)	1.515(5)	C(19) — N(1)	1.498(4)
C(8) — C(9)	1.514(5)	C(20) — N(1)	1.486(5)
C(9) — C(10)	1.515(5)	C(21) — N(1)	1.505(5)
C(10) — C(11)	1.519(5)		

Table S2e. Selected bond angles for C_{18}TAB phase III at 22 °C.

Atom — Atom — Atom	Angle / ˚	Atom — Atom — Atom	Angle / ˚
N(1) — C(1) — C(2)	116.7(2)	C(12) — C(13) — C(14)	113.8(3)
C(1) — C(2) — C(3)	108.5(3)	C(13) — C(14) — C(15)	114.3(4)
C(2) — C(3) — C(4)	115.0(3)	C(14) — C(15) — C(16)	114.4(3)
C(3) — C(4) — C(5)	114.1(3)	C(15) — C(16) — C(17)	115.2(4)
C(4) — C(5) — C(6)	115.1(3)	C(16) — C(17) — C(18)	114.3(4)
C(5) — C(6) — C(7)	113.7(3)	C(19) — N(1) — C(1)	106.5(2)
C(6) — C(7) — C(8)	114.5(3)	C(19) — N(1) — C(21)	108.7(3)
C(7) — C(8) — C(9)	114.5(4)	C(20) — N(1) — C(1)	112.3(3)
C(8) — C(9) — C(10)	114.2(3)	C(20) — N(1) — C(19)	109.1(3)
C(9) — C(10) — C(11)	114.0(3)	C(20) — N(1) — C(21)	109.4(2)
C(10) — C(11) — C(12)	113.9(3)	C(21) — N(1) — C(1)	110.6(3)
C(11) — C(12) — C(13)	114.1(3)		

Table S2f. Selected torsion angles for C_{18}TAB phase III at 22 °C.

Atom — Atom — Atom — Atom	Angle / ˚	Atom — Atom — Atom — Atom	Angle / ˚
N(1) — C(1) — C(2) — C(3)	164.6(4)	C(10) — C(11) — C(12) — C(13)	179.7(4)
C(1) — C(2) — C(3) — C(4)	172.1(4)	C(11) — C(12) — C(13) — C(14)	−179.8(4)
C(2) — C(3) — C(4) — C(5)	175.7(4)	C(12) — C(13) — C(14) — C(15)	179.3(4)
C(3) — C(4) — C(5) — C(6)	171.7(4)	C(13) — C(14) — C(15) — C(16)	179.8(4)
C(4) — C(5) — C(6) — C(7)	178.4(4)	C(14) — C(15) — C(16) — C(17)	179.5(4)
C(5) — C(6) — C(7) — C(8)	177.3(4)	C(15) — C(16) — C(17) — C(18)	−180.0(5)
C(6) — C(7) — C(8) — C(9)	−179.8(4)	C(2) — C(1) — N(1) — C(19)	171.1(4)
C(7) — C(8) — C(9) — C(10)	178.2(4)	C(2) — C(1) — N(1) — C(20)	−69.4(4)
C(8) — C(9) — C(10) — C(11)	178.8(4)	C(2) — C(1) — N(1) — C(21)	53.1(5)
C(9) — C(10) — C(11) — C(12)	179.6(4)		

Table S3a. Crystal data and structure refinement for C_{18}TAB phase II at 117 °C.

Identification code	xstr0480a
Empirical formula	$C_{21}H_{46}BrN$
Formula weight	392.5
Temperature / K	390
Crystal system	monoclinic
Space group	$P2_1/m$
a / Å	5.6617(3)
b / Å	7.3973(4)
c / Å	28.5605(18)
α / °	90
β / °	93.377(5)
γ / °	90
Volume / Å^3	1194.09(11)
Z	2
ρ_{calc} / g cm^{-3}	1.092
μ / mm^{-1}	2.327
F(000)	428
Crystal size / mm^3	0.2617 × 0.0573 × 0.0199
Radiation	Cu Kα (λ = 1.54184 Å)
2θ range for data collection / °	9.3 to 147.66
Index ranges	$-7 \le h \le 6$, $-9 \le k \le 8$, $-35 \le l \le 35$
Reflections collected	10389
Independent reflections	2534 [R_{int} = 0.0319, R_{sigma} = 0.0230]
Data/restraints/parameters	2534/175/198
Goodness-of-fit on F^2	1.022
Final R indexes [$I \ge 2\sigma(I)$]	R_1 = 0.0486, wR_2 = 0.1440
Final R indexes [all data]	R_1 = 0.0590, wR_2 = 0.1582
Largest diff. peak/hole / e Å^{-3}	0.71/−0.75

Table S3b. Fractional atomic coordinates and equivalent isotropic displacement parameters for C_{18}TAB phase II at 117 °C. U_{eq} is defined as ⅓ of the trace of the orthogonalised U_{ij} tensor.

Atom	*x*	*y*	*z*	*U*(eq) / Å^2
C(1)	0.8330(7)	¼	0.10899(15)	0.0752(10)
C(2)	0.9266(10)	¼	0.15905(19)	0.0987(15)
C(3)	0.7367(11)	¼	0.19187(19)	0.1074(17)
C(4)	0.7908(12)	¼	0.2428(2)	0.119(2)
C(5)	0.6076(13)	¼	0.2753(2)	0.138(3)
C(6)	0.6492(14)	¼	0.3254(2)	0.121(2)
C(7)	0.4638(15)	¼	0.3573(3)	0.157(4)
C(8)	0.4898(15)	¼	0.4066(2)	0.129(2)
C(9)	0.3112(15)	¼	0.4394(3)	0.162(4)
C(10)	0.3332(15)	¼	0.4880(3)	0.130(3)
C(11)	0.1542(16)	¼	0.5211(3)	0.170(4)
C(12)	0.1742(15)	¼	0.5694(2)	0.133(3)
C(13)	−0.0012(16)	¼	0.6026(3)	0.170(4)
C(14)	0.0213(16)	¼	0.6508(3)	0.133(3)
C(15)	−0.1548(19)	¼	0.6835(3)	0.203(6)
C(16)	−0.1293(18)	¼	0.7329(3)	0.145(3)
C(17)	−0.303(2)	¼	0.7663(4)	0.229(7)
C(18)	−0.278(2)	¼	0.8137(3)	0.204(6)
C(19)	0.8707(8)	¼	0.02577(16)	0.0911(13)
C(20)	1.1636(5)	0.4144(5)	0.07474(12)	0.0849(8)
N(1)	1.0113(5)	¼	0.07185(12)	0.0653(7)
Br(1)	0.63504(8)	¾	0.06534(2)	0.0876(2)
H(1)	0.734(1)	0.356(3)	0.1039(19)	0.090
H(2)	1.026(1)	0.356(4)	0.1641(2)	0.118
H(3)	0.640(1)	0.356(4)	0.1848(2)	0.129
H(4)	0.889(1)	0.356(4)	0.2490(3)	0.143
H(5)	0.511(1)	0.356(4)	0.2679(3)	0.165
H(6)	0.746(1)	0.356(4)	0.3329(3)	0.145
H(7)	0.370(1)	0.356(4)	0.3487(3)	0.188
H(8)	0.585(1)	0.356(4)	0.4147(3)	0.154
H(9)	0.217(1)	0.356(4)	0.4308(3)	0.195
H(10)	0.427(1)	0.356(4)	0.4968(3)	0.156
H(11)	0.061(2)	0.356(4)	0.5121(3)	0.204
H(12)	0.268(1)	0.356(4)	0.5780(3)	0.159
H(13)	−0.095(2)	0.356(4)	0.5940(3)	0.204
H(14)	0.115(2)	0.356(4)	0.6593(3)	0.160
H(15)	−0.251(2)	0.356(4)	0.6757(3)	0.243
H(16)	−0.033(2)	0.356(4)	0.7406(4)	0.174

H(17)	−0.397(3)	0.356(4)	0.7575(4)	0.274
H(18)	−0.192(3)	0.356(3)	0.8242(5)	0.306
H(18M)	−0.431(3)	¼	0.8265(7)	0.306
H(19)	0.773(1)	0.356(3)	0.0235(4)	0.137
H(19M)	0.977(2)	¼	0.0007(3)	0.137
H(20A)	1.2549	0.4153	0.1042	0.127
H(20B)	1.0659	0.5205	0.0724	0.127
H(20C)	1.2683	0.4135	0.0495	0.127

Table S3c. Anisotropic displacement parameters for C_{18}TAB phase II at 117 °C. The anisotropic displacement factor exponent has the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11} / Å^2	U_{22} / Å^2	U_{33} / Å^2	U_{23} / Å^2	U_{13} / Å^2	U_{12} / Å^2
C(1)	0.058(2)	0.089(3)	0.080(2)	0	0.0167(16)	0
C(2)	0.085(3)	0.129(4)	0.083(3)	0	0.013(2)	0
C(3)	0.100(4)	0.147(5)	0.077(3)	0	0.021(2)	0
C(4)	0.100(4)	0.168(6)	0.092(3)	0	0.025(3)	0
C(5)	0.115(5)	0.217(9)	0.083(3)	0	0.030(3)	0
C(6)	0.122(5)	0.152(6)	0.091(4)	0	0.030(3)	0
C(7)	0.117(5)	0.263(12)	0.092(4)	0	0.028(4)	0
C(8)	0.126(5)	0.165(7)	0.098(4)	0	0.036(4)	0
C(9)	0.119(5)	0.273(14)	0.098(5)	0	0.032(4)	0
C(10)	0.130(6)	0.163(7)	0.102(4)	0	0.036(4)	0
C(11)	0.129(6)	0.281(14)	0.104(5)	0	0.039(4)	0
C(12)	0.137(6)	0.162(8)	0.104(4)	0	0.042(4)	0
C(13)	0.131(6)	0.279(14)	0.102(5)	0	0.036(4)	0
C(14)	0.144(6)	0.156(7)	0.104(4)	0	0.044(4)	0
C(15)	0.160(9)	0.332(18)	0.122(6)	0	0.058(6)	0
C(16)	0.176(8)	0.152(7)	0.113(5)	0	0.055(5)	0
C(17)	0.210(12)	0.360(20)	0.121(7)	0	0.078(7)	0
C(18)	0.282(15)	0.210(12)	0.129(7)	0	0.086(8)	0
C(19)	0.078(3)	0.117(4)	0.079(3)	0	0.006(2)	0
C(20)	0.0733(17)	0.0741(19)	0.109(2)	0.0031(15)	0.0192(15)	−0.0096(13)
N(1)	0.0515(15)	0.0691(18)	0.0760(18)	0	0.0101(12)	0
Br(1)	0.0674(3)	0.0743(3)	0.1226(5)	0	0.0200(2)	0

Table S3d. Selected bond lengths for C_{18}TAB phase II at 117 °C.

Atom — Atom	Length / Å	Atom — Atom	Length / Å
N(1) — C(1)	1.507(5)	C(11) — C(12)	1.380(11)
C(1) — C(2)	1.495(7)	C(12) — C(13)	1.412(10)
C(2) — C(3)	1.467(8)	C(13) — C(14)	1.375(11)
C(3) — C(4)	1.469(9)	C(14) — C(15)	1.405(12)
C(4) — C(5)	1.431(9)	C(15) — C(16)	1.410(14)
C(5) — C(6)	1.436(10)	C(16) — C(17)	1.411(13)
C(6) — C(7)	1.430(10)	C(17) — C(18)	1.352(15)
C(7) — C(8)	1.408(11)	N(1) — C(19)	1.497(6)
C(8) — C(9)	1.419(10)	N(1) — C(20)	1.491(4)
C(9) — C(10)	1.386(10)	N(1) — C(20)[1]	1.491(4)
C(10) — C(11)	1.425(11)		

[1] $x, ½ - y, z$

Table S3e. Selected bond angles for C_{18}TAB phase II at 117 °C.

Atom — Atom — Atom	Angle / ˚	Atom — Atom — Atom	Angle / ˚
N(1) — C(1) — C(2)	117.3(4)	C(12) — C(13) — C(14)	130.1(9)
C(1) — C(2) — C(3)	112.3(5)	C(13) — C(14) — C(15)	129.6(10)
C(2) — C(3) — C(4)	121.0(5)	C(14) — C(15) — C(16)	129.0(11)
C(3) — C(4) — C(5)	121.6(6)	C(15) — C(16) — C(17)	130.0(11)
C(4) — C(5) — C(6)	124.3(7)	C(16) — C(17) — C(18)	129.8(14)
C(5) — C(6) — C(7)	123.5(7)	C(19) — N(1) — C(1)	106.0(3)
C(6) — C(7) — C(8)	126.9(8)	C(20) — N(1) — C(1)	111.7(2)
C(7) — C(8) — C(9)	128.6(8)	C(20)[1] — N(1) — C(1)	111.7(2)
C(8) — C(9) — C(10)	129.5(8)	C(20) — N(1) — C(19)	108.9(2)
C(9) — C(10) — C(11)	129.6(8)	C(20)[1] — N(1) — C(19)	108.9(2)
C(10) — C(11) — C(12)	130.1(9)	C(20) — N(1) — C(20)[1]	109.4(3)
C(11) — C(12) — C(13)	130.7(9)		

[1] $x, ½ - y, z$

Table S3f. Selected torsion angles for C_{18}TAB phase II at 117 °C.

Atom — Atom — Atom — Atom	Angle / ˚	Atom — Atom — Atom — Atom	Angle / ˚
N(1) — C(1) — C(2) — C(3)	180	C(10) — C(11) — C12 — C(14)	180
C(1) — C(2) — C(3) — C(4)	180	C(11) — C(12) — C(13) — C(15)	180
C(2) — C(3) — C(4) — C(5)	180	C(12) — C(13) — C(14) — C(16)	180
C(3) — C(4) — C(5) — C(6)	180	C(13) — C(14) — C(15) — C(17)	180
C(4) — C(5) — C(6) — C(7)	180	C(14) — C(15) — C(16) — C(18)	180
C(5) — C(6) — C(7) — C(8)	180	C(15) — C(16) — C(17) — C(18)	180
C(6) — C(7) — C(8) — C(9)	180	C(2) — C(1) — N(1) — C(19)	180
C(7) — C(8) — C(9) — C(10)	180	C(2) — C(1) — N(1) — C(20)	−61.5(2)
C(8) — C(9) — C(10) — C(11)	180	C(2) — C(1) — N(1) — C(20)[1]	61.5(2)
C(9) — C(10) — C(11) — C(12)	180		

[1] $x, ½ - y, z$

Table S4a. Crystal data and structure refinement for C_{16}TAB phase III at −123 °C.

Identification code	exp_283
Empirical formula	$C_{19}H_{42}BrN$
Formula weight	364.44
Temperature / K	150
Crystal system	monoclinic
Space group	$P2_1/c$
a / Å	5.59550(7)
b / Å	7.14921(12)
c / Å	51.7885(8)
α / °	90
β / °	94.7909(13)
γ / °	90
Volume / Å^3	2064.48(5)
Z	4
ρ_{calc} / g cm^{-3}	1.173
μ / mm^{-1}	2.656
F(000)	792
Crystal size / mm^3	0.58 × 0.2587 × 0.0493
Radiation	Cu Kα (λ = 1.54184 Å)
2θ range for data collection / °	10.284 to 147.344
Index ranges	$-6 \le h \le 6$, $-8 \le k \le 8$, $-64 \le l \le 63$
Reflections collected	31281
Independent reflections	4027 [R_{int} = 0.0589, R_{sigma} = 0.0248]
Data/restraints/parameters	4027/0/333
Goodness-of-fit on F^2	1.232
Final R indexes [$I \ge 2\sigma(I)$]	R_1 = 0.0428, wR_2 = 0.0795
Final R indexes [all data]	R_1 = 0.0475, wR_2 = 0.0816
Largest diff. peak/hole / e Å^{-3}	0.46/−0.40

Table S4b. Fractional atomic coordinates and equivalent isotropic displacement parameters for C_{16}TAB phase III at −123 °C. U_{eq} is defined as ⅓ of the trace of the orthogonalised U_{ij} tensor.

Atom	*x*	*y*	*z*	*U*(eq) / Å^2
C(1)	0.8280(3)	0.2542(4)	0.05922(4)	0.0181(4)
C(2)	0.9190(4)	0.2199(3)	0.08732(4)	0.0207(5)
C(3)	0.7217(4)	0.2791(4)	0.10437(4)	0.0246(5)
C(4)	0.7696(4)	0.2225(4)	0.13276(4)	0.0232(5)
C(5)	0.5814(4)	0.2998(3)	0.14946(4)	0.0216(5)
C(6)	0.6025(4)	0.2260(4)	0.17719(4)	0.0222(5)
C(7)	0.4150(4)	0.3071(4)	0.19370(4)	0.0212(5)
C(8)	0.4278(4)	0.2264(4)	0.22109(4)	0.0216(5)
C(9)	0.2410(4)	0.3090(4)	0.23762(4)	0.0218(5)
C(10)	0.2523(4)	0.2261(4)	0.26488(4)	0.0215(5)
C(11)	0.0670(4)	0.3092(4)	0.28157(4)	0.0213(5)
C(12)	0.0787(4)	0.2262(4)	0.30887(4)	0.0226(5)
C(13)	−0.1046(4)	0.3099(4)	0.32571(4)	0.0221(5)
C(14)	−0.0933(4)	0.2259(4)	0.35292(4)	0.0240(5)
C(15)	−0.2738(5)	0.3111(4)	0.37002(4)	0.0277(5)
C(16)	−0.2596(6)	0.2213(4)	0.39694(5)	0.0386(7)
C(17)	0.8803(4)	0.2569(4)	0.01337(4)	0.0233(5)
C(18)	1.1769(4)	0.4175(3)	0.04263(4)	0.0211(5)
C(19)	1.1619(4)	0.0754(3)	0.04195(4)	0.0223(5)
N(1)	1.0146(3)	0.2506(3)	0.03970(3)	0.0164(3)
Br(1)	0.63426(4)	0.75233(3)	0.03629(2)	0.02649(9)
H(1A)	0.748(4)	0.380(4)	0.0567(4)	0.019(4)
H(1B)	0.716(4)	0.159(4)	0.0537(4)	0.019(4)
H(2A)	1.063(5)	0.301(4)	0.0921(5)	0.023(5)
H(2B)	0.964(4)	0.088(4)	0.0902(5)	0.023(5)
H(3A)	0.699(5)	0.412(4)	0.1029(5)	0.028(5)
H(3B)	0.574(5)	0.216(4)	0.0983(5)	0.028(5)
H(4A)	0.927(5)	0.263(4)	0.1398(5)	0.030(5)
H(4B)	0.774(5)	0.085(4)	0.1345(5)	0.030(5)
H(5A)	0.593(5)	0.430(4)	0.1496(5)	0.028(5)
H(5B)	0.421(5)	0.270(4)	0.1420(5)	0.028(5)
H(6A)	0.765(5)	0.251(4)	0.1851(5)	0.030(5)
H(6B)	0.588(5)	0.088(4)	0.1773(5)	0.030(5)
H(7A)	0.435(5)	0.445(4)	0.1949(5)	0.029(5)
H(7B)	0.250(5)	0.286(4)	0.1857(5)	0.029(5)
H(8A)	0.585(5)	0.245(4)	0.2293(5)	0.024(4)
H(8B)	0.401(4)	0.089(4)	0.2197(5)	0.024(4)
H(9A)	0.260(4)	0.444(4)	0.2383(5)	0.023(5)

H(9B)	0.078(5)	0.286(3)	0.2292(5)	0.023(5)
H(10A)	0.411(5)	0.248(4)	0.2735(5)	0.027(5)
H(10B)	0.226(5)	0.086(4)	0.2642(5)	0.027(5)
H(11A)	0.084(5)	0.439(4)	0.2821(5)	0.028(5)
H(11B)	−0.098(5)	0.289(4)	0.2736(5)	0.028(5)
H(12A)	0.238(5)	0.246(4)	0.3173(5)	0.029(5)
H(12B)	0.056(5)	0.088(4)	0.3075(5)	0.029(5)
H(13A)	−0.077(4)	0.445(4)	0.3273(5)	0.026(5)
H(13B)	−0.272(5)	0.293(4)	0.3168(5)	0.026(5)
H(14A)	0.065(5)	0.238(4)	0.3609(5)	0.029(5)
H(14B)	−0.120(5)	0.093(4)	0.3518(5)	0.029(5)
H(15A)	−0.242(5)	0.448(4)	0.3711(5)	0.033(5)
H(15B)	−0.430(5)	0.297(4)	0.3620(5)	0.033(5)
H(16A)	−0.111(7)	0.243(5)	0.4060(7)	0.055(6)
H(16B)	−0.297(6)	0.083(5)	0.3950(6)	0.055(6)
H(16C)	−0.370(6)	0.278(5)	0.4062(7)	0.055(6)
H(17A)	0.779(5)	0.368(4)	0.0129(5)	0.025(2)
H(17B)	0.784(5)	0.145(4)	0.0116(5)	0.025(2)
H(17C)	0.999(5)	0.257(4)	0.0008(5)	0.025(2)
H(18A)	1.270(4)	0.415(4)	0.0591(5)	0.025(2)
H(18B)	1.081(5)	0.526(4)	0.0413(5)	0.025(2)
H(18C)	1.285(5)	0.410(4)	0.0290(5)	0.025(2)
H(19A)	1.057(5)	−0.029(4)	0.0403(5)	0.025(2)
H(19B)	1.266(4)	0.082(4)	0.0584(5)	0.025(2)
H(19C)	1.273(5)	0.080(4)	0.0279(5)	0.025(2)

Table S4c. Anisotropic displacement parameters for C_{16}TAB phase III at −123 °C. The anisotropic displacement factor exponent has the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11} / Å^2	U_{22} / Å^2	U_{33} / Å^2	U_{23} / Å^2	U_{13} / Å^2	U_{12} / Å^2
C(1)	0.0158(9)	0.0222(11)	0.0164(9)	−0.0002(8)	0.0023(7)	0.0006(10)
C(2)	0.0227(11)	0.0215(14)	0.0181(9)	0.0025(8)	0.0028(8)	0.0067(9)
C(3)	0.0240(11)	0.0310(16)	0.0190(10)	0.0019(9)	0.0036(8)	0.0067(10)
C(4)	0.0249(11)	0.0261(15)	0.0188(10)	0.0009(8)	0.0031(8)	0.0017(10)
C(5)	0.0244(12)	0.0216(14)	0.0190(10)	0.0007(8)	0.0033(8)	0.0022(9)
C(6)	0.0252(11)	0.0237(14)	0.0181(9)	0.0005(8)	0.0044(8)	0.0026(10)
C(7)	0.0231(11)	0.0228(13)	0.0181(9)	0.0008(8)	0.0034(8)	0.0018(9)
C(8)	0.0243(11)	0.0222(14)	0.0186(9)	−0.0002(8)	0.0037(8)	0.0020(10)
C(9)	0.0237(12)	0.0229(13)	0.0190(10)	0.0006(8)	0.0031(8)	0.0018(9)
C(10)	0.0241(11)	0.0222(14)	0.0188(9)	0.0016(8)	0.0040(8)	0.0015(9)
C(11)	0.0228(11)	0.0211(13)	0.0202(10)	0.0011(8)	0.0035(8)	0.0012(9)
C(12)	0.0256(11)	0.0230(14)	0.0197(10)	0.0006(8)	0.0051(8)	0.0022(10)
C(13)	0.0260(12)	0.0217(13)	0.0191(10)	0.0005(8)	0.0044(8)	0.0009(9)
C(14)	0.0298(12)	0.0223(14)	0.0204(10)	0.0021(9)	0.0054(8)	0.0015(10)
C(15)	0.0313(13)	0.0283(15)	0.0244(11)	−0.0012(9)	0.0078(9)	−0.0014(10)
C(16)	0.0548(18)	0.0384(19)	0.0244(12)	−0.0015(11)	0.0142(11)	−0.0096(14)
C(17)	0.0227(10)	0.0319(14)	0.0150(9)	−0.0012(9)	−0.0001(8)	0.0005(12)
C(18)	0.0204(12)	0.0161(13)	0.0268(11)	0.0003(8)	0.0024(9)	−0.0018(9)
C(19)	0.0195(11)	0.0201(13)	0.0274(11)	−0.0026(9)	0.0028(9)	0.0029(9)
N(1)	0.0155(8)	0.0177(9)	0.0160(7)	−0.0001(7)	0.0020(6)	0.0021(8)
Br(1)	0.01978(13)	0.01858(14)	0.04135(15)	0.00059(10)	0.00400(9)	0.00060(12)

Table S4d. Selected bond lengths for C_{16}TAB phase III at −123 °C.

Atom — Atom	Length / Å	Atom — Atom	Length / Å
N(1) — C(1)	1.513(2)	C(10) — C(11)	1.525(3)
C(1) — C(2)	1.521(3)	C(11) — C(12)	1.530(3)
C(2) — C(3)	1.530(3)	C(12) — C(13)	1.523(3)
C(3) — C(4)	1.527(3)	C(13) — C(14)	1.528(3)
C(4) — C(5)	1.521(3)	C(14) — C(15)	1.525(3)
C(5) — C(6)	1.525(3)	C(15) — C(16)	1.531(3)
C(6) — C(7)	1.522(3)	C(17) — N(1)	1.501(2)
C(7) — C(8)	1.527(3)	C(18) — N(1)	1.499(3)
C(8) — C(9)	1.524(3)	C(19) — N(1)	1.499(3)
C(9) — C(10)	1.527(3)		

Table S4e. Selected bond angles for C_{16}TAB phase III at −123 °C.

Atom — Atom — Atom	Angle / ˚	Atom — Atom — Atom	Angle / ˚
N(1) — C(1) — C(2)	116.22(16)	C(11) — C(12) — C(13)	113.46(19)
C(1) — C(2) — C(3)	107.91(17)	C(12) — C(13) — C(14)	113.31(19)
C(2) — C(3) — C(4)	113.92(19)	C(13) — C(14) — C(15)	113.6(2)
C(3) — C(4) — C(5)	112.14(19)	C(14) — C(15) — C(16)	112.0(2)
C(4) — C(5) — C(6)	114.01(19)	C(17) — N(1) — C(1)	106.59(15)
C(5) — C(6) — C(7)	113.23(19)	C(18) — N(1) — C(1)	111.41(17)
C(6) — C(7) — C(8)	113.37(19)	C(18) — N(1) — C(17)	108.72(17)
C(7) — C(8) — C(9)	113.21(19)	C(19) — N(1) — C(1)	111.61(17)
C(8) — C(9) — C(10)	113.05(19)	C(19) — N(1) — C(17)	109.01(17)
C(9) — C(10) — C(11)	113.29(19)	C(19) — N(1) — C(18)	109.41(16)
C(10) — C(11) — C(12)	113.23(19)		

Table S4f. Selected torsion angles for C_{16}TAB phase III at −123 °C.

Atom — Atom — Atom — Atom	Angle / ˚	Atom — Atom — Atom — Atom	Angle / ˚
N(1) — C(1) — C(2) — C(3)	165.4(2)	C(9) — C(10) — C(11) — C(12)	−179.9(2)
C(1) — C(2) — C(3) — C(4)	170.2(2)	C(10) — C(11) — C(12) — C(13)	179.5(2)
C(2) — C(3) — C(4) — C(5)	174.6(2)	C(11) — C(12) — C(13) — C(14)	179.7(2)
C(3) — C(4) — C(5) — C(6)	172.3(2)	C(12) — C(13) — C(14) — C(15)	179.1(2)
C(4) — C(5) — C(6) — C(7)	179.2(2)	C(13) — C(14) — C(15) — C(16)	179.1(2)
C(5) — C(6) — C(7) — C(8)	177.2(2)	C(2) — C(1) — N(1) — C(17)	171.2(2)
C(6) — C(7) — C(8) — C(9)	179.5(2)	C(2) — C(1) — N(1) — C(18)	−70.3(3)
C(7) — C(8) — C(9) — C(10)	179.3(2)	C(2) — C(1) — N(1) — C(19)	52.3(3)
C(8) — C(9) — C(10) — C(11)	179.6(2)		

Table S5a. Crystal data and structure refinement for C_{16}TAB phase III at 22 °C.

Identification code	exp_518
Empirical formula	$C_{19}H_{42}BrN$
Formula weight	364.44
Temperature / K	295
Crystal system	monoclinic
Space group	$P2_1/c$
a / Å	5.63257(8)
b / Å	7.26127(11)
c / Å	52.0364(9)
α / °	90
β / °	93.7545(14)
γ / °	90
Volume / Å^3	2123.70(6)
Z	4
ρ_{calc} / g cm^{-3}	1.140
μ / mm^{-1}	2.582
F(000)	792
Crystal size / mm^3	0.5774 × 0.2104 × 0.02
Radiation	Cu Kα (λ = 1.54184 Å)
2θ range for data collection / °	6.81 to 147.956
Index ranges	$-7 \le h \le 6$, $-8 \le k \le 9$, $-63 \le l \le 64$
Reflections collected	26213
Independent reflections	4232 [R_{int} = 0.0672, R_{sigma} = 0.0326]
Data/restraints/parameters	4232/9/334
Goodness-of-fit on F^2	1.228
Final R indexes [$I \ge 2\sigma(I)$]	R_1 = 0.0822, wR_2 = 0.1456
Final R indexes [all data]	R_1 = 0.0916, wR_2 = 0.1498
Largest diff. peak/hole / e Å^{-3}	0.95/−0.48

Table S5b. Fractional atomic coordinates and equivalent isotropic displacement parameters for C_{16}TAB phase III at 22 °C. U_{eq} is defined as ⅓ of the trace of the orthogonalised U_{ij} tensor.

Atom	x	y	z	U(eq) / Å^2
C(1)	0.8236(6)	0.2519(7)	0.05928(7)	0.0354(8)
C(2)	0.9119(7)	0.2204(6)	0.08695(8)	0.0366(9)
C(3)	0.7162(9)	0.2774(8)	0.10424(8)	0.0477(11)
C(4)	0.7634(8)	0.2280(8)	0.13239(8)	0.0491(12)
C(5)	0.5776(8)	0.2986(7)	0.14938(8)	0.0428(10)
C(6)	0.6005(8)	0.2279(7)	0.17697(8)	0.0424(10)
C(7)	0.4137(9)	0.3073(7)	0.19367(8)	0.0433(10)
C(8)	0.4270(8)	0.2322(8)	0.22095(8)	0.0459(10)
C(9)	0.2409(8)	0.3089(7)	0.23783(8)	0.0429(10)
C(10)	0.2525(8)	0.2300(7)	0.26483(8)	0.0445(10)
C(11)	0.0681(9)	0.3099(7)	0.28174(8)	0.0437(10)
C(12)	0.0785(8)	0.2278(7)	0.30872(8)	0.0438(10)
C(13)	−0.1017(9)	0.3096(7)	0.32583(8)	0.0432(10)
C(14)	−0.0897(9)	0.2282(7)	0.35293(9)	0.0478(11)
C(15)	−0.2685(10)	0.3094(8)	0.37022(10)	0.0566(13)
C(16)	−0.2553(13)	0.2234(9)	0.39704(11)	0.0800(2)
C(17)	0.8774(8)	0.2580(8)	0.01359(7)	0.0452(10)
C(18)	1.1693(9)	0.4155(6)	0.04221(9)	0.0412(10)
C(19)	1.1553(8)	0.0785(7)	0.04151(10)	0.0418(10)
N(1)	1.0094(5)	0.2505(5)	0.03954(5)	0.0311(6)
Br(1)	0.63071(7)	0.75152(7)	0.03617(2)	0.05070(18)
H(1A)	0.736(7)	0.370(6)	0.0559(8)	0.034(7)
H(1B)	0.709(8)	0.164(6)	0.0530(8)	0.034(7)
H(2A)	1.037(8)	0.316(7)	0.0906(9)	0.044(9)
H(2B)	0.944(8)	0.087(7)	0.0894(8)	0.044(9)
H(3A)	0.683(9)	0.406(8)	0.1031(10)	0.059(16)
H(3B)	0.568(9)	0.218(7)	0.0984(9)	0.054(14)
H(4A)	0.914(8)	0.276(6)	0.1388(8)	0.039(8)
H(4B)	0.800(8)	0.102(7)	0.1344(8)	0.039(8)
H(5A)	0.587(8)	0.432(7)	0.1502(9)	0.045(9)
H(5B)	0.425(8)	0.262(7)	0.1422(9)	0.045(9)
H(6A)	0.761(9)	0.259(7)	0.1845(9)	0.050(9)
H(6B)	0.589(8)	0.092(7)	0.1771(9)	0.050(9)
H(7A)	0.431(9)	0.440(7)	0.1948(9)	0.049(10)
H(7B)	0.259(9)	0.287(7)	0.1857(9)	0.049(10)
H(8A)	0.585(9)	0.238(7)	0.2293(9)	0.056(10)
H(8B)	0.412(9)	0.092(8)	0.2202(9)	0.056(10)
H(9A)	0.261(8)	0.436(7)	0.2384(9)	0.043(9)
H(9B)	0.082(8)	0.288(6)	0.2292(9)	0.043(9)

H(10A)	0.417(8)	0.253(7)	0.2736(9)	0.050(9)
H(10B)	0.236(9)	0.095(7)	0.2647(9)	0.050(9)
H(11A)	0.089(9)	0.440(8)	0.2832(9)	0.053(10)
H(11B)	−0.092(9)	0.292(7)	0.2738(9)	0.053(10)
H(12A)	0.234(9)	0.251(7)	0.3175(9)	0.054(10)
H(12B)	0.062(9)	0.094(8)	0.3076(9)	0.054(10)
H(13A)	−0.075(8)	0.438(7)	0.3274(9)	0.046(9)
H(13B)	−0.264(9)	0.297(6)	0.3179(9)	0.046(9)
H(14A)	0.068(9)	0.244(8)	0.3609(10)	0.059(10)
H(14B)	−0.112(9)	0.092(8)	0.3515(10)	0.059(10)
H(15A)	−0.248(9)	0.449(8)	0.3718(10)	0.063(11)
H(15B)	−0.440(1)	0.299(7)	0.3627(10)	0.063(11)
H(16A)	−0.094(6)	0.249(5)	0.4054(7)	0.101(14)
H(16B)	−0.283(7)	0.088(4)	0.3951(7)	0.101(14)
H(16C)	−0.381(6)	0.281(5)	0.4070(7)	0.101(14)
H(17A)	0.774(9)	0.350(7)	0.0135(9)	0.045(4)
H(17B)	0.790(8)	0.138(7)	0.0121(9)	0.045(4)
H(17C)	0.993(8)	0.262(7)	0.0003(9)	0.045(4)
H(18A)	1.264(8)	0.403(7)	0.0587(9)	0.045(4)
H(18B)	1.071(8)	0.524(7)	0.0423(9)	0.045(4)
H(18C)	1.276(8)	0.411(7)	0.0291(9)	0.045(4)
H(19A)	1.045(9)	−0.021(7)	0.0402(9)	0.045(4)
H(19B)	1.259(8)	0.080(7)	0.0576(9)	0.045(4)
H(19C)	1.254(8)	0.078(7)	0.0268(9)	0.045(4)

Table S5c. Anisotropic displacement parameters for C_{16}TAB phase III at 22 °C. The anisotropic displacement factor exponent has the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11} / Å^2	U_{22} / Å^2	U_{33} / Å^2	U_{23} / Å^2	U_{13} / Å^2	U_{12} / Å^2
C(1)	0.0276(17)	0.047(2)	0.0328(18)	0.0041(19)	0.0066(14)	0.0124(19)
C(2)	0.042(2)	0.031(2)	0.0367(19)	0.0039(16)	0.0073(16)	0.0071(17)
C(3)	0.048(2)	0.062(4)	0.034(2)	0.002(2)	0.0098(17)	0.012(2)
C(4)	0.045(2)	0.068(3)	0.035(2)	0.006(2)	0.0091(17)	0.016(2)
C(5)	0.048(2)	0.046(3)	0.035(2)	0.0001(18)	0.0098(18)	0.005(2)
C(6)	0.047(2)	0.045(3)	0.036(2)	0.0010(18)	0.0113(17)	0.002(2)
C(7)	0.048(2)	0.049(3)	0.034(2)	0.0001(18)	0.0099(18)	0.003(2)
C(8)	0.049(2)	0.055(3)	0.035(2)	0.001(2)	0.0124(17)	0.006(2)
C(9)	0.047(2)	0.049(3)	0.034(2)	−0.0004(18)	0.0106(17)	0.002(2)
C(10)	0.050(2)	0.048(3)	0.037(2)	0.003(2)	0.0123(17)	0.005(2)
C(11)	0.046(2)	0.050(3)	0.035(2)	0.0021(18)	0.0091(18)	0.001(2)
C(12)	0.051(2)	0.043(3)	0.039(2)	0.0042(19)	0.0124(18)	0.005(2)
C(13)	0.050(3)	0.043(3)	0.038(2)	−0.0008(18)	0.0119(18)	0.002(2)
C(14)	0.057(3)	0.046(3)	0.041(2)	−0.001(2)	0.0126(19)	−0.006(2)
C(15)	0.064(3)	0.058(3)	0.050(3)	−0.004(2)	0.021(2)	−0.004(3)
C(16)	0.119(5)	0.076(5)	0.049(3)	−0.002(3)	0.036(3)	−0.017(4)
C(17)	0.042(2)	0.065(3)	0.0288(18)	−0.002(2)	0.0032(16)	0.017(2)
C(18)	0.045(3)	0.032(2)	0.047(3)	0.0027(18)	0.007(2)	0.002(19)
C(19)	0.029(2)	0.043(3)	0.054(3)	−0.0040(2)	0.0090(19)	0.0119(18)
N(1)	0.0267(13)	0.0374(16)	0.0297(14)	0.0053(14)	0.0059(11)	0.0063(14)
Br(1)	0.0376(3)	0.0392(3)	0.0762(3)	0.0022(3)	0.0109(2)	0.0073(2)

Table S5d. Selected bond lengths for C_{16}TAB phase III at 22 °C.

Atom — Atom	Length / Å	Atom — Atom	Length / Å
N(1) — C(1)	1.513(4)	C(10) — C(11)	1.520(6)
C(1) — C(2)	1.510(5)	C(11) — C(12)	1.523(6)
C(2) — C(3)	1.525(6)	C(12) — C(13)	1.514(6)
C(3) — C(4)	1.514(6)	C(13) — C(14)	1.527(6)
C(4) — C(5)	1.504(6)	C(14) — C(15)	1.514(7)
C(5) — C(6)	1.522(6)	C(15) — C(16)	1.526(8)
C(6) — C(7)	1.521(6)	C(17) — N(1)	1.500(5)
C(7) — C(8)	1.518(6)	C(18) — N(1)	1.500(6)
C(8) — C(9)	1.517(6)	C(19) — N(1)	1.495(5)
C(9) — C(10)	1.515(6)		

Table S5e. Selected bond angles for C_{16}TAB phase III at 22 °C.

Atom — Atom — Atom	Angle / ˚	Atom — Atom — Atom	Angle / ˚
N(1) — C(1) — C(2)	116.6(3)	C(11) — C(12) — C(13)	113.7(4)
C(1) — C(2) — C(3)	108.4(3)	C(12) — C(13) — C(14)	113.6(4)
C(2) — C(3) — C(4)	114.7(4)	C(13) — C(14) — C(15)	114.0(4)
C(3) — C(4) — C(5)	113.8(4)	C(14) — C(15) — C(16)	112.9(5)
C(4) — C(5) — C(6)	114.8(4)	C(17) — N(1) — C(1)	106.7(3)
C(5) — C(6) — C(7)	113.1(4)	C(17) — N(1) — C(18)	108.3(4)
C(6) — C(7) — C(8)	113.9(4)	C(18) — N(1) — C(1)	111.7(3)
C(7) — C(8) — C(9)	114.6(4)	C(19) — N(1) — C(1)	111.1(3)
C(8) — C(9) — C(10)	114.1(4)	C(19) — N(1) — C(17)	109.3(4)
C(9) — C(10) — C(11)	113.8(4)	C(19) — N(1) — C(18)	109.7(3)
C(10) — C(11) — C(12)	113.4(4)		

Table S5f. Selected torsion angles for C_{16}TAB phase III at 22 °C.

Atom — Atom — Atom — Atom	Angle / ˚	Atom — Atom — Atom — Atom	Angle / ˚
N(1) — C(1) — C(2) — C(3)	164.9(4)	C(9) — C(10) — C(11) — C(12)	179.1(4)
C(1) — C(2) — C(3) — C(4)	171.5(5)	C(10) — C(11) — C(12) — C(13)	178.8(4)
C(2) — C(3) — C(4) — C(5)	175.4(5)	C(11) — C(12) — C(13) — C(14)	−179.6(4)
C(3) — C(4) — C(5) — C(6)	171.5(5)	C(12) — C(13) — C(14) — C(15)	179.8(5)
C(4) — C(5) — C(6) — C(7)	178.2(4)	C(13) — C(14) — C(15) — C(16)	179.1(5)
C(5) — C(6) — C(7) — C(8)	177.5(4)	C(2) — C(1) — N(1) — C(17)	172.3(4)
C(6) — C(7) — C(8) — C(9)	−179.6(4)	C(2) — C(1) — N(1) — C(18)	−69.6(5)
C(7) — C(8) — C(9) — C(10)	178.8(5)	C(2) — C(1) — N(1) — C(19)	53.3(5)
C(8) — C(9) — C(10) — C(11)	179.1(4)		

Table S6a. Crystal data and structure refinement for C_{16}TAB phase II at 107 °C.

Identification code	xstr0370
Empirical formula	$C_{19}H_{42}BrN$
Formula weight	364.44
Temperature / K	380
Crystal system	monoclinic
Space group	$P2_1/m$
a / Å	5.66305(12)
b / Å	7.38058(17)
c / Å	26.2866(8)
α / °	90
β / °	90.711(2)
γ / °	90
Volume / Å^3	1098.60(5)
Z	2
ρ_{calc} / g cm^{-3}	1.102
μ / mm^{-1}	2.496
F(000)	396.0
Crystal size / mm^3	0.2982 × 0.1808 × 0.0503
Radiation	Cu Kα (λ = 1.54184 Å)
2θ range for data collection / °	6.726 to 146.724
Index ranges	$-7 \le h \le 6$, $-8 \le k \le 8$, $-32 \le l \le 32$
Reflections collected	15422
Independent reflections	2359 [R_{int} = 0.0286, R_{sigma} = 0.0146]
Data/restraints/parameters	2359/154/180
Goodness-of-fit on F^2	1.095
Final R indexes [$I \ge 2\sigma(I)$]	R_1 = 0.0424, wR_2 = 0.1219
Final R indexes [all data]	R_1 = 0.0456, wR_2 = 0.1261
Largest diff. peak/hole / e Å^{-3}	0.83/−0.45

Table S6b. Fractional atomic coordinates and equivalent isotropic displacement parameters for C_{16}TAB phase II at 107 °C. U_{eq} is defined as ⅓ of the trace of the orthogonalised U_{ij} tensor.

Atom	*x*	*y*	*z*	*U*(eq) / Å^2
C(1)	0.8099(6)	¼	0.11872(14)	0.0729(8)
C(2)	0.8922(8)	¼	0.17217(17)	0.0998(13)
C(3)	0.6962(10)	¼	0.20884(18)	0.1085(15)
C(4)	0.7438(11)	¼	0.26340(2)	0.122(19)
C(5)	0.5541(12)	¼	0.30000(2)	0.136(2)
C(6)	0.5868(12)	¼	0.35330(2)	0.127(2)
C(7)	0.4000(13)	¼	0.38980(2)	0.151(3)
C(8)	0.4185(13)	¼	0.44240(2)	0.135(2)
C(9)	0.2347(14)	¼	0.47900(3)	0.164(3)
C(10)	0.2507(14)	¼	0.53160(2)	0.140(2)
C(11)	0.0708(14)	¼	0.56860(2)	0.173(4)
C(12)	0.0847(15)	¼	0.62050(3)	0.141(2)
C(13)	−0.0924(17)	¼	0.65770(3)	0.194(5)
C(14)	−0.0783(16)	¼	0.70950(3)	0.152(3)
C(15)	−0.252(2)	¼	0.74790(3)	0.238(6)
C(16)	−0.239(2)	¼	0.79800(3)	0.210(5)
C(17)	0.8649(7)	¼	0.02838(14)	0.0849(10)
C(18)	1.1468(4)	0.4149(4)	0.08078(11)	0.0812(7)
N(1)	0.9949(4)	¼	0.07784(10)	0.0622(6)
Br(1)	0.62017(6)	¾	0.07066(2)	0.0843(2)
H(1)	0.7124(13)	0.356(3)	0.1127(18)	0.087
H(2)	0.9894(15)	0.356(4)	0.1782(2)	0.120
H(3)	0.6013(15)	0.356(4)	0.2009(2)	0.130
H(4)	0.8400(16)	0.356(4)	0.2705(3)	0.147
H(5)	0.4607(17)	0.356(4)	0.2913(3)	0.163
H(6)	0.6808(17)	0.356(4)	0.3616(3)	0.153
H(7)	0.3084(18)	0.356(4)	0.3804(3)	0.182
H(8)	0.5110(18)	0.356(4)	0.4515(3)	0.162
H(9)	0.1425(19)	0.356(4)	0.4698(3)	0.196
H(10)	0.3435(18)	0.356(4)	0.5404(3)	0.168
H(11)	−0.0211(19)	0.356(4)	0.5593(3)	0.208
H(12)	0.177(19)	0.356(4)	0.6296(3)	0.170
H(13)	−0.185(2)	0.356(4)	0.6486(3)	0.233
H(14)	0.015(2)	0.356(4)	0.7185(4)	0.182
H(15)	−0.342(2)	0.356(4)	0.7379(4)	0.286
H(16)	−0.156(3)	0.356(3)	0.8096(5)	0.315
H(16M)	−0.395(3)	¼	0.8118(7)	0.315
H(17)	0.7678(13)	0.356(3)	0.0260(4)	0.127

H(17M)	0.9761(19)	¼	0.0010(4)	0.127
H(18A)	1.0493	0.5212	0.0788	0.122
H(18B)	1.2554	0.4147	0.0530	0.122
H(18C)	1.2333	0.4151	0.1124	0.122

Table S6c. Anisotropic displacement parameters for C_{16}TAB phase II at 107 °C. The anisotropic displacement factor exponent has the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11} / Å^2	U_{22} / Å^2	U_{33} / Å^2	U_{23} / Å^2	U_{13} / Å^2	U_{12} / Å^2
C(1)	0.0559(16)	0.079(2)	0.0834(19)	0	0.0115(14)	0
C(2)	0.083(3)	0.133(4)	0.083(2)	0	0.0078(19)	0
C(3)	0.097(3)	0.142(4)	0.087(3)	0	0.016(2)	0
C(4)	0.105(4)	0.173(6)	0.090(3)	0	0.022(2)	0
C(5)	0.117(4)	0.202(7)	0.089(3)	0	0.025(3)	0
C(6)	0.123(4)	0.165(6)	0.094(3)	0	0.023(3)	0
C(7)	0.121(5)	0.236(10)	0.097(3)	0	0.028(3)	0
C(8)	0.135(5)	0.168(7)	0.103(3)	0	0.037(3)	0
C(9)	0.132(5)	0.260(11)	0.100(4)	0	0.030(3)	0
C(10)	0.143(5)	0.172(7)	0.107(4)	0	0.038(4)	0
C(11)	0.137(5)	0.280(14)	0.103(4)	0	0.036(4)	0
C(12)	0.150(6)	0.160(6)	0.114(4)	0	0.042(4)	0
C(13)	0.165(7)	0.308(14)	0.112(4)	0	0.053(5)	0
C(14)	0.185(8)	0.150(6)	0.121(4)	0	0.052(5)	0
C(15)	0.216(11)	0.378(19)	0.123(5)	0	0.073(6)	0
C(16)	0.292(14)	0.209(10)	0.132(6)	0	0.086(7)	0
C(17)	0.074(2)	0.103(3)	0.078(2)	0	−0.0017(16)	0
C(18)	0.0675(13)	0.0668(15)	0.1093(18)	0.0020(12)	0.0089(12)	−0.0103(11)
N(1)	0.0491(12)	0.0612(13)	0.0766(14)	0	0.0059(10)	0
Br(1)	0.0628(3)	0.0678(3)	0.1227(4)	0	0.01166(19)	0

Table S6d. Selected bond lengths for C_{16}TAB phase II at 107 °C.

Atom — Atom	Length / Å	Atom — Atom	Length / Å
N(1) — C(1)	1.510(4)	C(10) — C(11)	1.418(9)
C(1) — C(2)	1.475(6)	C(11) — C(12)	1.366(10)
C(2) — C(3)	1.479(7)	C(12) — C(13)	1.409(10)
C(3) — C(4)	1.456(8)	C(13) — C(14)	1.363(11)
C(4) — C(5)	1.451(8)	C(14) — C(15)	1.415(11)
C(5) — C(6)	1.412(9)	C(15) — C(16)	1.319(13)
C(6) — C(7)	1.437(9)	C(17) — N(1)	1.486(5)
C(7) — C(8)	1.385(9)	C(18) — N(1)	1.492(3)
C(8) — C(9)	1.426(9)	N(1) — C(18)[1]	1.492(3)
C(9) — C(10)	1.384(10)		

[1] $x, ½ - y, z$

Table S6e. Selected bond angles for C_{16}TAB phase II at 107 °C.

Atom — Atom — Atom	Angle / ˚	Atom — Atom — Atom	Angle / ˚
N(1) — C(1) — C(2)	117.7(3)	C(11) — C(12) — C(13)	131.4(9)
C(1) — C(2) — C(3)	113.0(4)	C(12) — C(13) — C(14)	131.3(10)
C(2) — C(3) — C(4)	120.7(5)	C(13) — C(14) — C(15)	132.8(10)
C(3) — C(4) — C(5)	121.6(5)	C(14) — C(15) — C(16)	133.0(12)
C(4) — C(5) — C(6)	124.7(6)	C(17) — N(1) — C(1)	106.4(2)
C(5) — C(6) — C(7)	125.1(6)	C(17) — N(1) — C(18)	108.92(18)
C(6) — C(7) — C(8)	128.3(7)	C(17) — N(1) — C(18)[1]	108.92(18)
C(7) — C(8) — C(9)	128.8(7)	C(18) — N(1) — C(1)	111.57(17)
C(8) — C(9) — C(10)	129.4(8)	C(18)[1] — N(1) — C(1)	111.57(17)
C(9) — C(10) — C(11)	130.3(8)	C(18)[1] — N(1) — C(18)	109.4(3)
C(10) — C(11) — C(12)	130.8(8)		

[1] $x, ½ - y, z$

Table S6f. Selected torsion angles for C_{16}TAB phase II at 107 °C.

Atom — Atom — Atom — Atom	Angle / ˚	Atom — Atom — Atom — Atom	Angle / ˚
N(1) — C(1) — C(2) — C(3)	180	C(9) — C(10) — C(11) — C(12)	180
C(1) — C(2) — C(3) — C(4)	180	C(10) — C(11) — C(12) — C(13)	180
C(2) — C(3) — C(4) — C(5)	180	C(11) — C(12) — C(13) — C(14)	180
C(3) — C(4) — C(5) — C(6)	180	C(12) — C(13) — C(14) — C(15)	180
C(4) — C(5) — C(6) — C(7)	180	C(13) — C(14) — C(15) — C(16)	180
C(5) — C(6) — C(7) — C(8)	180	C(2) — C(1) — N(1) — C(17)	180
C(6) — C(7) — C(8) — C(9)	180	C(2) — C(1) — N(1) — C(18)	−61.34(18)
C(7) — C(8) — C(9) — C(10)	180	C(2) — C(1) — N(1) — C(18)[1]	61.34(18)
C(8) — C(9) — C(10) — C(11)	180		

[1] $x, ½ - y, z$

Table S7a. Crystal data and structure refinement for C_{14}TAB-D_{29} phase III at −123 °C.

Identification code	xstr0624
Empirical formula	$C_{17}H_9D_{29}BrN$
Formula weight	365.57
Temperature / K	150
Crystal system	monoclinic
Space group	$P2_1/c$
a / Å	5.59767(14)
b / Å	7.1390(2)
c / Å	47.0946(13)
α / °	90
β / °	92.401(2)
γ / °	90
Volume / Å^3	1880.33(9)
Z	4
ρ_{calc} / g cm^{-3}	1.291
μ / mm^{-1}	2.877
F(000)	728.0
Crystal size / mm^3	0.129 × 0.116 × 0.008
Radiation	Cu Kα (λ = 1.54184 Å)
2θ range for data collection / °	7.516 to 152.93
Index ranges	−7 ≤ h ≤ 7, −8 ≤ k ≤ 8, −59 ≤ l ≤ 59
Reflections collected	28898
Independent reflections	3868 [R_{int} = 0.0558, R_{sigma} = 0.0300]
Data/restraints/parameters	3868/0/301
Goodness-of-fit on F^2	1.019
Final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0409, wR_2 = 0.0966
Final R indexes [all data]	R_1 = 0.0520, wR_2 = 0.1056
Largest diff. peak/hole / e Å^{-3}	0.41/−0.46

Table S7b. Fractional atomic coordinates and equivalent isotropic displacement parameters for C_{14}TAB-D_{29} phase III at −123 °C. U_{eq} is defined as ⅓ of the trace of the orthogonalised U_{ij} tensor.

Atom	*x*	*y*	*z*	*U*(eq) / Å^2
C(1)	0.8054(3)	0.2542(3)	0.0650(4)	0.0184(4)
C(2)	0.8863(4)	0.2225(3)	0.0959(4)	0.0243(4)
C(3)	0.6813(4)	0.2786(3)	0.1146(4)	0.0271(5)
C(4)	0.7191(4)	0.2232(3)	0.1457(4)	0.0248(4)
C(5)	0.5230(4)	0.3006(3)	0.1639(4)	0.0250(4)
C(6)	0.5348(4)	0.2262(3)	0.1944(4)	0.0240(4)
C(7)	0.3401(4)	0.3085(4)	0.2125(4)	0.0238(4)
C(8)	0.3438(4)	0.2267(3)	0.2425(4)	0.0237(4)
C(9)	0.1509(4)	0.3102(3)	0.2607(4)	0.0244(4)
C(10)	0.1517(4)	0.2262(3)	0.2907(4)	0.0244(4)
C(11)	−0.0388(4)	0.3116(3)	0.3091(4)	0.0248(4)
C(12)	−0.0366(4)	0.2267(3)	0.3390(4)	0.0264(4)
C(13)	−0.2256(4)	0.3108(4)	0.3577(4)	0.0307(5)
C(14)	−0.2223(6)	0.2229(4)	0.3872(5)	0.0420(7)
C(15)	0.8752(4)	0.2562(3)	0.0148(4)	0.0244(4)
C(16)	1.1591(4)	0.4177(3)	0.0468(4)	0.0224(4)
C(17)	1.1463(4)	0.0754(3)	0.0463(4)	0.0229(4)
N(1)	0.9994(3)	0.2498(2)	0.0436(3)	0.0174(3)
Br(1)	0.62014(3)	0.75214(3)	0.03967(2)	0.02713(11)
D(1A)	0.732(4)	0.367(4)	0.0624(5)	0.017(4)
D(1B)	0.697(4)	0.150(4)	0.0590(5)	0.017(4)
D(2A)	1.033(5)	0.297(4)	0.1010(6)	0.030(5)
D(2B)	0.933(5)	0.084(4)	0.0991(5)	0.030(5)
D(3A)	0.666(5)	0.420(4)	0.1139(6)	0.033(5)
D(3B)	0.544(6)	0.225(4)	0.1075(7)	0.033(5)
D(4A)	0.868(6)	0.271(4)	0.1523(6)	0.028(5)
D(4B)	0.727(5)	0.085(4)	0.1476(5)	0.028(5)
D(5A)	0.533(5)	0.438(4)	0.1647(6)	0.030(5)
D(5B)	0.373(6)	0.272(4)	0.1553(6)	0.030(5)
D(6A)	0.693(5)	0.257(3)	0.2038(6)	0.023(4)
D(6B)	0.520(5)	0.089(4)	0.1943(5)	0.023(4)
D(7A)	0.359(5)	0.440(5)	0.2135(5)	0.029(5)
D(7B)	0.182(6)	0.282(4)	0.2030(6)	0.029(5)
D(8A)	0.496(6)	0.247(3)	0.2511(6)	0.023(4)
D(8B)	0.320(5)	0.090(4)	0.2413(5)	0.023(4)
D(9A)	0.167(5)	0.446(4)	0.2611(6)	0.029(5)
D(9B)	−0.003(6)	0.286(4)	0.2516(6)	0.029(5)
D(10A)	0.306(6)	0.251(4)	0.2999(6)	0.030(5)

D(10B)	0.125(5)	0.089(5)	0.2896(5)	0.030(5)
D(11A)	−0.016(5)	0.448(4)	0.3107(6)	0.029(5)
D(11B)	−0.199(5)	0.295(4)	0.2994(6)	0.029(5)
D(12A)	0.120(6)	0.246(4)	0.3478(6)	0.027(5)
D(12B)	−0.069(5)	0.095(4)	0.3368(5)	0.027(5)
D(13A)	−0.208(5)	0.448(5)	0.3593(6)	0.035(5)
D(13B)	−0.381(6)	0.292(4)	0.3487(6)	0.035(5)
D(14A)	−0.067(8)	0.243(4)	0.3975(9)	0.053(6)
D(14B)	−0.248(7)	0.093(6)	0.3855(7)	0.053(6)
D(14C)	−0.349(7)	0.283(5)	0.3988(8)	0.053(6)
H(15A)	0.776(5)	0.364(4)	0.0134(5)	0.028(2)
H(15B)	0.789(5)	0.152(4)	0.0129(6)	0.028(2)
H(15C)	1.000(6)	0.258(4)	0.0009(7)	0.028(2)
H(16A)	1.242(5)	0.416(4)	0.0648(6)	0.028(2)
H(16B)	1.067(5)	0.527(4)	0.0455(5)	0.028(2)
H(16C)	1.271(5)	0.414(4)	0.0319(6)	0.028(2)
H(17A)	1.047(5)	−0.035(4)	0.0455(5)	0.028(2)
H(17B)	1.246(5)	0.079(4)	0.0644(6)	0.028(2)
H(17C)	1.254(5)	0.073(4)	0.0309(6)	0.028(2)

Table S7c. Anisotropic displacement parameters for C_{14}TAB-D_{29} phase III at −123 °C. The anisotropic displacement factor exponent has the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11} / Å^2	U_{22} / Å^2	U_{33} / Å^2	U_{23} / Å^2	U_{13} / Å^2	U_{12} / Å^2
C(1)	0.0145(8)	0.0218(10)	0.0190(8)	0.0004(6)	0.0031(6)	0.0046(7)
C(2)	0.0230(10)	0.0303(12)	0.0196(8)	0.0024(7)	0.0020(7)	0.0038(8)
C(3)	0.0257(11)	0.0352(13)	0.0206(8)	0.0028(8)	0.0047(7)	0.0066(9)
C(4)	0.0238(10)	0.0300(12)	0.0209(8)	0.0023(7)	0.0033(7)	0.0028(8)
C(5)	0.0274(11)	0.0274(12)	0.0205(8)	0.0011(7)	0.0042(7)	0.0040(8)
C(6)	0.0263(11)	0.0252(12)	0.0209(8)	0.0017(7)	0.0051(7)	0.0023(8)
C(7)	0.0272(10)	0.0240(11)	0.0205(8)	0.0002(7)	0.0044(7)	0.0009(9)
C(8)	0.0256(10)	0.0249(12)	0.0208(8)	0.0017(7)	0.0046(7)	0.0027(8)
C(9)	0.0265(10)	0.0252(11)	0.0219(8)	0.0012(7)	0.0049(7)	0.0007(8)
C(10)	0.0268(10)	0.0243(13)	0.0226(9)	0.0012(7)	0.0051(7)	0.0012(8)
C(11)	0.0278(11)	0.0234(11)	0.0234(9)	−0.0002(7)	0.0044(7)	−0.0001(8)
C(12)	0.0314(12)	0.0244(12)	0.0239(9)	0.0008(7)	0.0065(8)	0.0004(8)
C(13)	0.0345(12)	0.0321(13)	0.0262(9)	−0.0021(8)	0.0089(8)	−0.0024(10)
C(14)	0.0589(18)	0.0422(17)	0.0258(10)	−0.0006(9)	0.0133(11)	−0.0096(13)
C(15)	0.0226(10)	0.0327(12)	0.0179(8)	−0.0015(7)	−0.0004(7)	−0.0001(9)
C(16)	0.0191(9)	0.0194(10)	0.0287(9)	0.0010(7)	0.0030(7)	−0.0035(8)
C(17)	0.0208(9)	0.0180(10)	0.0302(9)	−0.0020(7)	0.0046(7)	0.0022(8)
N(1)	0.0160(7)	0.0180(8)	0.0183(7)	−0.0007(5)	0.0029(5)	0.0005(6)
Br(1)	0.01942(16)	0.01832(16)	0.04385(16)	0.00067(8)	0.00378(9)	0.00046(8)

Table S7d. Selected bond lengths for C_{14}TAB-D_{29} phase III at −123 °C.

Atom — Atom	Length / Å	Atom — Atom	Length / Å
N(1) — C(1)	1.512(2)	C(9) — C(10)	1.532(3)
C(1) — C(2)	1.523(2)	C(10) — C(11)	1.529(3)
C(2) — C(3)	1.527(3)	C(11) — C(12)	1.532(3)
C(3) — C(4)	1.527(2)	C(12) — C(13)	1.528(3)
C(4) — C(5)	1.525(3)	C(13) — C(14)	1.525(3)
C(5) — C(6)	1.529(3)	C(15) — N(1)	1.500(2)
C(6) — C(7)	1.529(3)	C(16) — N(1)	1.499(3)
C(7) — C(8)	1.529(3)	C(17) — N(1)	1.495(3)
C(8) — C(9)	1.527(3)		

Table S7e. Selected bond angles for $C_{14}TAB\text{-}D_{29}$ phase III at −123 °C.

Atom — Atom — Atom	Angle / ˚	Atom — Atom — Atom	Angle / ˚
N(1) — C(1) — C(2)	116.16(15)	C(10) — C(11) — C(12)	112.59(18)
C(1) — C(2) — C(3)	108.07(16)	C(11) — C(12) — C(13)	113.26(19)
C(2) — C(3) — C(4)	114.05(17)	C(12) — C(13) — C(14)	112.4(2)
C(3) — C(4) — C(5)	111.86(17)	C(15) — N(1) — C(1)	106.51(14)
C(4) — C(5) — C(6)	113.43(18)	C(16) — N(1) — C(1)	111.03(14)
C(5) — C(6) — C(7)	112.71(18)	C(16) — N(1) — C(15)	108.56(15)
C(6) — C(7) — C(8)	112.75(18)	C(17) — N(1) — C(1)	111.70(14)
C(7) — C(8) — C(9)	112.80(18)	C(17) — N(1) — C(15)	109.45(15)
C(8) — C(9) — C(10)	112.89(19)	C(17) — N(1) — C(16)	109.50(15)
C(9) — C(10) — C(11)	113.01(19)		

Table S7f. Selected torsion angles for $C_{14}TAB\text{-}D_{29}$ phase III at −123 °C.

Atom — Atom — Atom — Atom	Angle / ˚	Atom — Atom — Atom — Atom	Angle / ˚
N(1) — C(1) — C(2) — C(3)	166.42(17)	C(8) — C(9) — C(10) — C(11)	179.14(19)
C(1) — C(2) — C(3) — C(4)	169.96(19)	C(9) — C(10) — C(11) — C(12)	179.96(19)
C(2) — C(3) — C(4) — C(5)	173.8(2)	C(10) — C(11) — C(12) — C(13)	179.9(2)
C(3) — C(4) — C(5) — C(6)	172.0(2)	C(11) — C(12) — C(13) — C(14)	179.4(2)
C(4) — C(5) — C(6) — C(7)	178.79(19)	C(2) — C(1) — N(1) — C(15)	172.02(18)
C(5) — C(6) — C(7) — C(8)	177.07(19)	C(2) — C(1) — N(1) — C(16)	−70.0(2)
C(6) — C(7) — C(8) — C(9)	179.44(19)	C(2) — C(1) — N(1) — C(17)	52.6(2)
C(7) — C(8) — C(9) — C(10)	179.09(19)		

Table S8a. Crystal data and structure refinement for C_{14}TAB phase III at −123 °C.

Identification code	xstr0252_exp_643
Empirical formula	$C_{17}H_{38}BrN$
Formula weight	336.39
Temperature / K	150
Crystal system	monoclinic
Space group	$P2_1/c$
a / Å	5.59763(9)
b / Å	7.15024(11)
c / Å	47.1556(8)
α / °	90
β / °	92.3068(14)
γ / °	90
Volume / Å^3	1885.84(5)
Z	4
ρ_{calc} / g cm^{-3}	1.185
μ / mm^{-1}	2.869
F(000)	728.0
Crystal size / mm^3	0.3599 × 0.1925 × 0.02
Radiation	Cu Kα (λ = 1.54184 Å)
2θ range for data collection / °	7.506 to 146.594
Index ranges	−6 ≤ h ≤ 6, −8 ≤ k ≤ 8, −58 ≤ l ≤ 58
Reflections collected	24241
Independent reflections	3717 [R_{int} = 0.0508, R_{sigma} = 0.0244]
Data/restraints/parameters	3717/0/301
Goodness-of-fit on F^2	1.303
Final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0539, wR_2 = 0.1128
Final R indexes [all data]	R_1 = 0.0587, wR_2 = 0.1152
Largest diff. peak/hole / e Å^{-3}	0.73/−0.40

Table S8b. Fractional atomic coordinates and equivalent isotropic displacement parameters for C_{14}TAB phase III at −123 °C. U_{eq} is defined as ⅓ of the trace of the orthogonalised U_{ij} tensor.

Atom	*x*	*y*	*z*	*U*(eq) / Å^2
C(1)	0.8046(5)	0.2535(5)	0.06502(6)	0.0178(6)
C(2)	0.8842(6)	0.2189(4)	0.09576(6)	0.0182(6)
C(3)	0.6811(6)	0.2802(5)	0.11449(6)	0.0223(7)
C(4)	0.7171(6)	0.2241(5)	0.14567(6)	0.0245(7)
C(5)	0.5233(6)	0.3002(5)	0.16396(6)	0.0212(7)
C(6)	0.5349(6)	0.2272(5)	0.19431(6)	0.0222(6)
C(7)	0.3404(6)	0.3074(5)	0.21251(6)	0.0211(6)
C(8)	0.3436(6)	0.2264(5)	0.24251(6)	0.0213(6)
C(9)	0.1504(6)	0.3097(5)	0.26080(6)	0.0217(7)
C(10)	0.1519(6)	0.2257(5)	0.29060(6)	0.0209(6)
C(11)	−0.0366(6)	0.3104(5)	0.30906(6)	0.0220(7)
C(12)	−0.0383(6)	0.2262(5)	0.33887(7)	0.0233(7)
C(13)	−0.2247(7)	0.3107(5)	0.35761(7)	0.0273(7)
C(14)	−0.2194(9)	0.2232(7)	0.38717(8)	0.0414(10)
C(15)	0.8751(6)	0.2568(5)	0.01476(6)	0.0224(6)
C(16)	1.1618(6)	0.4180(5)	0.04686(7)	0.0214(7)
C(17)	1.1429(6)	0.0755(5)	0.04595(7)	0.0211(7)
N(1)	0.9985(4)	0.2506(4)	0.04360(5)	0.0159(5)
Br(1)	0.61999(5)	0.75232(5)	0.03967(2)	0.02684(13)
H(1A)	0.733(6)	0.379(5)	0.0625(7)	0.018(6)
H(1B)	0.697(6)	0.155(5)	0.0591(7)	0.018(6)
H(2A)	1.028(7)	0.298(5)	0.1001(8)	0.022(7)
H(2B)	0.934(7)	0.089(6)	0.0986(7)	0.022(7)
H(3A)	0.662(7)	0.420(6)	0.1131(8)	0.023(7)
H(3B)	0.542(7)	0.216(5)	0.1079(8)	0.023(7)
H(4A)	0.870(8)	0.243(6)	0.1526(9)	0.034(8)
H(4B)	0.728(8)	0.084(6)	0.1472(8)	0.034(8)
H(5A)	0.532(7)	0.434(6)	0.1642(8)	0.027(7)
H(5B)	0.369(7)	0.265(6)	0.1555(8)	0.027(7)
H(6A)	0.695(7)	0.260(6)	0.2030(8)	0.028(7)
H(6B)	0.523(7)	0.092(6)	0.1938(8)	0.028(7)
H(7A)	0.356(7)	0.444(6)	0.2135(8)	0.027(7)
H(7B)	0.185(7)	0.287(6)	0.2035(8)	0.027(7)
H(8A)	0.503(7)	0.248(5)	0.2517(8)	0.020(6)
H(8B)	0.318(7)	0.090(5)	0.2416(7)	0.020(6)
H(9A)	0.171(7)	0.446(6)	0.2617(8)	0.023(7)
H(9B)	−0.005(8)	0.292(5)	0.2521(8)	0.023(7)
H(10A)	0.308(7)	0.249(6)	0.2995(8)	0.022(7)

H(10B)	0.135(6)	0.089(6)	0.2896(7)	0.022(7)
H(11A)	−0.015(7)	0.449(6)	0.3103(8)	0.028(7)
H(11B)	−0.199(7)	0.293(6)	0.2999(8)	0.028(7)
H(12A)	0.124(7)	0.234(6)	0.3482(8)	0.031(7)
H(12B)	−0.054(7)	0.092(6)	0.3374(8)	0.031(7)
H(13A)	−0.200(7)	0.446(6)	0.3595(8)	0.030(7)
H(13B)	−0.376(8)	0.298(6)	0.3488(8)	0.030(7)
H(14A)	−0.063(9)	0.248(7)	0.3976(10)	0.050(8)
H(14B)	−0.257(9)	0.092(8)	0.3855(10)	0.050(8)
H(14C)	−0.336(9)	0.285(7)	0.3974(10)	0.050(8)
H(15A)	0.771(7)	0.364(6)	0.0144(8)	0.023(3)
H(15B)	0.785(7)	0.144(6)	0.0128(8)	0.023(3)
H(15C)	1.001(7)	0.259(5)	0.0007(8)	0.023(3)
H(16A)	1.240(7)	0.415(5)	0.0652(8)	0.023(3)
H(16B)	1.056(7)	0.524(6)	0.0452(8)	0.023(3)
H(16C)	1.252(7)	0.413(6)	0.0319(8)	0.023(3)
H(17A)	1.044(7)	−0.041(6)	0.0448(8)	0.023(3)
H(17B)	1.241(7)	0.080(5)	0.0633(8)	0.023(3)
H(17C)	1.258(7)	0.072(5)	0.0311(8)	0.023(3)

Table S8c. Anisotropic displacement parameters for C_{14}TAB phase III at −123 °C. The anisotropic displacement factor exponent has the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11} / Å^2	U_{22} / Å^2	U_{33} / Å^2	U_{23} / Å^2	U_{13} / Å^2	U_{12} / Å^2
C(1)	0.0141(13)	0.0207(15)	0.0190(13)	0.0006(12)	0.0043(10)	−0.0020(14)
C(2)	0.0195(15)	0.0131(15)	0.0220(14)	0.0027(11)	0.0026(11)	0.0067(12)
C(3)	0.0222(16)	0.0243(17)	0.0208(14)	0.0000(12)	0.0041(12)	0.0040(14)
C(4)	0.0218(16)	0.0323(19)	0.0197(14)	−0.0002(13)	0.0041(12)	0.0033(15)
C(5)	0.0207(16)	0.0227(17)	0.0204(14)	0.0005(12)	0.0026(12)	0.0024(13)
C(6)	0.0222(16)	0.0245(17)	0.0203(14)	0.0013(12)	0.0046(11)	0.0004(14)
C(7)	0.0197(16)	0.0238(17)	0.0201(14)	0.0006(12)	0.0029(12)	0.0004(12)
C(8)	0.0232(16)	0.0205(16)	0.0205(14)	−0.0002(12)	0.0050(11)	0.0007(14)
C(9)	0.0214(16)	0.0236(17)	0.0203(14)	0.0000(12)	0.0039(12)	0.0012(13)
C(10)	0.0225(16)	0.0182(17)	0.0223(14)	0.0022(11)	0.0043(12)	0.0028(13)
C(11)	0.0254(17)	0.0211(16)	0.0197(14)	0.0020(12)	0.0046(12)	0.0000(13)
C(12)	0.0286(17)	0.0182(16)	0.0236(15)	0.0034(12)	0.0066(12)	0.0056(14)
C(13)	0.0283(19)	0.0273(18)	0.0268(16)	−0.0030(13)	0.0085(14)	−0.0019(14)
C(14)	0.055(3)	0.044(3)	0.0263(18)	−0.0039(17)	0.0149(17)	−0.015(2)
C(15)	0.0215(15)	0.0288(17)	0.0167(13)	−0.0015(13)	0.0001(11)	0.0006(16)
C(16)	0.0188(17)	0.0167(15)	0.0289(17)	0.0000(12)	0.0030(13)	−0.0024(13)
C(17)	0.0156(16)	0.0202(16)	0.0277(16)	−0.0034(12)	0.0036(13)	0.0038(13)
N(1)	0.0146(11)	0.0156(12)	0.0177(11)	−0.0004(10)	0.0026(9)	0.0041(11)
Br(1)	0.01817(19)	0.01797(19)	0.0446(2)	0.00079(15)	0.00421(13)	0.00155(16)

Table S8d. Selected bond lengths for C_{14}TAB phase III at −123 °C.

Atom — Atom	Length / Å	Atom — Atom	Length / Å
N(1) — C(1)	1.512(3)	C(9) — C(10)	1.528(4)
C(1) — C(2)	1.519(4)	C(10) — C(11)	1.521(4)
C(2) — C(3)	1.531(4)	C(11) — C(12)	1.530(4)
C(3) — C(4)	1.530(4)	C(12) — C(13)	1.520(5)
C(4) — C(5)	1.514(4)	C(13) — C(14)	1.527(5)
C(5) — C(6)	1.522(4)	C(15) — N(1)	1.501(4)
C(6) — C(7)	1.525(4)	C(16) — N(1)	1.510(4)
C(7) — C(8)	1.528(4)	C(17) — N(1)	1.492(4)
C(8) — C(9)	1.531(4)		

Table S8e. Selected bond angles for C_{14}TAB phase III at −123 °C.

Atom — Atom — Atom	Angle / ˚	Atom — Atom — Atom	Angle / ˚
N(1) — C(1) — C(2)	116.4(2)	C(10) — C(11) — C(12)	113.5(3)
C(1) — C(2) — C(3)	107.9(2)	C(11) — C(12) — C(13)	114.1(3)
C(2) — C(3) — C(4)	114.0(3)	C(12) — C(13) — C(14)	112.3(3)
C(3) — C(4) — C(5)	112.5(3)	C(15) — N(1) — C(1)	106.8(2)
C(4) — C(5) — C(6)	114.1(3)	C(15) — N(1) — C(16)	108.9(2)
C(5) — C(6) — C(7)	113.3(3)	C(16) — N(1) — C(1)	111.7(2)
C(6) — C(7) — C(8)	113.3(3)	C(17) — N(1) — C(1)	111.3(2)
C(7) — C(8) — C(9)	113.1(3)	C(17) — N(1) — C(15)	108.7(2)
C(8) — C(9) — C(10)	112.8(3)	C(17) — N(1) — C(16)	109.5(2)
C(9) — C(10) — C(11)	113.1(3)		

Table S8f. Selected torsion angles for C_{14}TAB phase III at −123 °C.

Atom — Atom — Atom — Atom	Angle / ˚	Atom — Atom — Atom — Atom	Angle / ˚
N(1) — C(1) — C(2) — C(3)	164.6(3)	C(8) — C(9) — C(10) — C(11)	179.0(3)
C(1) — C(2) — C(3) — C(4)	170.3(3)	C(9) — C(10) — C(11) — C(12)	179.5(3)
C(2) — C(3) — C(4) — C(5)	175.4(3)	C(10) — C(11) — C(12) — C(13)	179.6(3)
C(3) — C(4) — C(5) — C(6)	172.6(3)	C(11) — C(12) — C(13) — C(14)	−179.8(3)
C(4) — C(5) — C(6) — C(7)	179.2(3)	C(2) — C(1) — N(1) — C(15)	171.1(3)
C(5) — C(6) — C(7) — C(8)	176.9(3)	C(2) — C(1) — N(1) — C(16)	−70.0(3)
C(6) — C(7) — C(8) — C(9)	179.1(3)	C(2) — C(1) — N(1) — C(17)	52.7(4)
C(7) — C(8) — C(9) — C(10)	179.0(3)		

Table S9a. Crystal data and structure refinement for C_{14}TAB phase III at 22 °C.

Identification code	exp_644
Empirical formula	$C_{17}H_{38}BrN$
Formula weight	336.39
Temperature / K	295
Crystal system	monoclinic
Space group	$P2_1/c$
a / Å	5.63696(10)
b / Å	7.25318(13)
c / Å	47.4290(10)
α / °	90
β / °	91.0732(17)
γ / °	90
Volume / Å^3	1938.84(6)
Z	4
ρ_{calc} / g cm^{-3}	1.152
μ / mm^{-1}	2.791
F(000)	728.0
Crystal size / mm^3	0.3531 × 0.1939 × 0.02
Radiation	Cu Kα (λ = 1.54184 Å)
2θ range for data collection / °	7.456 to 146.602
Index ranges	−6 ≤ h ≤ 7, −9 ≤ k ≤ 9, −58 ≤ l ≤ 58
Reflections collected	25108
Independent reflections	3835 [R_{int} = 0.0497, R_{sigma} = 0.0250]
Data/restraints/parameters	3835/0/301
Goodness-of-fit on F^2	1.205
Final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0561, wR_2 = 0.1284
Final R indexes [all data]	R_1 = 0.0663, wR_2 = 0.1342
Largest diff. peak/hole / e Å^{-3}	0.93/−0.49

Table S9b. Fractional atomic coordinates and equivalent isotropic displacement parameters for C_{14}TAB phase III at 22 °C. U_{eq} is defined as ⅓ of the trace of the orthogonalised U_{ij} tensor.

Atom	x	y	z	U(eq) / Å^2
C(1)	0.7997(5)	0.2528(5)	0.06502(6)	0.0388(6)
C(2)	0.8772(6)	0.2223(5)	0.09529(7)	0.0440(7)
C(3)	0.6741(7)	0.2763(7)	0.11438(7)	0.0540(9)
C(4)	0.7115(7)	0.2289(7)	0.14520(7)	0.0542(9)
C(5)	0.5176(7)	0.2983(6)	0.16391(8)	0.0511(9)
C(6)	0.5319(7)	0.2312(6)	0.19406(7)	0.0511(8)
C(7)	0.3399(8)	0.3067(6)	0.21260(8)	0.0512(9)
C(8)	0.3428(7)	0.2319(6)	0.24246(8)	0.0517(8)
C(9)	0.1524(8)	0.3097(6)	0.26109(8)	0.0519(9)
C(10)	0.1533(7)	0.2289(6)	0.29061(7)	0.0504(8)
C(11)	−0.0342(8)	0.3098(6)	0.30952(8)	0.0521(9)
C(12)	−0.0343(8)	0.2293(6)	0.33911(8)	0.0548(9)
C(13)	−0.2189(9)	0.3086(7)	0.35823(9)	0.0627(11)
C(14)	−0.2141(14)	0.2277(10)	0.38740(11)	0.0925(19)
C(15)	0.8706(7)	0.2563(7)	0.01502(7)	0.0500(8)
C(16)	1.1524(7)	0.4159(5)	0.04609(8)	0.0468(8)
C(17)	1.1370(7)	0.0793(5)	0.04542(8)	0.0464(8)
N(1)	0.9922(4)	0.2508(4)	0.04331(5)	0.0352(5)
Br(1)	0.61573(6)	0.75147(5)	0.03947(2)	0.05454(16)
H(1A)	0.715(7)	0.378(6)	0.0617(8)	0.045(7)
H(1B)	0.696(7)	0.164(6)	0.0591(8)	0.045(7)
H(2A)	1.006(8)	0.311(6)	0.0989(9)	0.059(9)
H(2B)	0.919(8)	0.082(6)	0.0985(8)	0.059(9)
H(3A)	0.655(9)	0.422(7)	0.1127(10)	0.073(10)
H(3B)	0.536(9)	0.218(7)	0.1081(10)	0.073(10)
H(4A)	0.866(9)	0.265(7)	0.1536(10)	0.074(10)
H(4B)	0.728(9)	0.088(7)	0.1473(10)	0.074(10)
H(5A)	0.524(8)	0.436(7)	0.1631(9)	0.064(9)
H(5B)	0.366(9)	0.272(6)	0.1560(10)	0.064(9)
H(6A)	0.691(8)	0.262(6)	0.2023(9)	0.058(8)
H(6B)	0.516(8)	0.097(7)	0.1936(9)	0.058(8)
H(7A)	0.363(7)	0.442(7)	0.2136(8)	0.060(9)
H(7B)	0.185(8)	0.287(6)	0.2041(9)	0.060(9)
H(8A)	0.503(8)	0.246(6)	0.2519(9)	0.057(8)
H(8B)	0.324(8)	0.096(6)	0.2415(9)	0.057(8)
H(9A)	0.167(8)	0.452(7)	0.2615(9)	0.061(9)
H(9B)	−0.006(9)	0.290(6)	0.2528(9)	0.061(9)
H(10A)	0.307(8)	0.261(6)	0.2996(9)	0.061(9)
H(10B)	0.141(7)	0.088(7)	0.2904(8)	0.061(9)

H(11A)	−0.007(8)	0.450(7)	0.3104(9)	0.066(9)
H(11B)	−0.196(9)	0.294(6)	0.2998(9)	0.066(9)
H(12A)	0.133(9)	0.244(7)	0.3494(10)	0.074(10)
H(12B)	−0.055(9)	0.092(7)	0.3379(10)	0.074(10)
H(13A)	−0.206(9)	0.451(8)	0.3583(10)	0.079(11)
H(13B)	−0.388(10)	0.291(7)	0.3494(11)	0.079(11)
H(14A)	−0.058(11)	0.259(8)	0.3979(12)	0.091(10)
H(14B)	−0.334(10)	0.294(8)	0.3983(12)	0.091(10)
H(14C)	−0.242(10)	0.095(8)	0.3865(11)	0.091(10)
H(15A)	0.765(7)	0.361(6)	0.0137(8)	0.052(3)
H(15B)	0.783(7)	0.146(6)	0.0130(8)	0.052(3)
H(15C)	0.995(8)	0.262(5)	0.0004(9)	0.052(3)
H(16A)	1.238(7)	0.405(6)	0.0655(9)	0.052(3)
H(16B)	1.053(7)	0.521(6)	0.0459(8)	0.052(3)
H(16C)	1.262(7)	0.411(6)	0.0313(8)	0.052(3)
H(17A)	1.035(7)	−0.031(6)	0.0445(8)	0.052(3)
H(17B)	1.239(7)	0.086(6)	0.0635(9)	0.052(3)
H(17C)	1.247(7)	0.075(6)	0.0300(8)	0.052(3)

Table S9c. Anisotropic displacement parameters for C_{14}TAB phase III at 22 °C. The anisotropic displacement factor exponent has the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11} / Å^2	U_{22} / Å^2	U_{33} / Å^2	U_{23} / Å^2	U_{13} / Å^2	U_{12} / Å^2
C(1)	0.0307(14)	0.0470(17)	0.0389(14)	0.0016(14)	0.0062(11)	0.0056(15)
C(2)	0.0412(17)	0.0470(2)	0.0441(16)	0.0057(14)	0.0054(13)	0.0082(15)
C(3)	0.0510(2)	0.0700(3)	0.0406(17)	0.0016(17)	0.0098(14)	0.0110(2)
C(4)	0.0490(2)	0.0720(3)	0.0421(17)	0.0050(17)	0.0096(14)	0.0090(2)
C(5)	0.0500(2)	0.0610(2)	0.0430(17)	0.0012(16)	0.0092(15)	0.0072(17)
C(6)	0.0510(2)	0.0590(2)	0.0436(17)	0.0003(16)	0.0098(14)	0.0014(19)
C(7)	0.0510(2)	0.0580(2)	0.0448(18)	−0.0008(15)	0.0084(15)	0.0040(17)
C(8)	0.0540(2)	0.0580(2)	0.0439(17)	0.0008(16)	0.0113(15)	0.0039(19)
C(9)	0.0520(2)	0.0590(2)	0.0447(18)	−0.0001(16)	0.0098(15)	0.0025(18)
C(10)	0.0530(2)	0.0520(2)	0.0467(18)	0.0032(15)	0.0109(15)	0.0033(18)
C(11)	0.0530(2)	0.0540(2)	0.0494(19)	0.0001(16)	0.0117(16)	0.0008(17)
C(12)	0.0640(2)	0.0520(2)	0.0486(18)	0.0016(17)	0.0131(16)	0.0010(2)
C(13)	0.0690(3)	0.0590(3)	0.0600(2)	−0.0052(19)	0.0200(2)	−0.0040(2)
C(14)	0.1260(5)	0.0970(4)	0.0560(3)	−0.0090(3)	0.0340(3)	−0.0360(4)
C(15)	0.0476(19)	0.0660(2)	0.0361(15)	−0.0013(16)	0.0016(13)	0.0080(2)
C(16)	0.0410(2)	0.0401(18)	0.0600(2)	0.0021(15)	0.0063(16)	−0.0044(15)
C(17)	0.0366(19)	0.0431(19)	0.0600(2)	−0.0040(15)	0.0070(16)	0.0079(15)
N(1)	0.0304(11)	0.0370(13)	0.0383(12)	0.0009(11)	0.0046(9)	0.0055(11)
Br(1)	0.0394(2)	0.0417(2)	0.0828(3)	0.00181(19)	0.00825(16)	0.00374(18)

Table S9d. Selected bond lengths for C_{14}TAB phase III at 22 °C.

Atom — Atom	Length / Å	Atom — Atom	Length / Å
N(1) — C(1)	1.510(4)	C(9) — C(10)	1.518(5)
C(1) — C(2)	1.509(4)	C(10) — C(11)	1.517(5)
C(2) — C(3)	1.524(5)	C(11) — C(12)	1.520(5)
C(3) — C(4)	1.512(5)	C(12) — C(13)	1.507(6)
C(4) — C(5)	1.507(5)	C(13) — C(14)	1.503(7)
C(5) — C(6)	1.511(5)	C(15) — N(1)	1.496(4)
C(6) — C(7)	1.510(5)	C(16) — N(1)	1.504(4)
C(7) — C(8)	1.516(5)	C(17) — N(1)	1.490(4)
C(8) — C(9)	1.512(5)		

Table S9e. Selected bond angles for C_{14}TAB phase III at 22 °C.

Atom — Atom — Atom	Angle / ˚	Atom — Atom — Atom	Angle / ˚
N(1) — C(1) — C(2)	116.6(3)	C(10) — C(11) — C(12)	114.2(3)
C(1) — C(2) — C(3)	108.7(3)	C(11) — C(12) — C(13)	114.9(4)
C(2) — C(3) — C(4)	115.0(3)	C(12) — C(13) — C(14)	113.8(5)
C(3) — C(4) — C(5)	113.8(3)	C(15) — N(1) — C(1)	106.8(2)
C(4) — C(5) — C(6)	115.0(3)	C(15) — N(1) — C(16)	108.8(3)
C(5) — C(6) — C(7)	114.1(3)	C(16) — N(1) — C(1)	111.8(3)
C(6) — C(7) — C(8)	114.8(3)	C(17) — N(1) — C(1)	111.2(3)
C(7) — C(8) — C(9)	114.6(3)	C(17) — N(1) — C(15)	108.9(3)
C(8) — C(9) — C(10)	113.9(3)	C(17) — N(1) — C(16)	109.4(2)
C(9) — C(10) — C(11)	113.9(3)		

Table S9f. Selected torsion angles for C_{14}TAB phase III at 22 °C.

Atom — Atom — Atom — Atom	Angle / ˚	Atom — Atom — Atom — Atom	Angle / ˚
N(1) — C(1) — C(2) — C(3)	166.0(3)	C(8) — C(9) — C(10) — C(11)	178.7(4)
C(1) — C(2) — C(3) — C(4)	171.9(4)	C(9) — C(10) — C(11) — C(12)	180.0(4)
C(2) — C(3) — C(4) — C(5)	175.1(4)	C(10) — C(11) — C(12) — C(13)	179.8(4)
C(3) — C(4) — C(5) — C(6)	172.0(4)	C(11) — C(12) — C(13) — C(14)	−179.6(5)
C(4) — C(5) — C(6) — C(7)	178.4(4)	C(2) — C(1) — N(1) — C(15)	172.0(3)
C(5) — C(6) — C(7) — C(8)	176.5(4)	C(2) — C(1) — N(1) — C(16)	−69.2(4)
C(6) — C(7) — C(8) — C(9)	179.2(4)	C(2) — C(1) — N(1) — C(17)	53.4(4)
C(7) — C(8) — C(9) — C(10)	178.2(4)		

Table S10a. Crystal data and structure refinement for C_{14}TAB phase II at 107 °C.

Identification code	xstr0359
Empirical formula	$C_{17}H_{38}BrN$
Formula weight	336.39
Temperature / K	380
Crystal system	monoclinic
Space group	$P2_1/m$
a / Å	5.6621(2)
b / Å	7.3445(4)
c / Å	24.1054(13)
α / °	90
β / °	87.441(4)
γ / °	90
Volume / Å^3	1001.42(8)
Z	2
ρ_{calc} / g cm^{-3}	1.116
μ / mm^{-1}	2.701
F(000)	364.0
Crystal size / mm^3	0.2161 × 0.1229 × 0.02
Radiation	Cu Kα (λ = 1.54184 Å)
2θ range for data collection / °	7.342 to 147.428
Index ranges	$-7 \le h \le 6$, $-8 \le k \le 8$, $-29 \le l \le 29$
Reflections collected	14236
Independent reflections	2138 [R_{int} = 0.0468, R_{sigma} = 0.0223]
Data/restraints/parameters	2138/136/162
Goodness-of-fit on F^2	1.035
Final R indexes [$I \ge 2\sigma(I)$]	R_1 = 0.0494, wR_2 = 0.1389
Final R indexes [all data]	R_1 = 0.0537, wR_2 = 0.1453
Largest diff. peak/hole / e Å^{-3}	1.27/−0.45

Table S10b. Fractional atomic coordinates and equivalent isotropic displacement parameters for C_{14}TAB phase II at 107 °C. U_{eq} is defined as ⅓ of the trace of the orthogonalised U_{ij} tensor.

Atom	*x*	*y*	*z*	*U*(eq) / Å^2
C(1)	0.7812(7)	¼	0.13042(18)	0.0756(10)
C(2)	0.8578(11)	¼	0.18900(2)	0.1052(17)
C(3)	0.6483(12)	¼	0.22900(2)	0.1114(18)
C(4)	0.6891(14)	¼	0.28950(3)	0.129(3)
C(5)	0.4949(15)	¼	0.32950(3)	0.144(3)
C(6)	0.5198(16)	¼	0.38750(3)	0.132(3)
C(7)	0.3269(18)	¼	0.42870(3)	0.160(4)
C(8)	0.3406(17)	¼	0.48670(3)	0.145(3)
C(9)	0.1511(19)	¼	0.52740(3)	0.175(5)
C(10)	0.1574(18)	¼	0.58400(3)	0.145(3)
C(11)	−0.020(2)	¼	0.62580(4)	0.202(6)
C(12)	−0.018(2)	¼	0.68320(3)	0.154(4)
C(13)	−0.195(3)	¼	0.72480(4)	0.238(8)
C(14)	−0.193(2)	¼	0.77960(4)	0.201(6)
C(15)	0.8557(8)	¼	0.03154(18)	0.0851(12)
C(16)	1.1281(5)	0.4158(5)	0.08803(14)	0.0827(8)
N(1)	0.9759(5)	¼	0.08544(13)	0.0638(7)
Br(1)	0.60228(7)	¾	0.07696(2)	0.0847(2)
H(1)	0.6835(14)	0.3565(4)	0.1248(2)	0.091
H(2)	0.9544(16)	0.3565(4)	0.1953(3)	0.126
H(3)	0.5544(17)	0.3565(4)	0.2210(3)	0.134
H(4)	0.7862(18)	0.3566(4)	0.2954(3)	0.155
H(5)	0.4020(19)	0.3566(4)	0.3211(3)	0.172
H(6)	0.6127(19)	0.3565(4)	0.3961(4)	0.158
H(7)	0.236(2)	0.3565(4)	0.4194(4)	0.192
H(8)	0.433(2)	0.3566(4)	0.4954(4)	0.174
H(9)	0.061(2)	0.3565(4)	0.5174(4)	0.210
H(10)	0.250(2)	0.3566(4)	0.5926(4)	0.174
H(11)	−0.113(2)	0.3565(4)	0.6174(4)	0.243
H(12)	0.076(2)	0.3565(4)	0.6915(5)	0.185
H(13)	−0.285(3)	0.3565(4)	0.7150(5)	0.285
H(14)	−0.112(3)	0.3566(3)	0.7920(6)	0.302
H(14M)	−0.352(3)	¼	0.7951(9)	0.302
H(15)	0.7586(14)	0.3565(3)	0.0290(5)	0.128
H(15M)	0.972(2)	¼	0.0012(4)	0.128
H(16A)	1.2145	0.4129	0.1214	0.124
H(16B)	1.0305	0.5227	0.0880	0.124
H(16C)	1.2370	0.4183	0.0564	0.124

Table S10c. Anisotropic displacement parameters for C_{14}TAB phase II at 107 °C. Anisotropic displacement factor exponent has the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11} / Å^2	U_{22} / Å^2	U_{33} / Å^2	U_{23} / Å^2	U_{13} / Å^2	U_{12} / Å^2
C(1)	0.058(19)	0.085(3)	0.083(2)	0	0.006(16)	0
C(2)	0.092(3)	0.139(5)	0.083(3)	0	0.008(2)	0
C(3)	0.106(4)	0.138(5)	0.088(3)	0	0.010(3)	0
C(4)	0.109(4)	0.184(8)	0.092(3)	0	0.020(3)	0
C(5)	0.121(5)	0.215(10)	0.093(4)	0	0.023(3)	0
C(6)	0.129(6)	0.160(7)	0.104(4)	0	0.024(4)	0
C(7)	0.126(6)	0.244(13)	0.108(5)	0	0.026(4)	0
C(8)	0.149(7)	0.180(9)	0.101(4)	0	0.032(4)	0
C(9)	0.140(7)	0.273(15)	0.108(5)	0	0.035(4)	0
C(10)	0.156(7)	0.164(9)	0.112(5)	0	0.033(4)	0
C(11)	0.162(9)	0.317(19)	0.123(6)	0	0.046(6)	0
C(12)	0.180(9)	0.159(8)	0.120(5)	0	0.041(5)	0
C(13)	0.242(15)	0.33(2)	0.128(7)	0	0.088(9)	0
C(14)	0.255(16)	0.205(12)	0.138(7)	0	0.061(8)	0
C(15)	0.075(2)	0.097(3)	0.083(2)	0	−0.0046(19)	0
C(16)	0.0676(16)	0.0644(19)	0.1150(2)	0.0009(14)	0.0027(14)	−0.0102(13)
N(1)	0.0495(14)	0.0605(17)	0.0811(17)	0	0.0012(12)	0
Br(1)	0.0630(3)	0.0653(3)	0.1248(4)	0	0.0060(2)	0

Table S10d. Selected bond lengths for C_{14}TAB phase II at 107 °C.

Atom — Atom	Length / Å	Atom — Atom	Length / Å
N(1) — C(1)	1.511(5)	C(9) — C(10)	1.367(12)
C(1) — C(2)	1.496(7)	C(10) — C(11)	1.391(12)
C(2) — C(3)	1.495(9)	C(11) — C(12)	1.385(13)
C(3) — C(4)	1.486(9)	C(12) — C(13)	1.385(13)
C(4) — C(5)	1.429(9)	C(13) — C(14)	1.322(15)
C(5) — C(6)	1.412(11)	C(15) — N(1)	1.493(5)
C(6) — C(7)	1.442(11)	C(16) — N(1)	1.495(3)
C(7) — C(8)	1.403(11)	N(1) — C(16)[1]	1.495(3)
C(8) — C(9)	1.421(11)		

[1] $x, ½ - y, z$

Table S10e. Selected bond angles for C_{14}TAB phase II at 107 °C.

Atom — Atom — Atom	Angle / ˚	Atom — Atom — Atom	Angle / ˚
N(1) — C(1) — C(2)	116.4(4)	C(10) — C(11) — C(12)	133.3(12)
C(1) — C(2) — C(3)	110.7(5)	C(11) — C(12) — C(13)	133.2(13)
C(2) — C(3) — C(4)	118.6(6)	C(12) — C(13) — C(12)	133.2(15)
C(3) — C(4) — C(5)	120.9(7)	C(15) — N(1) — C(1)	106.1(3)
C(4) — C(5) — C(6)	124.1(8)	C(15) — N(1) — C(16)[1]	108.8(2)
C(5) — C(6) — C(7)	125.1(8)	C(15) — N(1) — C(16)	108.8(2)
C(6) — C(7) — C(8)	127.7(9)	C(16) — N(1) — C(1)	111.9(2)
C(7) — C(8) — C(9)	127.9(10)	C(16)[1] — N(1) — C(1)	111.9(2)
C(8) — C(9) — C(10)	129.6(10)	C(16)[1] — N(1) — C(16)	109.1(3)
C(9) — C(10) — C(11)	132.3(11)		

[1] $x, ½ - y, z$

Table S10f. Selected torsion angles for C_{14}TAB phase II at 107 °C.

Atom — Atom — Atom — Atom	Angle / ˚	Atom — Atom — Atom — Atom	Angle / ˚
N(1) — C(1) — C(2) — C(3)	180	C(8) — C(9) — C(10) — C(11)	180
C(1) — C(2) — C(3) — C(4)	180	C(9) — C(10) — C(11) — C(12)	180
C(2) — C(3) — C(4) — C(5)	180	C(10) — C(11) — C(12) — C(13)	180
C(3) — C(4) — C(5) — C(6)	180	C(11) — C(12) — C(13) — C(14)	180
C(4) — C(5) — C(6) — C(7)	180	C(2) — C(1) — N(1) — C(15)	180
C(5) — C(6) — C(7) — C(8)	180	C(2) — C(1) — N(1) — C(16)	−61.4(2)
C(6) — C(7) — C(8) — C(9)	180	C(2) — C(1) — N(1) — C(16)[1]	61.4(2)
C(7) — C(8) — C(9) — C(10)	180		

[1] $x, ½ - y, z$

Table S11a. Crystal data and structure refinement for C_{12}TAB phase III at −123 °C.

Identification code	xstr0475
Empirical formula	$C_{15}H_{34}BrN$
Formula weight	308.34
Temperature / K	150
Crystal system	monoclinic
Space group	$P2_1/c$
a / Å	5.59929(8)
b / Å	7.14079(10)
c / Å	42.5497(6)
α / °	90
β / °	89.2962(14)
γ / °	90
Volume / Å^3	1701.15(4)
Z	4
ρ_{calc} / g cm^{-3}	1.204
μ / mm^{-1}	3.138
F(000)	664.0
Crystal size / mm^3	0.263 × 0.1653 × 0.0131
Radiation	Cu Kα (λ = 1.54184 Å)
2θ range for data collection / °	12.482 to 147.254
Index ranges	−6 ≤ h ≤ 6, −8 ≤ k ≤ 8, −52 ≤ l ≤ 52
Reflections collected	23233
Independent reflections	3385 [R_{int} = 0.0289, R_{sigma} = 0.0163]
Data/restraints/parameters	3385/0/269
Goodness-of-fit on F^2	1.092
Final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0259, wR_2 = 0.0538
Final R indexes [all data]	R_1 = 0.0334, wR_2 = 0.0577
Largest diff. peak/hole / e Å^{-3}	0.34/−0.26

Table S11b. Fractional atomic coordinates and equivalent isotropic displacement parameters for C_{12}TAB phase III at −123 °C. U_{eq} is defined as ⅓ of the trace of the orthogonalised U_{ij} tensor.

Atom	*x*	*y*	*z*	*U*(eq) / Å^2
C(1)	0.7768(3)	0.2544(3)	0.0720(3)	0.0195(3)
C(2)	0.8434(3)	0.2218(3)	0.1060(4)	0.0237(4)
C(3)	0.6322(3)	0.2791(3)	0.1269(4)	0.0266(4)
C(4)	0.6555(3)	0.2230(3)	0.1613(4)	0.0248(4)
C(5)	0.4532(3)	0.3001(3)	0.1817(4)	0.0241(4)
C(6)	0.4515(3)	0.2266(3)	0.2153(4)	0.0240(4)
C(7)	0.2511(3)	0.3078(3)	0.2355(4)	0.0243(4)
C(8)	0.2413(3)	0.2274(3)	0.2688(4)	0.0243(4)
C(9)	0.0431(3)	0.3106(3)	0.2893(4)	0.0249(4)
C(10)	0.0312(3)	0.2277(3)	0.3222(4)	0.0256(4)
C(11)	−0.1652(4)	0.3107(3)	0.3430(4)	0.0300(4)
C(12)	−0.1748(5)	0.2230(3)	0.3756(5)	0.0402(5)
C(13)	0.8679(3)	0.2562(3)	0.0163(4)	0.0244(3)
C(14)	1.1381(3)	0.4176(3)	0.0516(4)	0.0226(4)
C(15)	1.1257(3)	0.0753(3)	0.0510(4)	0.0232(4)
N(1)	0.9795(2)	0.2504(2)	0.0482(3)	0.0179(3)
Br(1)	0.60268(3)	0.75223(3)	0.04384(2)	0.02716(7)
H(1A)	0.704(3)	0.375(3)	0.0692(4)	0.019(3)
H(1B)	0.671(3)	0.159(3)	0.0659(4)	0.019(3)
H(2A)	0.981(4)	0.299(3)	0.1119(5)	0.030(4)
H(2B)	0.883(4)	0.083(3)	0.1093(5)	0.030(4)
H(3A)	0.609(4)	0.413(3)	0.1252(5)	0.032(4)
H(3B)	0.491(4)	0.222(3)	0.1193(5)	0.032(4)
H(4A)	0.806(4)	0.268(3)	0.1694(5)	0.027(4)
H(4B)	0.654(3)	0.085(3)	0.1630(5)	0.027(4)
H(5A)	0.464(3)	0.433(3)	0.1819(4)	0.025(3)
H(5B)	0.303(4)	0.269(3)	0.1728(4)	0.025(3)
H(6A)	0.602(4)	0.254(3)	0.2248(5)	0.027(4)
H(6B)	0.443(4)	0.090(3)	0.2145(5)	0.027(4)
H(7A)	0.269(3)	0.444(3)	0.2367(5)	0.025(4)
H(7B)	0.100(4)	0.284(3)	0.2253(5)	0.025(4)
H(8A)	0.391(4)	0.252(3)	0.2787(5)	0.028(4)
H(8B)	0.223(4)	0.093(3)	0.2675(5)	0.028(4)
H(9A)	0.068(4)	0.447(3)	0.2908(5)	0.030(4)
H(9B)	−0.113(4)	0.296(3)	0.2786(5)	0.030(4)
H(10A)	0.186(4)	0.243(3)	0.3328(5)	0.028(4)
H(10B)	0.004(4)	0.092(3)	0.3200(5)	0.028(4)
H(11A)	−0.139(4)	0.448(3)	0.3447(5)	0.039(4)

H(11B)	−0.323(4)	0.294(3)	0.3325(5)	0.039(4)
H(12A)	−0.027(5)	0.243(4)	0.3871(6)	0.052(4)
H(12B)	−0.204(4)	0.089(4)	0.3738(6)	0.052(4)
H(12C)	−0.299(5)	0.284(3)	0.3882(6)	0.052(4)
H(13A)	0.768(4)	0.372(3)	0.0155(4)	0.027(16)
H(13B)	0.772(4)	0.148(3)	0.0146(5)	0.027(16)
H(13C)	0.997(4)	0.258(3)	0.0008(5)	0.027(16)
H(14A)	1.219(4)	0.413(3)	0.0718(5)	0.027(16)
H(14B)	1.041(4)	0.526(3)	0.0502(5)	0.027(16)
H(14C)	1.261(4)	0.415(3)	0.0355(5)	0.027(16)
H(15A)	1.021(4)	−0.033(3)	0.0490(4)	0.027(16)
H(15B)	1.210(4)	0.078(3)	0.0709(5)	0.027(16)
H(15C)	1.241(4)	0.078(3)	0.0338(5)	0.027(16)

Table S11c. Anisotropic displacement parameters for C_{12}TAB phase III at −123 °C. Anisotropic displacement factor exponent has the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11} / Å^2	U_{22} / Å^2	U_{33} / Å^2	U_{23} / Å^2	U_{13} / Å^2	U_{12} / Å^2
C(1)	0.0152(7)	0.0217(8)	0.0214(7)	0.0001(7)	0.0026(5)	0.0016(8)
C(2)	0.0220(8)	0.0275(10)	0.0214(7)	0.0029(7)	0.0018(6)	0.0037(7)
C(3)	0.0240(8)	0.0327(11)	0.0229(8)	0.0025(7)	0.0031(6)	0.0059(8)
C(4)	0.0249(8)	0.0275(10)	0.0220(8)	0.0015(7)	0.0017(6)	0.0020(8)
C(5)	0.0251(9)	0.0238(10)	0.0234(8)	0.0001(6)	0.0023(7)	0.0024(7)
C(6)	0.0249(8)	0.0257(10)	0.0213(7)	0.0008(7)	0.0037(6)	0.0025(8)
C(7)	0.0254(9)	0.0245(9)	0.0228(8)	0.0005(6)	0.0028(7)	0.0009(7)
C(8)	0.0254(8)	0.0243(10)	0.0230(8)	0.0013(7)	0.0038(6)	0.0008(7)
C(9)	0.0256(9)	0.0251(10)	0.0239(8)	0.0003(7)	0.0029(7)	−0.0003(7)
C(10)	0.0291(9)	0.0236(10)	0.0239(8)	0.0019(7)	0.0035(7)	0.0005(8)
C(11)	0.0322(10)	0.0292(10)	0.0284(9)	−0.0015(7)	0.0071(8)	−0.0021(8)
C(12)	0.0531(13)	0.0382(13)	0.0289(9)	−0.0020(9)	0.0125(9)	−0.0093(11)
C(13)	0.0231(8)	0.0321(10)	0.0179(7)	−0.0010(7)	−0.0012(6)	−0.0005(9)
C(14)	0.0189(9)	0.0196(9)	0.0292(9)	0.0005(7)	0.0015(7)	−0.0041(7)
C(15)	0.0211(9)	0.0195(9)	0.0288(9)	−0.0021(7)	0.0015(7)	0.0028(7)
N(1)	0.0159(6)	0.0186(6)	0.0191(6)	−0.0004(5)	0.0013(5)	0.0006(6)
Br(1)	0.01956(10)	0.01902(10)	0.04285(11)	0.00080(8)	0.00169(7)	0.00028(8)

Table S11d. Selected bond lengths for C_{12}TAB phase III at −123 °C.

Atom — Atom	Length / Å	Atom — Atom	Length / Å
N(1) — C(1)	1.5114(18)	C(8) — C(9)	1.524(2)
C(1) — C(2)	1.517(2)	C(9) — C(10)	1.521(2)
C(2) — C(3)	1.526(2)	C(10) — C(11)	1.523(3)
C(3) — C(4)	1.525(2)	C(11) — C(12)	1.523(3)
C(4) — C(5)	1.522(2)	C(13) — N(1)	1.5012(19)
C(5) — C(6)	1.522(2)	C(14) — N(1)	1.496(2)
C(6) — C(7)	1.520(2)	C(15) — N(1)	1.500(2
C(7) — C(8)	1.527(2)		

Table S11e. Selected bond angles for C_{12}TAB phase III at −123 °C.

Atom — Atom — Atom	Angle / ˚	Atom — Atom — Atom	Angle / ˚
N(1) — C(1) — C(2)	116.41(13)	C(9) — C(10) — C(11)	113.98(16)
C(1) — C(2) — C(3)	108.48(14)	C(10) — C(11) — C(12)	112.72(17)
C(2) — C(3) — C(4)	114.45(15)	C(13) — N(1) — C(1)	106.68(11)
C(3) — C(4) — C(5)	112.39(15)	C(14) — N(1) — C(1)	111.24(13)
C(4) — C(5) — C(6)	114.02(15)	C(14) — N(1) — C(13)	108.63(13)
C(5) — C(6) — C(7)	113.32(15)	C(14) — N(1) — C(15)	109.40(12)
C(6) — C(7) — C(8)	113.50(15)	C(15) — N(1) — C(1)	111.62(13)
C(7) — C(8) — C(9)	113.68(15)	C(15) — N(1) — C(13)	109.17(13
C(8) — C(9) — C(10)	113.51(16)		

Table S11f. Selected torsion angles for C_{12}TAB phase III at −123 °C.

Atom — Atom — Atom — Atom	Angle / ˚	Atom — Atom — Atom — Atom	Angle / ˚
N(1) — C(1) — C(2) — C(3)	165.91(16)	C(7) — C(8) — C(9) — C(10)	178.99(16)
C(1) — C(2) — C(3) — C(4)	169.92(16)	C(8) — C(9) — C(10) — C(11)	179.61(16)
C(2) — C(3) — C(4) — C(5)	174.21(16)	C(9) — C(10) — C(11) — C(12)	179.17(18)
C(3) — C(4) — C(5) — C(6)	172.36(16)	C(2) — C(1) — N(1) — C(13)	171.55(16)
C(4) — C(5) — C(6) — C(7)	178.92(16)	C(2) — C(1) — N(1) — C(14)	−70.14(19)
C(5) — C(6) — C(7) — C(8)	177.23(16)	C(2) — C(1) — N(1) — C(15)	52.4(2)
C(6) — C(7) — C(8) — C(9)	179.12(16)		

Table S12a. Crystal data and structure refinement for C_{12}TAB phase II at 22 °C.

Identification code	exp_807
Empirical formula	$C_{15}H_{34}BrN$
Formula weight	308.34
Temperature / K	295
Crystal system	monoclinic
Space group	$P2_1/m$
a / Å	5.64120(8)
b / Å	7.25452(11)
c / Å	21.5625(4)
α / °	90
β / °	86.9956(13)
γ / °	90
Volume / Å^3	881.21(2)
Z	2
ρ_{calc} / g cm^{-3}	1.162
μ / mm^{-1}	3.028
F(000)	332.0
Crystal size / mm^3	0.2837 × 0.1553 × 0.0229
Radiation	Cu Kα (λ = 1.54184 Å)
2θ range for data collection / °	8.212 to 147.114
Index ranges	−6 ≤ h ≤ 7, −8 ≤ k ≤ 8, −26 ≤ l ≤ 26
Reflections collected	12281
Independent reflections	1896 [R_{int} = 0.0269, R_{sigma} = 0.0142]
Data/restraints/parameters	1896/118/144
Goodness-of-fit on F^2	1.030
Final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0346, wR_2 = 0.1031
Final R indexes [all data]	R_1 = 0.0369, wR_2 = 0.1050
Largest diff. peak/hole / e Å^{-3}	0.71/−0.39

Table S12b. Fractional atomic coordinates and equivalent isotropic displacement parameters for C_{12}TAB phase II at 22 °C. U_{eq} is defined as ⅓ of the trace of the orthogonalised U_{ij} tensor.

Atom	*x*	*y*	*z*	*U*(eq) / Å^2
C(1)	0.7661(5)	¼	0.14442(14)	0.0457(7)
C(2)	0.8308(7)	¼	0.21082(18)	0.0696(11)
C(3)	0.6171(8)	¼	0.25382(18)	0.0764(12)
C(4)	0.6436(8)	¼	0.32172(19)	0.0771(12)
C(5)	0.4399(10)	¼	0.3641(2)	0.118(3)
C(6)	0.4469(9)	¼	0.4305(2)	0.0785(12)
C(7)	0.2441(11)	¼	0.4725(2)	0.144(4)
C(8)	0.2406(9)	¼	0.5383(2)	0.0828(14)
C(9)	0.0424(12)	¼	0.5806(2)	0.169(5)
C(10)	0.0361(11)	¼	0.6460(2)	0.0907(16)
C(11)	−0.1587(14)	¼	0.6894(3)	0.185(5)
C(12)	−0.1684(15)	¼	0.7531(3)	0.137(3)
C(13)	0.8593(6)	¼	0.03385(14)	0.0559(8)
C(14)	1.1199(4)	0.4184(3)	0.10048(11)	0.0528(5)
N(1)	0.9691(4)	¼	0.09556(11)	0.0409(5)
Br(1)	0.59453(6)	¾	0.08621(2)	0.05809(17)
H(1)	0.6699(13)	0.3579(4)	0.1372(2)	0.055
H(2)	0.9270(14)	0.3579(4)	0.2182(2)	0.083
H(3)	0.5243(14)	0.3578(4)	0.2441(3)	0.092
H(4)	0.7389(14)	0.3579(4)	0.3297(3)	0.093
H(5)	0.3481(15)	0.3578(4)	0.3539(3)	0.142
H(6)	0.5394(15)	0.3578(4)	0.4405(3)	0.094
H(7)	0.1537(16)	0.3578(4)	0.4615(3)	0.172
H(8)	0.3322(15)	0.3578(4)	0.5487(3)	0.099
H(9)	−0.0486(17)	0.3578(4)	0.5698(3)	0.202
H(10)	0.1277(16)	0.3578(4)	0.6565(4)	0.109
H(11)	−0.2479(18)	0.3578(4)	0.6777(3)	0.222
H(12)	−0.090(2)	0.3579(3)	0.7677(5)	0.206
H(12M)	−0.331(2)	¼	0.7686(7)	0.206
H(13)	0.7630(12)	0.3580(3)	0.0303(5)	0.084
H(13M)	0.9823(17)	¼	0.0014(4)	0.084
H(14A)	1.0225	0.5264	0.0982	0.079
H(14B)	1.2390	0.4198	0.0670	0.079
H(14C)	1.1952	0.4172	0.1394	0.079

Table S12c. Anisotropic displacement parameters for C_{12}TAB phase II at 22 °C. Anisotropic displacement factor exponent has the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11} / Å^2	U_{22} / Å^2	U_{33} / Å^2	U_{23} / Å^2	U_{13} / Å^2	U_{12} / Å^2
C(1)	0.0343(14)	0.0539(17)	0.0484(15)	0	0.0040(11)	0
C(2)	0.053(2)	0.105(3)	0.0499(18)	0	0.0031(15)	0
C(3)	0.062(2)	0.116(4)	0.051(19)	0	0.0077(16)	0
C(4)	0.064(2)	0.111(4)	0.055(2)	0	0.0084(17)	0
C(5)	0.071(3)	0.231(8)	0.052(2)	0	0.012(2)	0
C(6)	0.075(3)	0.101(4)	0.058(2)	0	0.0141(18)	0
C(7)	0.078(4)	0.294(12)	0.057(3)	0	0.018(2)	0
C(8)	0.084(3)	0.102(4)	0.060(2)	0	0.019(2)	0
C(9)	0.090(4)	0.351(17)	0.061(3)	0	0.024(3)	0
C(10)	0.108(4)	0.097(4)	0.064(2)	0	0.026(2)	0
C(11)	0.111(5)	0.367(17)	0.072(3)	0	0.038(4)	0
C(12)	0.190(8)	0.138(6)	0.077(3)	0	0.056(4)	0
C(13)	0.0508(18)	0.074(2)	0.0426(15)	0	−0.0024(13)	0
C(14)	0.0453(11)	0.0454(13)	0.0672(13)	0.0022(10)	0.0020(9)	−0.0081(9)
N(1)	0.0325(11)	0.0433(13)	0.0464(12)	0	0.0015(9)	0
Br(1)	0.0429(2)	0.0452(2)	0.0855(3)	0	0.00271(16)	0

Table S12d. Selected bond lengths for C_{12}TAB phase II at 22 °C.

Atom — Atom	Length / Å	Atom — Atom	Length / Å
N(1) — C(1)	1.515(4)	C(8) — C(9)	1.406(7)
C(1) — C(2)	1.496(5)	C(9) — C(10)	1.408(7)
C(2) — C(3)	1.482(6)	C(10) — C(11)	1.406(8)
C(3) — C(4)	1.479(6)	C(11) — C(12)	1.371(9)
C(4) — C(5)	1.430(6)	N(1) — C(13)	1.497(4)
C(5) — C(6)	1.434(6)	N(1) — C(14)	1.496(3)
C(6) — C(7)	1.422(7)	N(1) — C(14)[1]	1.496(3)
C(7) — C(8)	1.417(7)		

[1] $x, ½ - y, z$

Table S12e. Selected bond angles for C_{12}TAB phase II at 22 °C.

Atom — Atom — Atom	Angle / ˚	Atom — Atom — Atom	Angle / ˚
N(1) — C(1) — C(2)	116.9(3)	C(9) — C(10) — C(11)	130.1(7)
C(1) — C(2) — C(3)	111.6(3)	C(10) — C(11) — C(12)	130.9(8)
C(2) — C(3) — C(4)	119.9(4)	C(1) — N(1) — C(13)	106.6(2)
C(3) — C(4) — C(5)	120.9(4)	C(1) — N(1) — C(14)	111.28(15)
C(4) — C(5) — C(6)	125.0(5)	C(1) — N(1) — C(14)1	111.28(15)
C(5) — C(6) — C(7)	124.9(5)	C(13) — N(1) — C(14)	109.06(16)
C(6) — C(7) — C(8)	127.3(6)	C(13) — N(1) — C(14)1	109.06(16)
C(7) — C(8) — C(9)	128.2(6)	C(14) — N(1) — C(14)1	109.5(2)
C(8) — C(9) — C(10)	128.9(7)		

[1] $x, ½ - y, z$

Table S12f. Selected torsion angles for C_{12}TAB phase II at 22 °C.

Atom — Atom — Atom — Atom	Angle / ˚	Atom — Atom — Atom — Atom	Angle / ˚
N(1) — C(1) — C(2) — C(3)	180	C(7) — C(8) — C(9) — C(10)	180
C(1) — C(2) — C(3) — C(4)	180	C(8) — C(9) — C(10) — C(11)	180
C(2) — C(3) — C(4) — C(5)	180	C(9) — C(10) — C(11) — C(12)	180
C(3) — C(4) — C(5) — C(6)	180	C(2) — C(1) — N(1) — C(13)	180
C(4) — C(5) — C(6) — C(7)	180	C(2) — C(1) — N(1) — C(14)	−61.23(16)
C(5) — C(6) — C(7) — C(8)	180	C(2) — C(1) — N(1) — C(14)[1]	61.22(16)
C(6) — C(7) — C(8) — C(9)	180		

[1] $x, ½ - y, z$

Table S13a. Crystal data and structure refinement for C_{10}TAB phase III at −173 °C.

Identification code	exp_836
Empirical formula	$C_{13}H_{30}BrN$
Formula weight	280.29
Temperature / K	100
Crystal system	monoclinic
Space group	$P2_1/c$
a / Å	5.58903(14)
b / Å	7.10956(17)
c / Å	38.0171(9)
α / °	90
β / °	85.779(2)
γ / °	90
Volume / Å^3	1506.53(6)
Z	4
ρ_{calc} / g cm^{-3}	1.236
μ / mm^{-1}	3.494
F(000)	600.0
Crystal size / mm^3	0.3203 × 0.27 × 0.0457
Radiation	Cu Kα (λ = 1.54184 Å)
2θ range for data collection / °	9.33 to 146.97
Index ranges	−6 ≤ h ≤ 6, −8 ≤ k ≤ 8, −47 ≤ l ≤ 46
Reflections collected	19936
Independent reflections	2935 [R_{int} = 0.0464, R_{sigma} = 0.0212]
Data/restraints/parameters	2935/0/237
1.237	1.237
Final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0438, wR_2 = 0.0929
Final R indexes [all data]	R_1 = 0.0479, wR_2 = 0.0949
Largest diff. peak/hole / e Å^{-3}	0.60/−0.48

Table S13b. Fractional atomic coordinates and equivalent isotropic displacement parameters for C_{10}TAB phase III at −173 °C. U_{eq} is defined as ⅓ of the trace of the orthogonalised U_{ij} tensor.

Atom	*x*	*y*	*z*	*U*(eq) / Å^2
C(1)	0.7431(5)	0.2546(4)	0.08080(7)	0.0177(6)
C(2)	0.7934(6)	0.2205(4)	0.11900(8)	0.0200(6)
C(3)	0.5732(6)	0.2807(5)	0.14245(8)	0.0223(6)
C(4)	0.5793(6)	0.2231(4)	0.18103(8)	0.0214(6)
C(5)	0.3683(6)	0.3011(4)	0.20392(8)	0.0206(6)
C(6)	0.3505(6)	0.2272(4)	0.24159(8)	0.0215(6)
C(7)	0.1417(6)	0.3095(4)	0.26445(8)	0.0219(6)
C(8)	0.1138(6)	0.2276(4)	0.30164(8)	0.0214(6)
C(9)	−0.0925(6)	0.3114(5)	0.32480(8)	0.0244(7)
C(10)	−0.1186(7)	0.2237(5)	0.36138(9)	0.0321(8)
C(11)	0.8605(5)	0.2555(5)	0.01825(8)	0.0207(6)
C(12)	1.1154(6)	0.4187(4)	0.05780(8)	0.0202(6)
C(13)	1.1019(6)	0.0749(4)	0.05725(8)	0.0198(6)
N(1)	0.9570(4)	0.2504(3)	0.05407(6)	0.0163(5)
Br(1)	0.58241(5)	0.75251(4)	0.04890(2)	0.02177(12)
H(1A)	0.671(6)	0.378(5)	0.0769(8)	0.012(5)
H(1B)	0.639(6)	0.161(5)	0.0735(8)	0.012(5)
H(2A)	0.925(7)	0.298(5)	0.1257(9)	0.023(6)
H(2B)	0.828(6)	0.089(5)	0.1225(9)	0.023(6)
H(3A)	0.558(6)	0.414(5)	0.1412(9)	0.021(6)
H(3B)	0.434(7)	0.224(5)	0.1338(9)	0.021(6)
H(4A)	0.727(7)	0.270(5)	0.1898(9)	0.022(6)
H(4B)	0.584(6)	0.087(5)	0.1823(9)	0.022(6)
H(5A)	0.381(6)	0.430(6)	0.2045(8)	0.023(6)
H(5B)	0.225(7)	0.271(5)	0.1937(9)	0.023(6)
H(6A)	0.500(7)	0.255(5)	0.2528(10)	0.023(6)
H(6B)	0.331(6)	0.091(5)	0.2407(9)	0.023(6)
H(7A)	0.158(6)	0.453(5)	0.2663(8)	0.021(6)
H(7B)	−0.009(7)	0.290(5)	0.2535(9)	0.021(6)
H(8A)	0.263(7)	0.245(5)	0.3133(9)	0.021(6)
H(8B)	0.096(6)	0.096(6)	0.3001(8)	0.021(6)
H(9A)	−0.065(7)	0.452(5)	0.3268(9)	0.027(7)
H(9B)	−0.242(7)	0.301(5)	0.3137(9)	0.027(7)
H(10A)	0.022(8)	0.238(6)	0.3741(11)	0.038(6)
H(10B)	−0.148(7)	0.085(6)	0.3600(10)	0.038(6)
H(10C)	−0.253(7)	0.288(6)	0.3772(10)	0.038(6)
H(11A)	0.759(6)	0.367(5)	0.0166(8)	0.020(3)
H(11B)	0.766(6)	0.144(5)	0.0154(8)	0.020(3)

H(11C)	0.998(7)	0.256(5)	0.0001(9)	0.020(3)
H(12A)	1.183(6)	0.416(5)	0.0807(9)	0.020(3)
H(12B)	1.017(6)	0.527(5)	0.0558(8)	0.020(3)
H(12C)	1.239(6)	0.413(5)	0.0385(9)	0.020(3)
H(13A)	1.001(6)	−0.035(5)	0.0555(8)	0.020(3)
H(13B)	1.178(6)	0.073(5)	0.0797(9)	0.020(3)
H(13C)	1.225(6)	0.075(5)	0.0383(9)	0.020(3)

Table S13c. Anisotropic displacement parameters for C_{10}TAB phase III at −173 °C. Anisotropic displacement factor exponent has the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11} / Å^2	U_{22} / Å^2	U_{33} / Å^2	U_{23} / Å^2	U_{13} / Å^2	U_{12} / Å^2
C(1)	0.0142(13)	0.0164(14)	0.0224(14)	0.0000(11)	−0.0011(10)	−0.0008(13)
C(2)	0.0192(15)	0.0160(15)	0.0248(15)	0.0018(11)	−0.0030(11)	0.0041(12)
C(3)	0.0191(15)	0.0205(16)	0.0272(15)	0.0010(12)	−0.0020(12)	0.0044(13)
C(4)	0.0202(15)	0.0192(16)	0.0251(15)	0.0011(11)	−0.0026(11)	0.0017(13)
C(5)	0.0205(16)	0.0146(15)	0.0267(15)	0.0011(11)	−0.0031(12)	0.0004(12)
C(6)	0.0221(15)	0.0184(16)	0.0237(14)	0.0009(11)	−0.0011(11)	−0.0006(13)
C(7)	0.0220(17)	0.0177(15)	0.0260(15)	0.0009(11)	−0.0011(12)	−0.0011(12)
C(8)	0.0244(16)	0.0146(15)	0.0252(15)	0.0006(11)	−0.0016(12)	0.0038(13)
C(9)	0.0226(18)	0.0199(15)	0.0302(16)	−0.0011(12)	0.0007(13)	−0.0012(13)
C(10)	0.038(2)	0.0296(19)	0.0280(17)	−0.0021(14)	0.0044(14)	−0.0048(17)
C(11)	0.0191(14)	0.0222(15)	0.0212(14)	−0.0015(12)	−0.0043(11)	0.0025(15)
C(12)	0.0187(17)	0.0137(14)	0.0280(16)	0.0002(11)	−0.0015(12)	−0.0008(13)
C(13)	0.0164(16)	0.0131(14)	0.0301(16)	−0.0014(11)	−0.0034(12)	0.0034(12)
N(1)	0.0140(11)	0.0138(11)	0.0213(11)	0.0003(9)	−0.0021(9)	0.0008(11)
Br(1)	0.01674(18)	0.01278(17)	0.03593(19)	0.00057(12)	−0.00296(12)	0.00079(14)

Table S13d. Selected bond lengths for C_{10}TAB phase III at −173 °C.

Atom — Atom	Length / Å	Atom — Atom	Length / Å
N(1) — C(1)	1.511(4)	C(7) — C(8)	1.527(4)
C(1) — C(2)	1.519(4)	C(8) — C(9)	1.520(4)
C(2) — C(3)	1.527(4)	C(9) — C(10)	1.521(5)
C(3) — C(4)	1.526(4)	N(1) — C(11)	1.501(3)
C(4) — C(5)	1.518(4)	N(1) — C(12)	1.502(4)
C(5) — C(6)	1.522(4)	N(1) — C(13)	1.497(4)
C(6) — C(7)	1.520(4)		

Table S13e. Selected bond angles for C_{10}TAB phase III at −173 °C.

Atom — Atom — Atom	Angle / ˚	Atom — Atom — Atom	Angle / ˚
N(1) — C(1) — C(2)	116.5(2)	C(8) — C(9) — C(10)	112.8(3)
C(1) — C(2) — C(3)	108.4(2)	C(1) — N(1) — C(11)	106.9(2)
C(2) — C(3) — C(4)	114.3(3)	C(1) — N(1) — C(12)	111.3(2)
C(3) — C(4) — C(5)	112.4(3)	C(1) — N(1) — C(13)	111.6(2)
C(4) — C(5) — C(6)	114.0(3)	C(11) — N(1) — C(12)	108.7(2)
C(5) — C(6) — C(7)	113.5(3)	C(11) — N(1) — C(13)	109.0(2)
C(6) — C(7) — C(8)	113.9(3)	C(12) — N(1) — C(13)	109.3(2)
C(7) — C(8) — C(9)	114.1(3)		

Table S13f. Selected torsion angles for C_{10}TAB phase III at −173 °C.

Atom — Atom — Atom — Atom	Angle / ˚	Atom — Atom — Atom — Atom	Angle / ˚
N(1) — C(1) — C(2) — C(3)	165.2(3)	C(6) — C(7) — C(8) — C(9)	179.1(3)
C(1) — C(2) — C(3) — C(4)	169.8(3)	C(7) — C(8) — C(9) — C(10)	178.7(3)
C(2) — C(3) — C(4) — C(5)	174.8(3)	C(2) — C(1) — N(1) — C(11)	170.9(3)
C(3) — C(4) — C(5) — C(6)	172.8(3)	C(2) — C(1) — N(1) — C(12)	−70.6(3)
C(4) — C(5) — C(6) — C(7)	178.8(3)	C(2) — C(1) — N(1) — C(13)	51.8(3)
C(5) — C(6) — C(7) — C(8)	176.6(3)		

Table S14a. Crystal data and structure refinement for C_{10}TAB phase III at −123 °C.

Identification code	xstr0483
Empirical formula	$C_{13}H_{30}BrN$
Formula weight	280.29
Temperature / K	150
Crystal system	monoclinic
Space group	$P2_1/c$
a / Å	5.60055(7)
b / Å	7.13788(7)
c / Å	38.1311(4)
α / °	90
β / °	85.4663(10)
γ / °	90
Volume / Å^3	1519.56(3)
Z	4
ρ_{calc} / g cm^{-3}	1.225
μ / mm^{-1}	3.465
F(000)	600.0
Crystal size / mm^3	0.5307 × 0.2158 × 0.0557
Radiation	Cu Kα (λ = 1.54184 Å)
2θ range for data collection / °	9.306 to 153.006
Index ranges	$-7 \le h \le 6$, $-8 \le k \le 8$, $-47 \le l \le 47$
Reflections collected	26935
Independent reflections	3154 [R_{int} = 0.0337, R_{sigma} = 0.0155]
Data/restraints/parameters	3154/0/239
Goodness-of-fit on F^2	1.052
Final R indexes [$I \ge 2\sigma(I)$]	R_1 = 0.0222, wR_2 = 0.0588
Final R indexes [all data]	R_1 = 0.0260, wR_2 = 0.0618
Largest diff. peak/hole / e Å^{-3}	0.42/−0.29

Table S14b. Fractional atomic coordinates and equivalent isotropic displacement parameters for C_{10}TAB phase III at −123 °C. U_{eq} is defined as ⅓ of the trace of the orthogonalised U_{ij} tensor.

Atom	*x*	*y*	*z*	*U*(eq) / Å^2
C(1)	0.7768(3)	0.2544(3)	0.07198(3)	0.0195(3)
C(2)	0.8434(3)	0.2218(3)	0.10600(4)	0.0237(4)
C(1)	0.7414(2)	0.2543(17)	0.08072(3)	0.0194(3)
C(2)	0.7922(3)	0.2218(2)	0.11884(3)	0.0242(3)
C(3)	0.5712(3)	0.2797(2)	0.14230(4)	0.0275(3)
C(4)	0.5783(3)	0.2231(2)	0.18079(3)	0.0254(3)
C(5)	0.3670(3)	0.3013(2)	0.20381(3)	0.0254(3)
C(6)	0.3506(3)	0.2269(2)	0.24144(4)	0.0250(3)
C(7)	0.1410(3)	0.3094(2)	0.26444(3)	0.0252(3)
C(8)	0.1165(3)	0.2279(2)	0.30162(4)	0.0263(3)
C(9)	−0.0904(3)	0.3109(2)	0.32483(4)	0.0302(3)
C(10)	−0.1156(4)	0.2235(3)	0.36145(4)	0.0413(4)
C(11)	0.8589(3)	0.2555(19)	0.01836(3)	0.0250(3)
C(12)	1.1128(2)	0.4178(19)	0.05768(4)	0.0232(3)
C(13)	1.1005(3)	0.0754(19)	0.05697(4)	0.0238(3)
N(1)	0.9553(2)	0.2503(13)	0.05401(3)	0.0181(2)
Br(1)	0.58107(2)	0.75220(2)	0.04889(2)	0.02682(7)
H(1A)	0.673(3)	0.372(2)	0.0776(4)	0.022(3)
H(1B)	0.635(3)	0.160(2)	0.0731(4)	0.022(3)
H(2A)	0.933(4)	0.298(3)	0.1251(5)	0.037(3)
H(2B)	0.829(3)	0.088(3)	0.1225(4)	0.037(3)
H(3A)	0.554(3)	0.417(3)	0.1408(5)	0.037(3)
H(3B)	0.435(4)	0.227(2)	0.1339(5)	0.037(3)
H(4A)	0.726(4)	0.266(2)	0.1900(5)	0.028(3)
H(4B)	0.579(3)	0.086(2)	0.1828(4)	0.028(3)
H(5A)	0.374(3)	0.438(3)	0.2039(4)	0.033(3)
H(5B)	0.224(4)	0.269(2)	0.1939(5)	0.033(3)
H(6A)	0.496(4)	0.254(2)	0.2522(5)	0.030(3)
H(6B)	0.336(3)	0.095(3)	0.2411(4)	0.030(3)
H(7A)	0.163(3)	0.444(3)	0.2659(5)	0.036(3)
H(7B)	−0.013(4)	0.288(2)	0.2534(5)	0.036(3)
H(8A)	0.266(4)	0.249(2)	0.3131(5)	0.031(3)
H(8B)	0.095(3)	0.093(3)	0.2999(4)	0.031(3)
H(9A)	−0.076(3)	0.443(3)	0.3269(5)	0.041(4)
H(9B)	−0.231(4)	0.297(3)	0.3141(5)	0.041(4)
H(10A)	0.028(5)	0.241(3)	0.3737(7)	0.053(4)
H(10B)	−0.154(4)	0.093(3)	0.3592(5)	0.053(4)
H(10C)	−0.241(4)	0.283(3)	0.3765(6)	0.053(4)

H(11A)	0.766(3)	0.368(2)	0.0172(4)	0.028(3)
H(11B)	0.763(3)	0.147(2)	0.0162(4)	0.028(3)
H(11C)	0.996(4)	0.259(1)	0.0009(5)	0.028(3)
H(12A)	1.179(3)	0.413(2)	0.0799(4)	0.027(2)
H(12B)	1.020(3)	0.527(3)	0.0559(4)	0.027(2)
H(12C)	1.241(3)	0.414(2)	0.0390(4)	0.027(2)
H(13A)	1.002(3)	−0.028(3)	0.0556(4)	0.027(2)
H(13B)	1.175(3)	0.076(2)	0.0790(4)	0.027(2)
H(13C)	1.228(3)	0.078(2)	0.0383(4)	0.027(2)

Table S14c. Anisotropic displacement parameters for C_{10}TAB phase III at −123 °C. Anisotropic displacement factor exponent has the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11} / Å^2	U_{22} / Å^2	U_{33} / Å^2	U_{23} / Å^2	U_{13} / Å^2	U_{12} / Å^2
C(1)	0.0149(6)	0.0225(7)	0.0204(6)	0.0003(4)	0.0004(5)	0.0014(5)
C(2)	0.0218(7)	0.0287(7)	0.0220(6)	0.0026(5)	−0.0003(5)	0.0037(5)
C(3)	0.0252(8)	0.0348(7)	0.0218(6)	0.0024(5)	0.0014(5)	0.0062(6)
C(4)	0.0254(7)	0.0289(7)	0.0216(6)	0.0022(5)	0.0005(5)	0.0025(5)
C(5)	0.0264(7)	0.0268(7)	0.0227(6)	0.0009(5)	0.0008(5)	0.0021(6)
C(6)	0.0250(7)	0.0273(7)	0.0221(6)	0.0015(5)	0.0019(5)	0.0018(5)
C(7)	0.0272(7)	0.0252(7)	0.0228(6)	0.0003(5)	0.0008(5)	0.0003(6)
C(8)	0.0302(8)	0.0244(7)	0.0236(6)	0.0018(5)	0.0022(5)	0.0007(5)
C(9)	0.0326(9)	0.0294(7)	0.0277(7)	−0.0010(6)	0.0040(6)	−0.0011(6)
C(10)	0.0546(12)	0.0407(9)	0.0266(7)	−0.0014(6)	0.0097(7)	−0.0099(8)
C(11)	0.0252(7)	0.0326(8)	0.0175(6)	−0.0005(4)	−0.0030(5)	−0.0004(5)
C(12)	0.0202(7)	0.0196(6)	0.0296(6)	0.0002(5)	−0.0010(5)	−0.0039(5)
C(13)	0.0207(7)	0.0191(6)	0.0315(6)	−0.0021(5)	−0.0014(5)	0.0028(5)
N(1)	0.0162(5)	0.0188(5)	0.0192(5)	−0.0011(3)	−0.0006(4)	0.0005(4)
Br(1)	0.01952(10)	0.01912(10)	0.04162(11)	0.00064(5)	−0.00127(6)	0.00009(5)

Table S14d. Selected bond lengths for C_{10}TAB phase III at −123 °C.

Atom — Atom	Length / Å	Atom — Atom	Length / Å
N(1) — C(1)	1.5098(16)	C(7) — C(8)	1.5286(18)
C(1) — C(2)	1.5205(17)	C(8) — C(9)	1.521(2)
C(2) — C(3)	1.5255(19)	C(9) — C(10)	1.525(2)
C(3) — C(4)	1.5259(18)	N(1) — C(11)	1.5019(16)
C(4) — C(5)	1.5227(19)	N(1) — C(12)	1.4992(16)
C(5) — C(6)	1.5259(18)	N(1) — C(13)	1.4991(16)
C(6) — C(7)	1.5263(19)		

Table S14e. Selected bond angles for C_{10}TAB phase III at −123 °C.

Atom — Atom — Atom	Angle / ˚	Atom — Atom — Atom	Angle / ˚
N(1) — C(1) — C(2)	116.35(11)	C(8) — C(9) — C(10)	112.61(14)
C(1) — C(2) — C(3)	108.36(11)	C(1) — N(1) — C(11)	106.72(10)
C(2) — C(3) — C(4)	114.25(12)	C(1) — N(1) — C(12)	111.30(9)
C(3) — C(4) — C(5)	112.30(12)	C(1) — N(1) — C(13)	111.77(10)
C(4) — C(5) — C(6)	113.64(12)	C(11) — N(1) — C(12)	108.72(10)
C(5) — C(6) — C(7)	113.11(12)	C(11) — N(1) — C(13)	108.96(10)
C(6) — C(7) — C(8)	113.27(12)	C(12) — N(1) — C(13)	109.28(11)
C(7) — C(8) — C(9)	113.59(13)		

Table S14f. Selected torsion angles for C_{10}TAB phase III at −123 °C.

Atom — Atom — Atom — Atom	Angle / ˚	Atom — Atom — Atom — Atom	Angle / ˚
N(1) — C(1) — C(2) — C(3)	165.73(11)	C(6) — C(7) — C(8) — C(9)	179.39(13)
C(1) — C(2) — C(3) — C(4)	169.69(12)	C(7) — C(8) — C(9) — C(10)	178.38(14)
C(2) — C(3) — C(4) — C(5)	173.99(13)	C(2) — C(1) — N(1) — C(11)	171.50(11)
C(3) — C(4) — C(5) — C(6)	172.48(13)	C(2) — C(1) — N(1) — C(12)	−70.03(14)
C(4) — C(5) — C(6) — C(7)	178.85(13)	C(2) — C(1) — N(1) — C(13)	52.47(14)
C(5) — C(6) — C(7) — C(8)	177.12(13)		

Table S15a. Crystal data and structure refinement for C_{10}TAB phase II at −23 °C.

Identification code	xstr0483d
Empirical formula	$C_{13}H_{30}BrN$
Formula weight	280.29
Temperature / K	250
Crystal system	monoclinic
Space group	$P2_1/m$
a / Å	5.62642(7)
b / Å	7.20481(8)
c / Å	19.3396(2)
α / °	90
β / °	83.4072(11)
γ / °	90
Volume / Å^3	778.792(16)
Z	2
ρ_{calc} / g cm^{-3}	1.195
μ / mm^{-1}	3.380
F(000)	300.0
Crystal size / mm^3	0.3595 × 0.2503 × 0.0426
Radiation	Cu Kα (λ = 1.54184 Å)
2θ range for data collection / °	9.206 to 147.838
Index ranges	$-7 \le h \le 7$, $-9 \le k \le 9$, $-23 \le l \le 23$
Reflections collected	12138
Independent reflections	1673 [R_{int} = 0.0253, R_{sigma} = 0.0111]
Data/restraints/parameters	1673/103/126
Goodness-of-fit on F^2	1.045
Final R indexes [$I \ge 2\sigma(I)$]	R_1 = 0.0335, wR_2 = 0.0997
Final R indexes [all data]	R_1 = 0.0341, wR_2 = 0.1007
Largest diff. peak/hole / e Å^{-3}	0.49/−0.61

Table S15b. Fractional atomic coordinates and equivalent isotropic displacement parameters for C_{10}TAB phase III at −23 °C. U_{eq} is defined as ⅓ of the trace of the orthogonalised U_{ij} tensor.

Atom	*x*	*y*	*z*	*U*(eq) / Å^2
C(1)	0.7315(5)	¼	0.16189(16)	0.0387(6)
C(2)	0.7811(7)	¼	0.2367(2)	0.0607(10)
C(3)	0.5571(8)	¼	0.2849(2)	0.0683(12)
C(4)	0.5704(8)	¼	0.3608(2)	0.0673(12)
C(5)	0.3549(10)	¼	0.4086(2)	0.1150(3)
C(6)	0.3487(9)	¼	0.4834(2)	0.0692(12)
C(7)	0.1357(12)	¼	0.5308(3)	0.1530(5)
C(8)	0.1203(1)	¼	0.6047(2)	0.0800(15)
C(9)	−0.0889(1)	¼	0.6529(3)	0.1760(5)
C(10)	−0.1086(1)	¼	0.7251(3)	0.1250(3)
C(11)	0.8505(6)	¼	0.03785(16)	0.0463(7)
C(12)	1.0968(4)	0.4193(3)	0.11255(13)	0.0450(5)
N(1)	0.9466(4)	¼	0.10722(13)	0.0347(5)
Br(1)	0.57381(5)	¾	0.09618(2)	0.04870(17)
H(1)	0.636(1)	0.359(4)	0.1542(2)	0.046
H(2)	0.877(1)	0.359(4)	0.2446(3)	0.073
H(3)	0.466(1)	0.359(4)	0.2742(3)	0.082
H(4)	0.664(1)	0.359(4)	0.3699(3)	0.081
H(5)	0.265(1)	0.359(4)	0.3973(3)	0.139
H(6)	0.440(1)	0.359(4)	0.4942(3)	0.083
H(7)	0.047(1)	0.359(4)	0.5188(3)	0.184
H(8)	0.210(1)	0.359(4)	0.6162(4)	0.096
H(9)	−0.176(1)	0.359(4)	0.6402(4)	0.211
H(10)	−0.032(2)	0.359(3)	0.7411(6)	0.187
H(10M)	−0.274(2)	¼	0.7436(8)	0.187
H(11)	0.755(1)	0.359(3)	0.0339(6)	0.070
H(11M)	0.981(1)	¼	0.0013(5)	0.070
H(12A)	1.162	0.419	0.1563	0.067
H(12B)	1.000	0.528	0.1095	0.067
H(12C)	1.225	0.420	0.0752	0.067

Table S15c. Anisotropic displacement parameters for C_{10}TAB phase II at −23 °C. Anisotropic displacement factor exponent has the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11} / Å^2	U_{22} / Å^2	U_{33} / Å^2	U_{23} / Å^2	U_{13} / Å^2	U_{12} / Å^2
C(1)	0.0280(14)	0.0445(17)	0.0424(15)	0	0.0014(11)	0
C(2)	0.0450(19)	0.0930(3)	0.0429(17)	0	0.0000(14)	0
C(3)	0.048(2)	0.108(4)	0.0470(19)	0	0.0041(16)	0
C(4)	0.055(2)	0.097(3)	0.047(2)	0	0.0051(16)	0
C(5)	0.062(3)	0.234(10)	0.046(2)	0	0.0110(19)	0
C(6)	0.067(3)	0.087(3)	0.049(2)	0	0.0109(18)	0
C(7)	0.071(4)	0.330(14)	0.052(3)	0	0.017(2)	0
C(8)	0.096(4)	0.081(4)	0.055(2)	0	0.024(2)	0
C(9)	0.096(5)	0.364(17)	0.059(3)	0	0.030(3)	0
C(10)	0.166(7)	0.124(6)	0.069(3)	0	0.053(4)	0
C(11)	0.0445(17)	0.057(2)	0.0380(15)	0	−0.0044(12)	0
C(12)	0.0376(11)	0.0377(13)	0.0588(12)	0.0018(10)	−0.0020(9)	−0.0069(9)
N(1)	0.0278(11)	0.0346(13)	0.0409(12)	0	−0.0008(9)	0
Br(1)	0.03540(2)	0.03680(2)	0.07300(3)	0	−0.00207(16)	0

Table S15d. Selected bond lengths for C_{10}TAB phase II at −23 °C.

Atom — Atom	Length / Å	Atom — Atom	Length / Å
N(1) — C(1)	1.513(4)	C(7) — C(8)	1.420(7)
C(1) — C(2)	1.505(5)	C(8) — C(9)	1.415(8)
C(2) — C(3)	1.479(5)	C(9) — C(10)	1.389(9)
C(3) — C(4)	1.478(6)	N(1) — C(11)	1.503(4)
C(4) — C(5)	1.438(6)	N(1) — C(12)	1.494(3)
C(5) — C(6)	1.442(6)	N(1) — C(12)[1]	1.494(3)
C(6) — C(7)	1.424(7)		

[1] $x, \frac{1}{2} - y, z$

Table S15e. Selected bond angles for C_{10}TAB phase II at −23 °C.

Atom — Atom — Atom	Angle / ˚	Atom — Atom — Atom	Angle / ˚
N(1) — C(1) — C(2)	116.7(3)	C(8) — C(9) — C(10)	128.8(8)
C(1) — C(2) — C(3)	111.5(3)	C(1) — N(1) — C(11)	106.4(2)
C(2) — C(3) — C(4)	119.3(4)	C(1) — N(1) — C(12)	111.42(15)
C(3) — C(4) — C(5)	120.3(4)	C(1) — N(1) — C(12)[1]	111.42(15)
C(4) — C(5) — C(6)	124.5(5)	C(11) — N(1) — C(12)	109.02(16)
C(5) — C(6) — C(7)	124.6(5)	C(11) — N(1) — C(12)[1]	109.02(16)
C(6) — C(7) — C(8)	126.7(6)	C(12) — N(1) — C(12)[1]	109.4(2)
C(7) — C(8) — C(9)	127.8(7)		

[1] $x, \frac{1}{2} - y, z$

Table S15f. Selected torsion angles for C_{10}TAB phase II at −23 °C.

Atom — Atom — Atom — Atom	Angle / ˚	Atom — Atom — Atom — Atom	Angle / ˚
N(1) — C(1) — C(2) — C(3)	180	C(6) — C(7) — C(8) — C(9)	180
C(1) — C(2) — C(3) — C(4)	180	C(7) — C(8) — C(9) — C(10)	180
C(2) — C(3) — C(4) — C(5)	180	C(2) — C(1) — N(1) — C(11)	180
C(3) — C(4) — C(5) — C(6)	180	C(2) — C(1) — N(1) — C(12)	−61.27(16)
C(4) — C(5) — C(6) — C(7)	180	C(2) — C(1) — N(1) — C(12)[1]	61.28(17)
C(5) — C(6) — C(7) — C(8)	180		

[1] $x, ½ - y, z$

Table S16a. Crystal data and structure refinement for C_{10}TAB phase II at 22 °C.

Identification code	exp_825
Empirical formula	$C_{13}H_{30}BrN$
Formula weight	280.29
Temperature / K	295
Crystal system	monoclinic
Space group	$P2_1/m$
a / Å	5.63155(10)
b / Å	7.25188(14)
c / Å	19.6559(4)
α / °	90
β / °	81.2424(17)
γ / °	90
Volume / Å^3	793.38(3)
Z	2
ρ_{calc} / g cm^{-3}	1.173
μ / mm^{-1}	3.318
F(000)	300.0
Crystal size / mm^3	0.4807 × 0.2163 × 0.0207
Radiation	Cu Kα (λ = 1.54184 Å)
2θ range for data collection / °	9.104 to 147.612
Index ranges	−7 ≤ h ≤ 6, −9 ≤ k ≤ 9, −24 ≤ l ≤ 24
Reflections collected	11361
Independent reflections	1710 [R_{int} = 0.0444, R_{sigma} = 0.0192]
Data/restraints/parameters	1710/105/126
Goodness-of-fit on F^2	1.080
Final R indexes [$I \geq 2\sigma$ (I)]	R_1 = 0.0362, wR_2 = 0.1042
Final R indexes [all data]	R_1 = 0.0373, wR_2 = 0.1058
Largest diff. peak/hole / e Å^{-3}	0.98/−0.38

Table S16b. Fractional atomic coordinates and equivalent isotropic displacement parameters for C_{10}TAB phase II at 22 °C. U_{eq} is defined as ⅓ of the trace of the orthogonalised U_{ij} tensor.

Atom	*x*	*y*	*z*	*U*(eq) / Å^2
C(1)	0.7202(5)	¼	0.16214(17)	0.0536(7)
C(2)	0.7688(8)	¼	0.2351(2)	0.0766(11)
C(3)	0.5448(9)	¼	0.2851(2)	0.0879(14)
C(4)	0.5602(10)	¼	0.3595(2)	0.0922(15)
C(5)	0.3444(12)	¼	0.4098(3)	0.129(3)
C(6)	0.3464(11)	¼	0.4825(3)	0.1001(17)
C(7)	0.1327(14)	¼	0.5329(3)	0.165(4)
C(8)	0.1285(15)	¼	0.6057(3)	0.118(2)
C(9)	−0.0788(18)	¼	0.6568(4)	0.192(5)
C(10)	−0.0910(2)	¼	0.7277(4)	0.182(5)
C(11)	0.8424(6)	¼	0.03897(17)	0.0609(8)
C(12)	1.0872(4)	0.4181(4)	0.10998(13)	0.0595(6)
N(1)	0.9368(4)	¼	0.10614(13)	0.0464(5)
Br(1)	0.56574(6)	¾	0.09468(2)	0.06251(18)
H(1)	0.6253(13)	0.3580(4)	0.1553(2)	0.064
H(2)	0.8642(14)	0.3579(4)	0.2418(3)	0.092
H(3)	0.4531(14)	0.3579(4)	0.2759(3)	0.105
H(4)	0.6542(15)	0.3579(4)	0.3674(3)	0.111
H(5)	0.2539(17)	0.3578(4)	0.3997(3)	0.155
H(6)	0.4374(16)	0.3579(4)	0.4923(4)	0.120
H(7)	0.0425(19)	0.3578(4)	0.5226(4)	0.197
H(8)	0.2201(19)	0.3579(4)	0.6150(5)	0.141
H(9)	−0.167(2)	0.3579(4)	0.6456(5)	0.230
H(10)	−0.013(3)	0.3579(3)	0.7419(7)	0.273
H(10M)	−0.256(3)	¼	0.7490(9)	0.273
H(11)	0.7466(12)	0.3580(3)	0.0359(5)	0.091
H(11M)	0.9748(16)	¼	0.0019(5)	0.091
H(12A)	1.150	0.418	0.1527	0.089
H(12B)	0.991	0.526	0.1074	0.089
H(12C)	1.218	0.418	0.0723	0.089

Table S16c. Anisotropic displacement parameters for C_{10}TAB phase II at 22 °C. Anisotropic displacement factor exponent has the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11} / Å^2	U_{22} / Å^2	U_{33} / Å^2	U_{23} / Å^2	U_{13} / Å^2	U_{12} / Å^2
C(1)	0.0386(14)	0.0607(19)	0.0590(16)	0	0.0002(12)	0
C(2)	0.0600(2)	0.1060(3)	0.0620(2)	0	−0.0013(16)	0
C(3)	0.069(3)	0.127(4)	0.0640(2)	0	0.0029(19)	0
C(4)	0.080(3)	0.123(4)	0.066(2)	0	0.0110(2)	0
C(5)	0.092(4)	0.222(9)	0.066(3)	0	0.0120(2)	0
C(6)	0.105(4)	0.115(4)	0.071(3)	0	0.0160(3)	0
C(7)	0.107(5)	0.300(14)	0.074(3)	0	0.025(3)	0
C(8)	0.149(6)	0.112(5)	0.077(3)	0	0.032(3)	0
C(9)	0.149(8)	0.321(16)	0.085(4)	0	0.044(5)	0
C(10)	0.241(11)	0.178(9)	0.096(5)	0	0.068(6)	0
C(11)	0.0564(18)	0.071(2)	0.0558(17)	0	−0.0105(14)	0
C(12)	0.0498(12)	0.0513(14)	0.0761(14)	0.0019(11)	−0.0051(10)	−0.0085(10)
N(1)	0.0378(11)	0.0453(13)	0.0552(13)	0	−0.0039(10)	0
Br(1)	0.04580(2)	0.04850(2)	0.09150(3)	0	−0.00491(17)	0

Table S16d. Selected bond lengths for C_{10}TAB phase II at 22 °C.

Atom — Atom	Length / Å	Atom — Atom	Length / Å
N(1) — C(1)	1.513(4)	C(7) — C(8)	1.428(10)
C(1) — C(2)	1.500(5)	C(8) — C(9)	1.419(9)
C(2) — C(3)	1.476(6)	C(9) — C(10)	1.384(12)
C(3) — C(4)	1.479(7)	N(1) — C(11)	1.496(4)
C(4) — C(5)	1.444(7)	N(1) — C(12)	1.493(3)
C(5) — C(6)	1.432(8)	N(1) — C(12)[1]	1.493(3)
C(6) — C(7)	1.438(8)		

[1] $x, \frac{1}{2} - y, z$

Table S16e. Selected bond angles for C_{10}TAB phase II at 22 °C.

Atom — Atom — Atom	Angle / ˚	Atom — Atom — Atom	Angle / ˚
N(1) — C(1) — C(2)	116.8(3)	C(8) — C(9) — C(10)	128.5(11)
C(1) — C(2) — C(3)	112.0(4)	C(1) — N(1) — C(11)	106.7(2)
C(2) — C(3) — C(4)	119.1(4)	C(1) — N(1) — C(12)	111.34(16)
C(3) — C(4) — C(5)	120.4(5)	C(1) — N(1) — C(12)[1]	111.34(16)
C(4) — C(5) — C(6)	123.3(6)	C(11) — N(1) — C(12)	108.98(17)
C(5) — C(6) — C(7)	123.7(7)	C(11) — N(1) — C(12)[1]	108.97(17)
C(6) — C(7) — C(8)	125.1(8)	C(12) — N(1) — C(12)[1]	109.5(3)
C(7) — C(8) — C(9)	126.6(9)		

[1] $x, \frac{1}{2} - y, z$

Table S16f. Selected torsion angles for C_{10}TAB phase II at 22 °C.

Atom — Atom — Atom — Atom	Angle / ˚	Atom — Atom — Atom — Atom	Angle / ˚
N(1) — C(1) — C(2) — C(3)	180	C(6) — C(7) — C(8) — C(9)	180
C(1) — C(2) — C(3) — C(4)	180	C(7) — C(8) — C(9) — C(10)	180
C(2) — C(3) — C(4) — C(5)	180	C(2) — C(1) — N(1) — C(11)	180
C(3) — C(4) — C(5) — C(6)	180	C(2) — C(1) — N(1) — C(12)	−61.23(17)
C(4) — C(5) — C(6) — C(7)	180	C(2) — C(1) — N(1) — C(12)[1]	61.23(17)
C(5) — C(6) — C(7) — C(8)	180		

[1] $x, ½ - y, z$

Table S17a. Crystal data and structure refinement for C_{10}TAB phase II at 102 °C.

Identification code	exp_828
Empirical formula	$C_{13}H_{30}BrN$
Formula weight	280.29
Temperature / K	375
Crystal system	monoclinic
Space group	$P2_1/m$
a / Å	5.65600(12)
b / Å	7.31429(17)
c / Å	20.2631(6)
α / °	90
β / °	76.970(3)
γ / °	90
Volume / Å^3	816.70(4)
Z	2
ρ_{calc} / g cm^{-3}	1.140
μ / mm^{-1}	3.223
F(000)	300.0
Crystal size / mm^3	0.495 × 0.2112 × 0.0131
Radiation	Cu Kα (λ = 1.54184 Å)
2θ range for data collection / °	8.958 to 146.87
Index ranges	−6 ≤ h ≤ 7, −9 ≤ k ≤ 8, −24 ≤ l ≤ 25
Reflections collected	11983
Independent reflections	1758 [R_{int} = 0.0292, R_{sigma} = 0.0132]
Data/restraints/parameters	1758/105/126
Goodness-of-fit on F^2	1.073
Final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0431, wR_2 = 0.1308
Final R indexes [all data]	R_1 = 0.0474, wR_2 = 0.1379
Largest diff. peak/hole / e Å^{-3}	1.08/−0.50

Table S17b. Fractional atomic coordinates and equivalent isotropic displacement parameters for C_{10}TAB phase II at 102 °C. U_{eq} is defined as ⅓ of the trace of the orthogonalised U_{ij} tensor.

Atom	*x*	*y*	*z*	*U*(eq) / Å^2
C(1)	0.6989(8)	¼	0.1624(2)	0.0847(11)
C(2)	0.7432(12)	¼	0.2312(3)	0.1123(18)
C(3)	0.5204(14)	¼	0.2843(3)	0.130(2)
C(4)	0.5362(18)	¼	0.3572(4)	0.159(3)
C(5)	0.3251(19)	¼	0.4117(4)	0.170(4)
C(6)	0.340(2)	¼	0.4793(4)	0.165(4)
C(7)	0.135(2)	¼	0.5361(5)	0.187(5)
C(8)	0.145(3)	¼	0.6071(4)	0.188(4)
C(9)	−0.056(3)	¼	0.6620(5)	0.230(7)
C(10)	−0.045(3)	¼	0.7301(5)	0.264(8)
C(11)	0.8257(8)	¼	0.0405(2)	0.0874(12)
C(12)	1.0710(5)	0.4169(5)	0.10428(18)	0.0883(9)
N(1)	0.9187(5)	¼	0.10450(17)	0.0684(7)
Br(1)	0.54928(8)	¾	0.09384(3)	0.0896(3)
H(1)	0.6039(15)	0.3570(4)	0.1567(3)	0.102
H(2)	0.8388(17)	0.3570(4)	0.2362(4)	0.135
H(3)	0.4254(18)	0.3569(4)	0.2786(5)	0.156
H(4)	0.633(2)	0.3570(4)	0.3612(5)	0.190
H(5)	0.233(2)	0.3570(4)	0.4041(5)	0.204
H(6)	0.432(2)	0.3570(4)	0.4865(5)	0.198
H(7)	0.039(3)	0.3570(4)	0.5307(6)	0.225
H(8)	0.242(3)	0.3570(4)	0.6113(7)	0.226
H(9)	−0.150(3)	0.3570(4)	0.6559(7)	0.276
H(10)	0.040(4)	0.3570(3)	0.7397(8)	0.396
H(10M)	−0.206(4)	¼	0.7581(10)	0.396
H(11)	0.7290(14)	0.3570(3)	0.0393(6)	0.131
H(11M)	0.9604(18)	¼	0.0020(4)	0.131
H(12A)	1.139	0.4162	0.1435	0.132
H(12B)	0.972	0.5239	0.1050	0.132
H(12C)	1.199	0.4177	0.0641	0.132

Table S17c. Anisotropic displacement parameters for C_{10}TAB phase II at 102 °C. Anisotropic displacement factor exponent has the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11} / Å^2	U_{22} / Å^2	U_{33} / Å^2	U_{23} / Å^2	U_{13} / Å^2	U_{12} / Å^2
C(1)	0.065(2)	0.088(3)	0.096(3)	0	−0.0068(19)	0
C(2)	0.104(4)	0.132(5)	0.097(3)	0	−0.013(3)	0
C(3)	0.128(5)	0.156(7)	0.100(4)	0	−0.010(3)	0
C(4)	0.149(7)	0.202(10)	0.106(4)	0	0.012(4)	0
C(5)	0.152(7)	0.224(11)	0.114(5)	0	0.014(4)	0
C(6)	0.196(10)	0.174(9)	0.108(5)	0	0.002(5)	0
C(7)	0.155(8)	0.260(14)	0.128(6)	0	0.007(5)	0
C(8)	0.252(12)	0.178(10)	0.109(5)	0	0.014(6)	0
C(9)	0.238(14)	0.297(18)	0.122(6)	0	0.030(7)	0
C(10)	0.360(20)	0.268(18)	0.126(7)	0	0.015(10)	0
C(11)	0.079(3)	0.095(3)	0.091(3)	0	−0.024(2)	0
C(12)	0.0740(17)	0.0644(19)	0.126(2)	0.0016(16)	−0.0205(16)	−0.0104(13)
N(1)	0.0537(15)	0.0614(18)	0.0891(19)	0	−0.0144(13)	0
Br(1)	0.0671(3)	0.0657(3)	0.1333(5)	0	−0.0169(3)	0

Table S17d. Selected bond lengths for C_{10}TAB phase II at 102 °C.

Atom — Atom	Length / Å	Atom — Atom	Length / Å
N(1) — C(1)	1.505(5)	C(7) — C(8)	1.454(16)
C(1) — C(2)	1.471(8)	C(8) — C(9)	1.401(15)
C(2) — C(3)	1.461(10)	C(9) — C(10)	1.396(18)
C(3) — C(4)	1.500(11)	N(1) — C(11)	1.505(5)
C(4) — C(5)	1.433(12)	N(1) — C(12)	1.493(4)
C(5) — C(6)	1.391(13)	N(1) — C(12)[1]	1.493(4)
C(6) — C(7)	1.438(14)		

[1] $x, \frac{1}{2}-y, z$

Table S17e. Selected bond angles for C_{10}TAB phase II at 102 °C.

Atom — Atom — Atom	Angle / ˚	Atom — Atom — Atom	Angle / ˚
N(1) — C(1) — C(2)	116.8(4)	C(8) — C(9) — C(10)	125.2(15)
C(1) — C(2) — C(3)	113.3(5)	C(1) — N(1) — C(11)	106.5(3)
C(2) — C(3) — C(4)	119.5(7)	C(1) — N(1) — C(12)	112.2(2)
C(3) — C(4) — C(5)	122.4(9)	C(1) — N(1) — C(12)[1]	112.2(2)
C(4) — C(5) — C(6)	122.4(10)	C(11) — N(1) — C(12)	108.1(2)
C(5) — C(6) — C(7)	124.8(11)	C(11) — N(1) — C(12)[1]	108.1(2)
C(6) — C(7) — C(8)	125.8(12)	C(12) — N(1) — C(12)[1]	109.6(3)
C(7) — C(8) — C(9)	125.4(13)		

[1] $x, \frac{1}{2}-y, z$

Table S17f. Selected torsion angles for C_{10}TAB phase II at 102 °C.

Atom — Atom — Atom — Atom	Angle / ˚	Atom — Atom — Atom — Atom	Angle / ˚
N(1) — C(1) — C(2) — C(3)	180	C(6) — C(7) — C(8) — C(9)	180
C(1) — C(2) — C(3) — C(4)	180	C(7) — C(8) — C(9) — C(10)	180
C(2) — C(3) — C(4) — C(5)	180	C(2) — C(1) — N(1) — C(11)	180
C(3) — C(4) — C(5) — C(6)	180	C(2) — C(1) — N(1) — C(12)	−61.9(2)
C(4) — C(5) — C(6) — C(7)	180	C(2) — C(1) — N(1) — C(12)[1]	61.9(2)
C(5) — C(6) — C(7) — C(8)	180		

[1] $x, ½ - y, z$

Table S18a. Crystal data and structure refinement for C_1TAB at −123 °C.

Identification code	xstr0600
Empirical formula	$C_4H_{12}BrN$
Formula weight	154.06
Temperature / K	150
Crystal system	tetragonal
Space group	$P4/nmm$
a / Å	7.6596(2)
b / Å	7.6596(2)
c / Å	5.4588(2)
α / °	90
β / °	90
γ / °	90
Volume / Å^3	320.27(2)
Z	2
ρ_{calc} / g cm^{-3}	1.597
μ / mm^{-1}	7.706
F(000)	156.0
Crystal size / mm^3	0.121 × 0.065 × 0.029
Radiation	Cu Kα (λ = 1.54184 Å)
2θ range for data collection / °	16.238 to 147.264
Index ranges	$-9 \le h \le 9$, $-8 \le k \le 9$, $-6 \le l \le 6$
Reflections collected	2896
Independent reflections	209 [R_{int} = 0.0468, R_{sigma} = 0.0179]
Data/restraints/parameters	209/3/17
Goodness-of-fit on F^2	1.170
Final R indexes [$I \ge 2\sigma(I)$]	R_1 = 0.0221, wR_2 = 0.0603
Final R indexes [all data]	R_1 = 0.0233, wR_2 = 0.0615
Largest diff. peak/hole / e Å^{-3}	0.87/−0.29

Table S18b. Fractional atomic coordinates and equivalent isotropic displacement parameters for C_1TAB at −123 °C with a centrosymmetric choice of origin for space group $P4/nmm$. The N atom is on Wyckoff site 2a with $\bar{4}m2$ point-group symmetry and the Br atom is on Wyckoff site 2c with $4mm$ point-group symmetry. U_{eq} is defined as ⅓ of the trace of the orthogonalised U_{ij} tensor.

Atom	x	y	z	U(eq) / Å^2
Br(1)	¼	¼	0.62394(9)	0.0234(3)
N(1)	¾	¼	0	0.0193(9)
C(1)	0.5913(4)	¼	0.1584(5)	0.0280(7)
H(1A)	0.591(3)	0.354(3)	0.263(3)	0.042
H(1B)	0.487(2)	¼	0.056(4)	0.042

Table S18c. Anisotropic displacement parameters for C_1TAB at −123 °C. Anisotropic displacement factor exponent has the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11} / Å^2	U_{22} / Å^2	U_{33} / Å^2	U_{23} / Å^2	U_{13} / Å^2	U_{12} / Å^2
Br(1)	0.0234(3)	0.0234(3)	0.0234(4)	0	0	0
N(1)	0.0181(14)	0.0181(14)	0.0220(2)	0	0	0
C(1)	0.0175(15)	0.0377(19)	0.0287(13)	0	0.0029(12)	0

Table S18d. Selected bond lengths for C_1TAB at −123 °C.

Atom — Atom	Length / Å	Atom — Atom	Length / Å
N(1) — C(1)	1.492(3)	N(1) — C(1)^2	1.492(3)
N(1) — C(1)^1	1.492(3)	N(1) — C(1)^3	1.492(3)

^{1} $½ + y, x − ½, −z$; ^{2} $½ + y, 1 − x, −z$; ^{3} $^3⁄_2 + x, y, z$

Table S18e. Selected bond angles for C_1TAB at −123 °C.

Atom — Atom — Atom	Angle / ˚	Atom — Atom — Atom	Angle / ˚
C(1) — N(1) — C(1)1	109.63(11)	C(1)1 — N(1) — C(1)2	109.63(11)
C(1) — N(1) — C(1)2	109.2(2)	C(1)1 — N(1) — C(1)3	109.2(2)
C(1) — N(1) — C(1)3	109.63(11)	C(1)2 — N(1) — C(1)3	109.63(11)

^{1} $½ + y, x − ½, −z$; ^{2} $½ + y, 1 − x, −z$; ^{3} $^3⁄_2 + x, y, z$

Table S19. Lattice parameter data for C_{18}TAB as a function of temperature obtained from LeBail fits to the PXRD data shown in Fig. S6.

T / °C	a / Å	b / Å	c / Å	α / °	β / °	γ / °	V / Z / Å^3
27	5.62803(11)	7.26435(18)	56.7286(8)	90	95.9210(13)	90	576.73(2)
37	5.62839(9)	7.27595(10)	56.7484(9)	90	95.820(2)	90	577.99(2)
47	5.63183(15)	7.28603(9)	56.7632(9)	90	95.757(3)	90	579.36(2)
57	5.63726(10)	7.29704(10)	56.7719(8)	90	95.611(2)	90	581.04(2)
67	5.64119(10)	7.30834(10)	56.7910(9)	90	95.525(2)	90	582.62(2)
77	5.64417(8)	7.32058(8)	56.8060(7)	90	95.4048(13)	90	584.18(13)
87	5.64795(8)	7.33383(7)	56.8292(7)	90	95.2632(12)	90	586.00(12)
97	5.65471(10)	7.35314(10)	28.4329(5)	90	94.926(2)	90	588.93(2)
107	5.66148(9)	7.38714(10)	28.4975(5)	90	93.940(2)	90	594.51(2)
117	6.489(2)	= a	33.213(9)	90	90	90	699.3(5)
127	6.4935(14)	= a	33.357(6)	90	90	90	703.3(3)
137	6.495(2)	= a	33.500(9)	90	90	90	706.7(5)
147	6.4988(13)	= a	33.652(6)	90	90	90	710.6(3)
157	6.5039(13)	= a	33.826(6)	90	90	90	715.4(3)
167	6.507(2)	= a	33.973(10)	90	90	90	719.1(5)
177	6.509(3)	= a	34.141(11)	90	90	90	723.3(7)
187	6.511(3)	= a	34.446(11)	90	90	90	730.1(7)
197	6.516(3)	= a	34.665(11)	90	90	90	735.8(7)
207	6.520(4)	= a	34.888(12)	90	90	90	741.5(9)
217	6.522(7)	= a	35.268(18)	90	90	90	750.1(16)
227	6.522(8)	= a	35.76(3)	90	90	90	760.5(19)

Table S20. Lattice parameter data for C_{16}TAB as a function of temperature obtained from LeBail fits to the PXRD data shown in Fig. S7. The results from fits to several additional data sets collected in 5° C intervals are also given.

T / °C	a / Å	b / Å	c / Å	α / °	β / °	γ / °	V / Z / Å^3
27	5.62939(12)	7.25543(14)	51.9919(10)	90	93.7823(11)	90	529.73(2)
37	5.63305(12)	7.26500(14)	52.0153(11)	90	93.6874(11)	90	531.07(2)
47	5.63695(13)	7.27534(16)	52.0415(12)	90	93.5975(11)	90	532.51(2)
57	5.64022(15)	7.28655(17)	52.0638(13)	90	93.4667(12)	90	533.77(2)
67	5.64361(17)	7.29926(20)	52.0891(17)	90	93.2912(16)	90	535.56(3)
72	5.64584(14)	7.30523(16)	26.0558(6)	90	93.1758(13)	90	536.50(2)
77	5.64855(17)	7.31491(20)	26.0703(8)	90	92.9490(14)	90	537.88(3)
82	5.65195(16)	7.33150(18)	26.1122(7)	90	92.4277(14)	90	540.53(3)
87	5.65339(16)	7.34015(18)	26.1356(7)	90	92.1639(15)	90	541.88(3)
92	5.65505(16)	7.35100(18)	26.1678(8)	90	91.8590(13)	90	543.62(3)
97	5.65681(16)	7.36143(18)	26.2011(7)	90	91.5357(14)	90	545.34(3)
102	5.65962(15)	7.37011(18)	26.2321(7)	90	91.2497(14)	90	546.97(2)
107	5.66047(22)	7.37717(26)	26.2467(11)	90	90.9354(19)	90	547.93(4)
112	6.4674(2)	= a	30.223(3)	90	90	90	632.06(4)
117	6.4728(4)	= a	30.277(4)	90	90	90	634.25(10)
127	6.4798(2)	= a	30.383(3)	90	90	90	637.86(8)
137	6.4809(3)	= a	30.546(4)	90	90	90	641.50(10)
147	6.4962(2)	= a	30.717(5)	90	90	90	648.14(11)
157	6.4910(3)	= a	30.842(3)	90	90	90	649.73(8)
167	6.4984(2)	= a	30.957(4)	90	90	90	653.64(8)
177	6.5001(2)	= a	31.118(3)	90	90	90	657.37(6)
187	6.5135(10)	= a	31.262(5)	90	90	90	663.15(18)
197	6.5082(2)	= a	31.439(3)	90	90	90	665.82(7)
207	6.5118(3)	= a	31.667(4)	90	90	90	671.41(9)
217	6.5291(10)	= a	32.080(7)	90	90	90	683.77(22)
227	6.5258(8)	= a	32.114(6)	90	90	90	683.80(17)

Table S21. Lattice parameter data for C_{14}TAB as a function of temperature obtained from LeBail fits to the PXRD data shown in Fig. S8.

T / °C	a / Å	b / Å	c / Å	α / °	β / °	γ / °	V / Z / Å^3
7	5.63086(9)	7.23745(8)	47.3587(9)	90	91.3425(14)	90	482.370(13)
17	5.63383(8)	7.24647(8)	47.3873(9)	90	91.2233(14)	90	483.565(13)
27	5.63327(8)	7.24817(7)	47.3841(7)	90	91.1440(13)	90	483.418(11)
37	5.63909(17)	7.26485(19)	47.4376(14)	90	90.9395(14)	90	485.78(2)
47	5.64449(16)	7.28203(19)	23.7646(7)	90	90.5236(13)	90	488.38(2)
57	5.64343(7)	7.29077(9)	23.8028(4)	90	90.1123(19)	90	489.681(12)
67	5.64565(8)	7.30475(8)	23.8542(4)	90	89.4546(13)	90	491.851(12)
77	5.64894(9)	7.31825(8)	23.9087(4)	90	88.9485(14)	90	494.114(13)
87	5.65178(8)	7.33171(8)	23.9725(5)	90	88.3964(14)	90	496.483(13)
97	5.65826(19)	7.3504(2)	24.0504(10)	90	87.7418(17)	90	499.74(3)
107	6.4857(7)	= a	27.487(4)	90	90	90	578.10(12)
117	6.4910(7)	= a	27.650(4)	90	90	90	582.48(13)
127	6.4950(6)	= a	27.774(4)	90	90	90	585.83(11)
137	6.4990(7)	= a	27.925(4)	90	90	90	589.74(13)
147	6.5019(7)	= a	28.069(4)	90	90	90	593.31(13)
157	6.5030(6)	= a	28.198(4)	90	90	90	596.24(12)
167	6.5084(8)	= a	28.353(5)	90	90	90	600.51(15)
177	6.5109(9)	= a	28.536(6)	90	90	90	604.83(17)
187	6.5153(7)	= a	28.777(5)	90	90	90	610.78(14)
197	6.5237(9)	= a	29.113(6)	90	90	90	619.50(17)
207	6.5147(2)	= a	29.451(4)	90	90	90	624.96(10)
217	6.5266(3)	= a	29.957(5)	90	90	90	638.02(11)
227	6.5421(13)	= a	30.856(8)	90	90	90	660.3(3)

Table S22. Lattice parameter data for C_{12}TAB as a function of temperature obtained from LeBail fits to the PXRD data shown in Fig. S9.

T / °C	a / Å	b / Å	c / Å	α / °	β / °	γ / °	V / Z / Å^3
−123	5.58553(13)	7.16916(17)	42.5653(9)	90	89.2789(17)	90	426.082(16)
−43	5.61795(8)	7.19830(9)	42.7284(6)	90	88.6763(12)	90	431.865(10)
−33	5.62114(8)	7.20463(8)	42.7535(6)	90	88.5793(12)	90	432.727(10)
−23	5.62425(8)	7.21147(9)	42.7830(7)	90	88.4742(13)	90	433.656(11)
−13	5.62708(7)	7.21781(8)	42.8111(6)	90	88.3552(11)	90	434.516(9)
−3	5.62927(7)	7.22586(7)	42.8483(7)	90	88.1909(12)	90	435.515(10)
7	5.63411(8)	7.23543(8)	21.4591(4)	90	87.8601(14)	90	437.087(12)
17	5.63764(7)	7.24798(6)	21.5315(4)	90	87.2300(12)	90	439.391(10)
27	5.64047(7)	7.25824(7)	21.5777(4)	90	86.8292(12)	90	441.019(11)
37	5.64326(7)	7.26892(7)	21.6269(4)	90	86.4392(13)	90	442.717(10)
47	5.64541(7)	7.27945(7)	21.6800(4)	90	86.0249(13)	90	444.403(11)
57	5.64754(8)	7.29067(7)	21.7403(4)	90	85.5573(13)	90	446.226(11)
67	5.64918(8)	7.30190(8)	21.8113(5)	90	85.0034(14)	90	448.146(13)
⋮							
107	6.48632(6)	= a	24.8619(9)	90	90	90	523.00(2)
117	6.49088(6)	= a	24.9601(9)	90	90	90	525.80(2)
127	6.49537(6)	= a	25.0597(9)	90	90	90	528.63(2)
137	6.49876(8)	= a	25.1657(9)	90	90	90	531.42(2)
147	6.50165(9)	= a	25.2743(8)	90	90	90	534.19(2)
157	6.50491(7)	= a	25.3760(8)	90	90	90	536.88(2)
167	6.50775(8)	= a	25.4641(8)	90	90	90	539.21(2)

Table S23. Lattice parameter data for C_{10}TAB as a function of temperature obtained from LeBail fits to the PXRD data shown in Fig. S10.

T / °C	a / Å	b / Å	c / Å	α / °	β / °	γ / °	V / Z / Å^3
−123	5.60054(9)	7.13901(9)	38.1249(6)	90	85.4228(14)	90	379.865(10)
−93	5.60779(7)	7.15540(7)	38.1948(5)	90	85.1923(10)	90	381.803(8)
−83	5.61067(7)	7.16137(7)	38.2206(5)	90	85.1121(10)	90	382.530(8)
−73	5.61302(7)	7.16699(7)	38.2509(5)	90	85.0219(10)	90	383.242(8)
−63	5.61586(7)	7.17304(7)	38.2819(5)	90	84.9242(10)	90	384.014(8)
−53	5.61909(7)	7.17961(7)	38.3191(5)	90	84.7842(10)	90	384.875(8)
−43	5.62134(7)	7.18849(7)	19.2294(3)	90	84.1946(10)	90	386.528(8)
−33	5.62329(7)	7.19715(7)	19.2924(3)	90	83.7038(10)	90	388.044(8)
−23	5.62528(7)	7.20529(7)	19.3435(3)	90	83.3349(11)	90	389.364(8)
−13	5.62708(7)	7.21404(7)	19.3945(3)	90	82.9784(11)	90	390.699(8)
−3	5.62887(6)	7.22284(7)	19.4465(3)	90	82.6153(10)	90	392.034(8)
7	5.63015(6)	7.23204(6)	19.5050(3)	90	82.2185(10)	90	393.440(8)
17	5.63024(6)	7.24076(7)	19.5648(3)	90	81.8083(17)	90	394.733(9)
27	5.63276(7)	7.25090(8)	19.6400(3)	90	81.2947(11)	90	396.453(9)
37	5.63399(7)	7.26046(8)	19.7182(3)	90	80.7574(12)	90	398.055(9)
47	5.63515(8)	7.27030(9)	19.8088(4)	90	80.1437(14)	90	399.786(11)
52	5.63493(10)	7.27571(10)	19.8662(5)	90	79.7632(17)	90	400.757(14)
57	5.63469(10)	7.28060(11)	19.9294(4)	91.163(2)	79.3625(18)	90.052(1)	401.68(17)
62	5.6369(2)	7.2859(2)	19.9758(10)	90	79.036(4)	90	402.71(3)
67	5.63657(10)	7.29116(11)	20.0300(5)	90	78.6455(19)	90	403.533(14)
77	5.63887(7)	7.30141(8)	20.1385(4)	90	77.8934(13)	90	405.35(2)
87	5.64305(7)	7.31199(8)	20.2290(3)	90	77.2276(11)	90	407.017(9)
97	5.65058(7)	7.31968(8)	20.2629(3)	90	76.8776(12)	90	408.098(9)
107	6.47579(8)	= a	44.0128(16)	90	90	90	461.428(19)
117	6.48008(8)	= a	44.1985(17)	90	90	90	463.990(19)
127	6.48400(9)	= a	44.3842(19)	90	90	90	466.50(2)
137	6.48728(10)	= a	44.572(2)	90	90	90	468.95(3)
147	6.49068(14)	= a	44.770(3)	90	90	90	471.53(3)
157	6.49233(11)	= a	22.555(4)	90	90	90	475.34(9)
167	6.49720(12)	= a	22.5885(11)	90	90	90	476.77(3)
177	6.50162(10)	= a	22.6717(10)	90	90	90	479.18(2)
187	6.50509(9)	= a	22.7722(11)	90	90	90	481.82(2)
197	6.50830(9)	= a	22.8923(12)	90	90	90	484.84(3)

Table S24. Lattice parameter data for C_1TAB as a function of temperature obtained from LeBail fits to variable temperature PXRD data. No phase transitions were observed.

T / °C	a / Å	b / Å	c / Å	α / °	β / °	γ / °	V / Z / Å^3
−153	7.64689(9)	= a	5.44685(8)	90	90	90	159.252(4)
−143	7.65055(9)	= a	5.44997(8)	90	90	90	159.496(4)
−133	7.65420(10)	= a	5.45290(8)	90	90	90	159.734(4)
−123	7.65783(10)	= a	5.45598(9)	90	90	90	159.975(4)
−113	7.66178(10)	= a	5.45921(9)	90	90	90	160.236(4)
−103	7.66582(10)	= a	5.46257(9)	90	90	90	160.504(4)
−93	7.66979(10)	= a	5.46569(9)	90	90	90	160.761(4)
−83	7.67378(10)	= a	5.46894(9)	90	90	90	161.024(4)
−73	7.67799(10)	= a	5.47236(9)	90	90	90	161.302(4)
−63	7.68196(10)	= a	5.47546(9)	90	90	90	161.560(4)
−53	7.68616(11)	= a	5.47885(9)	90	90	90	161.837(4)
−43	7.69021(10)	= a	5.48213(9)	90	90	90	162.104(4)
−33	7.69442(10)	= a	5.48557(9)	90	90	90	162.384(4)
−23	7.69873(11)	= a	5.48887(10)	90	90	90	162.664(4)
−13	7.70270(11)	= a	5.49194(10)	90	90	90	162.923(4)
−3	7.70737(11)	= a	5.49550(10)	90	90	90	163.226(4)
7	7.71207(11)	= a	5.49895(10)	90	90	90	163.528(4)
17	7.71670(11)	= a	5.50264(10)	90	90	90	163.834(5)
27	7.72337(9)	= a	5.50669(7)	90	90	90	164.238(4)
37	7.72812(9)	= a	5.51041(7)	90	90	90	164.551(4)
47	7.73281(9)	= a	5.51399(8)	90	90	90	164.858(4)
57	7.73750(10)	= a	5.51769(8)	90	90	90	165.169(4)
67	7.74218(10)	= a	5.52131(8)	90	90	90	165.477(4)
77	7.74693(10)	= a	5.52496(8)	90	90	90	165.790(4)
87	7.75155(10)	= a	5.52857(8)	90	90	90	166.096(4)
97	7.75663(10)	= a	5.53249(8)	90	90	90	166.432(4)
107	7.76155(10)	= a	5.53623(8)	90	90	90	166.756(4)
117	7.76673(10)	= a	5.54020(8)	90	90	90	167.098(4)
127	7.77189(10)	= a	5.54413(8)	90	90	90	167.439(4)
137	7.77696(11)	= a	5.54797(9)	90	90	90	167.774(4)
147	7.78136(11)	= a	5.55145(9)	90	90	90	168.069(4)
157	7.78665(11)	= a	5.55546(9)	90	90	90	168.419(4)
167	7.79203(11)	= a	5.55955(9)	90	90	90	168.776(4)
177	7.79741(11)	= a	5.56369(9)	90	90	90	169.135(5)
187	7.80290(12)	= a	5.56774(10)	90	90	90	169.496(5)
197	7.80840(12)	= a	5.57175(10)	90	90	90	169.858(5)
207	7.81350(12)	= a	5.57570(10)	90	90	90	170.200(5)

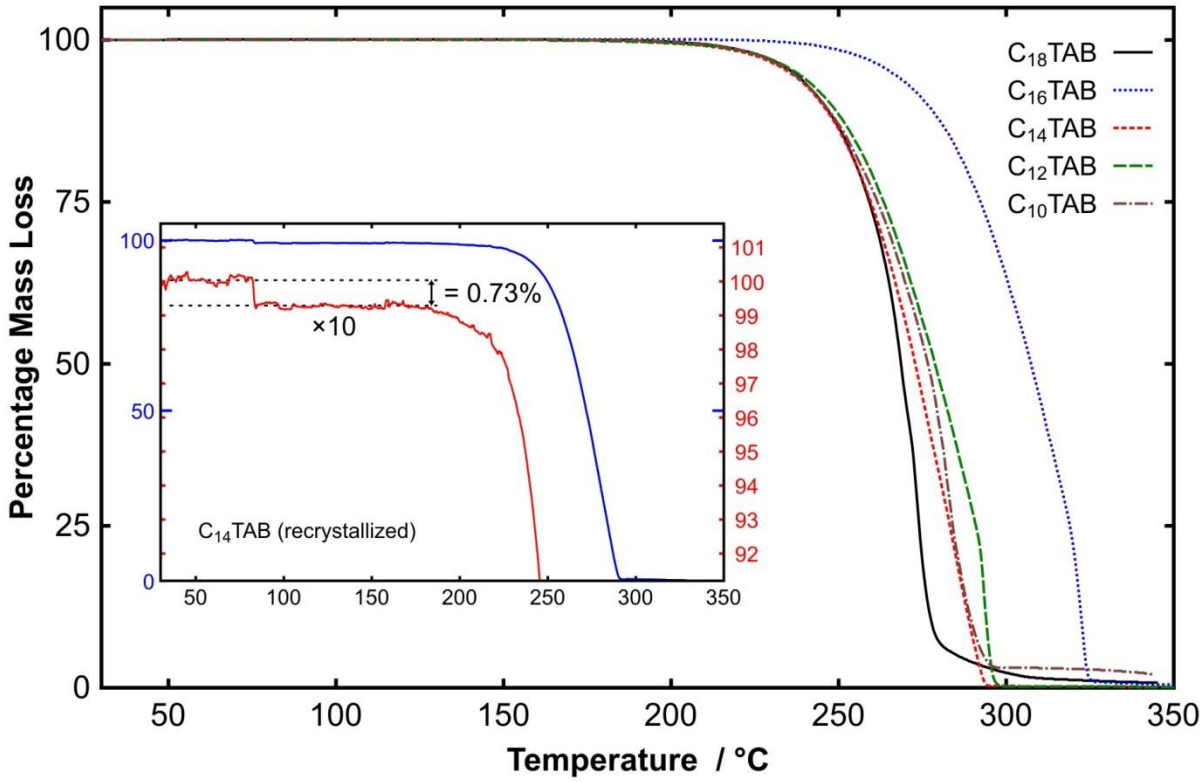


Fig. S1. TGA data on samples of C_{18}TAB to C_{10}TAB demonstrating sample stability to around 200 °C. The data demonstrates absence of any hydrate phase within the samples as supplied. With the sole exception of C_{16}TAB that decomposed at about 325 °C, possibly due to a much larger crystallite size; the other C_nTAB samples all decomposed below 300 °C. The inset figure shows TGA data for a sample of C_{14}TAB recrystallized from water, again showing absence of hydrate formation; the 0.73% mass loss (visible on the enlarged scale inset) at approximately 80 °C is consistent with the loss of loosely-bound water from the surface of the crystallites, which can be removed by vacuum drying.

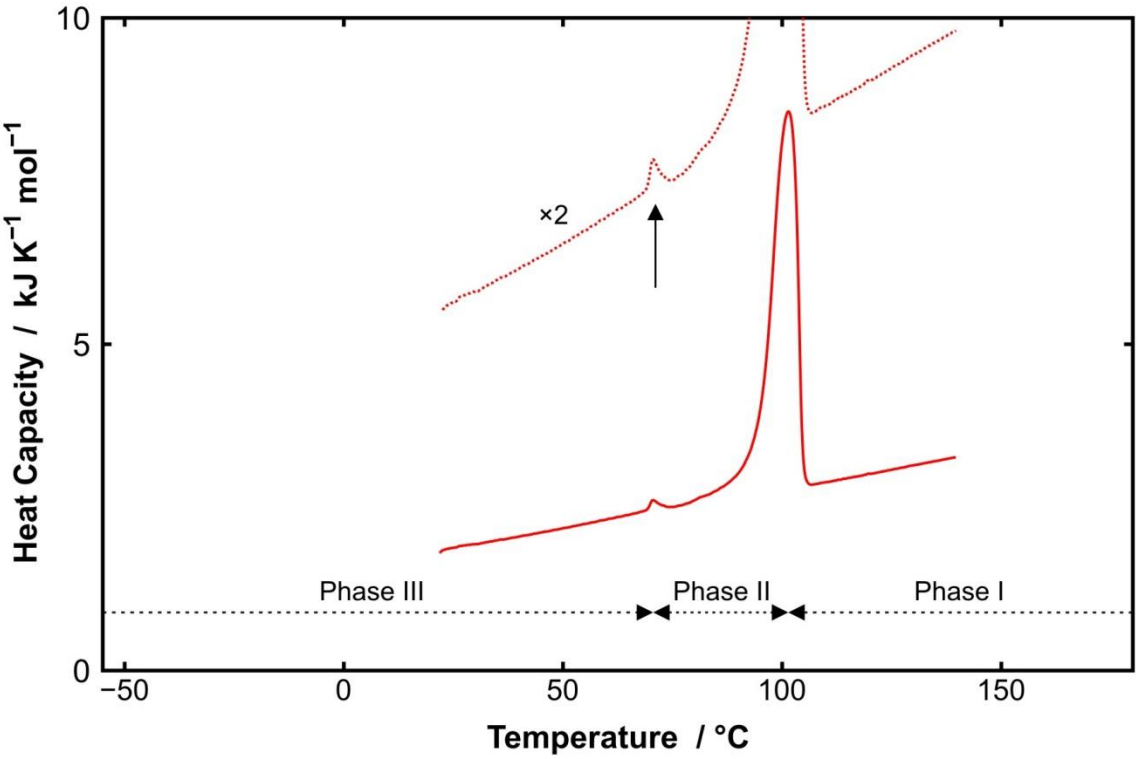


Fig. S2. DSC data on heating a 9.502 mg sample of C_{18}TAB from 20 °C to 140 °C at 10 °C min^{-1} shown as a solid line. The dotted curve shows the data expanded on a vertical scale (×2) to highlight weaker features. In addition to the major peak at 101.4 °C (ΔH = 41.1 kJ mol^{-1}), a weaker transition indicated with an arrow was observed at 70.5 °C (ΔH = 0.4 kJ mol^{-1}).

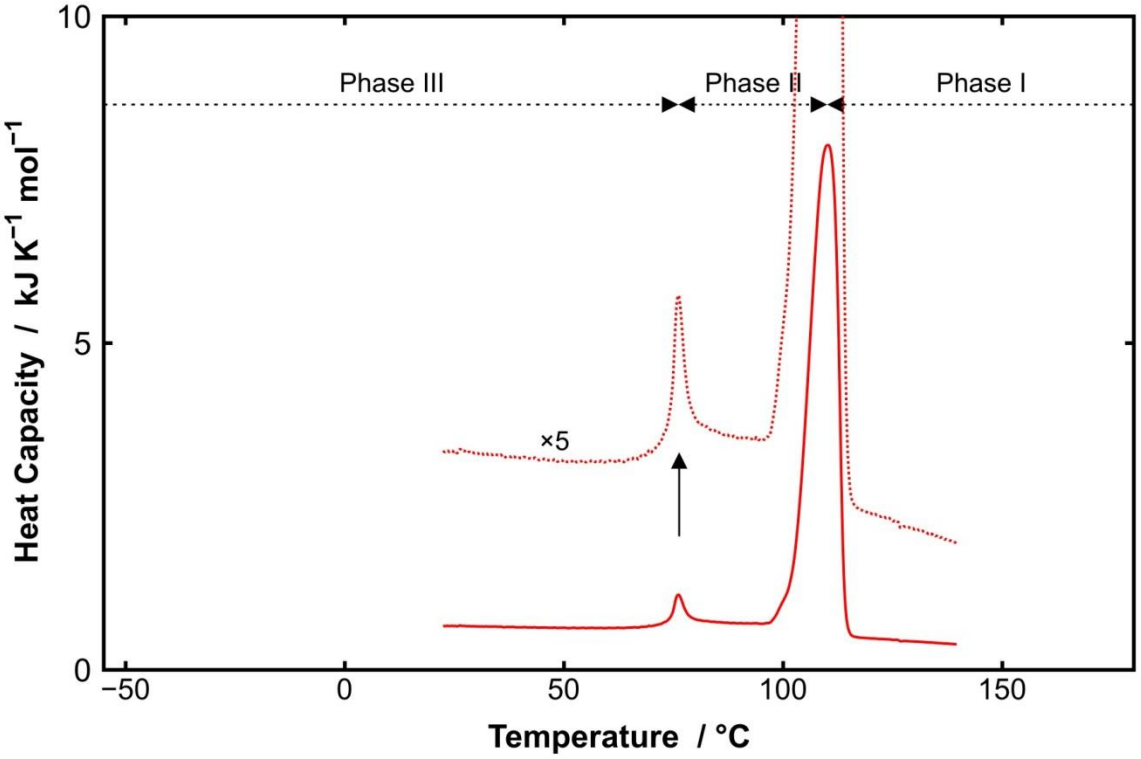


Fig. S3. DSC data on heating a 10.302 mg sample of C_{16}TAB from 20 °C to 140 °C at 10 °C min^{-1} shown as a solid line. The dotted curve shows the data expanded on a vertical scale (×5) to highlight weaker features. In addition to the major peak at 110.4 °C (ΔH = 52.9 kJ mol^{-1}), a weaker transition indicated with an arrow was observed at 76.2 °C (ΔH = 1.5 kJ mol^{-1}).

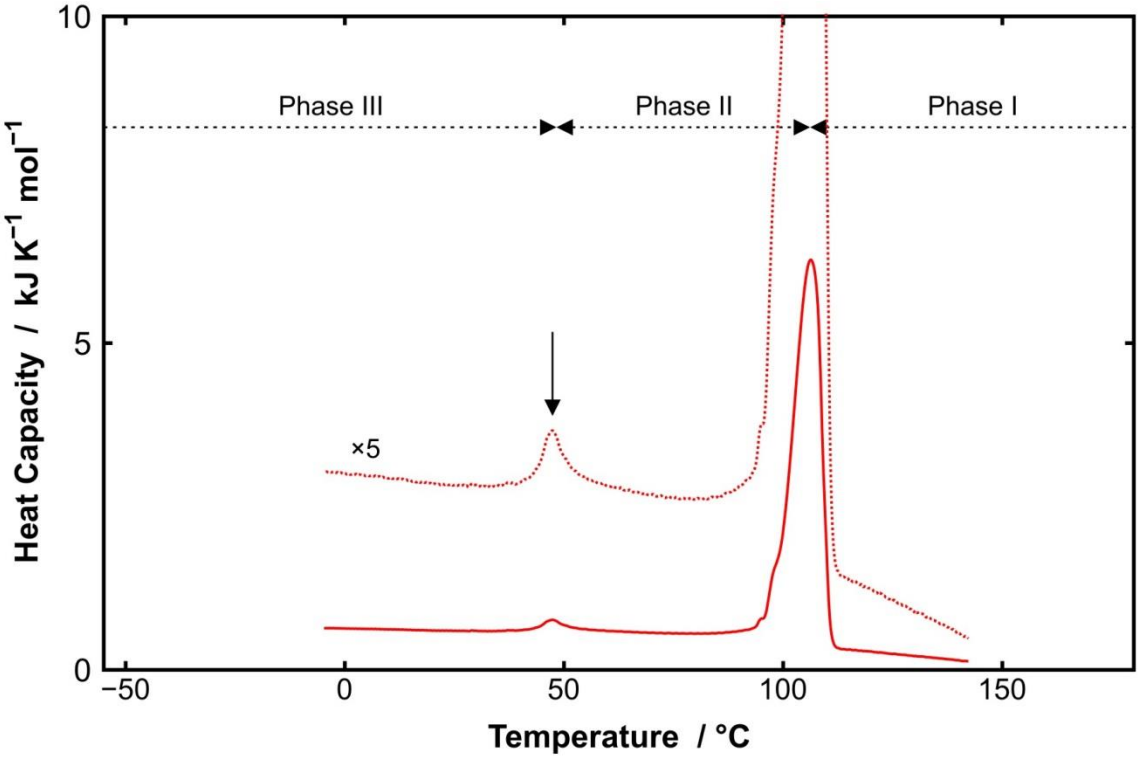


Fig. S4. DSC data on heating an 8.636 mg sample of C_{14}TAB from −10 °C to 140 °C at 10 °C min^{-1} shown as a solid line. The dotted curve shows the data expanded on a vertical scale (×5) to highlight weaker features. In addition to the major peak at 103.7 °C (ΔH = 46.6 kJ mol^{-1}), a weaker transition indicated with an arrow was observed at 44.8 °C (ΔH = 1.2 kJ mol^{-1}).

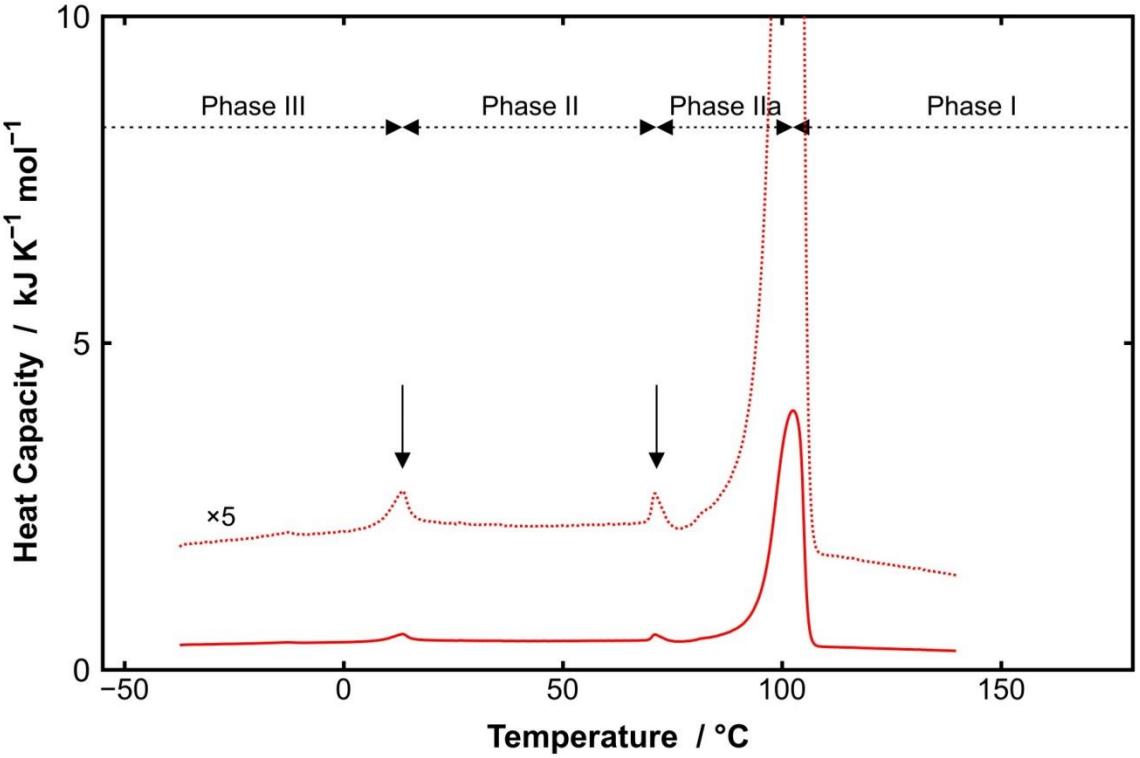


Fig. S5. DSC data on heating a 9.349 mg sample of C_{12}TAB from −40 °C to 140 °C at 10 °C min^{-1} shown as a solid line. The dotted curve shows the data expanded on a vertical scale (×5) to highlight weaker features. In addition to the major peak at 102.5 °C (ΔH = 35.6 kJ mol^{-1}), two weaker transitions indicated with arrows were observed at 13.4 °C (ΔH = 0.7 kJ mol^{-1}) and 71.0 °C (ΔH = 0.3 kJ mol^{-1}).

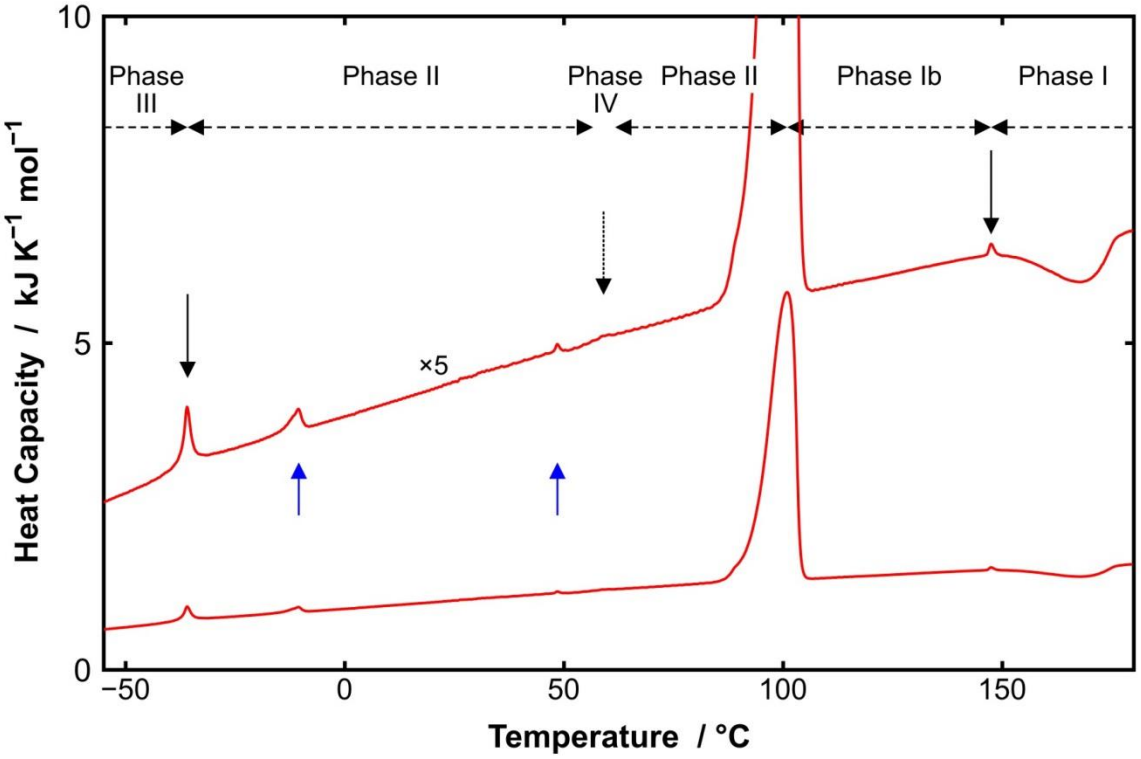


Fig. S6. DSC data on heating a 9.349 mg sample of C_{10}TAB from −60 °C to 180 °C at 10 °C min^{-1} shown as a solid line. The dotted curve shows the data expanded on a vertical scale (×5) to highlight weaker features. In addition to the major peak at 100.9 °C (ΔH = 32.3 kJ mol^{-1}), two weaker transitions that were also seen in PXRD data are indicated with solid down arrows at −36.0 °C (ΔH = 0.6 kJ mol^{-1}) and 147.4 °C (ΔH = 0.07 kJ mol^{-1}). Other features indicated with blue up arrows were observed at −10.7 °C and 48.4 °C. The re-entrant transition associated with the presence of phase IV (indicated with a dashed down arrow) is hardly discernible in this data.

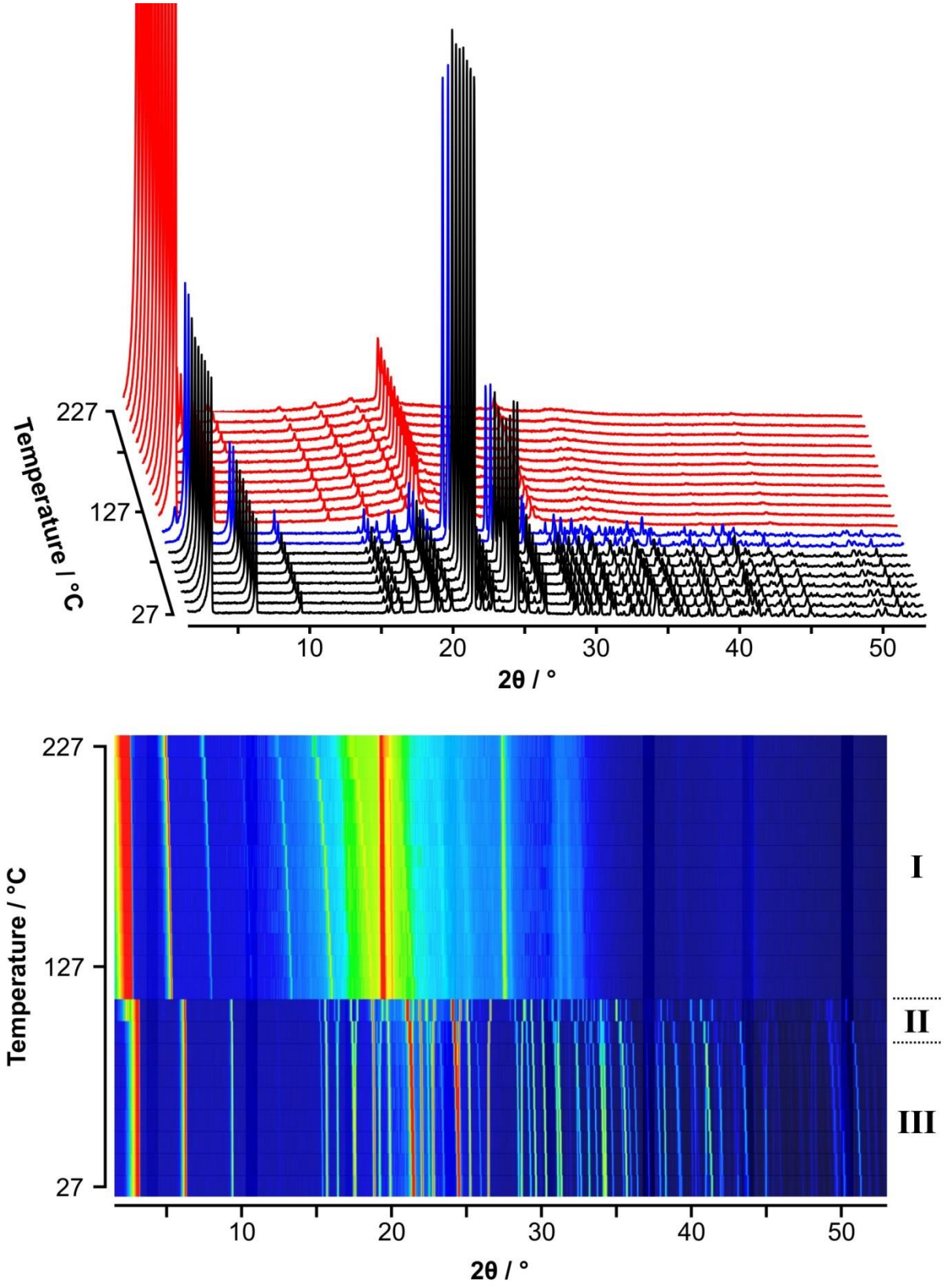


Fig. S7. PXRD data on a sample of C_{18}TAB as a function of temperature measured in a 0.7 mm capillary on a Stoe Stadi-P diffractometer with Cu Kα_1 radiation. In the upper plot, curves are shown in red, blue, and black for phases I, II, and III of the sample, respectively. The lower plot shows the same diffraction data as a surface plot using a non-linear colour scale from blue to red to show low versus high counts.

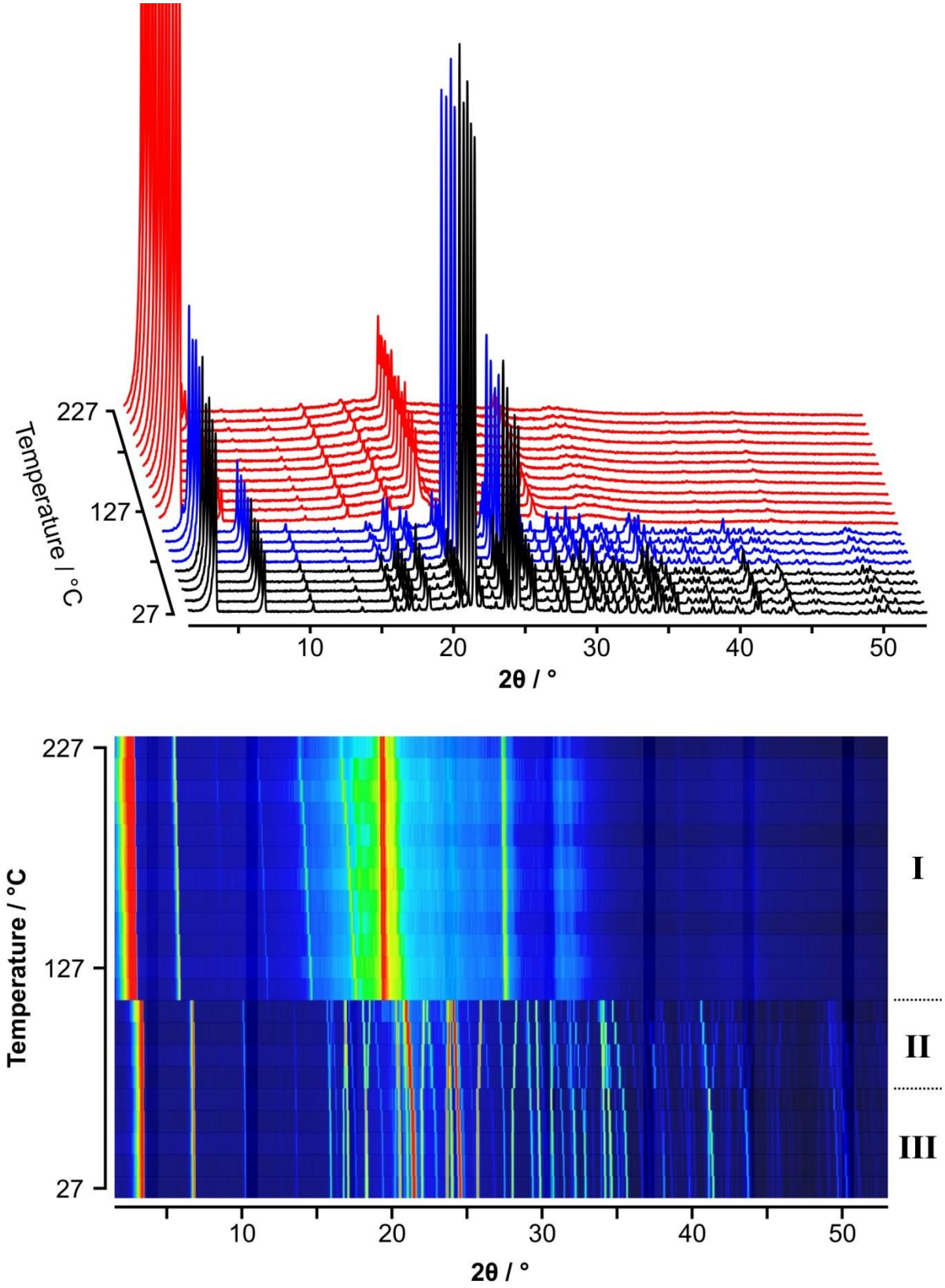


Fig. S8. PXRD data on a sample of C_{16}TAB as a function of temperature measured in a 0.7 mm capillary on a Stoe Stadi-P diffractometer with Cu Kα_1 radiation. In the upper plot, curves are shown in red, blue, and black for phases I, II, and III of the sample, respectively. The lower plot shows the same diffraction data as a surface plot using a non-linear colour scale from blue to red to show low versus high counts.

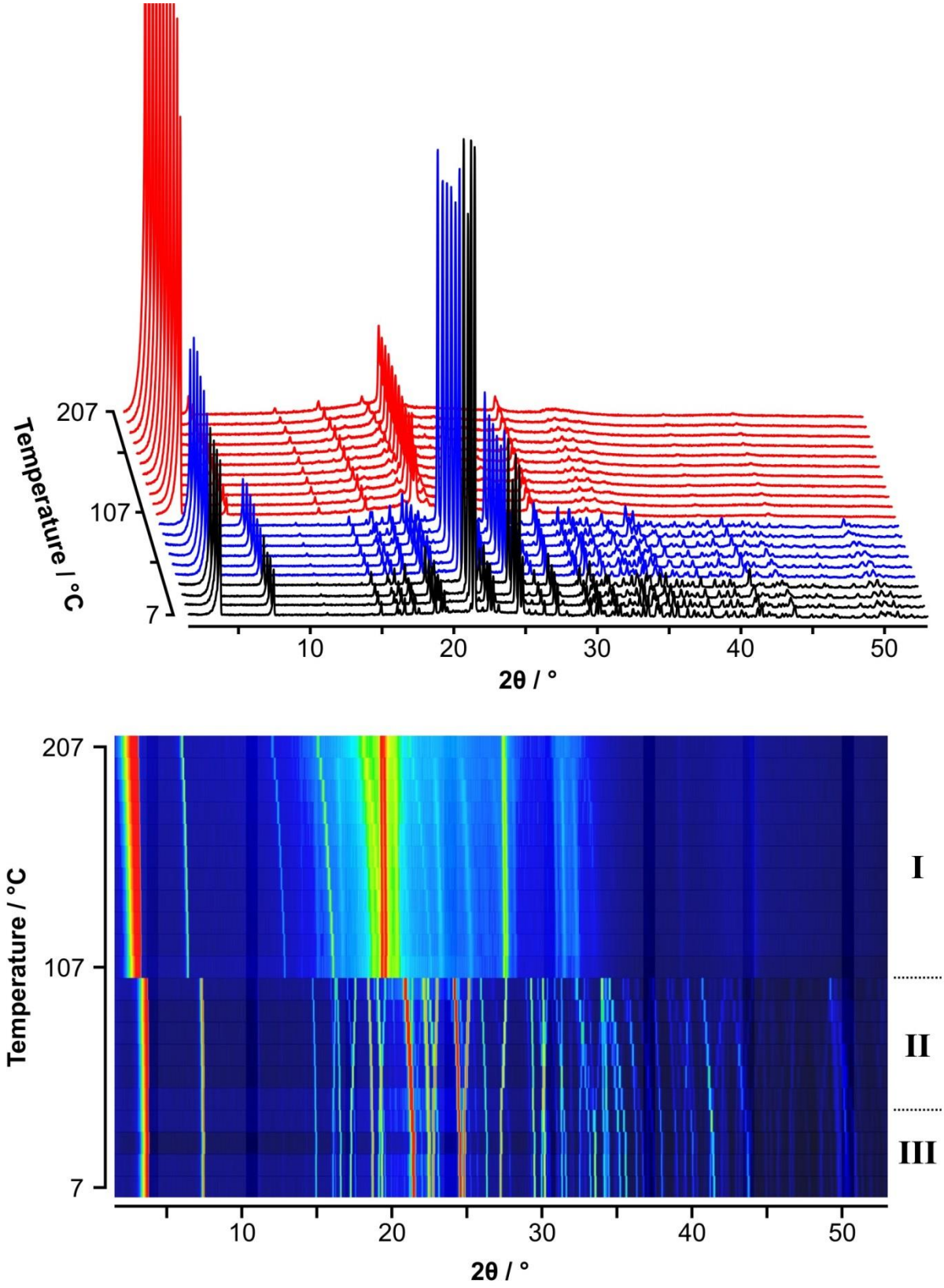


Fig. S9. PXRD data on a sample of C_{14}TAB as a function of temperature measured in a 0.7 mm capillary on a Stoe Stadi-P diffractometer with Cu Kα_1 radiation. In the upper plot, curves are shown in red, blue, and black for phases I, II, and III of the sample, respectively. The lower plot shows the same diffraction data as a surface plot using a non-linear colour scale from blue to red to show low versus high counts.

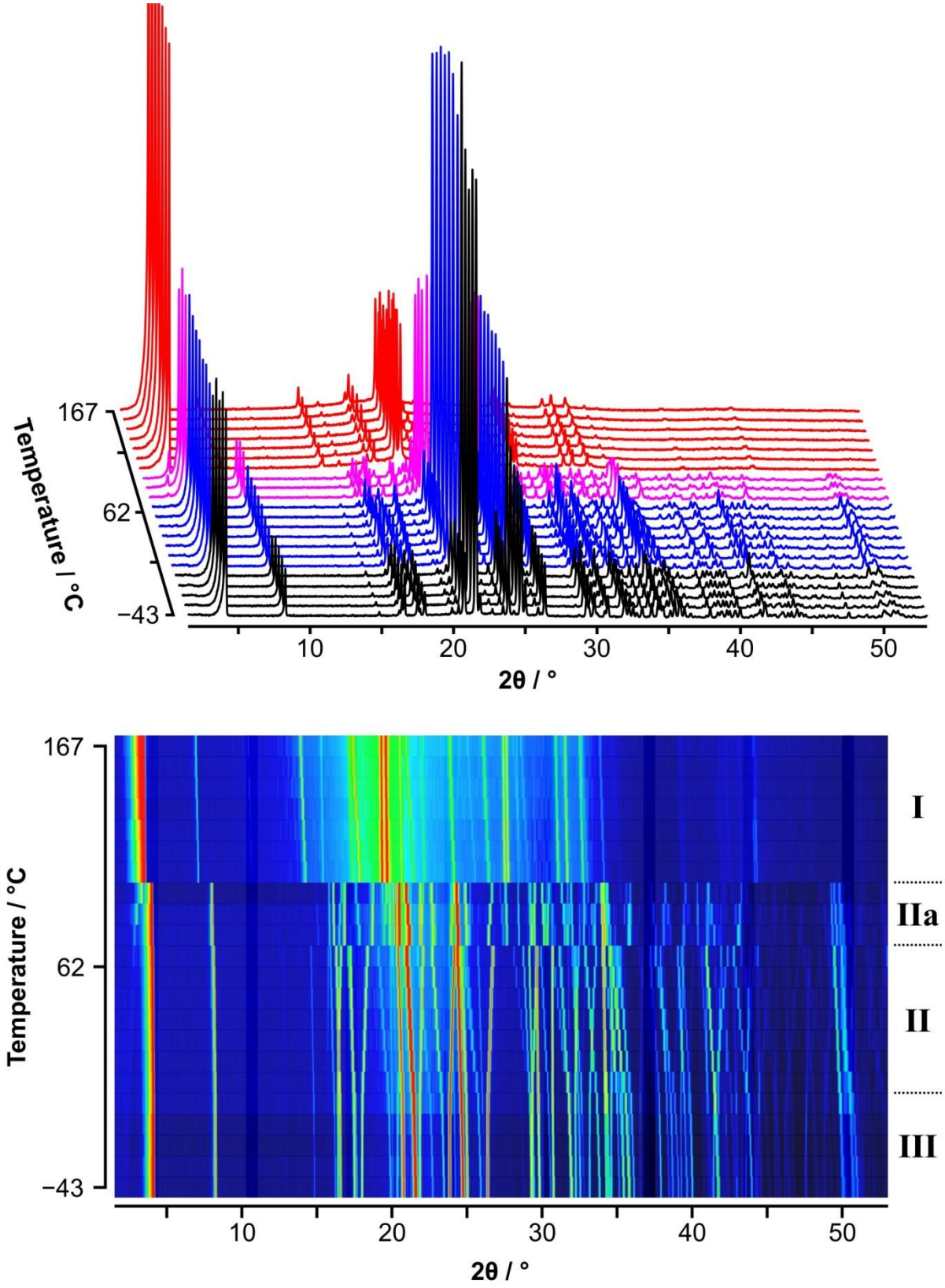


Fig. S10. PXRD data on a sample of C_{12}TAB as a function of temperature measured in a 0.7 mm capillary on a Stoe Stadi-P diffractometer with Cu Kα_1 radiation. In the upper plot, curves are shown in red, magenta, blue, and black for phases I, IIa, II, and III of the sample, respectively. The lower plot shows the same diffraction data as a surface plot using a non-linear colour scale from blue to red to show low versus high counts.

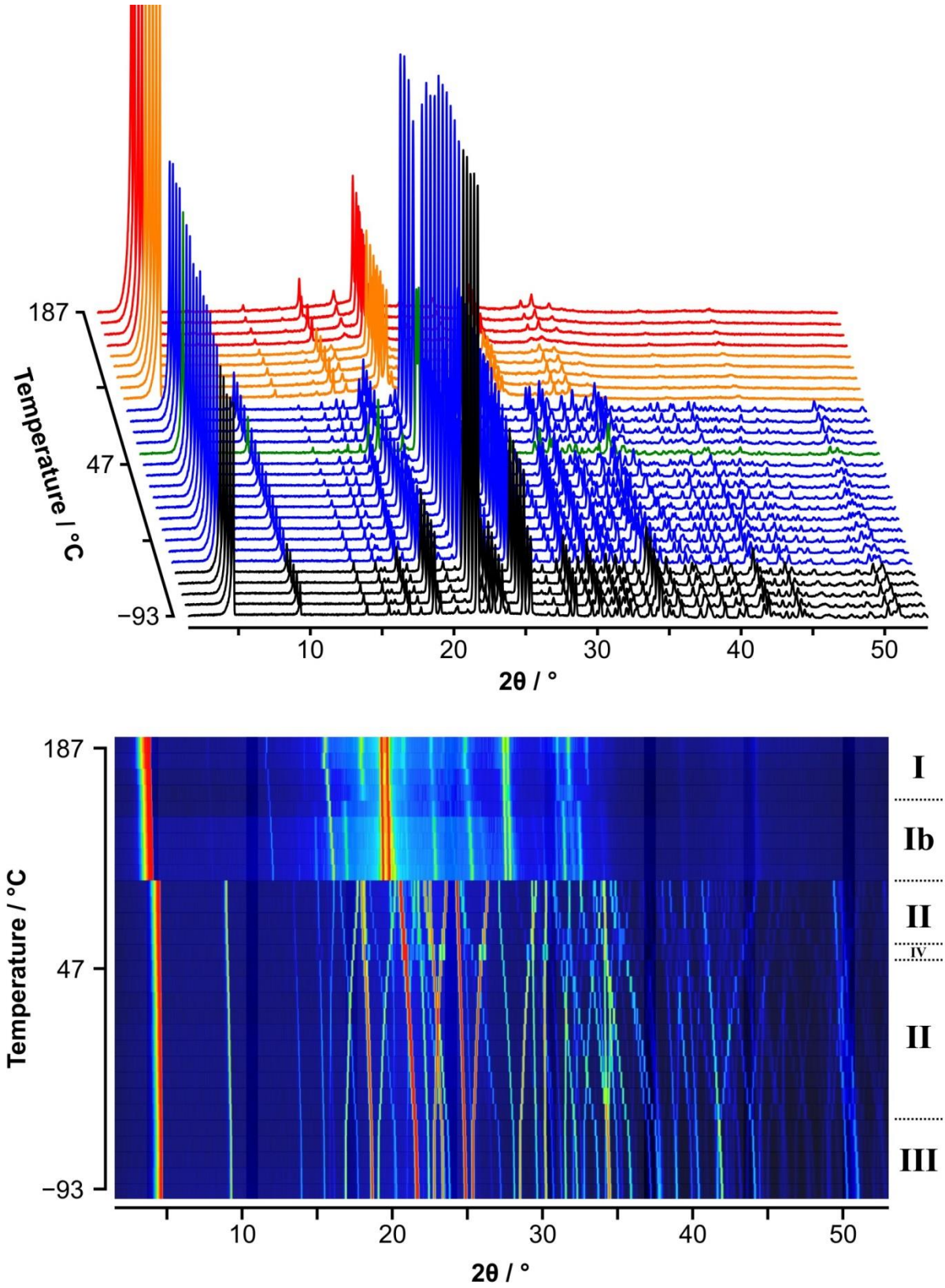


Fig. S11. PXRD data for a sample of C_{10}TAB as a function of temperature measured in a 0.7 mm capillary on a Stoe Stadi-P diffractometer with Cu Kα_1 radiation. In the upper plot, curves are shown in red, orange, blue, and black for phases I, Ib, II, and III of the sample, respectively. Phase IV, exhibiting re-entrant behaviour, is shown in green. The lower plot shows the same diffraction data as a surface plot using a non-linear colour scale from blue to red to show low versus high counts.

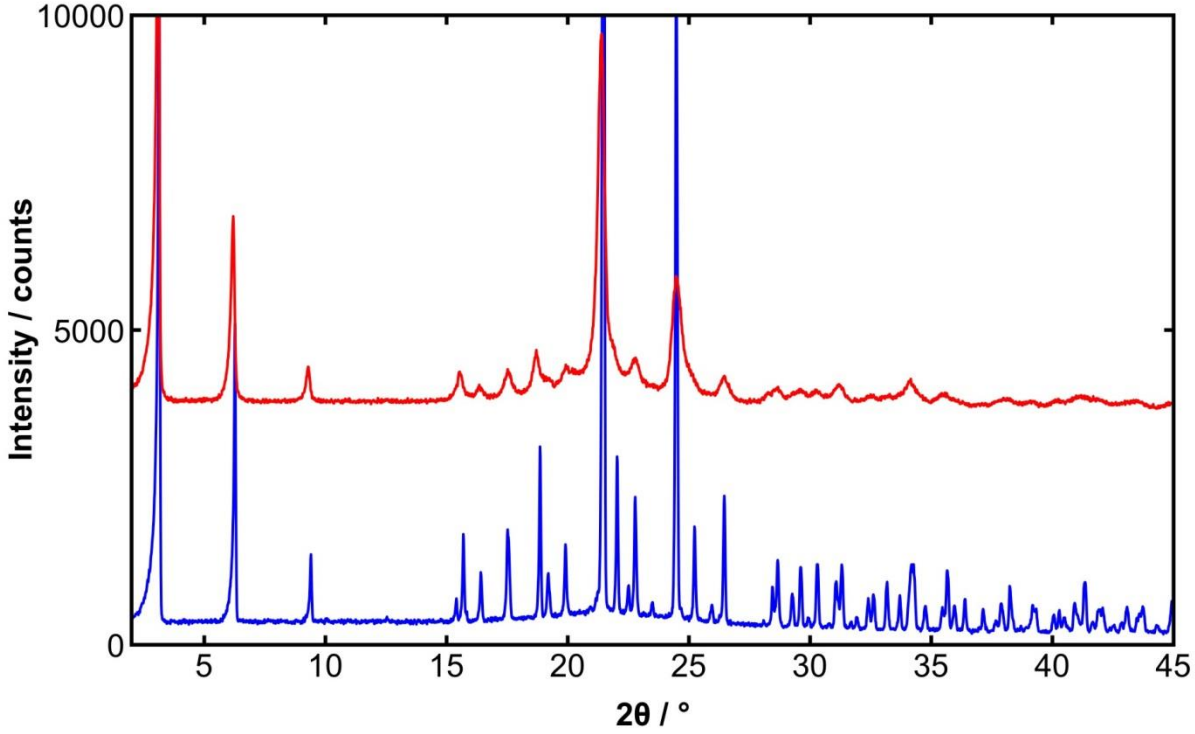


Fig. S12. PXRD patterns measured on a Stoe Stadi-P diffractometer with Cu $K\alpha_1$ radiation for a capillary sample of C_{18}TAB at 27 °C before (lower curve in blue) and after (upper curve in red, offset by 3500 counts) heating to phase I and cooling back to room temperature.

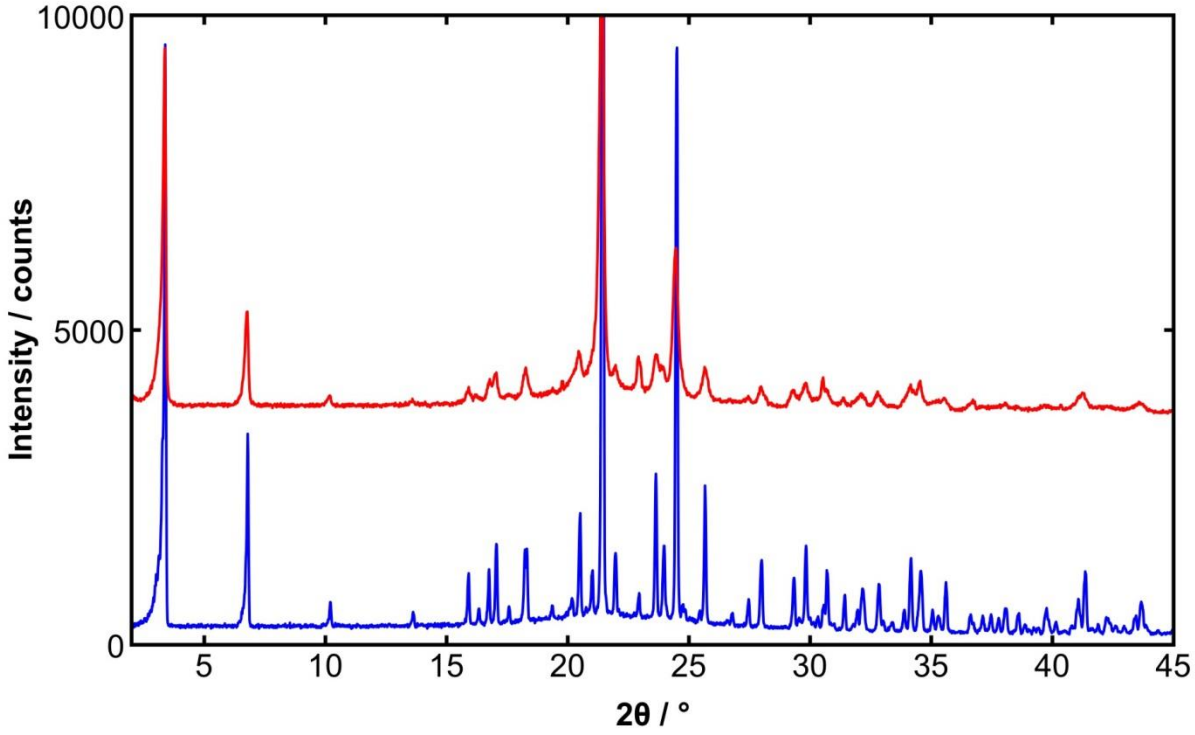


Fig. S13. PXRD patterns measured on a Stoe Stadi-P diffractometer with Cu $K\alpha_1$ radiation for a capillary sample of C_{16}TAB at 27 °C before (lower curve in blue) and after (upper curve in red offset, offset by 3500 counts) heating to phase I and cooling back to room temperature.

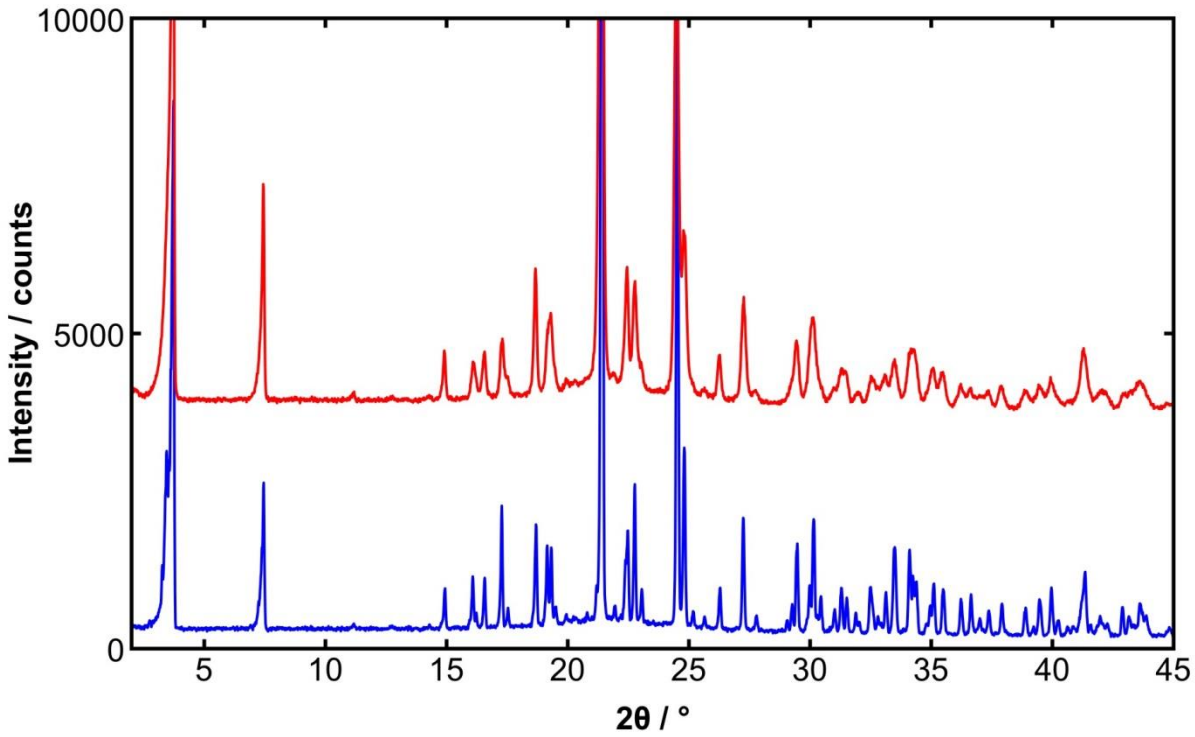


Fig. S14. PXRD patterns measured on a Stoe Stadi-P diffractometer with Cu $K\alpha_1$ radiation for a capillary sample of C_{14}TAB at 27 °C before (lower curve in blue) and after (upper curve in red offset, offset by 3500 counts) heating to phase I and cooling back to room temperature.

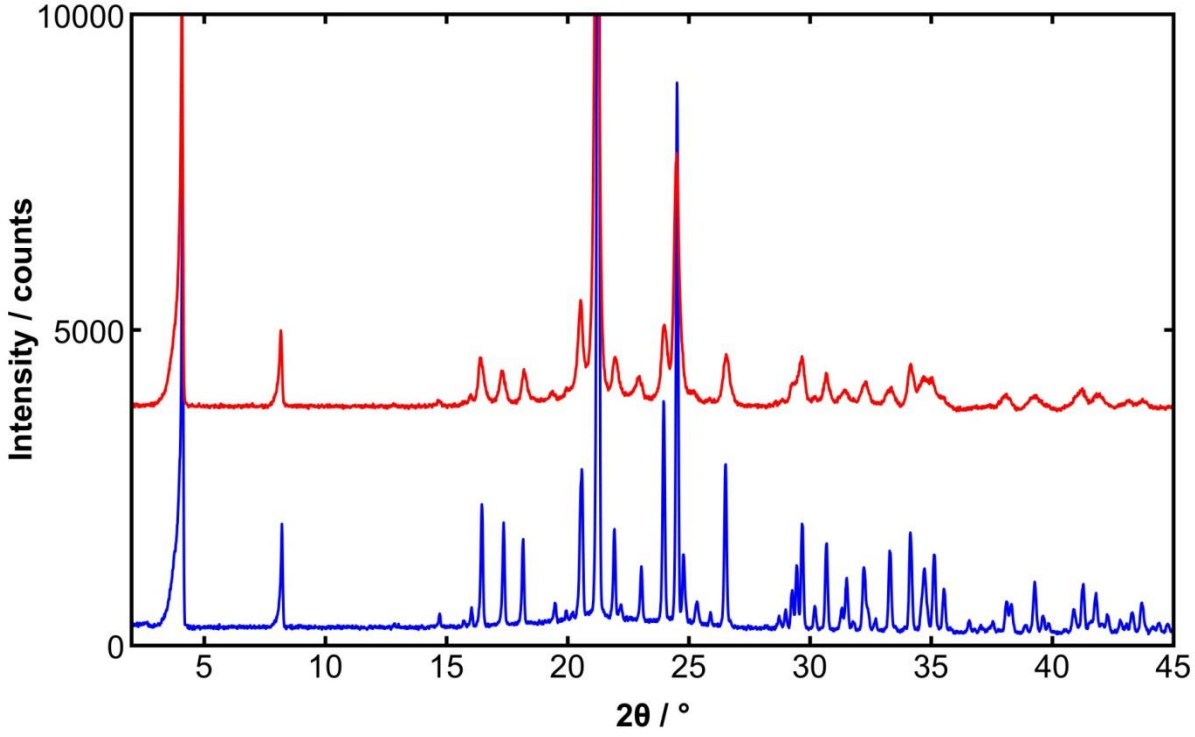


Fig. S15. PXRD patterns measured on a Stoe Stadi-P diffractometer with Cu $K\alpha_1$ radiation for a capillary sample of C_{12}TAB at 27 °C before (lower curve in blue) and after (upper curve in red offset, offset by 3500 counts) heating to phase I and cooling back to room temperature.

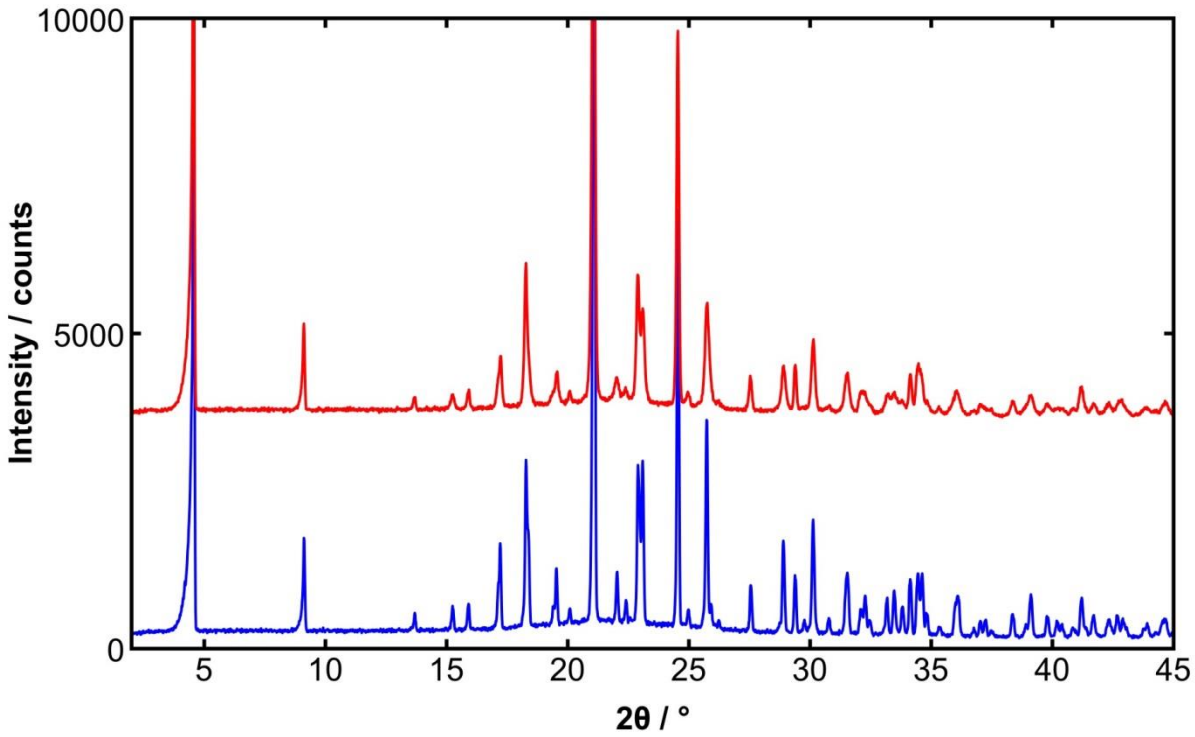


Fig. S16. PXRD patterns measured on a Stoe Stadi-P diffractometer with Cu $K\alpha_1$ radiation for a capillary sample of C_{10}TAB at 27 °C before (lower curve in blue) and after (upper curve in red offset, offset by 3500 counts) heating to phase I and cooling back to room temperature.

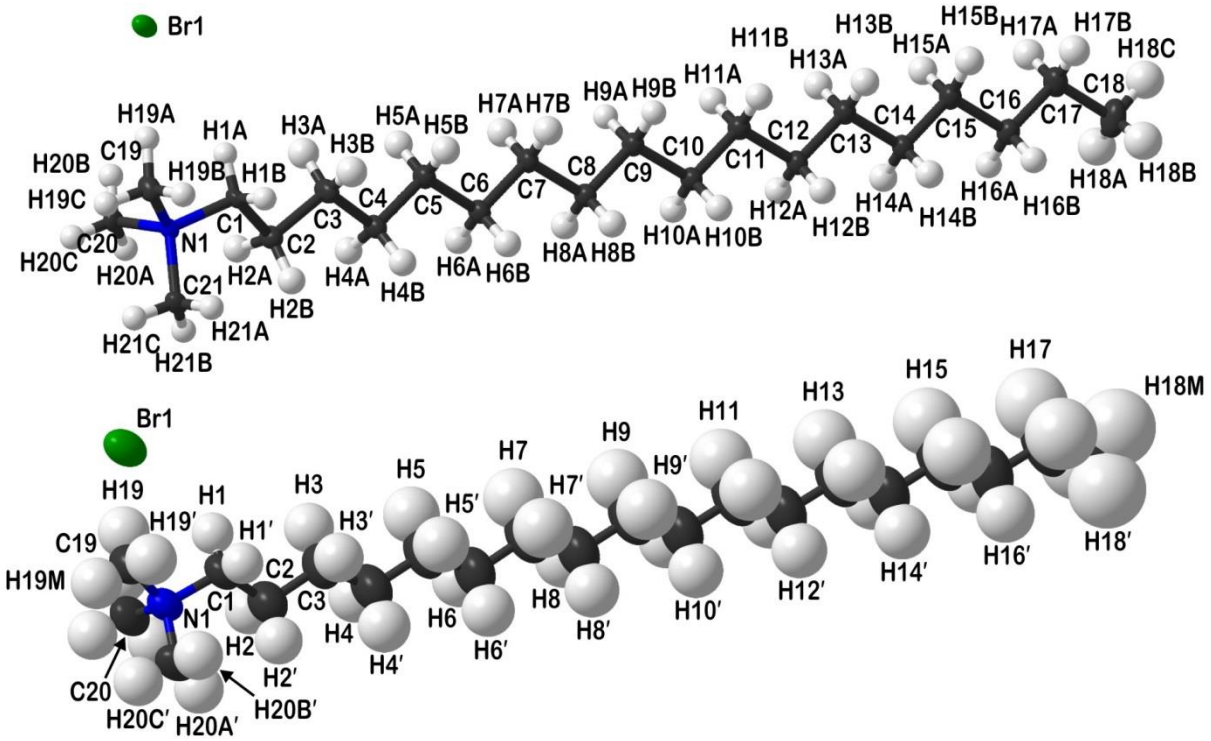


Fig. S17. Labelling of the atoms in the structures of C_{18}TAB in phase III at −123 °C (upper) and phase II at 117 °C (lower). For phase II, atoms related by mirror symmetry are labelled with a prime (′) and hydrogen atoms on the mirror plane are labelled with an M. Some atoms cannot be labelled due to crowding. Thermal ellipsoids are drawn at 50% probability (including H atoms) using Mercury.[10] For phase III, hydrogen atoms on one side of the alkyl chain are labelled with an A and on the other side with a B.

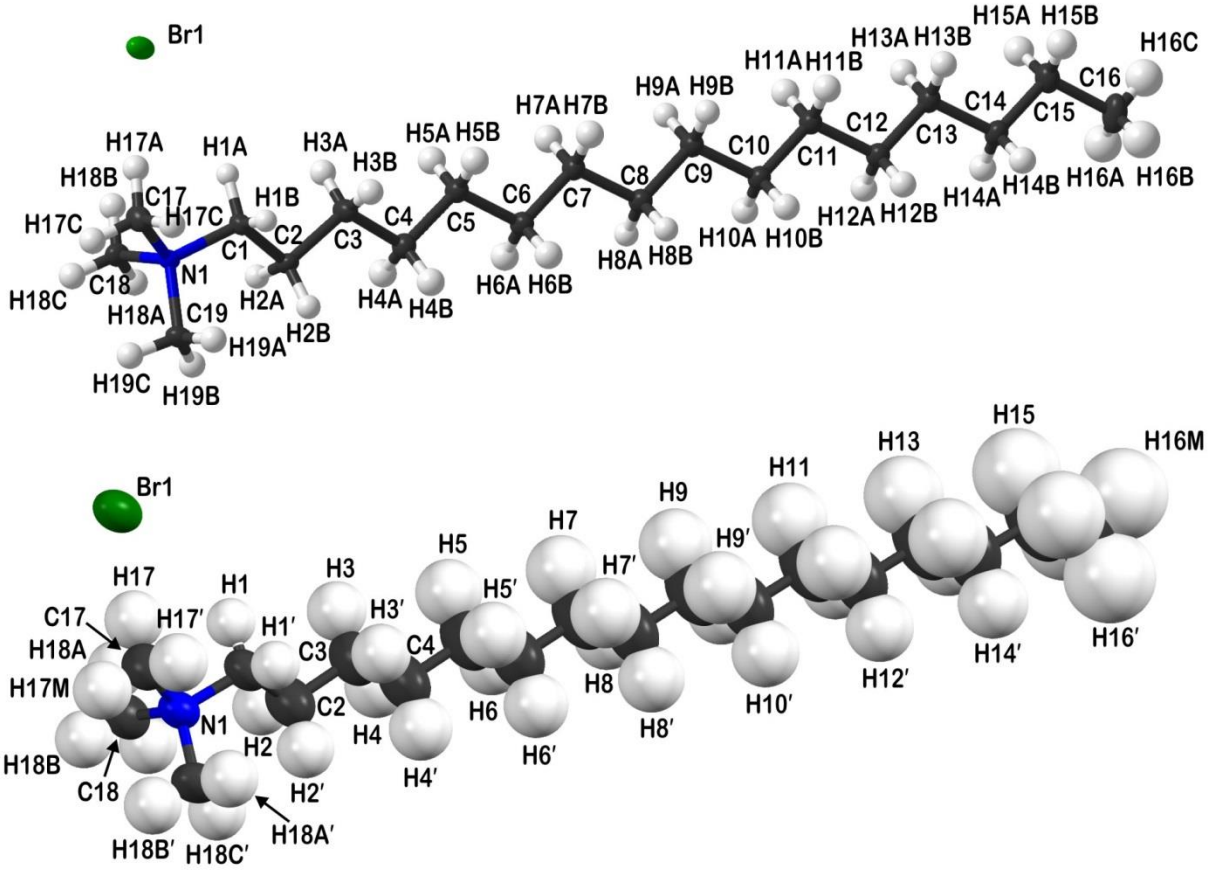


Fig. S18. Labelling of the atoms in the structures of C_{16}TAB in phase III at −123 °C (upper) and phase II at 117 °C (lower). For phase II, atoms related by mirror symmetry are labelled with a prime (′) and hydrogen atoms on the mirror plane are labelled with an M. Some atoms cannot be labelled due to crowding. Thermal ellipsoids are drawn at 50% probability (including H atoms) using Mercury.[10] For phase III, hydrogen atoms on one side of the alkyl chain are labelled with an A and on the other side with a B.

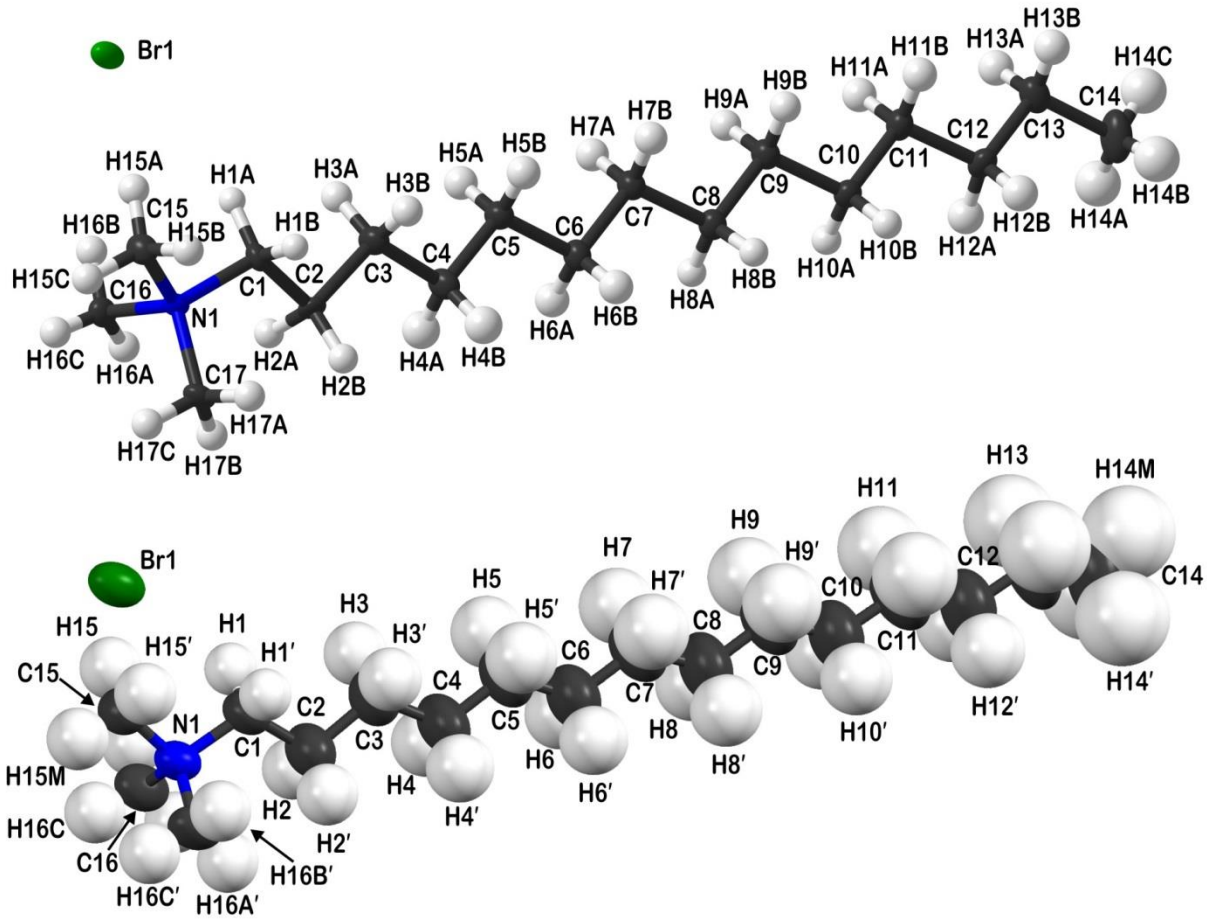


Fig. S19. Labelling of the atoms in the structures of C_{14}TAB in phase III at −123 °C (upper) and phase II at 107 °C (lower). For phase II, atoms related by mirror symmetry are labelled with a prime (′) and hydrogen atoms on the mirror plane are labelled with an M. Some atoms cannot be labelled due to crowding. Thermal ellipsoids are drawn at 50% probability (including H atoms) using Mercury.[10] For phase III, hydrogen atoms on one side of the alkyl chain are labelled with an A and on the other side with a B.

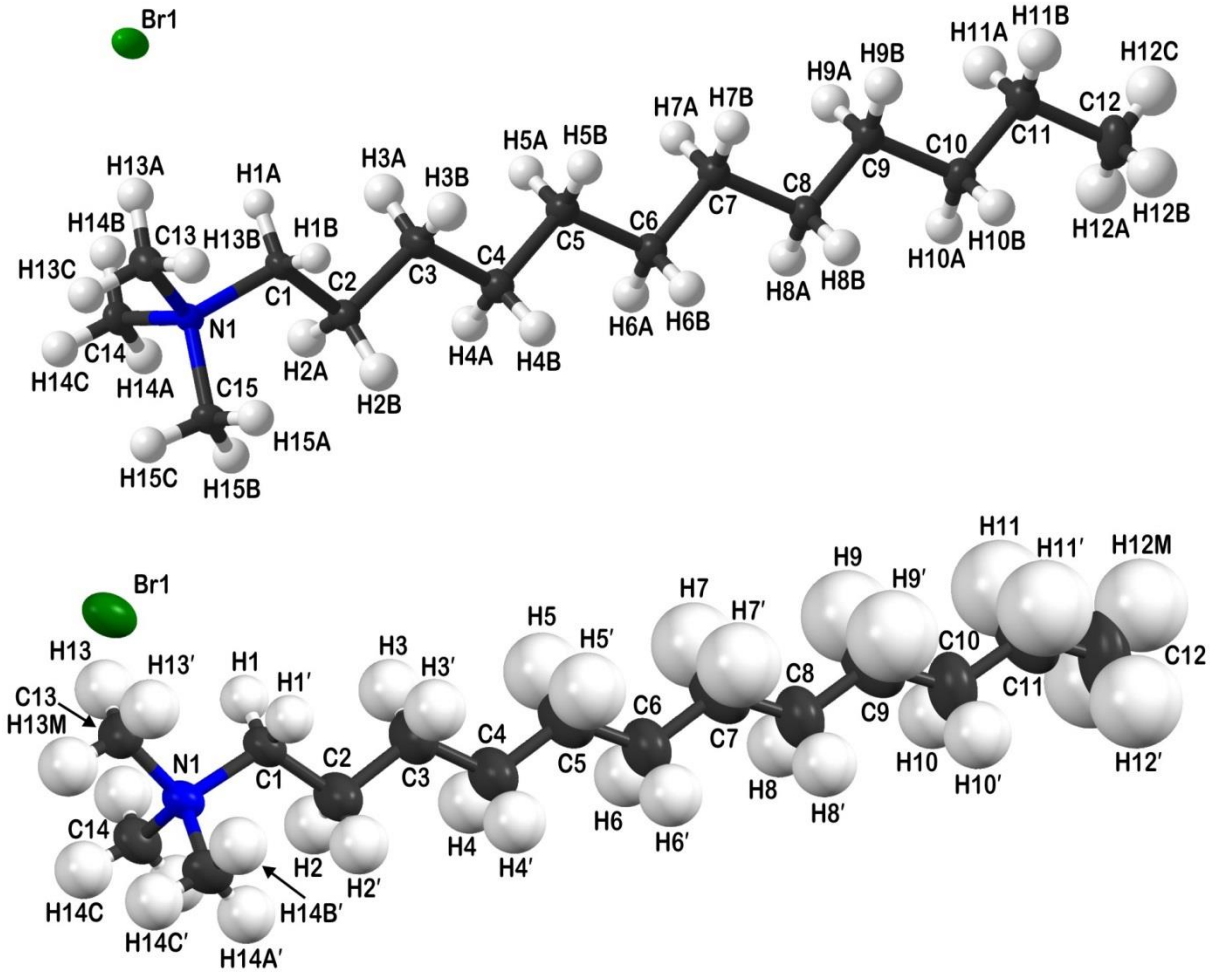


Fig. S20. Labelling of the atoms in the structures of C_{12}TAB in phase III at −123 °C (upper) and phase II at 22 °C (lower). For phase II, atoms related by mirror symmetry are labelled with a prime (′) and hydrogen atoms on the mirror plane are labelled with an M. Some atoms cannot be labelled due to crowding. Thermal ellipsoids are drawn at 50% probability (including H atoms) using Mercury.[10] For phase III, hydrogen atoms on one side of the alkyl chain are labelled with an A and on the other side with a B.

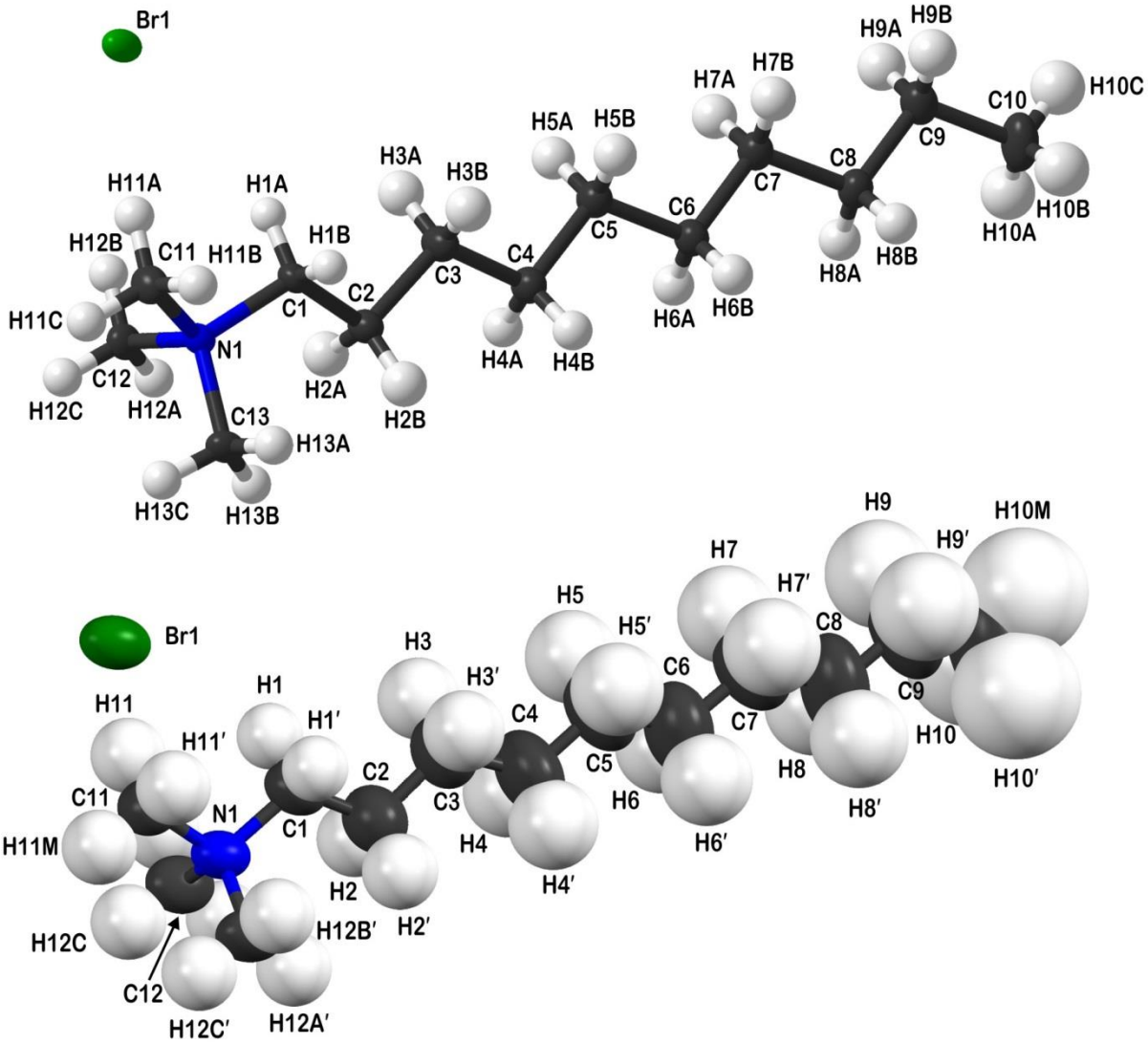


Fig. S21. Labelling of the atoms in the structures of C_{10}TAB in phase III at −123 °C (upper) and phase II at 102 °C (lower). For phase II, atoms related by mirror symmetry are labelled with a prime (′) and hydrogen atoms on the mirror plane are labelled with an M. Some atoms cannot be labelled due to crowding. Thermal ellipsoids are drawn at 50% probability (including H atoms) using Mercury.[10] For phase III, hydrogen atoms on one side of the alkyl chain are labelled with an A and on the other side with a B.

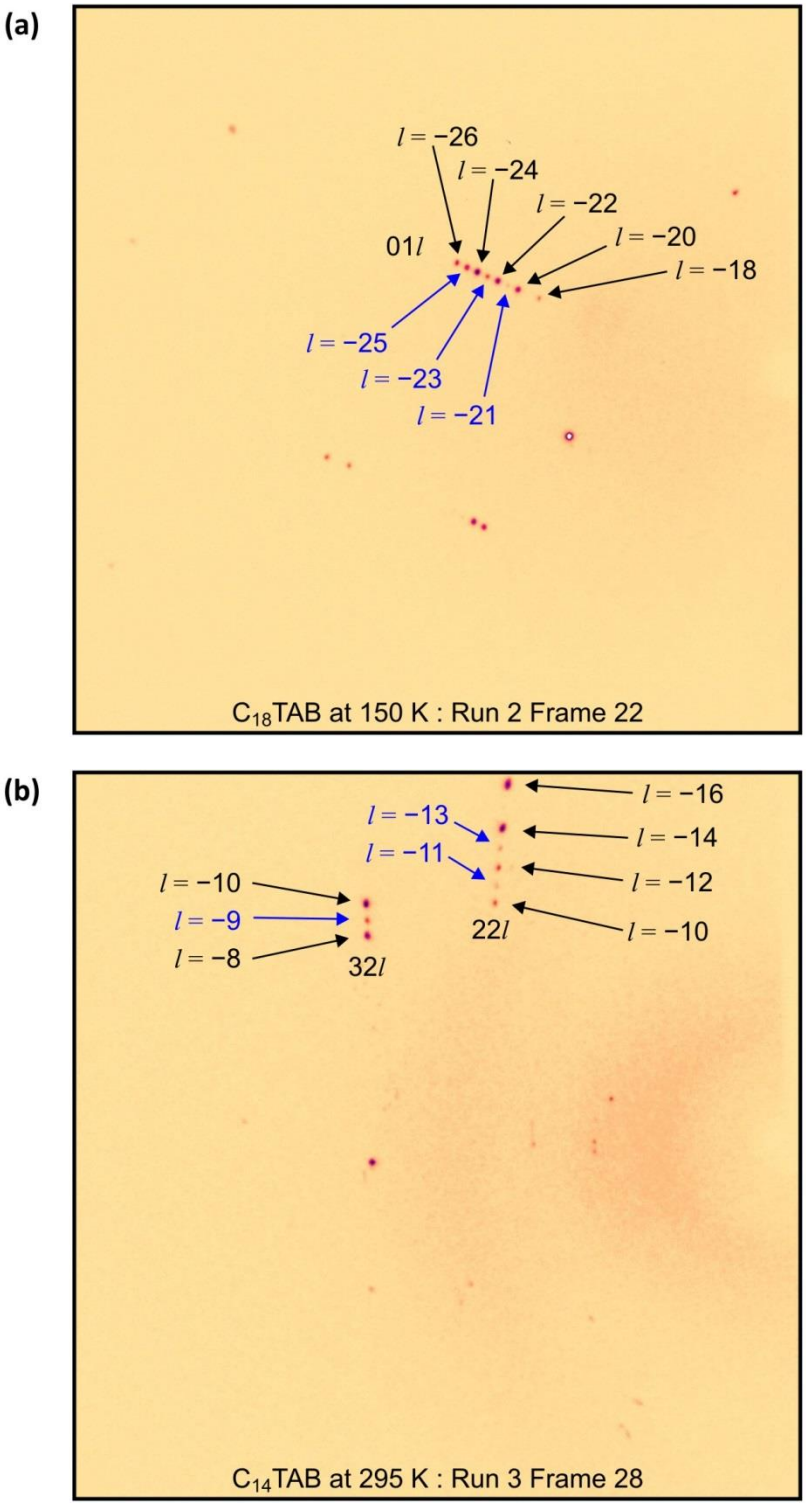


Fig. S22. **(a)** A frame of single-crystal X-ray diffraction data measured for C_{18}TAB at −123 °C. A sequence of 01l reflections is highlighted with arrows with the values of l shown. The reflections highlighted by the blue arrows with l odd are ones indicative of the doubled-length unit cell along c in phase III. **(b)** A frame of single-crystal X-ray diffraction data from C_{14}TAB at 22 °C with a sequence of both 22l and 32l reflections highlighted with arrows with the values of l shown. As for (a), reflections highlighted by the blue arrows with l odd are ones indicative of the doubled-length unit cell along c in phase III. Although hkl reflections with l odd are relatively weak in phase III of C_nTAB, these images demonstrate that they are clearly visible.

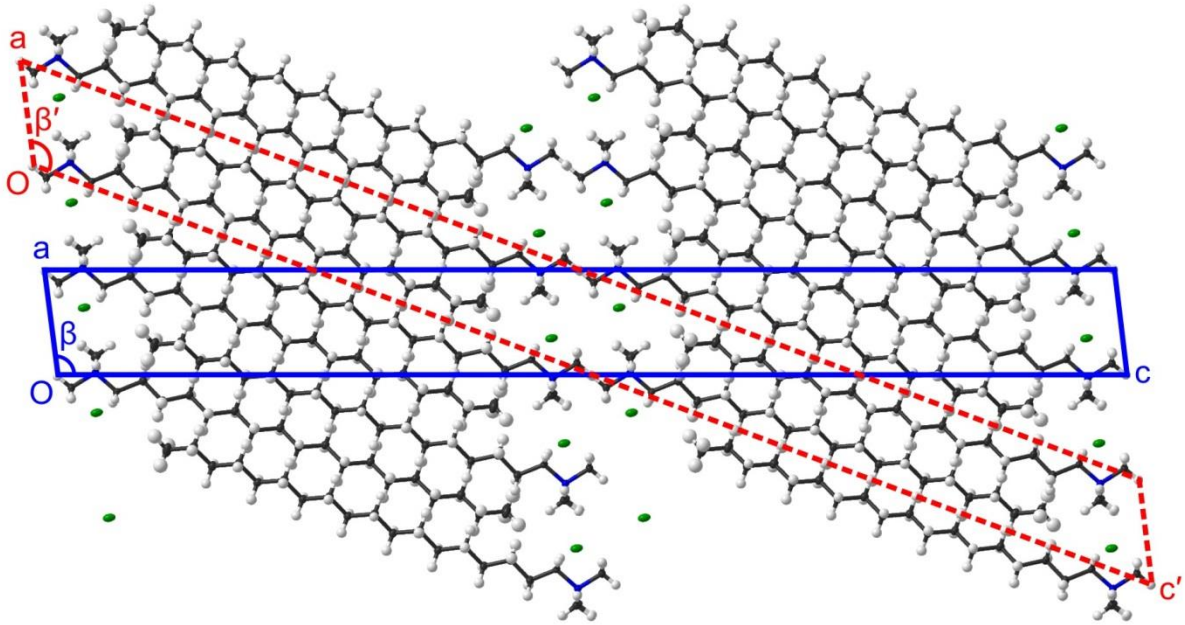


Fig. S23. Relationship between the crystallographic cell used for the least-squares refinement of the crystal structure of phase III of C_{18}TAB, where the monoclinic angle close to 90° reduces correlation between parameters, and the cell relevant to the chemical structure with the alkyl chain approximately parallel to *c*′ as used to illustrate the tilt of the molecules with respect to the ionic plane as used in Fig. 3.

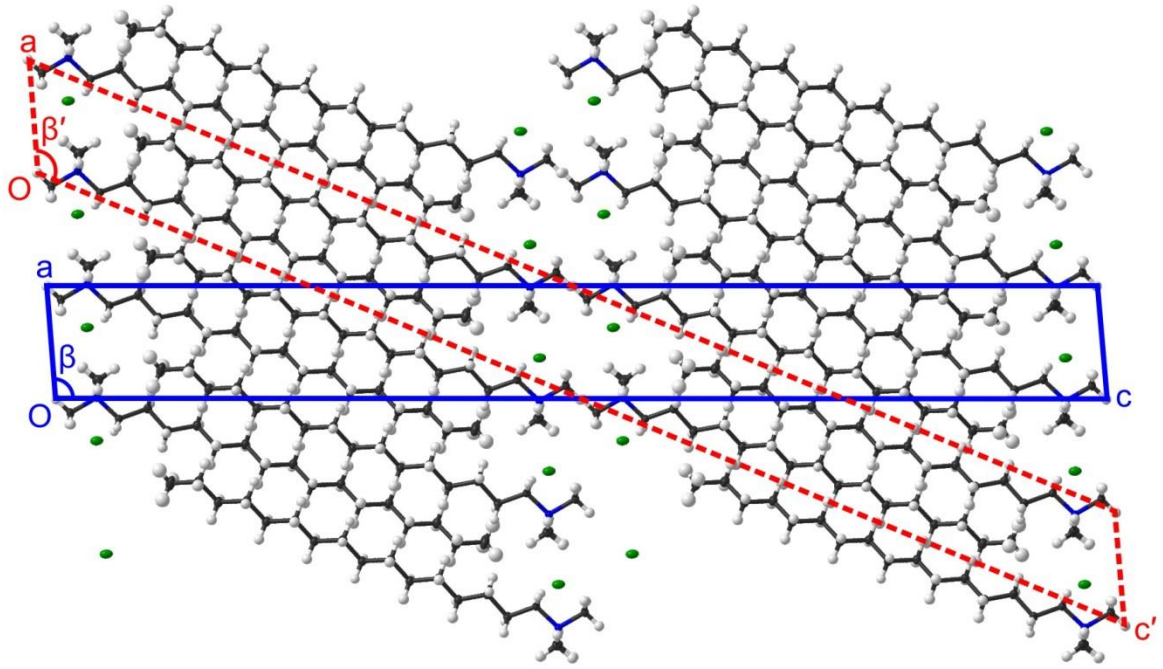


Fig. S24. Relationship between the crystallographic cell used for the least-squares refinement of the crystal structure of phase III of C_{16}TAB, where the monoclinic angle close to 90° reduces correlation between parameters, and the cell relevant to the chemical structure with the alkyl chain approximately parallel to *c*′ as used to illustrate the tilt of the molecules with respect to the ionic plane as used in Fig. 3.

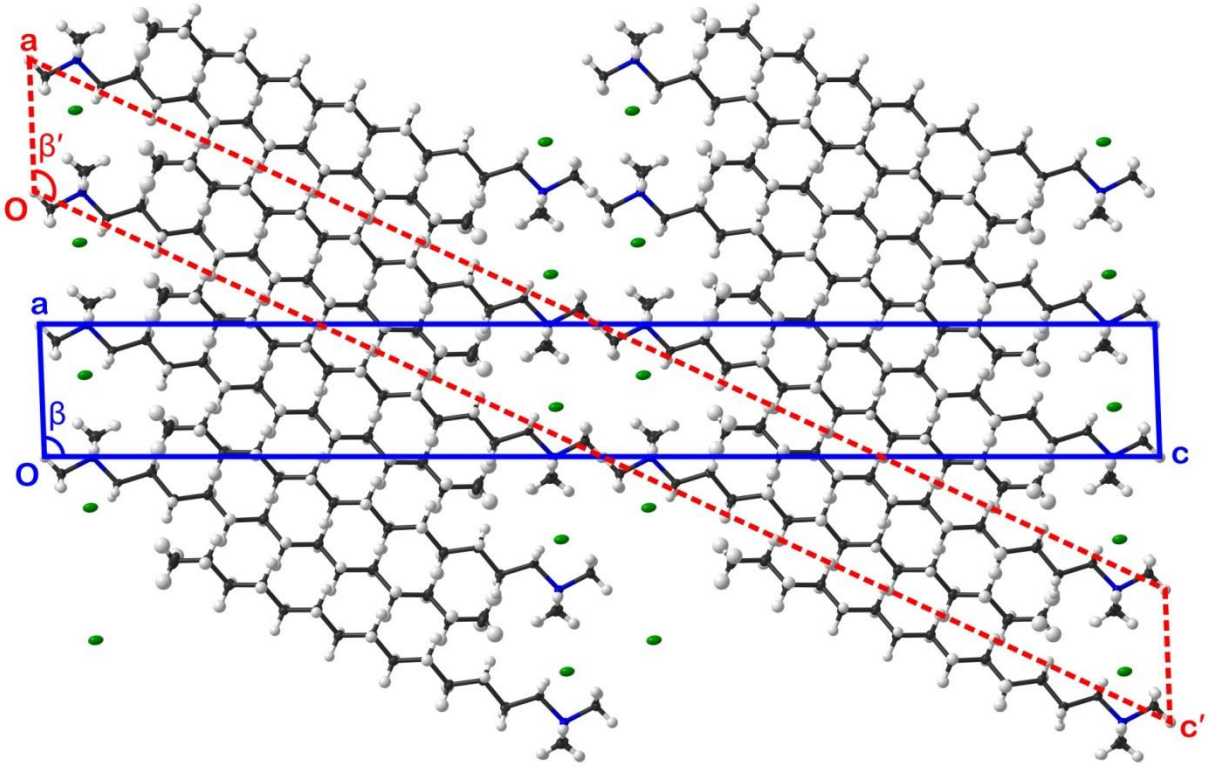


Fig. S25. Relationship between the crystallographic cell used for the least-squares refinement of the crystal structure of phase III of C_{14}TAB, where the monoclinic angle close to 90° reduces correlation between parameters, and the cell relevant to the chemical structure with the alkyl chain approximately parallel to *c*′ as used to illustrate the tilt of the molecules with respect to the ionic plane as used in Fig. 3.

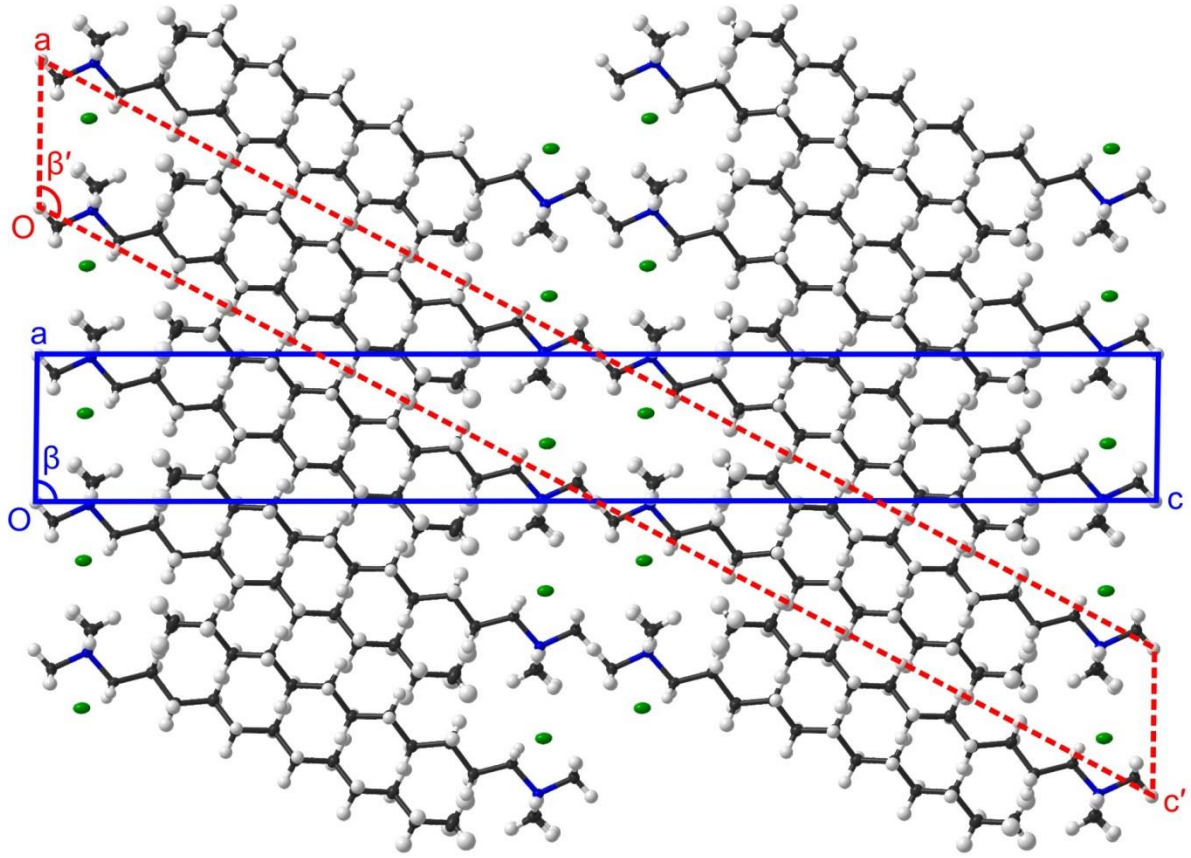


Fig. S26. Relationship between the crystallographic cell used for the least-squares refinement of the crystal structure of phase III of C_{12}TAB, where the monoclinic angle close to 90° reduces correlation between the parameters, and the cell relevant to the chemical structure with the alkyl chains approximately parallel to *c*′ as used to illustrate the tilt of the molecules with respect to the ionic plane as used in Fig. 3 in the paper. Note that in contrast to the unit cells shown in blue in Figs. S23-S25, a non-standard monoclinic β angle less than 90° is used so that structures with different alkyl-chain length can be compared directly.

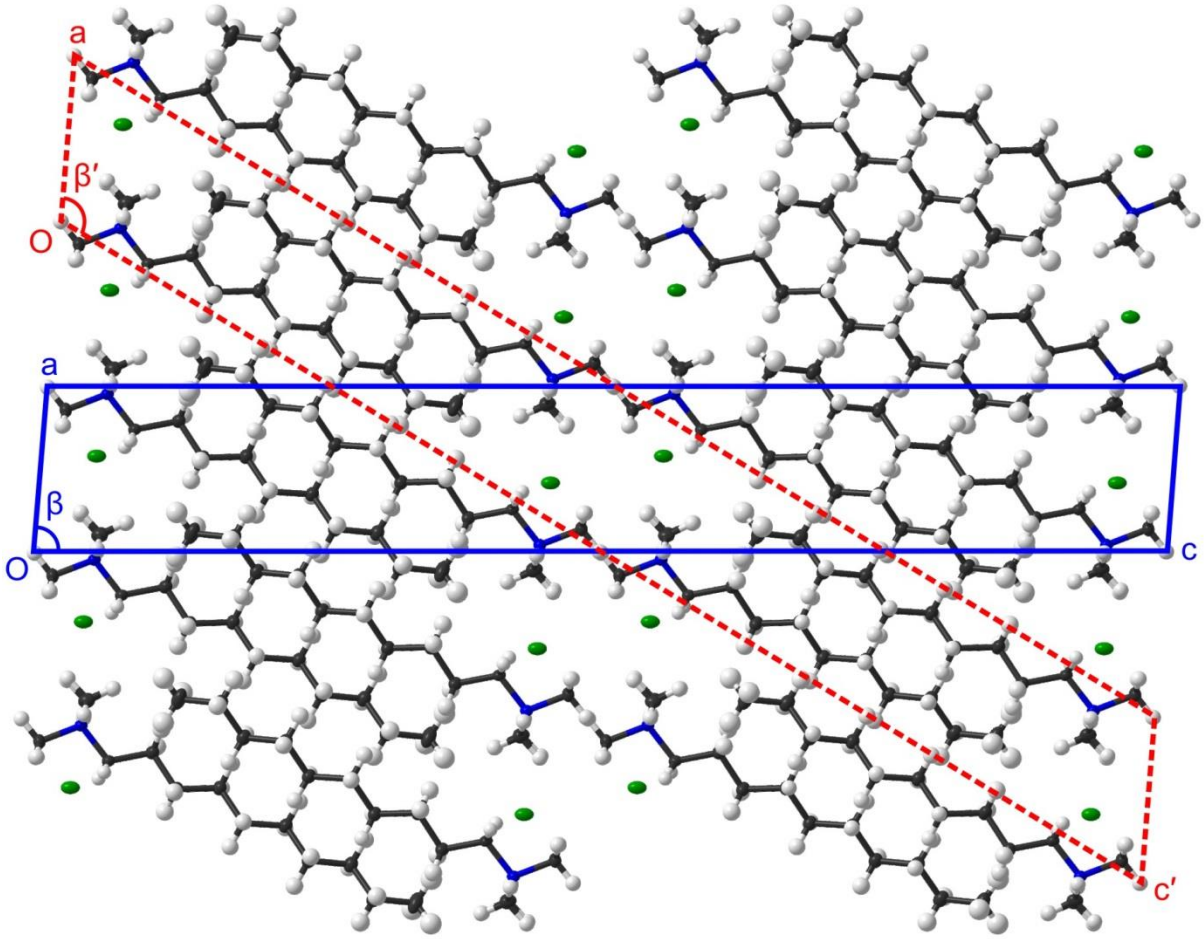


Fig. S27. Relationship between the crystallographic cell used for the least-squares refinement of the crystal structure of phase III of C_{10}TAB, where the monoclinic angle close to 90° reduces correlation between parameters, and the cell relevant to the chemical structure with the alkyl chain approximately parallel to *c*′ as used to illustrate the tilt of the molecules with respect to the ionic plane as used in Fig. 3. Note that in contrast to the unit cells shown in blue in Figs. S23-S25, a non-standard monoclinic β angle less than 90° is used (as in Fig. S36) so that structures with different alkyl-chain length can be compared directly.

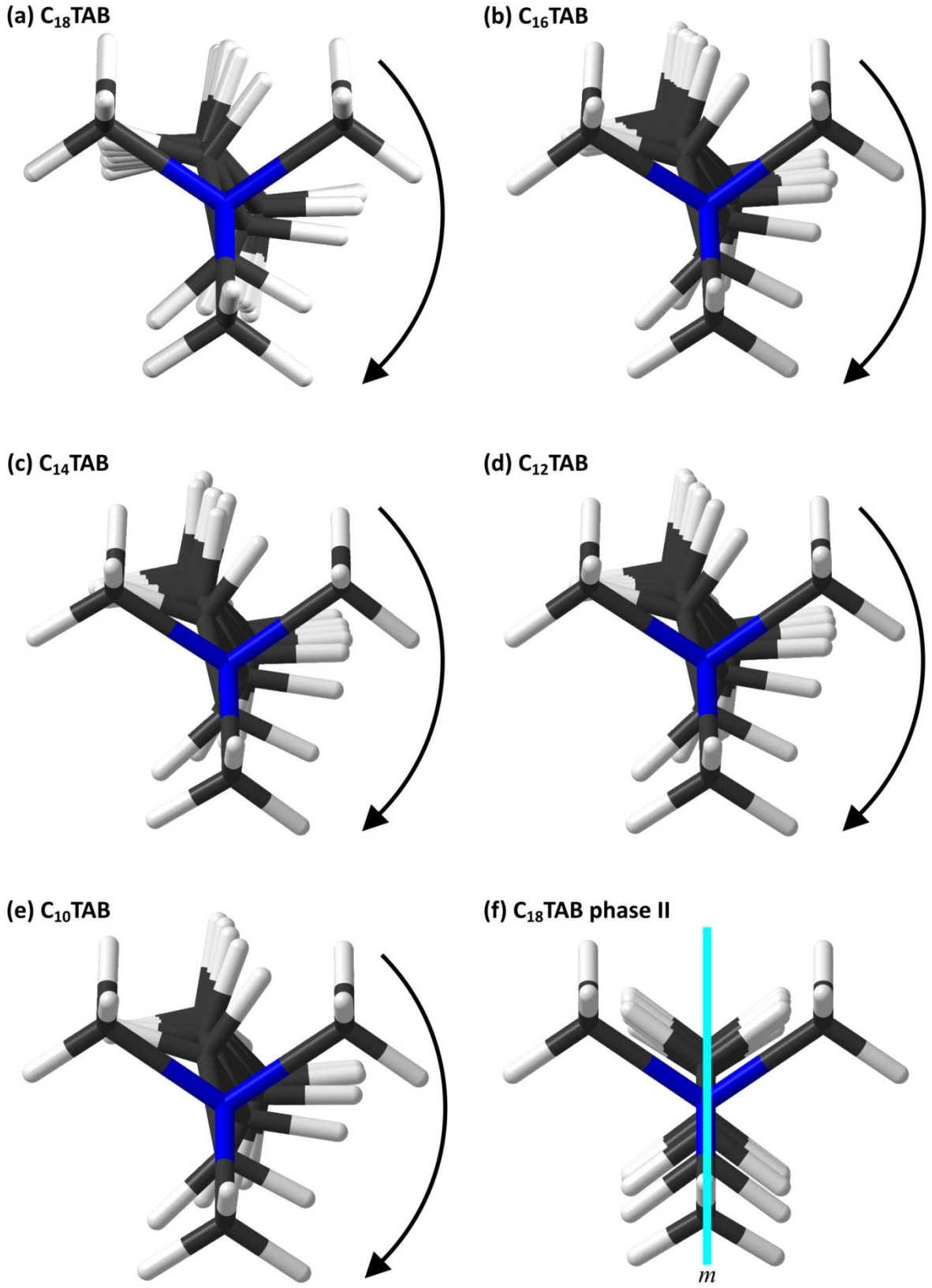


Fig. S28. (a) to (e) show a view down the length of the alkyl chain for C_nTAB for n = 18 to 10, respectively, at −123 °C. For clarity, a stick representation is used. The appearance and degree of twist is very similar for each surfactant molecule. The slight twist of the chain with respect to the head group explains the doubling of the unit cell observed in phase III for all C_nTAB and the 108° C1–C2–C3 bond angle *cf*. mean of 113°. For comparison, (f) shows the loss of twist and the consequent mirror symmetry in phase II as typified by C_{18}TAB at 107 °C.

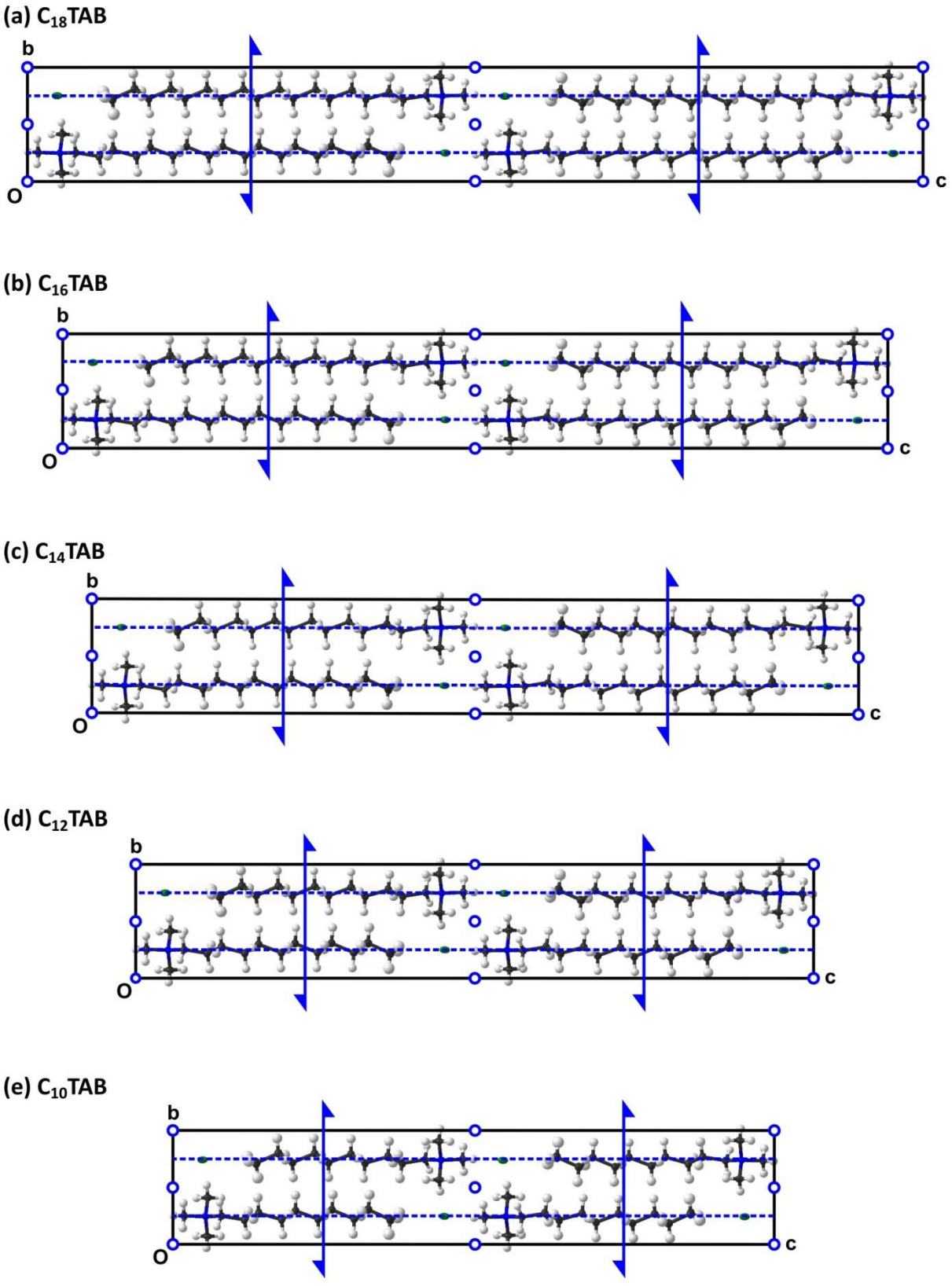
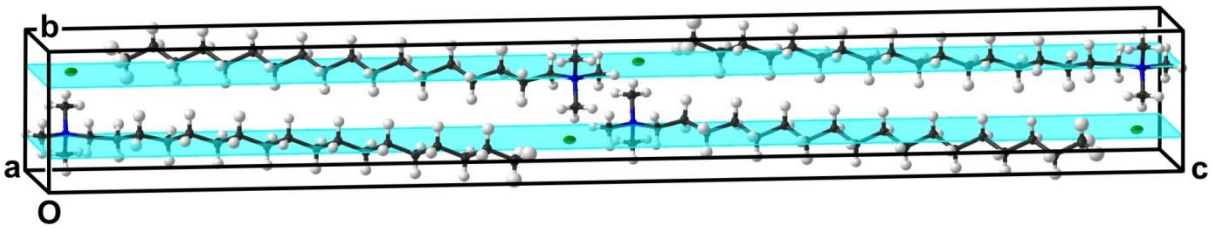
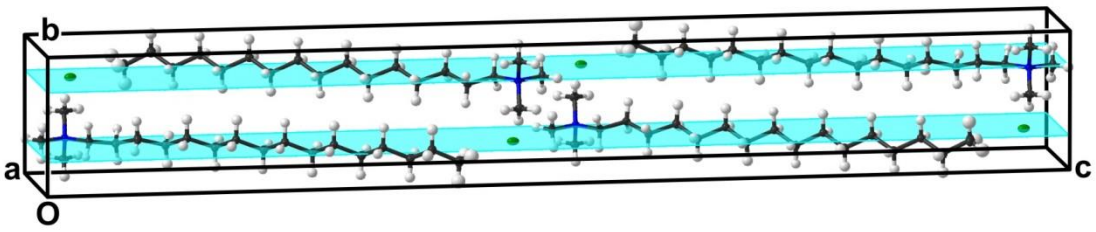


Fig. S29 (a)-(e). Figure showing the symmetry elements present in phase III of C_nTAB at −123 °C, space-group symmetry $P2_1/c$, as viewed from the origin along **a**. Open circles indicate centres of inversion, dashed lines show the *c*-glide planes, and half-arrows give the position of the 2_1 screw axes perpendicular to the glide planes.

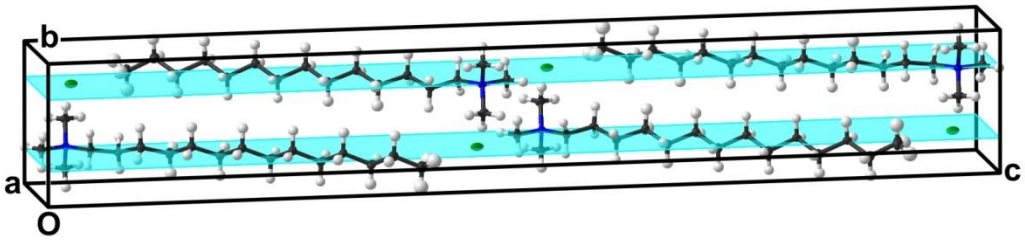
(a) C_{18}TAB



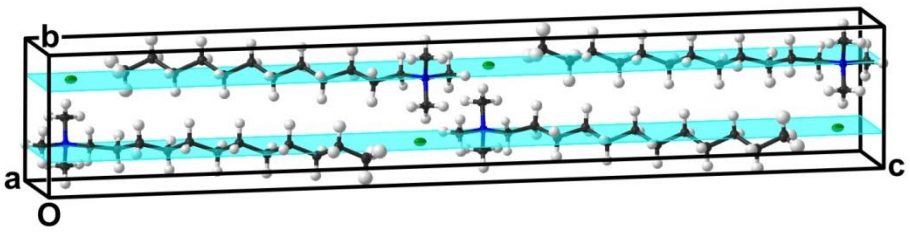
(b) C_{16}TAB



(c) C_{14}TAB



(d) C_{12}TAB



(e) C_{10}TAB

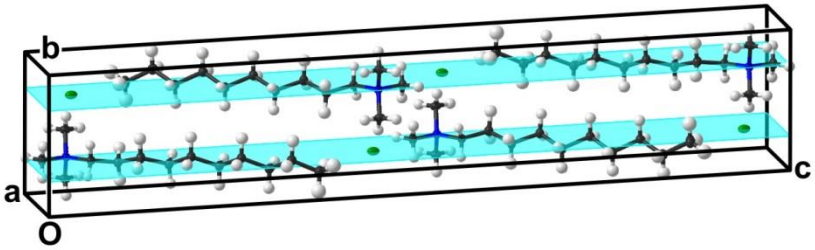


Fig. S30 (a) to (e). Oblique view of the unit cells of phase III of C_nTAB at −123 °C showing the *c*-glide plane within the unit cell. The presence of this symmetry element leads to the unit cell being two molecules in length in phase III compared to one molecule in length in phase II, in which the *c*-glide plane has become a mirror plane.

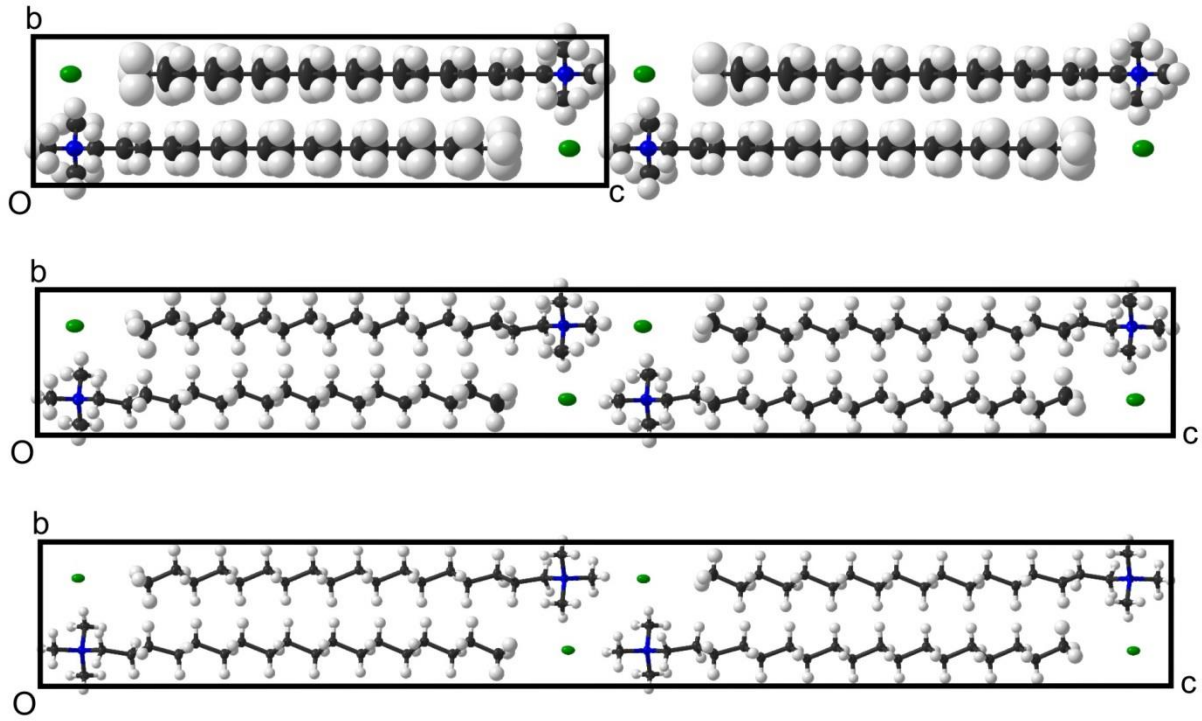


Fig. S31. Evolution of molecular motion in C_{18}TAB with increasing temperature seen in views of the unit cell along **a**: phase III at −123 °C (bottom), phase III at 22 °C (middle), and phase II at 117 °C (top), where the unit cell is halved due to the loss of the *c*-glide plane present in phase III. Thermal ellipsoids are drawn at 50% probability (including H atoms) using Mercury.[10]

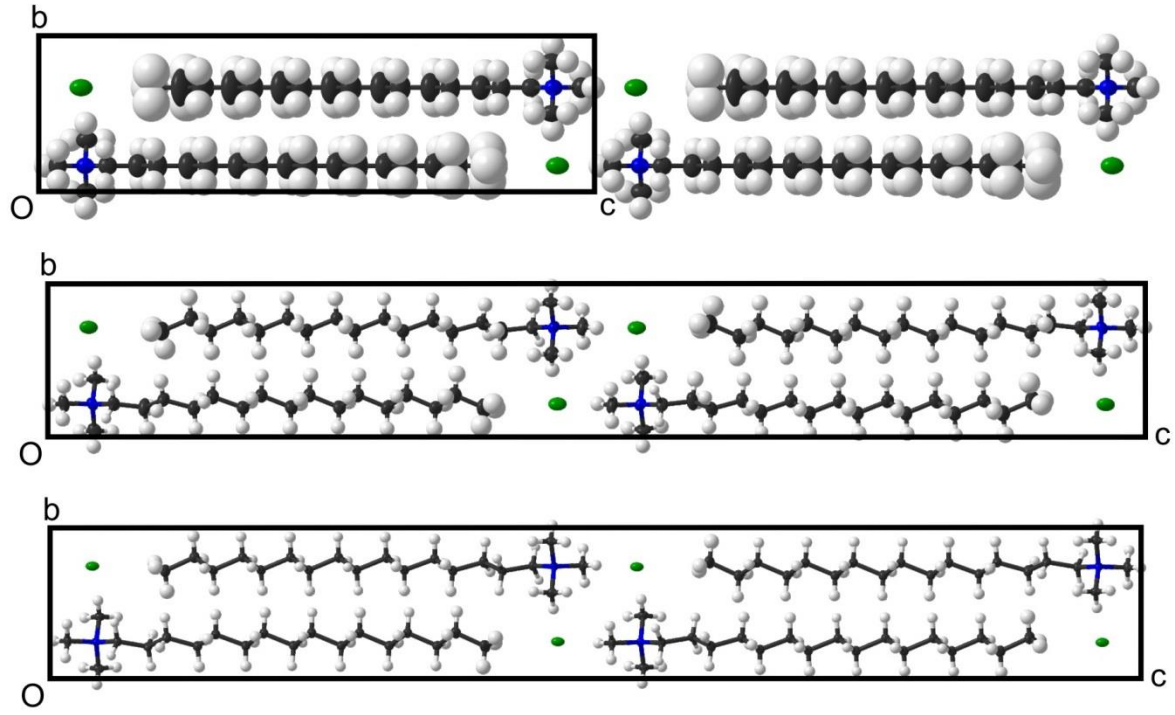


Fig. S32. Evolution of molecular motion in C_{16}TAB with increasing temperature seen in views of the unit cell along **a**: phase III at −123 °C (bottom), phase III at 22 °C (middle), and phase II at 117 °C (top), where the unit cell is halved in phase II due to the loss of the *c*-glide plane present in phase III. Thermal ellipsoids are drawn at 50% probability (including H atoms) using Mercury.[10]

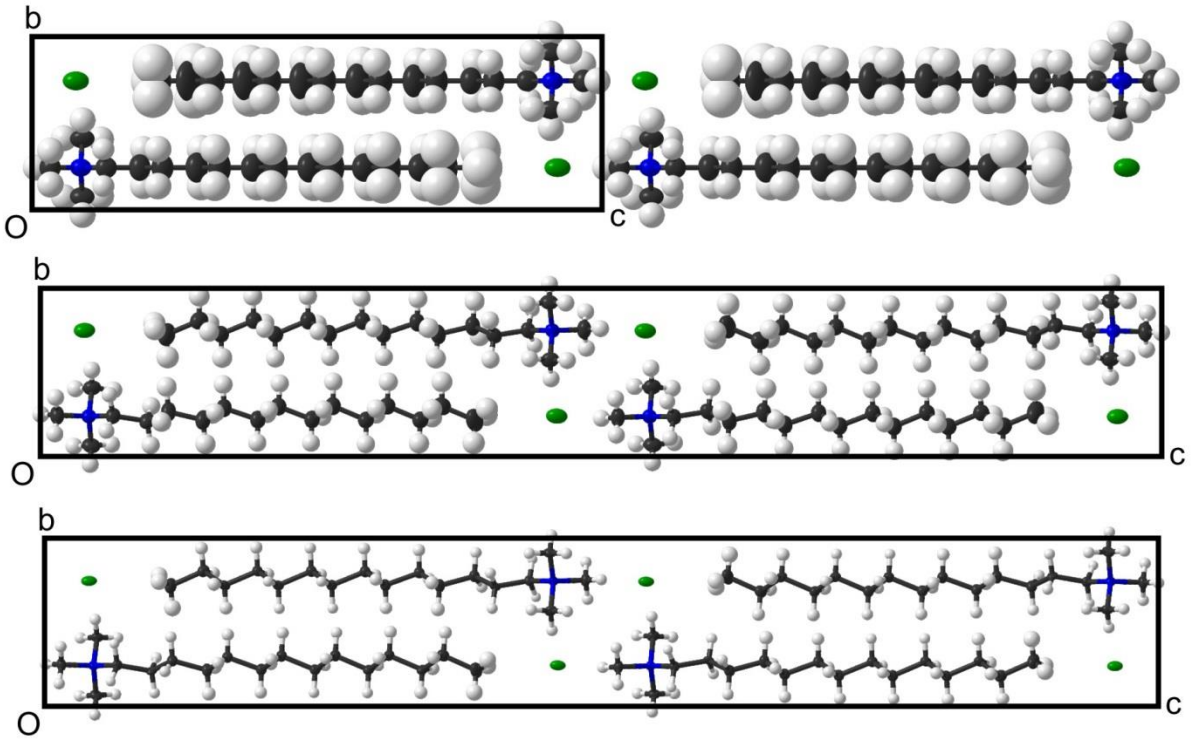


Fig. S33. Evolution of molecular motion in C_{14}TAB with increasing temperature seen in views of the unit cell along **a**: phase III at −123 °C (bottom), phase III at 22 °C (middle), and phase II at 107 °C (top), where the unit cell is halved in phase II due to the loss of the *c*-glide plane present in phase III. Thermal ellipsoids are drawn at 50% probability (including H atoms) using Mercury.[10]

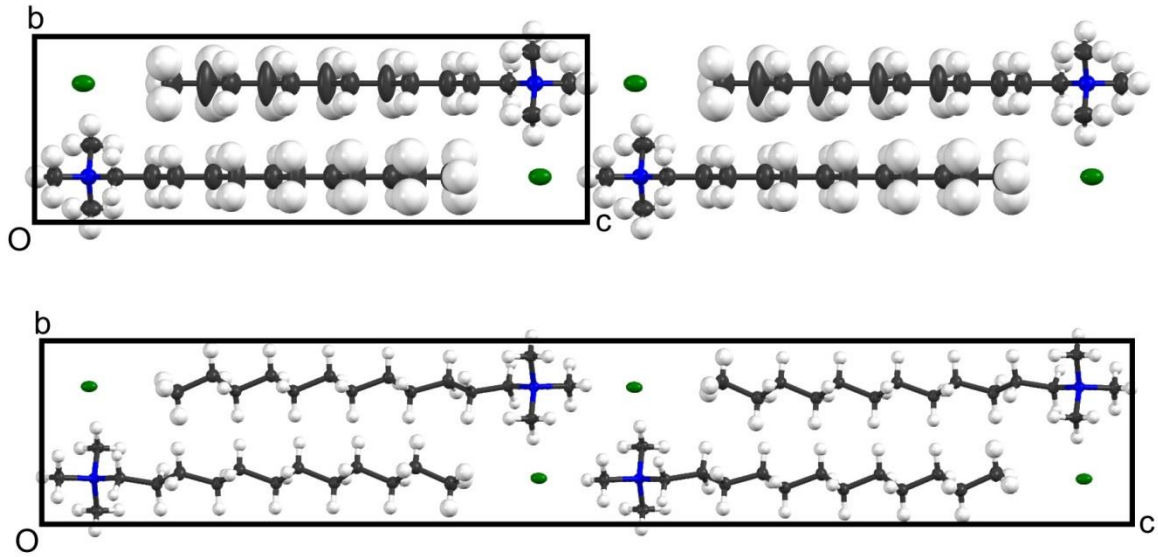


Fig. S34. Evolution of molecular motion in C_{12}TAB with increasing temperature seen in views of the unit cell along **a**: phase III at −123 °C (bottom) and phase II at 22 °C (top), where the unit cell is halved in phase II due to the loss of the *c*-glide plane present in phase III. In contrast to the previous 3 figures (Figs. S31-33) and the following figure (Fig. S35), a structure cannot be shown just below the transition temperature to phase I due to the incommensurate nature of the structure of phase IIb. Thermal ellipsoids are drawn at 50% probability (including H atoms) using Mercury.[10]

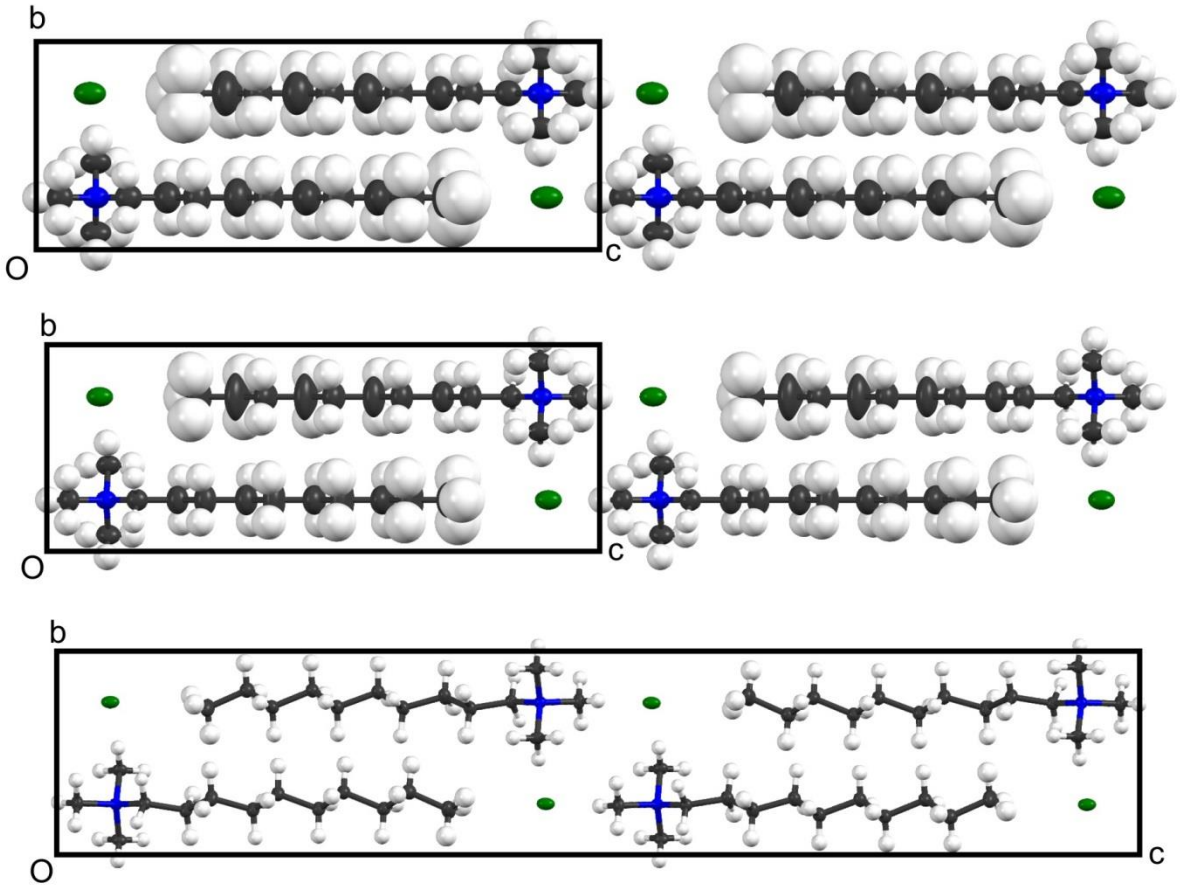


Fig. S35. Evolution of molecular motion in C_{10}TAB with increasing temperature seen in views of the unit cell along **a**: phase III at −123 °C (bottom), phase II at 22 °C (middle), and phase II at 102 °C (top), where the unit cell is halved in phase II due to the loss of the *c*-glide plane present in phase III. The two measurements on phase II lie below and above the re-entrant phase transition at about 57 °C. At both 22 °C and 102 °C, the structure of phase II appears to be the same but with larger anisotropic thermal displacements at the higher temperature. Thermal ellipsoids are drawn at 50% probability (including H atoms) using Mercury.[10]

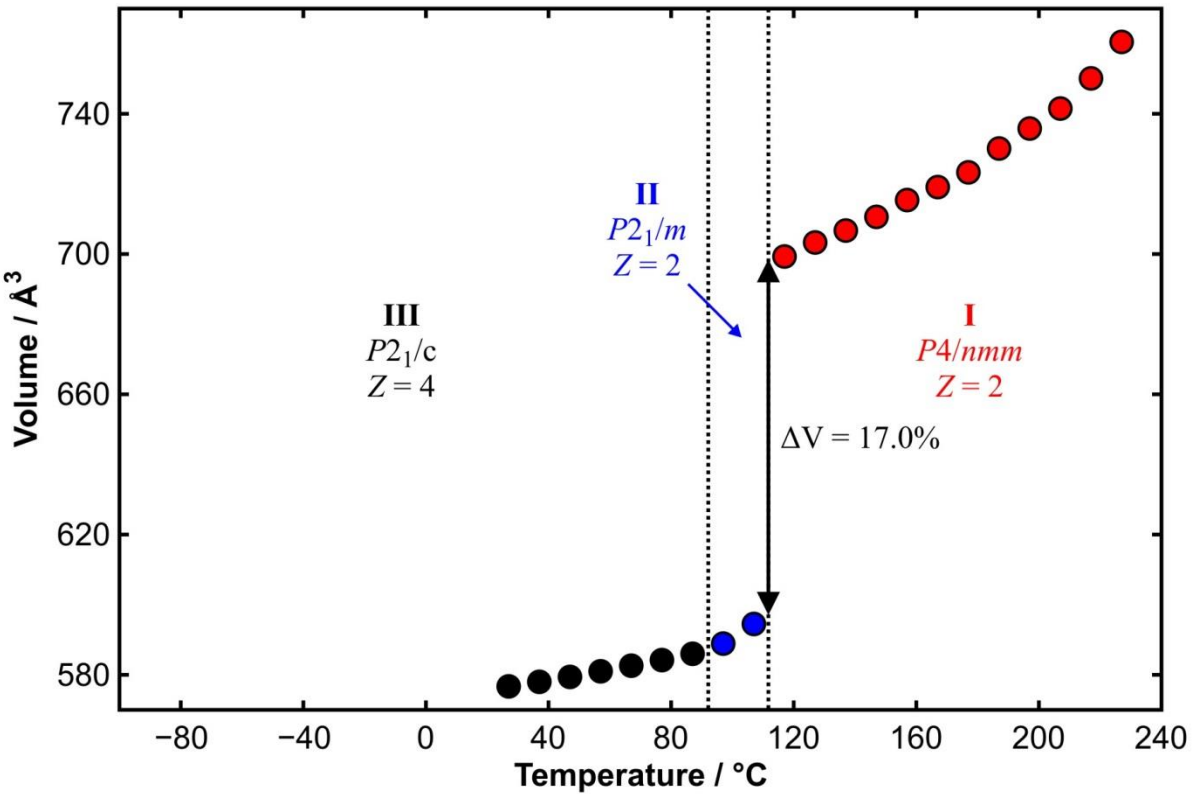


Fig. S36. Molecular volume for C_{18}TAB as a function of temperature (from Table 19). Figures S36 to S40 are drawn with the same temperature and volume scales, but with a volume-offset that depends on the alkyl-chain length *n*, to aid comparison between the C_nTABs. *Z* is the number of molecules in the unit cell for the identified structures.

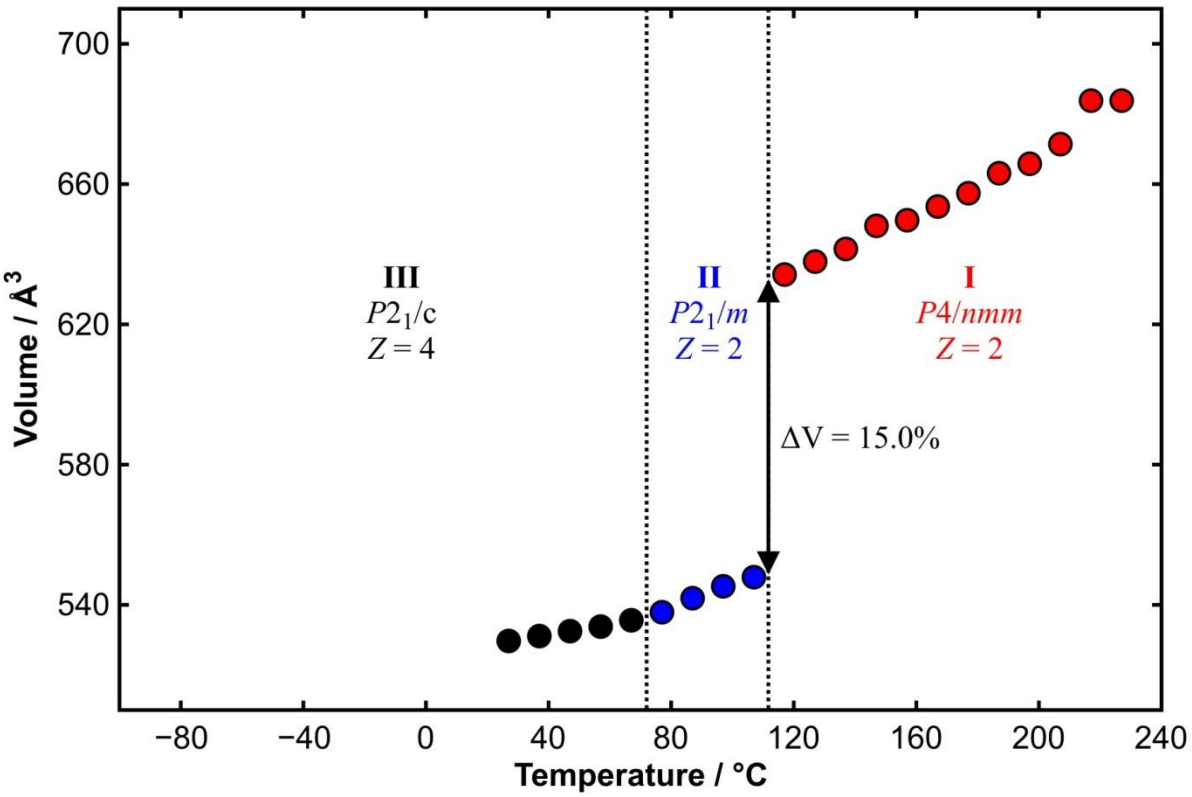


Fig. S37. Molecular volume for C_{16}TAB as a function of temperature (from Table 20). *Z* is the number of molecules in the unit cell for the identified structures.

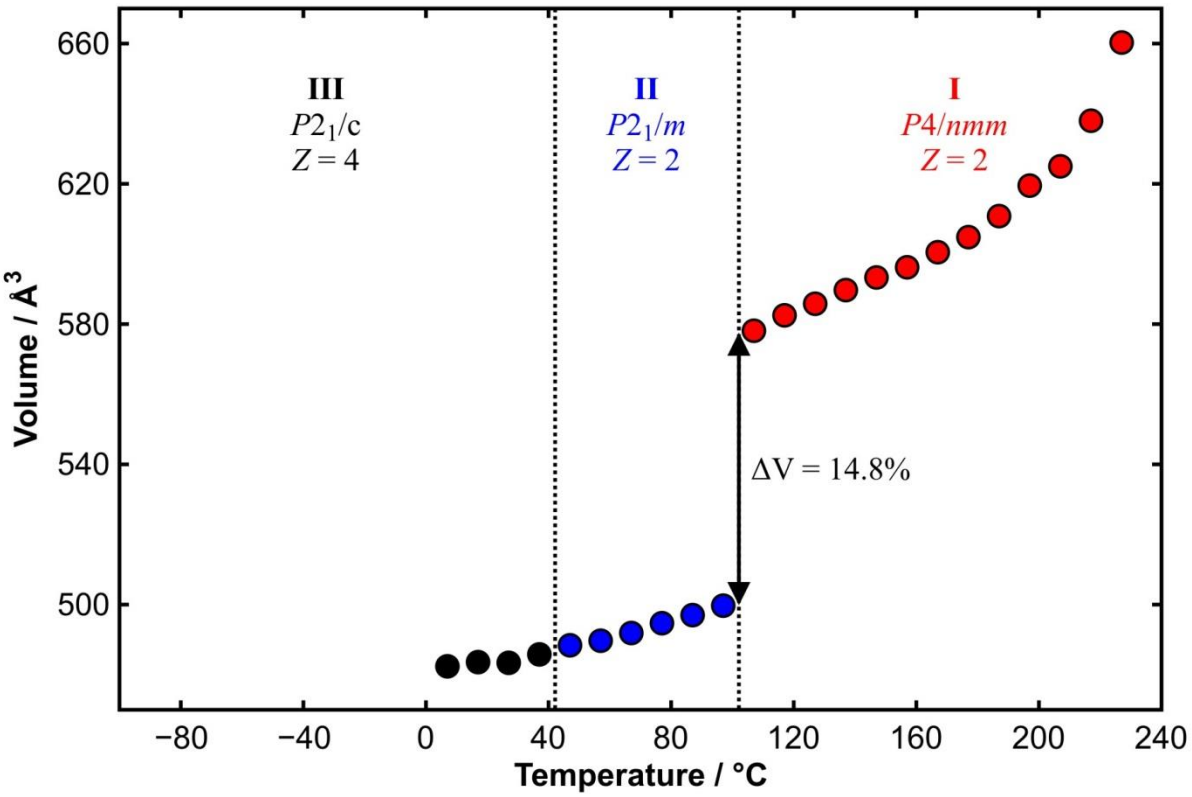


Fig. S38. Molecular volume for C_{14}TAB as a function of temperature (from Table 21). *Z* is the number of molecules in the unit cell for the identified structures.

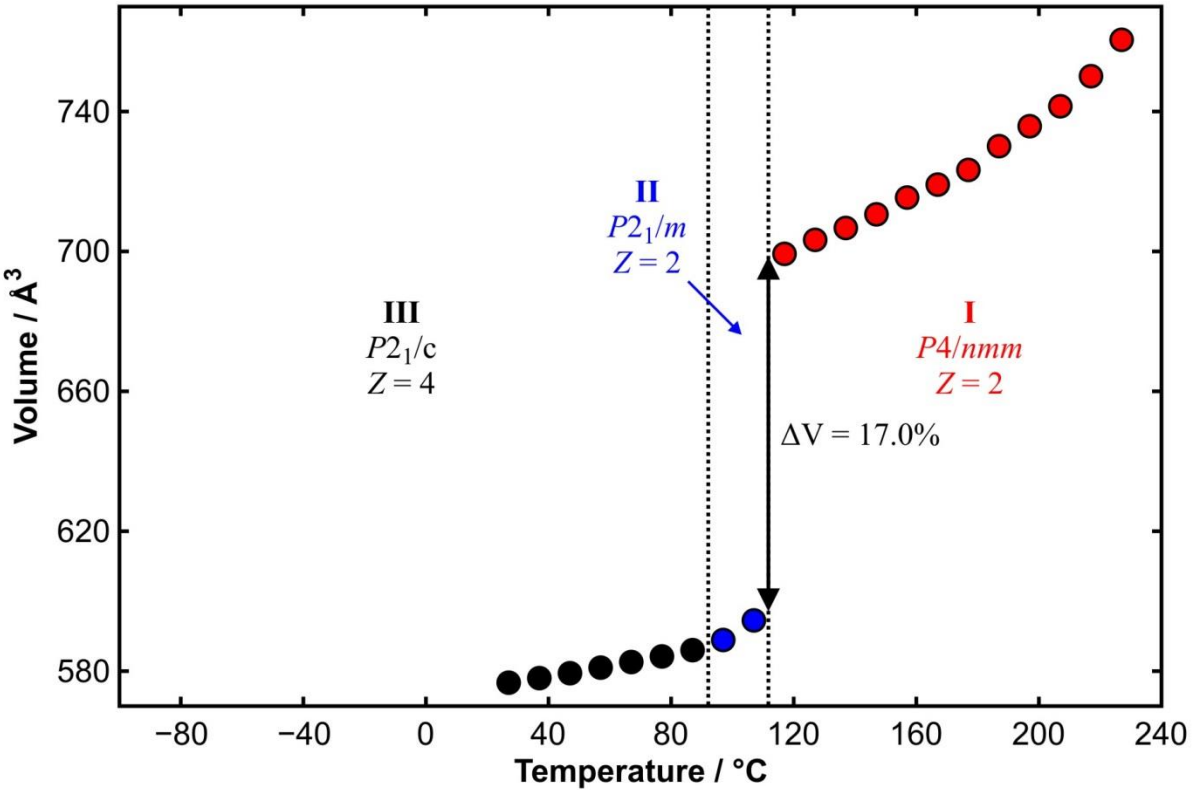


Fig. S39. Molecular volume for C_{12}TAB as a function of temperature (from Table 22). *Z* is the number of molecules in the unit cell for the identified structures.

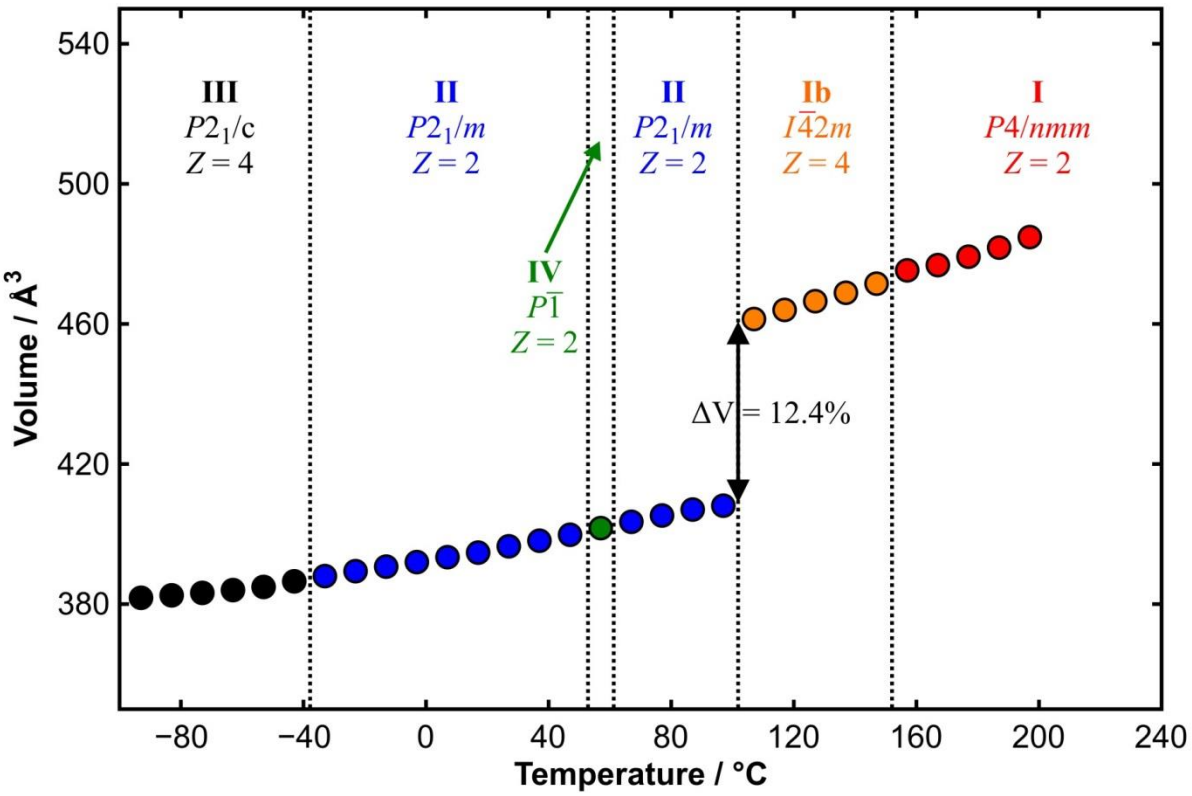


Fig. S40. Molecular volume of C_{10}TAB as a function of temperature (from Table 23). The colour scheme for the data points is the same as that used to display the PXRD data in Fig. S10 (upper). *Z* is the number of molecules in the unit cell for the identified structures.

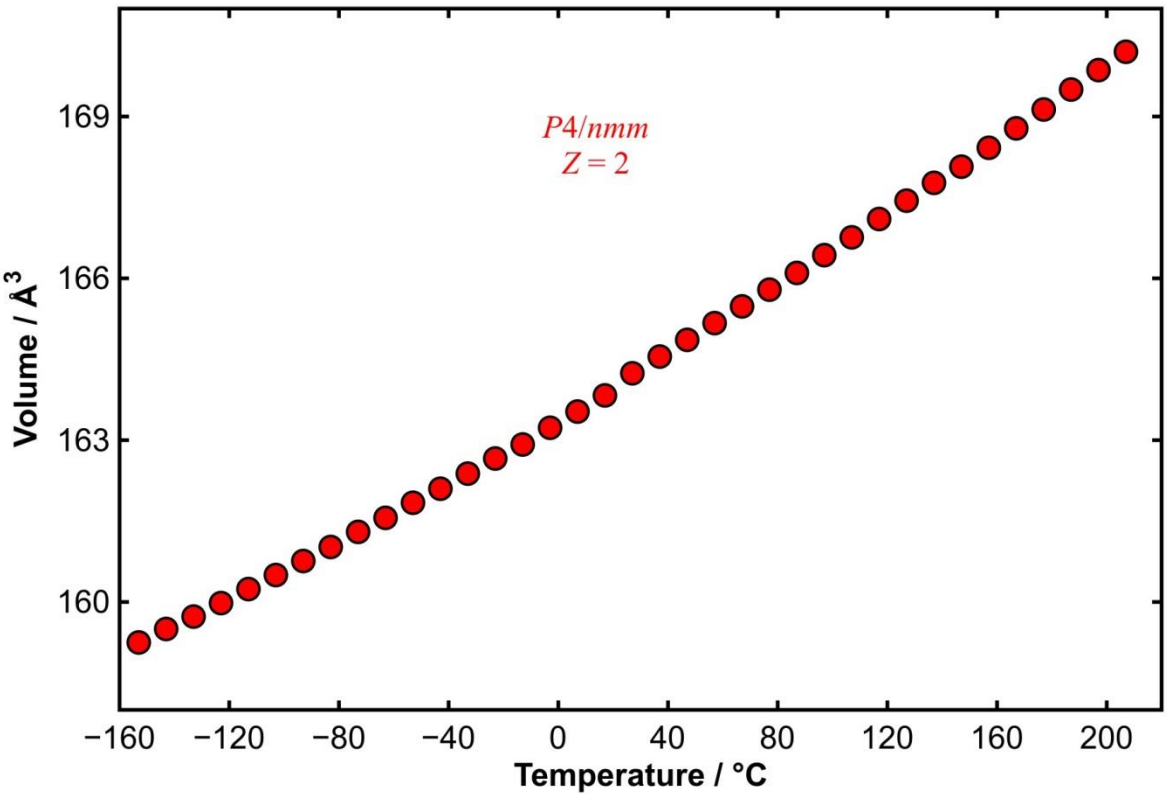


Fig. S41. Molecular volume for C_1TAB as a function of temperature (from Table 24).

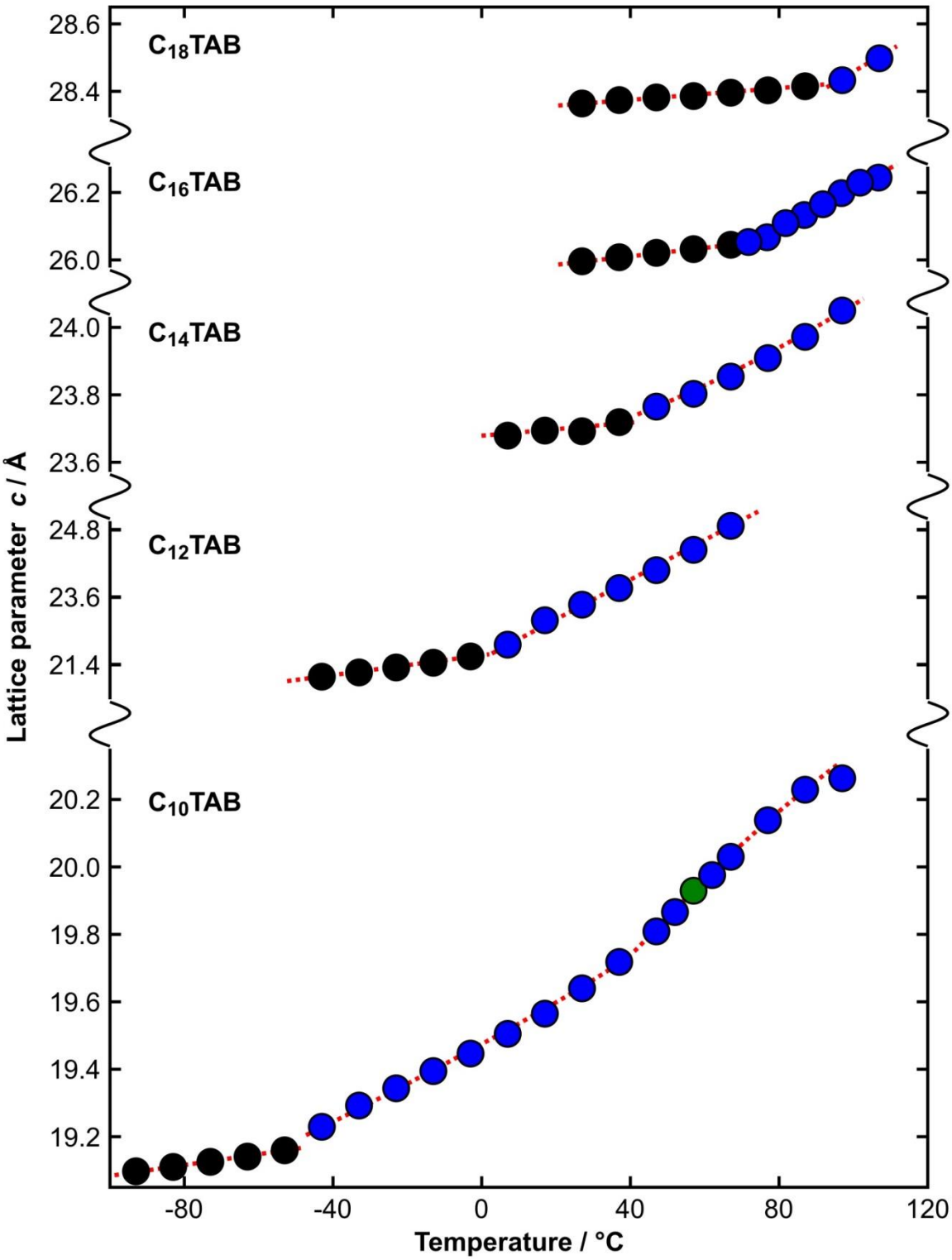


Fig. S42. Lattice parameter *c* for phase II (blue points) and *c*/2 for phase III (black points) as a function of temperature (from data in Tables 19-24). The value of *c* for the re-entrant phase IV of C_{10}TAB is shown in green. Dotted lines in red are a guide to the eye. The transition from phase III to phase II results in a noticeable change in gradient. The decrease in the transition temperature from phase III to II with decreasing alkyl-chain length *n* is evident.

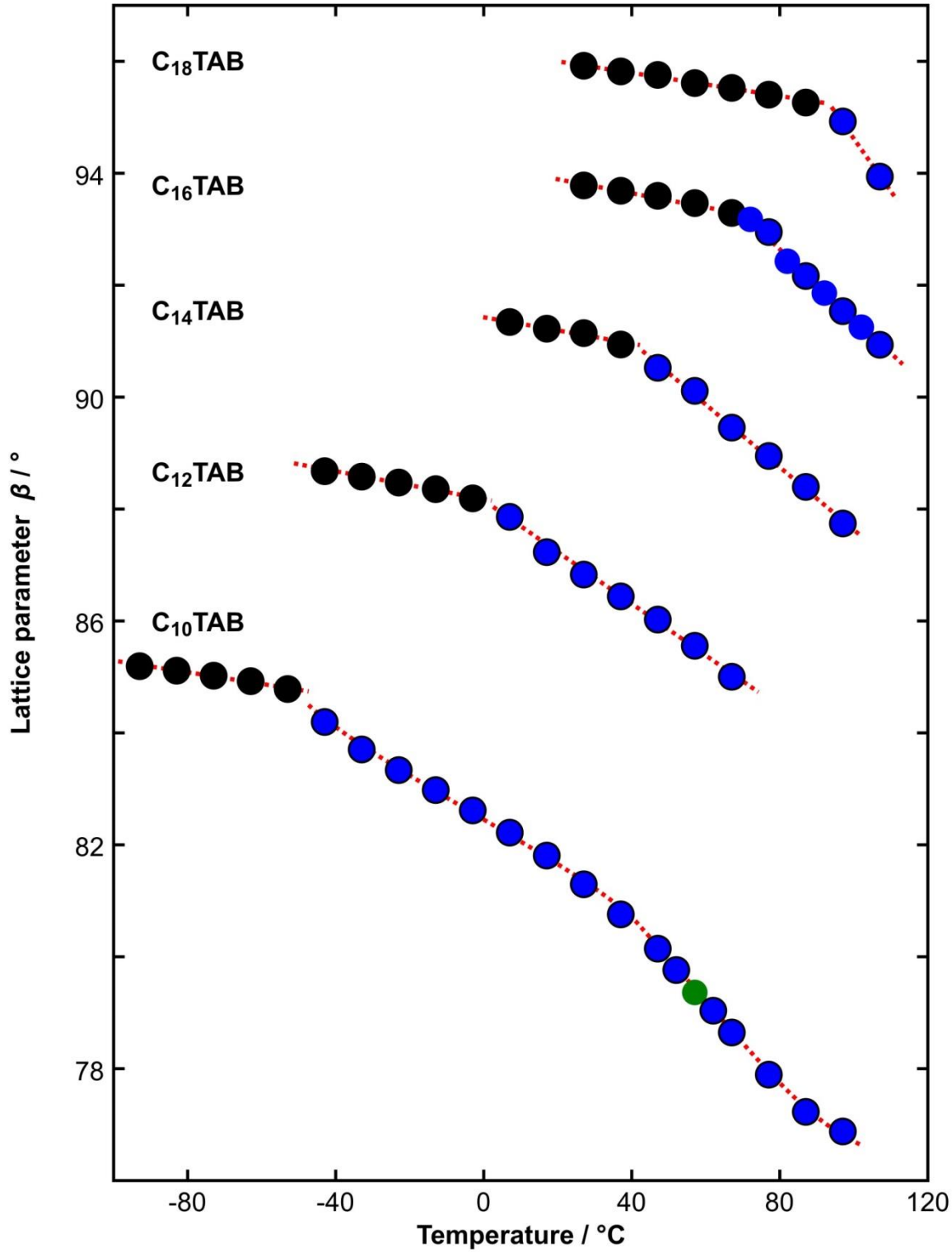


Fig. S43. Lattice parameter β for phases II (blue points) and III (black points) of C_nTAB as a function of temperature (from data in Tables 19-24). The value of β for the re-entrant phase IV of C_{10}TAB is shown in green. Dotted lines in red are a guide to the eye. As for the lattice parameter *c*, the transition from phase III to phase II results in a noticeable change in gradient. The decrease in the phase III to II transition temperature with decreasing alkyl-chain length *n* is evident.

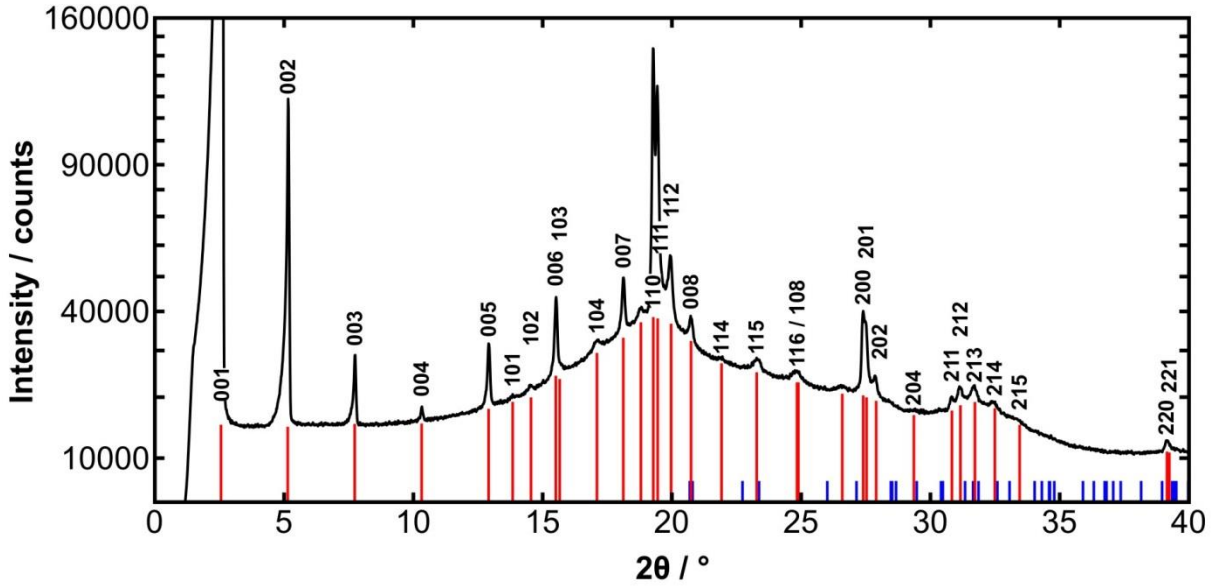


Fig. S44. Indexed PXRD data on C_{18}TAB phase I at 177 °C in space group *P*4/*nmm*. The observed indexed peaks (indicated with red vertical lines) provide the information on space-group symmetry. Blue vertical lines show the position of peaks that were not observed but would be allowed by the space-group symmetry for the same cell. These unobserved peaks occur predominantly at higher angles. 00*l* reflections can be readily picked out by eye. It is also clearly seen that the intensity of diffraction peaks generally decreases strongly with increasing angle, which is indicative of large motional disorder. Although data were measured to 65° in 2θ, there is little intensity above 40° for phase I (*cf*. Fig. S7) in contrast to the observation of peaks at high angles for the other phases. To help visualise weak peaks in the presence of strong ones, $I^{½}$ is plotted versus 2θ but with counts shown on the vertical axis; this non-linear scale starts above zero due to the relatively high background.

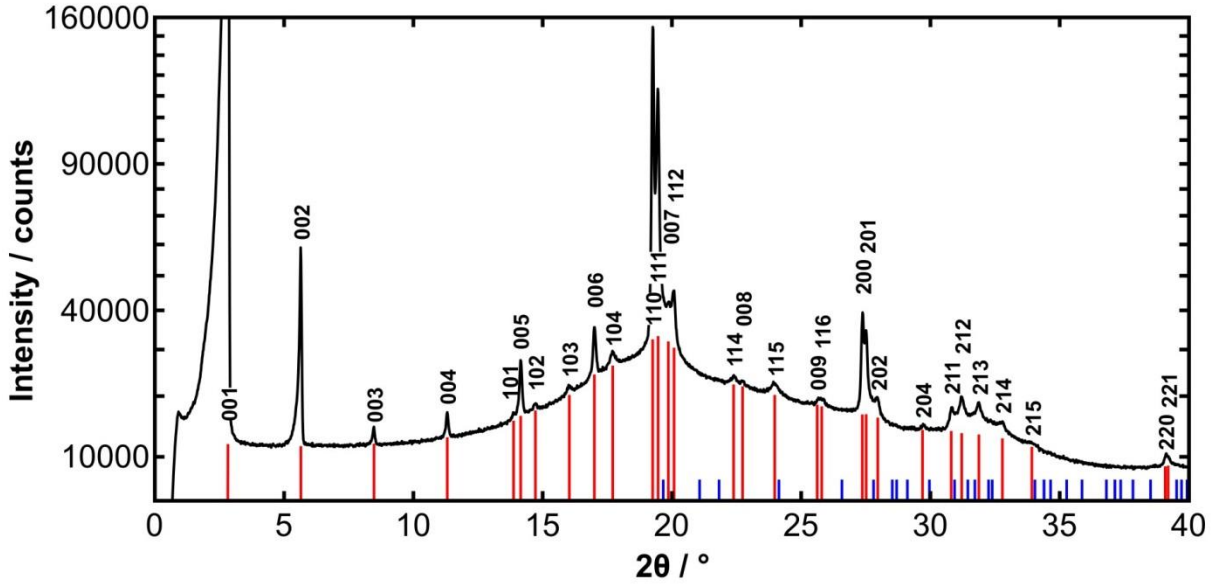


Fig. S45. Indexed PXRD data for C_{16}TAB phase I at 187 °C in space group *P*4/*nmm*. The labelling of indexed peaks is as described in the caption to Fig. S44, which shares common features with these data.

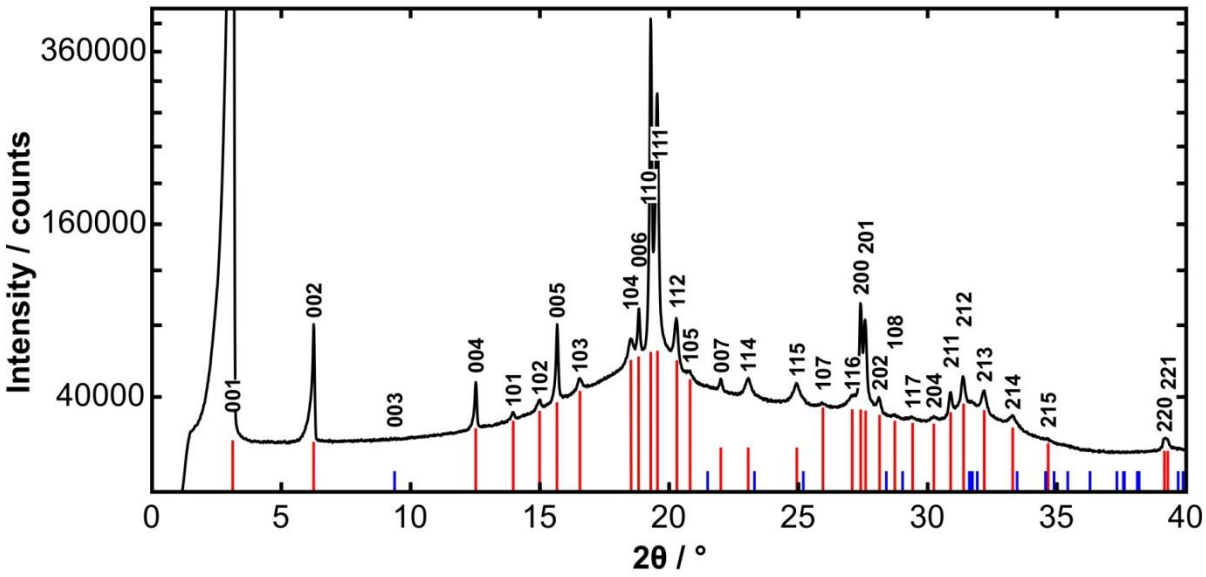


Fig. S46. Indexed PXRD data for C_{14}TAB phase I at 157 °C in space group *P*4/*nmm*. The labelling of indexed peaks is as described in the caption to Fig. S44, which shares common features with these data.

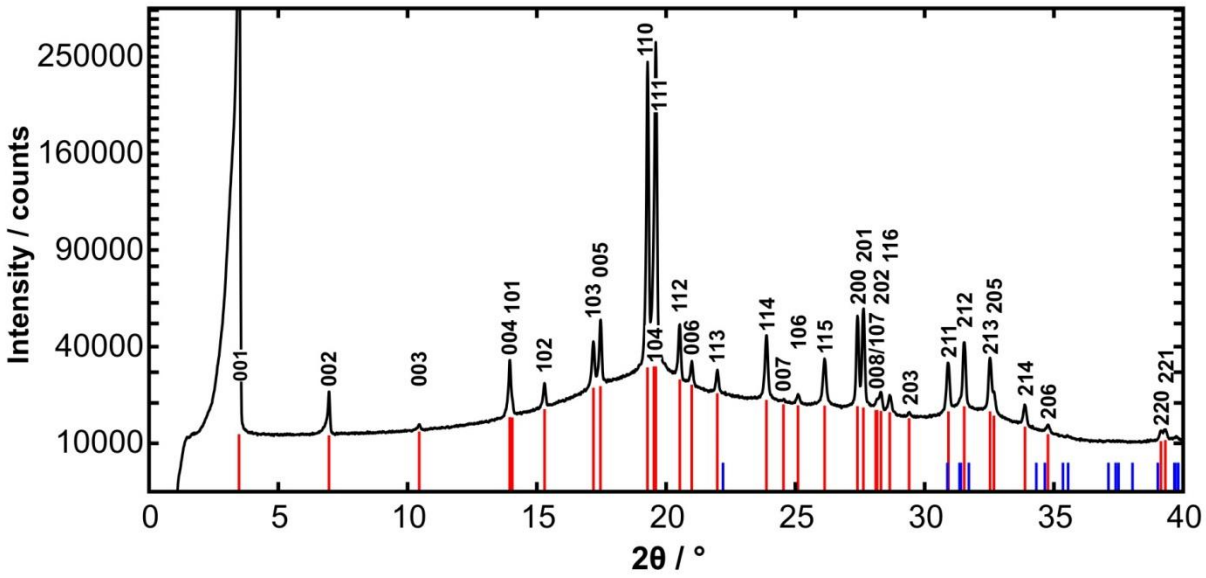


Fig. S47. Indexed PXRD data for C_{12}TAB phase I at 157 °C in space group *P*4/*nmm*. The labelling of indexed peaks is as described in the caption to Fig. S44, which shares common features with these data.

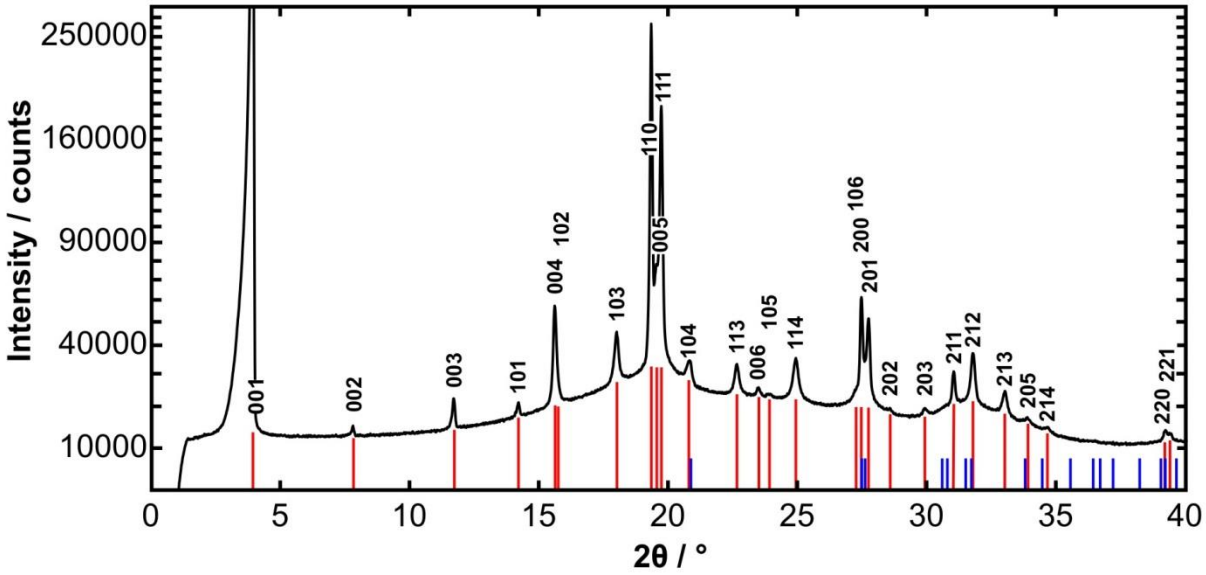


Fig. S48. Indexed PXRD data for C_{10}TAB phase I at 167 °C in space group *P*4/*nmm*. The labelling of indexed peaks is as described in the caption to Fig. S44, which shares common features with these data.

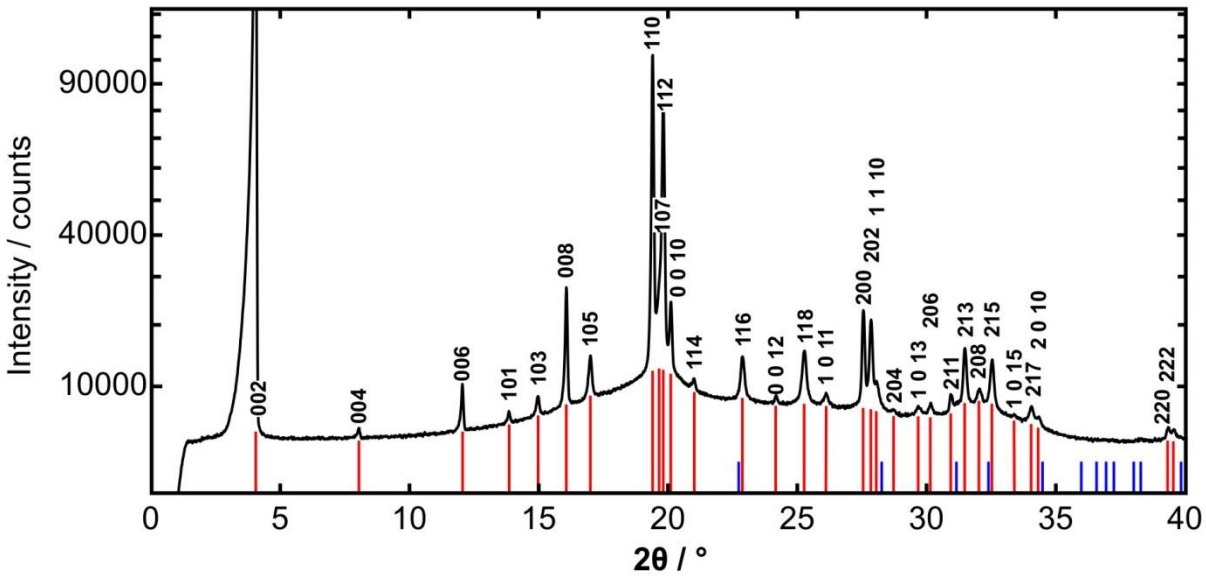


Fig. S49. Indexed PXRD data for C_{10}TAB phase Ib at 117 °C in space group $I\bar{4}2m$. Phase Ib of C_{10}TAB is very similar to that of phase I with a similar pattern and intensity of 00*l* reflections (as seen in the previous figure). The peaks observed at about 13.8°, 14.9°, and 16.9° in 2θ are significant in identification of this phase as they can only be indexed with a doubled-length unit cell along the *c* axis resulting in an *I*-centred space group. As for Fig. S44, red vertical lines show the position of observed indexed peaks; blue vertical lines show the position of peaks that were not observed but would be allowed by the space-group symmetry for the same cell.

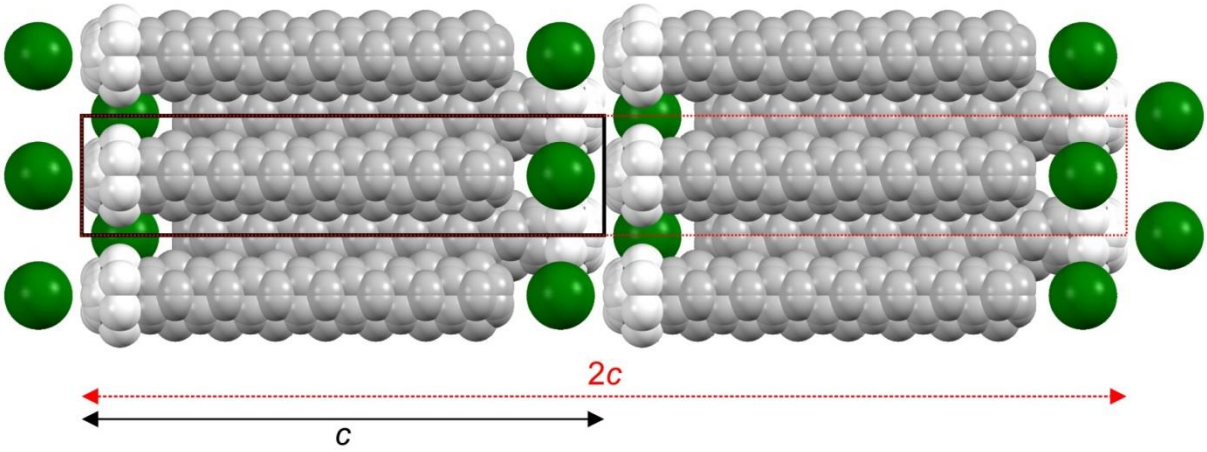


Fig. S50. Space-filling view of the proposed rotator structure of C_{14}TAB phase I with space-group symmetry *P*4/*nmm* seen perpendicular to the rotating alkyl-chain axis. The unit cell outlined in thick black corresponds to the single-length cell of phase I seen for all C_nTAB (*n* = 10, 12, 14, 16, and 18). The unit cell outlined with a dotted red line corresponds to the double-length body-centred unit cell found for phase Ib of C_{10}TAB, which can be explained in terms of a rotating alkyl chain plus a cationic head group ($–N^+Me_3$) that is more ordered than in phase I. The packing of rotating alkyl chains is similar to that proposed previously for the high-temperature tetragonal phase of *n*-alkyl ammonium chlorides, also with space-group symmetry *P*4/*nmm*.[25]

[25] D. F. R. Gilson, A. S. Kertes, R. St. J. Manley, J. Tsau and G. Donnay, *Can. J. Chem*., 1976, **54**, 765–768.

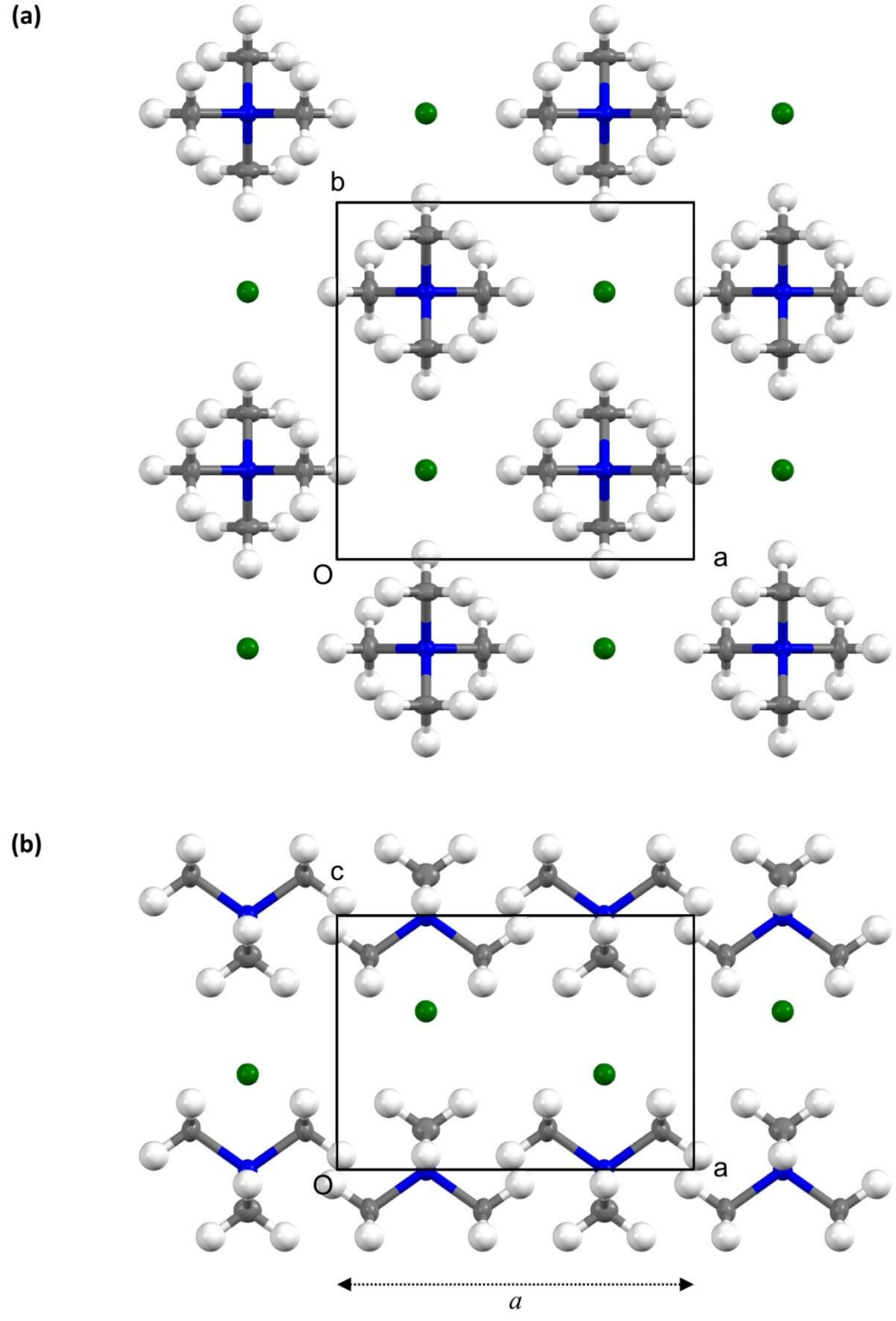


Fig. S51. **(a)** and **(b)** show the structure of C_1TAB at −123 °C with space-group symmetry *P*4/*nmm* as viewed down **c** and **b**, respectively. Thermal ellipsoids are drawn at 50% probability. The lattice parameter *a* is significantly bigger than the value observed for the plastic phase I of C_nTAB (*n* = 10, 12, 14, 16, and 18) due to the subtle difference in the packing of the ions (see Fig. S60 for a comparison).

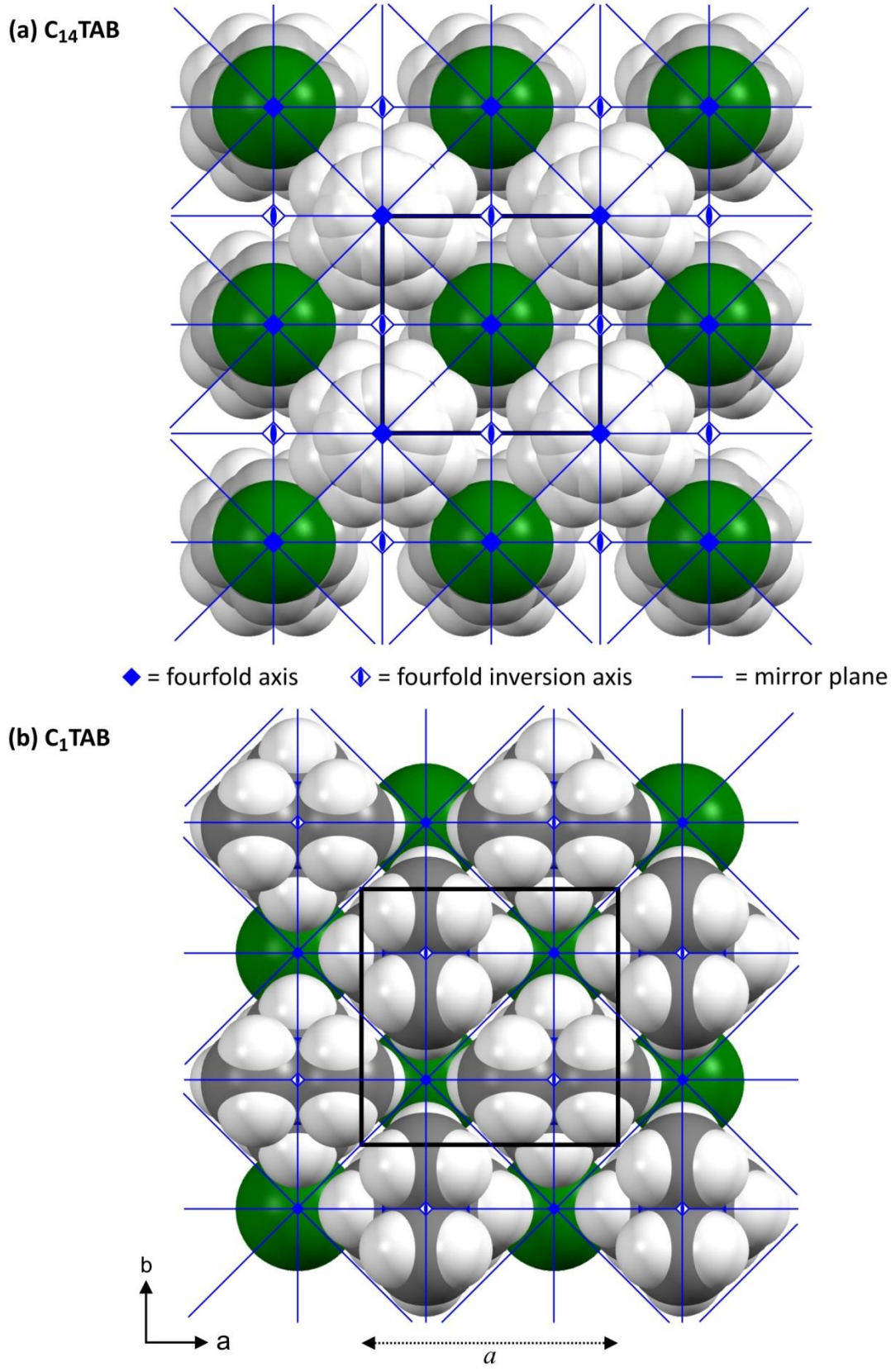


Fig. S52. **(a)** Space-filling view of the proposed rotator structure of C_{14}TAB phase I with space-group symmetry *P*4/*nmm* seen down *c*. Selected symmetry elements, *viz*. fourfold axes, fourfold-inversion axes, and mirror planes perpendicular to unit-cell axes, are shown in blue. **(b)** On the same scale, C_1TAB is shown for comparison with the unit cell with the centrosymmetric origin used in the description of the structure in thick black.

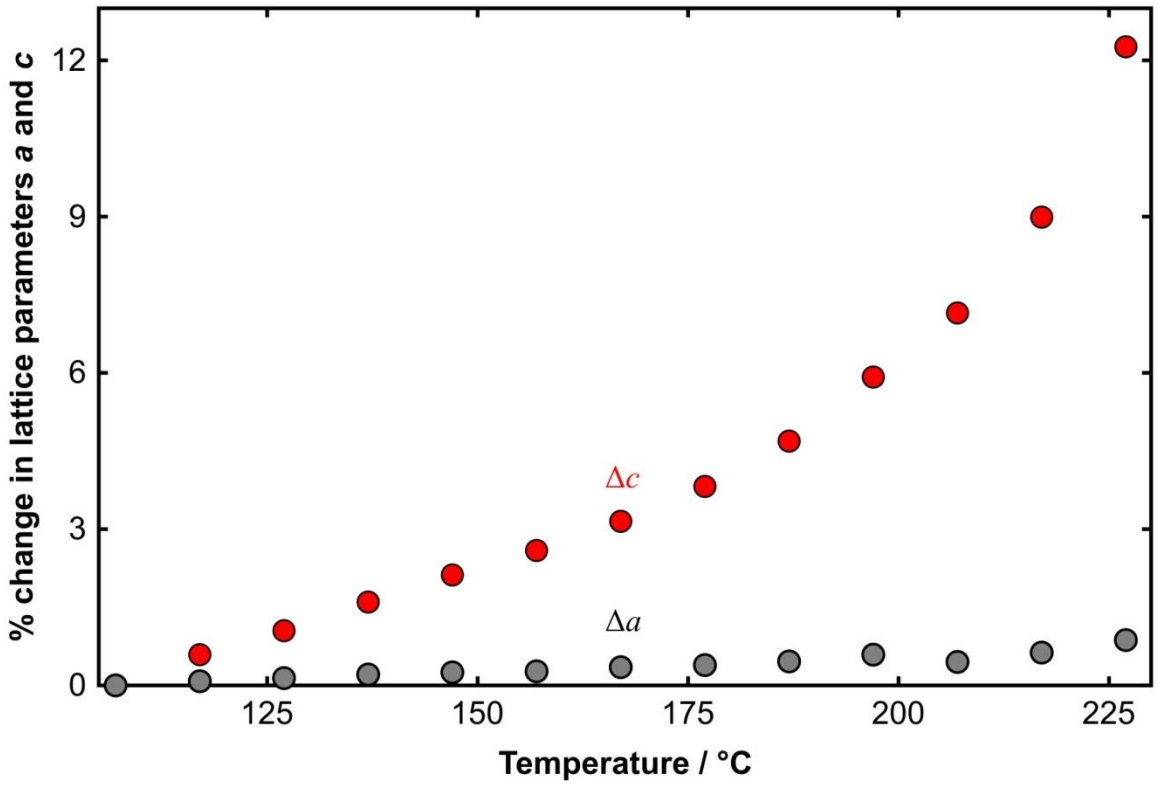


Fig. S53. Percentage change in tetragonal lattice parameters *a* (grey points) and *c* (red points) for C_{14}TAB as a function of temperature. The rapid increase in *c* with increasing temperature above 200 °C is indicative of sample decomposition, which occurs due to increasing separation of the ionic planes. In the plastic phase I, there is little change in the value of *a* with temperature for all C_nTAB in this study, this almost temperature-independent distance being determined by the effective diameter, Ø = (*a* / √2) = 4.60 Å at 177 °C, of the dynamically-disordered alkyl trimethylammonium cation and not by its length.

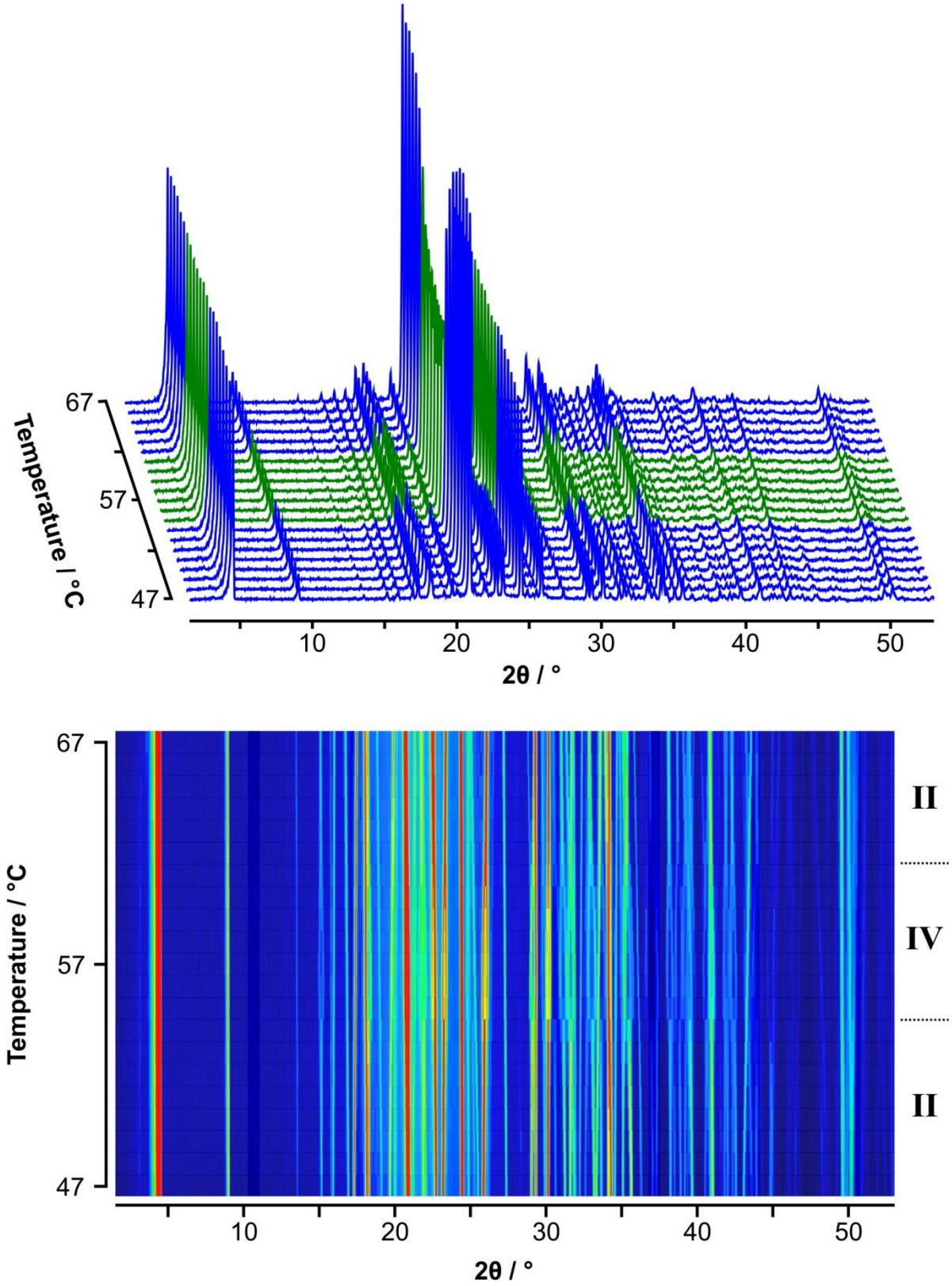


Fig. S54. PXRD data as a function of temperature in 1 °C steps for a sample of C_{10}TAB measured using a 0.7 mm capillary on a Stoe Stadi-P diffractometer with Cu Kα_1 radiation. The re-entrant phase transition is more clearly seen in the upper figure, where diffraction patterns of the monoclinic phase II are shown in blue curves and those of the triclinic phase IV are shown in green.

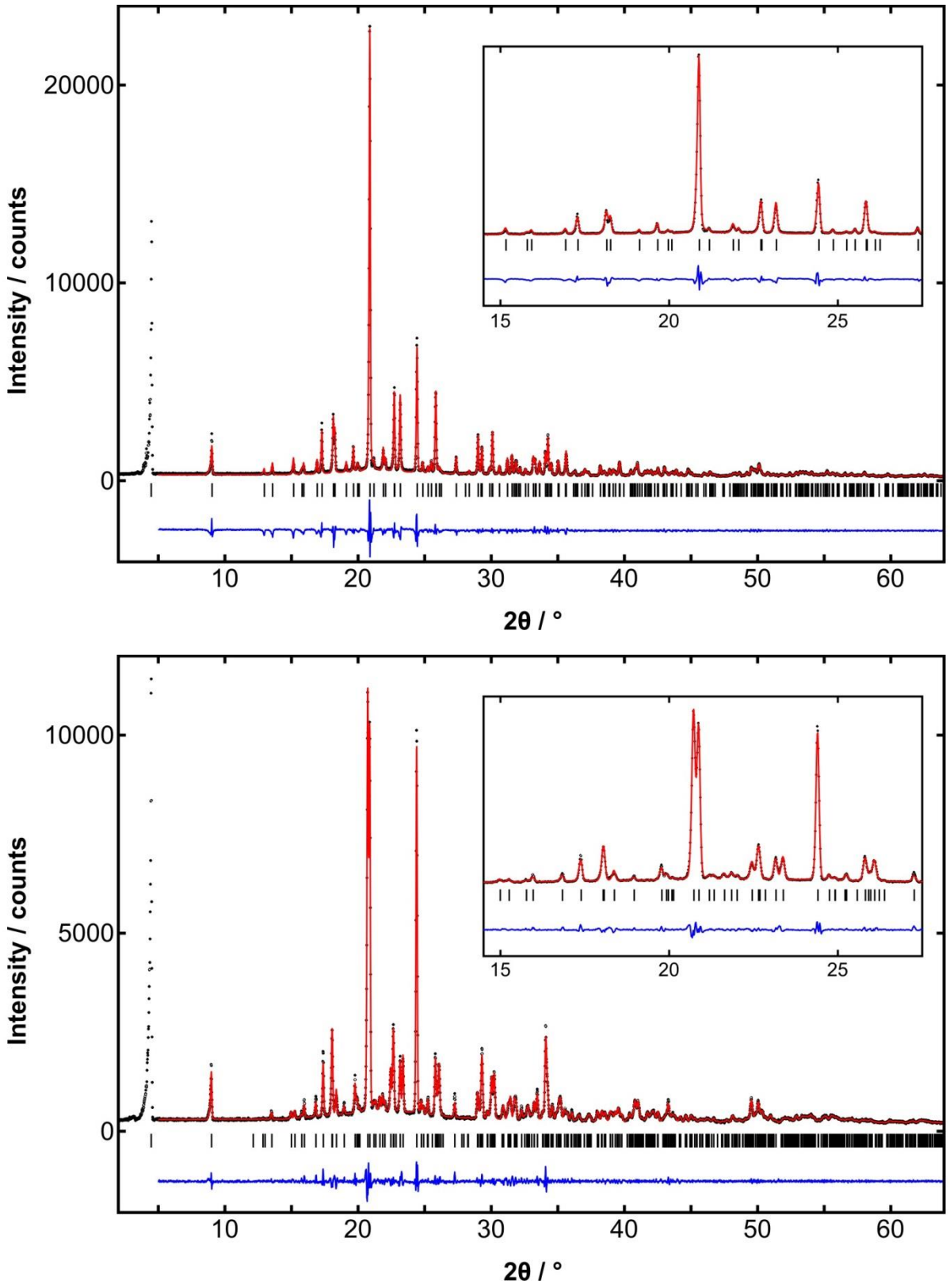


Fig. S55. Upper plot shows a LeBail fit to the laboratory PXRD data for C_{10}TAB at 53 °C measured on a Stadi-P diffractometer with Cu Kα_1 radiation using the monoclinic cell of phase II. Lower plot shows a LeBail fit to data for C_{10}TAB at 57 °C using the triclinic cell of the re-entrant phase IV. The insets show the excellent fit to the peak positions with the split peaks in the lower plot well-accounted for by the triclinic distortion.

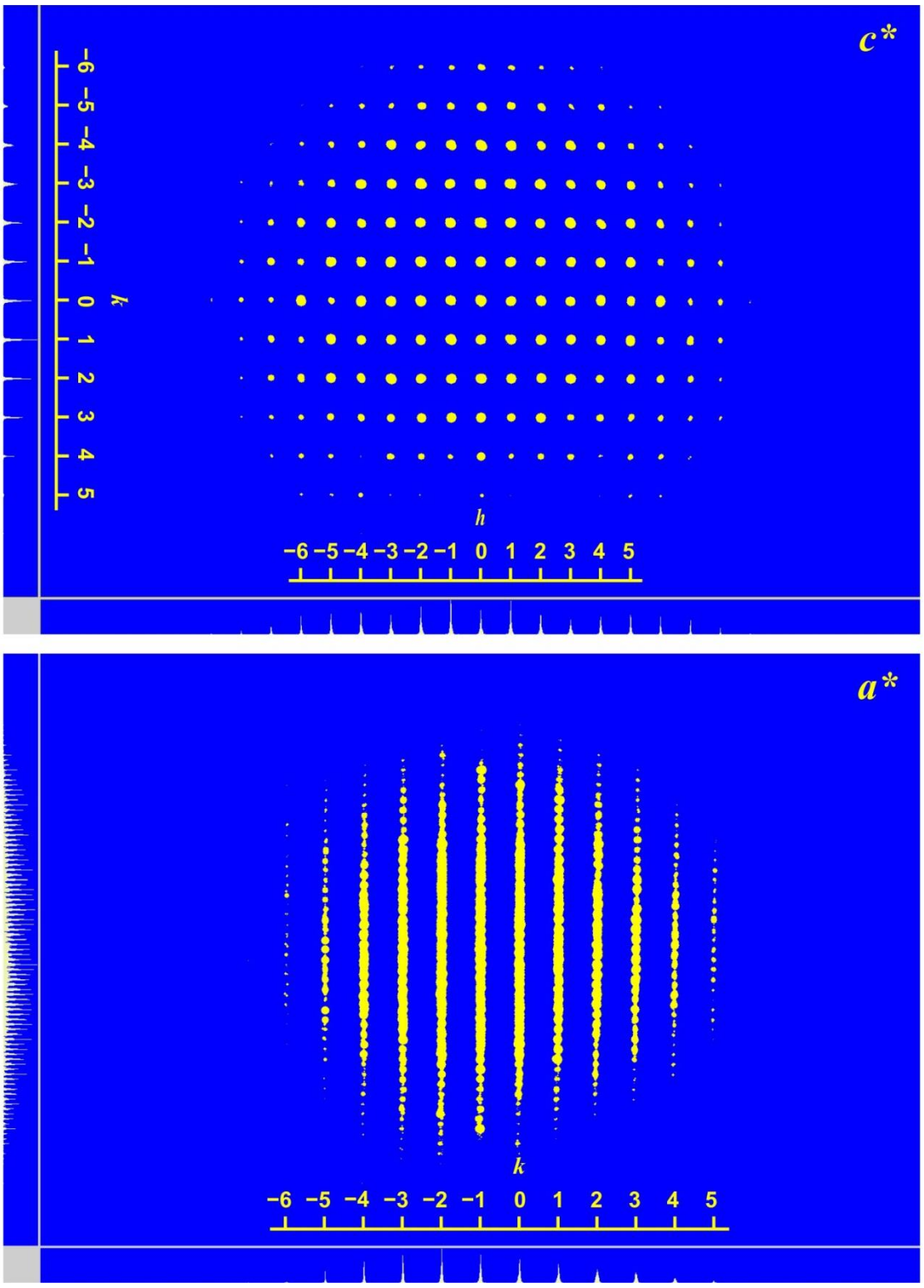


Fig. S56. Whole sphere of reciprocal-space data viewed down *c** (upper) and *a** (lower) using the Ewald Explorer software within CrysAlis^{Pro} for C_{12}TAB phase IIa at 97 °C. From these two figures, it is evident that spots in reciprocal space can be assigned integer indices in h and k but not l.

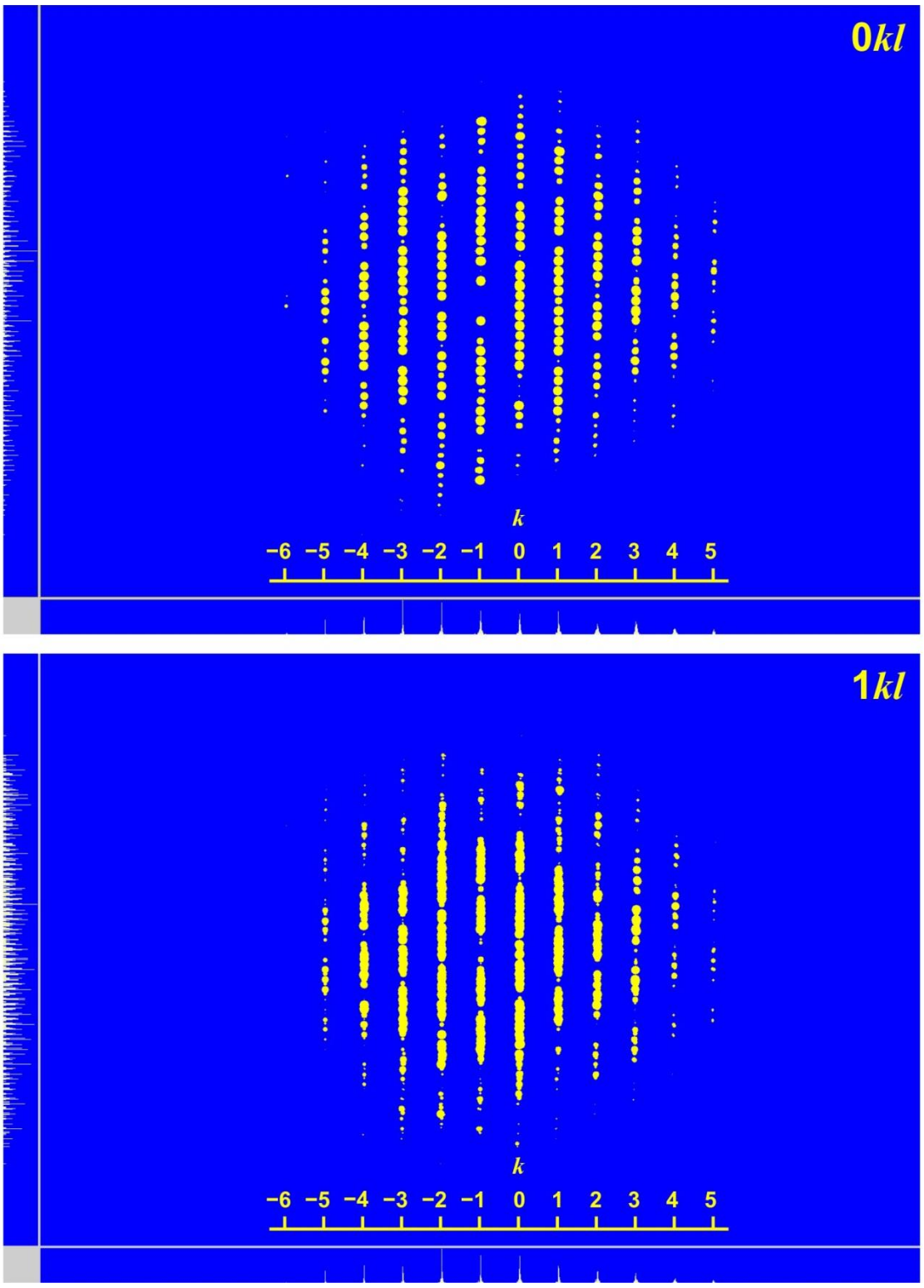


Fig. S57. Similar to Fig. S56, but now showing individual 0kl and 1kl planes of reciprocal-space data for C_{12}TAB phase IIa at 97 °C. While the upper figure appears to show commensurate behaviour in that integer indices l can be assigned along vertical rows of spots, it is clear that the same integers cannot be used in the adjacent plane seen in the lower figure, thus indicating an incommensurate phase for C_{12}TAB at this temperature.

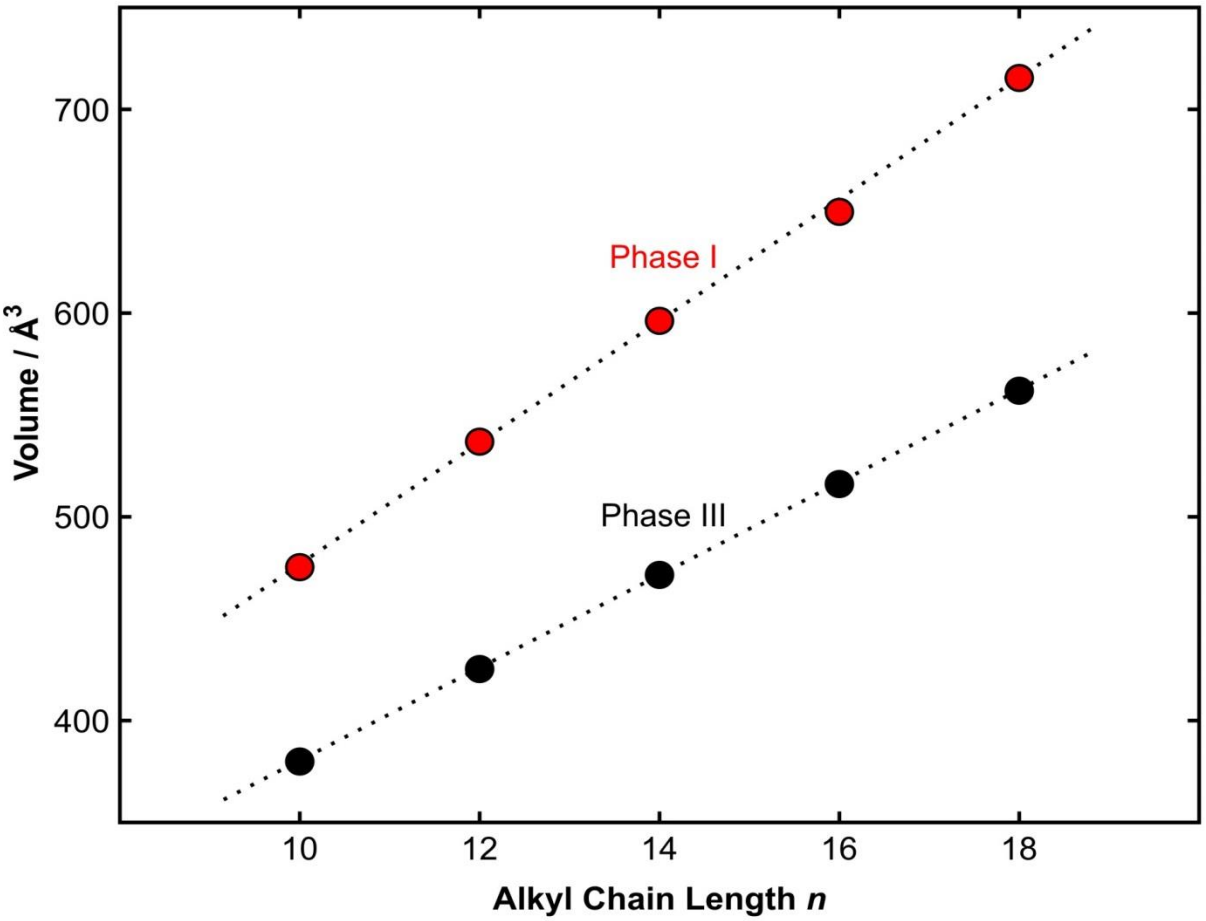


Fig. S58. Molecular volume as a function of alkyl-chain length *n* for C_nTAB in phase III at −123 °C (black points) and in phase I at 157 °C (red points). The dotted lines show the best straight-line fit through each set of data points. The slope of the line provides the volume increment, V_{CH_2}, per –CH_2– unit: 22.7 Å^3 at −123 °C and 29.7 Å^3 at 157 °C.

Fig. S59. View of the low-temperature set-up on the Stoe Stadi-P diffractometer equipped with a single Mythen 1K detector. The instrument has been modified so that the incident beam height is higher than normal to allow for the mounting of different sample environment stages. In addition, the set-up employs screw-in brass stubs with internal diameters from 0.2 to 1.2 mm (in 0.1 mm steps) as developed for use on the high-resolution PXRD beamlines BM16/ID31 at ESRF, and also used on, for example, the high-resolution PXRD beamline I11 at the Diamond synchrotron. The vertical axis of the Stadi-P is perfect for the use of the Oxford Instruments CryojetHT device that enables samples to be measured from about −173 °C to 227 °C. However, the rotating goniometer head disrupts the laminar shield flow of the CryojetHT. As a preventative measure against ice formation during data collection at the lowest temperatures, a conical polytetrafluoroethylene (PTFE/Teflon^{TM}) cone is fitted as shown, on which ice may form as a skirt at its outer edge only.

Fig. S60. Views of the X-ray capillary containing C_{10}TAB before (left) and after (right) prolonged heating to high temperature (> 167 °C) for several hours. The slight change in colour is evidence of the start of sample degradation. This degradation was only observed for C_{10}TAB and not for the longer alkyl chain surfactants.

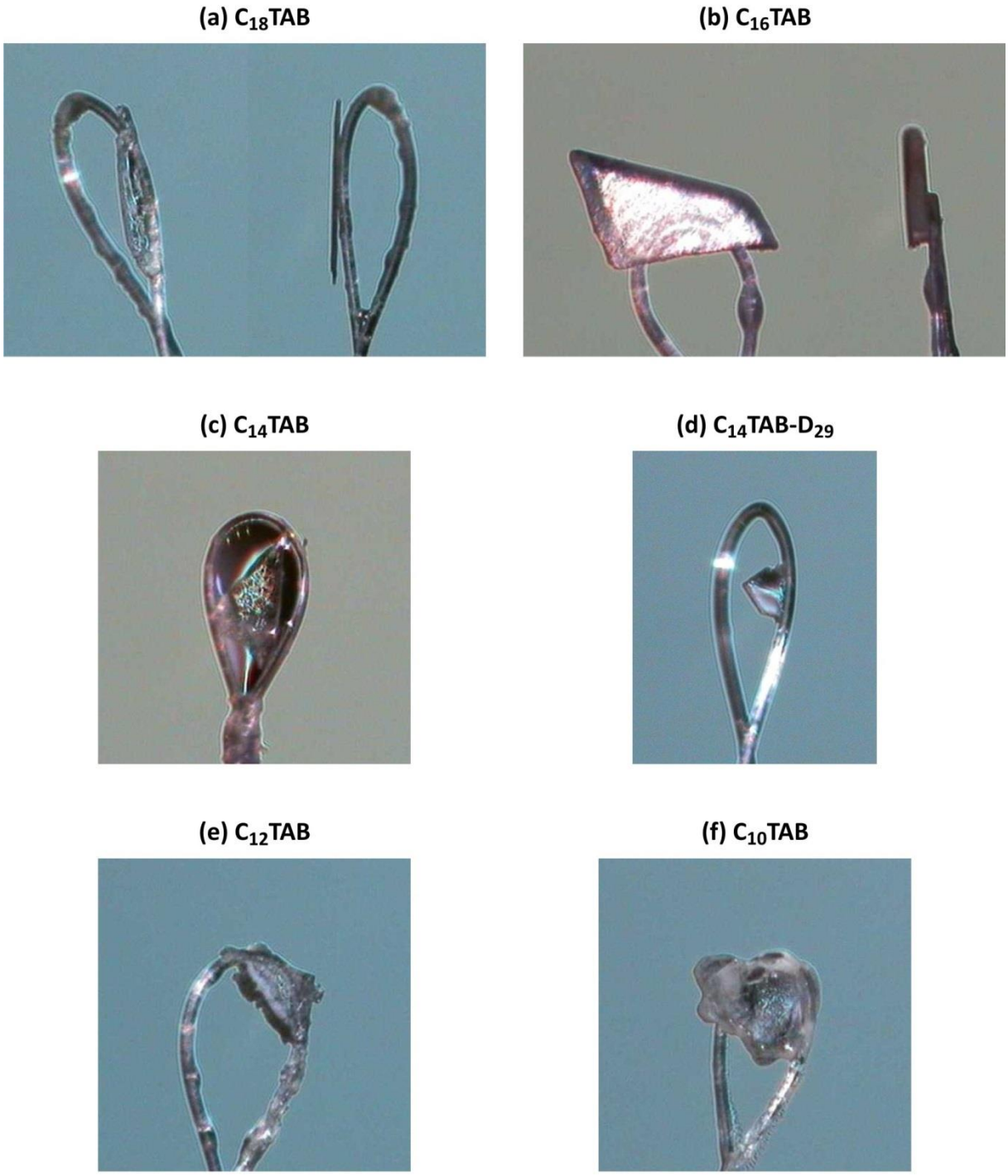


Fig. S61 (a)-(f). Views of various crystals of C_nTAB used in the single-crystal structure determination experiments; crystals varied in size but were always relatively thin and plate-like as emphasised by the twin views shown in (a) and (b). Crystals are shown mounted on 20 µm nylon loops (Ø ≈ 0.3 mm) from Hampton Research using Fomblin® (perfluorinated polyether) oil.[26] With modern instrumentation, crystals with orders of magnitude smaller volume (*e.g.* plate- and needle-shaped crystals) can be measured compared to those used in previous decades for single-crystal X-ray diffraction.

[26] Fomblin YR-1800 (CAS No. 69991-67-9) from Alfa Aesar, Cat. No. L17548.

CIF S1. C18TAB_−123C_Transformed.cif

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 C20   0.0217  0.0198  0.0277  0.0005  0.0151 -0.0027
 C21   0.0252  0.0205  0.0279 -0.0018  0.0172  0.0001
 N1    0.0166  0.0202  0.0165 -0.0011  0.0094 -0.0001
 Br1   0.0259  0.0201  0.0451  0.0008  0.0231  0.0007
```

CIF S2. C16TAB_−123C_Transformed.cif

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data_modified_cif_file_C16TAB_150K
_space_group_crystal_system        'monoclinic'
_space_group_IT_number             14
_space_group_name_H-M_alt          'P 1 21/c 1'

loop_
  _space_group_symop_operation_xyz
 'x, y, z'
 '-x, y+1/2, -z+1/2'
 '-x, -y, -z'
 'x, -y-1/2, z-1/2'

_cell_length_a          5.59550
_cell_length_b          7.14921
_cell_length_c         58.10872
_cell_angle_alpha      90
_cell_angle_beta      117.362
_cell_angle_gamma      90
_cell_volume         2064.48

loop_
  _atom_site_label
  _atom_site_type_symbol
  _atom_site_fract_x
  _atom_site_fract_y
  _atom_site_fract_z
  _atom_site_U_iso_or_equiv
  _atom_site_adp_type
  _atom_site_occupancy
 H1A   H    0.97480   0.38000   0.05670  0.0190 Uiso 1
 H1B   H    0.93080   0.15900   0.05370  0.0190 Uiso 1
 H2A   H    1.43140   0.30100   0.09210  0.0230 Uiso 1
 H2B   H    1.32480   0.08800   0.09020  0.0230 Uiso 1
 H3A   H    1.11060   0.41200   0.10290  0.0280 Uiso 1
 H3B   H    0.96720   0.21600   0.09830  0.0280 Uiso 1
 H4A   H    1.48620   0.26300   0.13980  0.0300 Uiso 1
 H4B   H    1.31200   0.08500   0.13450  0.0300 Uiso 1
 H5A   H    1.19140   0.43000   0.14960  0.0280 Uiso 1
 H5B   H    0.98900   0.27000   0.14200  0.0280 Uiso 1
 H6A   H    1.50540   0.25100   0.18510  0.0300 Uiso 1
 H6B   H    1.29720   0.08800   0.17730  0.0300 Uiso 1
 H7A   H    1.21460   0.44500   0.19490  0.0290 Uiso 1
 H7B   H    0.99280   0.28600   0.18570  0.0290 Uiso 1
 H8A   H    1.50220   0.24500   0.22930  0.0240 Uiso 1
 H8B   H    1.27980   0.08900   0.21970  0.0240 Uiso 1
 H9A   H    1.21320   0.44400   0.23830  0.0230 Uiso 1
 H9B   H    0.99480   0.28600   0.22920  0.0230 Uiso 1
 H10A  H    1.50500   0.24800   0.27350  0.0270 Uiso 1
 H10B  H    1.28280   0.08600   0.26420  0.0270 Uiso 1
 H11A  H    1.21240   0.43900   0.28210  0.0280 Uiso 1
 H11B  H    0.99640   0.28900   0.27360  0.0280 Uiso 1
 H12A  H    1.50720   0.24600   0.31730  0.0290 Uiso 1
 H12B  H    1.28600   0.08800   0.30750  0.0290 Uiso 1
 H13A  H    1.23220   0.44500   0.32730  0.0260 Uiso 1
 H13B  H    0.99520   0.29300   0.31680  0.0260 Uiso 1
 H14A  H    1.50860   0.23800   0.36090  0.0290 Uiso 1
 H14B  H    1.28720   0.09300   0.35180  0.0290 Uiso 1
 H15A  H    1.24240   0.44800   0.37110  0.0330 Uiso 1
 H15B  H    1.01800   0.29700   0.36200  0.0330 Uiso 1
 H16A  H    1.51300   0.24300   0.40600  0.0550 Uiso 1
 H16B  H    1.28300   0.08300   0.39500  0.0550 Uiso 1
 H16C  H    1.25480   0.27800   0.40620  0.0550 Uiso 1
 H17A  H    0.83060   0.36800   0.01290  0.0250 Uiso 1
 H17B  H    0.83040   0.14500   0.01160  0.0250 Uiso 1
 H17C  H    1.00220   0.25700   0.00080  0.0250 Uiso 1
 H18A  H    1.50640   0.41500   0.05910  0.0250 Uiso 1
 H18B  H    1.24620   0.52600   0.04130  0.0250 Uiso 1
 H18C  H    1.40100   0.41000   0.02900  0.0250 Uiso 1
 H19A  H    1.21820  -0.02900   0.04030  0.0250 Uiso 1
```

```
 H19B  H    1.49960   0.08200   0.05840  0.0250 Uiso 1
 H19C  H    1.38460   0.08000   0.02790  0.0250 Uiso 1
 C1    C    1.06488   0.25420   0.05922  0.0181 Uani 1
 C2    C    1.26828   0.21990   0.08732  0.0207 Uani 1
 C3    C    1.13918   0.27910   0.10437  0.0246 Uani 1
 C4    C    1.30064   0.22250   0.13276  0.0232 Uani 1
 C5    C    1.17924   0.29980   0.14946  0.0216 Uani 1
 C6    C    1.31126   0.22600   0.17719  0.0222 Uani 1
 C7    C    1.18980   0.30710   0.19370  0.0212 Uani 1
 C8    C    1.31216   0.22640   0.22109  0.0216 Uani 1
 C9    C    1.19148   0.30900   0.23762  0.0218 Uani 1
 C10   C    1.31182   0.22610   0.26488  0.0215 Uani 1
 C11   C    1.19328   0.30920   0.28157  0.0213 Uani 1
 C12   C    1.31418   0.22620   0.30887  0.0226 Uani 1
 C13   C    1.19824   0.30990   0.32571  0.0221 Uani 1
 C14   C    1.31838   0.22590   0.35292  0.0240 Uani 1
 C15   C    1.20628   0.31110   0.37002  0.0277 Uani 1
 C16   C    1.32816   0.22130   0.39694  0.0386 Uani 1
 C17   C    0.93378   0.25690   0.01337  0.0233 Uani 1
 C18   C    1.34742   0.41750   0.04263  0.0211 Uani 1
 C19   C    1.32970   0.07540   0.04195  0.0223 Uani 1
 N1    N    1.17340   0.25060   0.03970  0.0164 Uani 1
 Br1   Br   0.77942   0.75233   0.03629  0.0265 Uani 1

loop_
  _atom_site_aniso_label
  _atom_site_aniso_U_11
  _atom_site_aniso_U_22
  _atom_site_aniso_U_33
  _atom_site_aniso_U_23
  _atom_site_aniso_U_13
  _atom_site_aniso_U_12
 C1    0.0166  0.0222  0.0164 -0.0002  0.0084  0.0005
 C2    0.0226  0.0215  0.0181  0.0025  0.0095  0.0069
 C3    0.0244  0.0310  0.0190  0.0019  0.0105  0.0067
 C4    0.0247  0.0261  0.0188  0.0009  0.0100  0.0019
 C5    0.0245  0.0216  0.0190  0.0007  0.0103  0.0022
 C6    0.0257  0.0237  0.0181  0.0005  0.0109  0.0025
 C7    0.0234  0.0228  0.0181  0.0008  0.0100  0.0019
 C8    0.0246  0.0222  0.0186 -0.0002  0.0105  0.0017
 C9    0.0238  0.0229  0.0190  0.0006  0.0101  0.0018
 C10   0.0247  0.0222  0.0188  0.0016  0.0108  0.0020
 C11   0.0235  0.0211  0.0202  0.0011  0.0109  0.0015
 C12   0.0268  0.0230  0.0197  0.0006  0.0121  0.0022
 C13   0.0265  0.0217  0.0191  0.0005  0.0113  0.0010
 C14   0.0304  0.0223  0.0204  0.0021  0.0127  0.0021
 C15   0.0338  0.0283  0.0244 -0.0012  0.0163 -0.0017
 C16   0.0569  0.0384  0.0244 -0.0015  0.0221 -0.0091
 C17   0.0202  0.0319  0.0150 -0.0012  0.0057  0.0000
 C18   0.0218  0.0161  0.0268  0.0003  0.0125 -0.0015
 C19   0.0215  0.0201  0.0274 -0.0026  0.0130  0.0016
 N1    0.0161  0.0177  0.0160 -0.0001  0.0079  0.0018
 Br1   0.0246  0.0186  0.0414  0.0006  0.0195  0.0008
```

CIF S3. C14TAB_−123C_Transformed.cif

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data_modified_cif_file_C14TAB_150K
_space_group_crystal_system        'monoclinic'
_space_group_IT_number             14
_space_group_name_H-M_alt          'P 1 21/c 1'

loop_
  _space_group_symop_operation_xyz
 'x, y, z'
 '-x, y+1/2, -z+1/2'
 '-x, -y, -z'
 'x, -y-1/2, z-1/2'

_cell_length_a          5.59763
_cell_length_b          7.15024
_cell_length_c         53.00926
_cell_angle_alpha      90
_cell_angle_beta      117.271
_cell_angle_gamma      90
_cell_volume         1885.84

loop_
  _atom_site_label
  _atom_site_type_symbol
  _atom_site_fract_x
  _atom_site_fract_y
  _atom_site_fract_z
  _atom_site_U_iso_or_equiv
  _atom_site_adp_type
  _atom_site_occupancy
 H1A   H    0.98300   0.37900   0.06250  0.0180 Uiso 1
 H1B   H    0.93340   0.15500   0.05910  0.0180 Uiso 1
 H2A   H    1.42840   0.29800   0.10010  0.0220 Uiso 1
 H2B   H    1.32840   0.08900   0.09860  0.0220 Uiso 1
 H3A   H    1.11440   0.42000   0.11310  0.0230 Uiso 1
 H3B   H    0.97360   0.21600   0.10790  0.0230 Uiso 1
 H4A   H    1.48040   0.24300   0.15260  0.0340 Uiso 1
 H4B   H    1.31680   0.08400   0.14720  0.0340 Uiso 1
 H5A   H    1.18880   0.43400   0.16420  0.0270 Uiso 1
 H5B   H    0.99100   0.26500   0.15550  0.0270 Uiso 1
 H6A   H    1.50700   0.26000   0.20300  0.0280 Uiso 1
 H6B   H    1.29820   0.09200   0.19380  0.0280 Uiso 1
 H7A   H    1.21000   0.44400   0.21350  0.0270 Uiso 1
 H7B   H    0.99900   0.28700   0.20350  0.0270 Uiso 1
 H8A   H    1.50980   0.24800   0.25170  0.0200 Uiso 1
 H8B   H    1.28440   0.09000   0.24160  0.0200 Uiso 1
 H9A   H    1.21780   0.44600   0.26170  0.0230 Uiso 1
 H9B   H    1.00340   0.29200   0.25210  0.0230 Uiso 1
 H10A  H    1.50600   0.24900   0.29950  0.0220 Uiso 1
 H10B  H    1.29340   0.08900   0.28960  0.0220 Uiso 1
 H11A  H    1.22620   0.44900   0.31030  0.0280 Uiso 1
 H11B  H    1.00060   0.29300   0.29990  0.0280 Uiso 1
 H12A  H    1.51680   0.23400   0.34820  0.0310 Uiso 1
 H12B  H    1.29560   0.09200   0.33740  0.0310 Uiso 1
 H13A  H    1.23800   0.44600   0.35950  0.0300 Uiso 1
 H13B  H    1.01920   0.29800   0.34880  0.0300 Uiso 1
 H14A  H    1.52740   0.24800   0.39760  0.0500 Uiso 1
 H14B  H    1.28500   0.09200   0.38550  0.0500 Uiso 1
 H14C  H    1.25360   0.28500   0.39740  0.0500 Uiso 1
 H15A  H    0.82860   0.36400   0.01440  0.0230 Uiso 1
 H15B  H    0.83620   0.14400   0.01280  0.0230 Uiso 1
 H15C  H    1.00380   0.25900   0.00070  0.0230 Uiso 1
 H16A  H    1.50080   0.41500   0.06520  0.0230 Uiso 1
 H16B  H    1.23680   0.52400   0.04520  0.0230 Uiso 1
 H16C  H    1.37960   0.41300   0.03190  0.0230 Uiso 1
 H17A  H    1.22320  -0.04100   0.04480  0.0230 Uiso 1
 H17B  H    1.49420   0.08000   0.06330  0.0230 Uiso 1
 H17C  H    1.38240   0.07200   0.03110  0.0230 Uiso 1
 C1    C    1.06468   0.25350   0.06502  0.0178 Uani 1
 C2    C    1.26724   0.21890   0.09576  0.0182 Uani 1
```

```
 C3    C    1.13906   0.28020   0.11449  0.0223 Uani 1
 C4    C    1.29978   0.22410   0.14567  0.0245 Uani 1
 C5    C    1.17914   0.30020   0.16396  0.0212 Uani 1
 C6    C    1.31214   0.22720   0.19431  0.0222 Uani 1
 C7    C    1.19044   0.30740   0.21251  0.0211 Uani 1
 C8    C    1.31364   0.22640   0.24251  0.0213 Uani 1
 C9    C    1.19360   0.30970   0.26080  0.0217 Uani 1
 C10   C    1.31430   0.22570   0.29060  0.0209 Uani 1
 C11   C    1.19964   0.31040   0.30906  0.0220 Uani 1
 C12   C    1.31718   0.22620   0.33887  0.0233 Uani 1
 C13   C    1.20574   0.31070   0.35761  0.0273 Uani 1
 C14   C    1.32928   0.22320   0.38717  0.0414 Uani 1
 C15   C    0.93414   0.25680   0.01476  0.0224 Uani 1
 C16   C    1.34924   0.41800   0.04686  0.0214 Uani 1
 C17   C    1.32670   0.07550   0.04595  0.0211 Uani 1
 N1    N    1.17290   0.25060   0.04360  0.0159 Uani 1
 Br1   Br   0.77867   0.75232   0.03967  0.0268 Uani 1

loop_
  _atom_site_aniso_label
  _atom_site_aniso_U_11
  _atom_site_aniso_U_22
  _atom_site_aniso_U_33
  _atom_site_aniso_U_23
  _atom_site_aniso_U_13
  _atom_site_aniso_U_12
 C1    0.0178  0.0207  0.0190  0.0006  0.0119 -0.0015
 C2    0.0213  0.0131  0.0220  0.0027  0.0116  0.0071
 C3    0.0244  0.0243  0.0208  0.0000  0.0124  0.0036
 C4    0.0238  0.0323  0.0197 -0.0002  0.0120  0.0029
 C5    0.0220  0.0227  0.0204  0.0005  0.0109  0.0023
 C6    0.0246  0.0245  0.0203  0.0013  0.0127  0.0009
 C7    0.0214  0.0238  0.0201  0.0006  0.0111  0.0006
 C8    0.0258  0.0205  0.0205 -0.0002  0.0131  0.0005
 C9    0.0235  0.0236  0.0203  0.0000  0.0120  0.0011
 C10   0.0250  0.0182  0.0223  0.0022  0.0132  0.0034
 C11   0.0271  0.0211  0.0197  0.0020  0.0124  0.0008
 C12   0.0318  0.0182  0.0236  0.0034  0.0158  0.0064
 C13   0.0336  0.0273  0.0268 -0.0030  0.0189 -0.0030
 C14   0.0594  0.0440  0.0263 -0.0039  0.0244 -0.0150
 C15   0.0201  0.0288  0.0167 -0.0015  0.0071 -0.0001
 C16   0.0223  0.0167  0.0289  0.0000  0.0149 -0.0021
 C17   0.0200  0.0202  0.0277 -0.0034  0.0149  0.0019
 N1    0.0167  0.0156  0.0177 -0.0004  0.0098  0.0035
 Br1   0.0255  0.0180  0.0446  0.0008  0.0226  0.0017
```

CIF S4. C12TAB_−123C_Transformed.cif

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data_modified_cif_file_C12TAB_150K
_space_group_crystal_system        'monoclinic'
_space_group_IT_number             14
_space_group_name_H-M_alt          'P 1 21/c 1'

loop_
  _space_group_symop_operation_xyz
 'x, y, z'
 '-x, y+1/2, -z+1/2'
 '-x, -y, -z'
 'x, -y-1/2, z-1/2'

_cell_length_a          5.59929
_cell_length_b          7.14079
_cell_length_c         47.84034
_cell_angle_alpha      90
_cell_angle_beta      117.209
_cell_angle_gamma      90
_cell_volume         1701.15

loop_
  _atom_site_label
  _atom_site_type_symbol
  _atom_site_fract_x
  _atom_site_fract_y
  _atom_site_fract_z
  _atom_site_U_iso_or_equiv
  _atom_site_adp_type
  _atom_site_occupancy
 H1A   H    0.98080   0.37500   0.06920  0.0190 Uiso 1
 H1B   H    0.93460   0.15900   0.06590  0.0190 Uiso 1
 H2A   H    1.42860   0.29900   0.11190  0.0300 Uiso 1
 H2B   H    1.32020   0.08300   0.10930  0.0300 Uiso 1
 H3A   H    1.10980   0.41300   0.12520  0.0320 Uiso 1
 H3B   H    0.96820   0.22200   0.11930  0.0320 Uiso 1
 H4A   H    1.48360   0.26800   0.16940  0.0270 Uiso 1
 H4B   H    1.30600   0.08500   0.16300  0.0270 Uiso 1
 H5A   H    1.19160   0.43300   0.18190  0.0250 Uiso 1
 H5B   H    0.99420   0.26900   0.17280  0.0250 Uiso 1
 H6A   H    1.50120   0.25400   0.22480  0.0270 Uiso 1
 H6B   H    1.30100   0.09000   0.21450  0.0270 Uiso 1
 H7A   H    1.21580   0.44400   0.23670  0.0250 Uiso 1
 H7B   H    1.00120   0.28400   0.22530  0.0250 Uiso 1
 H8A   H    1.50580   0.25200   0.27870  0.0280 Uiso 1
 H8B   H    1.29300   0.09300   0.26750  0.0280 Uiso 1
 H9A   H    1.23120   0.44700   0.29080  0.0300 Uiso 1
 H9B   H    1.00140   0.29600   0.27860  0.0300 Uiso 1
 H10A  H    1.51720   0.24300   0.33280  0.0280 Uiso 1
 H10B  H    1.28400   0.09200   0.32000  0.0280 Uiso 1
 H11A  H    1.23980   0.44800   0.34470  0.0390 Uiso 1
 H11B  H    1.00700   0.29400   0.33250  0.0390 Uiso 1
 H12A  H    1.52140   0.24300   0.38710  0.0520 Uiso 1
 H12B  H    1.29120   0.08900   0.37380  0.0520 Uiso 1
 H12C  H    1.25380   0.28400   0.38820  0.0520 Uiso 1
 H13A  H    0.83000   0.37200   0.01550  0.0269 Uiso 1
 H13B  H    0.83040   0.14800   0.01460  0.0269 Uiso 1
 H13C  H    1.00020   0.25800   0.00080  0.0269 Uiso 1
 H14A  H    1.50620   0.41300   0.07180  0.0269 Uiso 1
 H14B  H    1.24180   0.52600   0.05020  0.0269 Uiso 1
 H14C  H    1.40300   0.41500   0.03550  0.0269 Uiso 1
 H15A  H    1.21700  -0.03300   0.04900  0.0269 Uiso 1
 H15B  H    1.49360   0.07800   0.07090  0.0269 Uiso 1
 H15C  H    1.37620   0.07800   0.03380  0.0269 Uiso 1
 C1    C    1.06472   0.25440   0.07198  0.0195 Uani 1
 C2    C    1.26740   0.22180   0.10600  0.0237 Uani 1
 C3    C    1.13972   0.27910   0.12688  0.0266 Uani 1
 C4    C    1.30070   0.22300   0.16130  0.0248 Uani 1
 C5    C    1.18004   0.30010   0.18171  0.0241 Uani 1
 C6    C    1.31266   0.22660   0.21529  0.0240 Uani 1
```

```
 C7    C    1.19310   0.30780   0.23550  0.0243 Uani 1
 C8    C    1.31634   0.22740   0.26876  0.0243 Uani 1
 C9    C    1.20018   0.31060   0.28927  0.0249 Uani 1
 C10   C    1.31996   0.22770   0.32219  0.0256 Uani 1
 C11   C    1.20672   0.31070   0.34298  0.0300 Uani 1
 C12   C    1.32756   0.22300   0.37559  0.0402 Uani 1
 C13   C    0.93314   0.25620   0.01631  0.0244 Uani 1
 C14   C    1.34442   0.41760   0.05158  0.0226 Uani 1
 C15   C    1.32970   0.07530   0.05100  0.0232 Uani 1
 N1    N    1.17226   0.25040   0.04819  0.0179 Uani 1
 Br1   Br   0.77804   0.75223   0.04384  0.0272 Uani 1

loop_
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  _atom_site_aniso_U_11
  _atom_site_aniso_U_22
  _atom_site_aniso_U_33
  _atom_site_aniso_U_23
  _atom_site_aniso_U_13
  _atom_site_aniso_U_12
 C1    0.0189  0.0217  0.0214  0.0001  0.0123  0.0015
 C2    0.0236  0.0275  0.0214  0.0029  0.0116  0.0046
 C3    0.0266  0.0327  0.0229  0.0025  0.0135  0.0064
 C4    0.0259  0.0275  0.0220  0.0015  0.0118  0.0025
 C5    0.0269  0.0238  0.0234  0.0001  0.0130  0.0022
 C6    0.0274  0.0257  0.0213  0.0008  0.0133  0.0026
 C7    0.0274  0.0245  0.0228  0.0005  0.0132  0.0010
 C8    0.0283  0.0243  0.0230  0.0013  0.0141  0.0013
 C9    0.0279  0.0251  0.0239  0.0003  0.0138 -0.0001
 C10   0.0312  0.0236  0.0239  0.0019  0.0143  0.0013
 C11   0.0376  0.0292  0.0284 -0.0015  0.0196 -0.0026
 C12   0.0587  0.0382  0.0289 -0.0020  0.0246 -0.0092
 C13   0.0212  0.0321  0.0179 -0.0010  0.0073 -0.0009
 C14   0.0226  0.0196  0.0292  0.0005  0.0150 -0.0034
 C15   0.0243  0.0195  0.0288 -0.0021  0.0148  0.0015
 N1    0.0178  0.0186  0.0191 -0.0004  0.0101  0.0003
 Br1   0.0263  0.0190  0.0429  0.0008  0.0216  0.0006
```

CIF S5. C10TAB_−123C_Transformed.cif

```
data_modified_cif_file_C10TAB_150K
_space_group_crystal_system        'monoclinic'
_space_group_IT_number             14
_space_group_name_H-M_alt          'P 1 21/c 1'

loop_
  _space_group_symop_operation_xyz
 'x, y, z'
 '-x, y+1/2, -z+1/2'
 '-x, -y, -z'
 'x, -y-1/2, z-1/2'

_cell_length_a          5.60055
_cell_length_b          7.13788
_cell_length_c         42.67077
_cell_angle_alpha      90
_cell_angle_beta      117.024
_cell_angle_gamma      90
_cell_volume         1519.56

loop_
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  _atom_site_type_symbol
  _atom_site_fract_x
  _atom_site_fract_y
  _atom_site_fract_z
  _atom_site_U_iso_or_equiv
  _atom_site_adp_type
  _atom_site_occupancy
 H1A   H    0.98340   0.37200   0.07760  0.0220 Uiso 1
 H1B   H    0.92740   0.16000   0.07310  0.0220 Uiso 1
 H2A   H    1.43340   0.29800   0.12510  0.0370 Uiso 1
 H2B   H    1.31900   0.08800   0.12250  0.0370 Uiso 1
 H3A   H    1.11720   0.41700   0.14080  0.0370 Uiso 1
 H3B   H    0.97060   0.22700   0.13390  0.0370 Uiso 1
 H4A   H    1.48600   0.26600   0.19000  0.0280 Uiso 1
 H4B   H    1.31020   0.08600   0.18280  0.0280 Uiso 1
 H5A   H    1.18960   0.43800   0.20390  0.0330 Uiso 1
 H5B   H    0.99960   0.26900   0.19390  0.0330 Uiso 1
 H6A   H    1.50480   0.25400   0.25220  0.0300 Uiso 1
 H6B   H    1.30040   0.09500   0.24110  0.0300 Uiso 1
 H7A   H    1.22660   0.44400   0.26590  0.0360 Uiso 1
 H7B   H    1.00060   0.28800   0.25340  0.0360 Uiso 1
 H8A   H    1.51840   0.24900   0.31310  0.0310 Uiso 1
 H8B   H    1.29460   0.09300   0.29990  0.0310 Uiso 1
 H9A   H    1.23160   0.44300   0.32690  0.0410 Uiso 1
 H9B   H    1.02540   0.29700   0.31410  0.0410 Uiso 1
 H10A  H    1.52280   0.24100   0.37370  0.0530 Uiso 1
 H10B  H    1.28280   0.09300   0.35920  0.0530 Uiso 1
 H10C  H    1.26500   0.28300   0.37650  0.0530 Uiso 1
 H11A  H    0.83480   0.36800   0.01720  0.0280 Uiso 1
 H11B  H    0.82780   0.14700   0.01620  0.0280 Uiso 1
 H11C  H    0.99960   0.25900   0.00090  0.0280 Uiso 1
 H12A  H    1.49860   0.41300   0.07990  0.0270 Uiso 1
 H12B  H    1.24360   0.52700   0.05590  0.0270 Uiso 1
 H12C  H    1.39700   0.41400   0.03900  0.0270 Uiso 1
 H13A  H    1.22440  -0.02800   0.05560  0.0270 Uiso 1
 H13B  H    1.49100   0.07600   0.07900  0.0270 Uiso 1
 H13C  H    1.38120   0.07800   0.03830  0.0270 Uiso 1
 C1    C    1.06428   0.25425   0.08072  0.0194 Uani 1
 C2    C    1.26756   0.22180   0.11884  0.0242 Uani 1
 C3    C    1.14040   0.27970   0.14230  0.0275 Uani 1
 C4    C    1.30146   0.22310   0.18079  0.0254 Uani 1
 C5    C    1.18224   0.30130   0.20381  0.0254 Uani 1
 C6    C    1.31636   0.22690   0.24144  0.0250 Uani 1
 C7    C    1.19876   0.30940   0.26444  0.0252 Uani 1
 C8    C    1.32298   0.22790   0.30162  0.0263 Uani 1
 C9    C    1.20892   0.31090   0.32483  0.0302 Uani 1
 C10   C    1.33020   0.22350   0.36145  0.0413 Uani 1
```

```
 C11   C    0.93234   0.25553   0.01836  0.0250 Uani 1
 C12   C    1.34352   0.41778   0.05768  0.0232 Uani 1
 C13   C    1.32838   0.07537   0.05697  0.0238 Uani 1
 N1    N    1.17134   0.25028   0.05401  0.0181 Uani 1
 Br1   Br   0.77663   0.75220   0.04889  0.0268 Uani 1

loop_
  _atom_site_aniso_label
  _atom_site_aniso_U_11
  _atom_site_aniso_U_22
  _atom_site_aniso_U_33
  _atom_site_aniso_U_23
  _atom_site_aniso_U_13
  _atom_site_aniso_U_12
 C1    0.0179  0.0225  0.0204  0.0003  0.0111  0.0014
 C2    0.0232  0.0287  0.0220  0.0026  0.0113  0.0047
 C3    0.0274  0.0348  0.0218  0.0024  0.0127  0.0068
 C4    0.0267  0.0289  0.0216  0.0022  0.0118  0.0034
 C5    0.0281  0.0268  0.0227  0.0009  0.0126  0.0023
 C6    0.0278  0.0273  0.0221  0.0015  0.0133  0.0024
 C7    0.0288  0.0252  0.0228  0.0003  0.0127  0.0004
 C8    0.0327  0.0244  0.0236  0.0018  0.0144  0.0016
 C9    0.0374  0.0294  0.0277 -0.0010  0.0181 -0.0015
 C10   0.0600  0.0407  0.0266 -0.0014  0.0226 -0.0096
 C11   0.0221  0.0326  0.0175 -0.0005  0.0065 -0.0006
 C12   0.0234  0.0196  0.0296  0.0002  0.0146 -0.0034
 C13   0.0239  0.0191  0.0315 -0.0021  0.0153  0.0014
 N1    0.0177  0.0188  0.0192 -0.0011  0.0095 -0.0001
 Br1   0.0259  0.0191  0.0416  0.0006  0.0207  0.0004
```