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Uniaxial negative thermal expansion induced by moiety twisting in an organic crystal

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1. Synthesis of compound 1

Compound **1** was synthesized following the procedure reported previously.¹ 1-Ethynylcyclopentanol (8.7 mmol, 1 ml, Aldrich), CuCl (1 mmol, 101 mg, Aldrich) and 20 ml dry pyridine were taken in Schlenk tube. The tube was flushed with oxygen gas and then shaken for 24 hours on a mechanical stirrer. After completion of reaction the solvent was removed under reduced pressure. The dark green oily material was dissolved in diethyl ether and extracted with water. The organic layer was separated and dried on anhydrous MgSo₄. The clear solution was filtered and solvent was removed under reduced pressure. Resulted yellow semi-solid compound was crystallized from hexane-chloroform mixture. The single crystals for variable temperature X-ray diffraction were grown by sublimation of colourless solid at 90-100 °C under vacuum.

¹H NMR (400 MHz, DMSO-d₆): δ 5.38 (singlet, 2H); δ 1.62 – 1.78 (multiplet, 16 H) ¹³C NMR (CDCl₃): δ 82.17; δ 73. 66; δ 66.27; δ 41.27; δ 22.36.

2. Single crystal X-ray diffraction:

Single crystal X-ray data were collected on Bruker SMART Apex diffractometer equipped with a CCD area detector. A crystal was glued to a thin glass fiber and enveloped in a temperature-controlled stream of dry nitrogen gas during intensity data collection. The temperature of the crystal was controlled using an Oxford Cryosystream Plus cryostat. The single-crystal data were initially recorded at 100 K and then successive datasets were collected at intervals of 20K as the temperature was slowly increased to 340K.

2.1 Crystal data of 1 at 100 K

C₁₄H₁₈O₂, *M* = 218.28, colorless block, $0.38 \times 0.19 \times 0.10 \text{ mm}^3$, monoclinic, space group *P*2₁/*n* (No. 14), *a* = 7.1352(6), *b* = 11.9641(10), *c* = 14.4049(12) Å, *β* = 97.3660(10)°, *V* = 1219.54(18) Å³, *Z* = 4, *D*_c = 1.189 g/cm³, *F*₀₀₀ = 472, Bruker APEX-II CCD, MoK_α radiation, λ = 0.71073 Å, *T* = 100(2)K, $2\theta_{max}$ = 55.1°, 6909 reflections collected, 2641 unique (R_{int} = 0.0197). The structure was solved and refined using the programs SHELXS-97 (Sheldrick, 1990) and SHELXL-97 (Sheldrick, 1997) respectively. The program X-Seed (Barbour, 1999) was used

as an interface to the SHELX programs, and X-Seed (Barbour, 2017) was used to prepare the figures. Final *GooF* = 1.065, *R1* = 0.0667, *wR2* = 0.1593, *R* indices based on 2211 reflections with I >2sigma(I) (refinement on F^2), 145 parameters, 0 restraints. Lp and absorption corrections applied, μ = 0.078 mm⁻¹.

2.2 Crystal data of 1 at 120 K

C₁₄H₁₈O₂, M = 218.28, colorless block, $0.38 \times 0.19 \times 0.10 \text{ mm}^3$, monoclinic, space group $P2_{1/n}$ (No. 14), a = 7.1268(7), b = 11.9819(11), c = 14.4375(13) Å, $\beta = 97.4320(10)^\circ$, V = 1222.5(2) Å³, Z = 4, $D_c = 1.186$ g/cm³, $F_{000} = 472$, Bruker APEX-II CCD, MoK_a radiation, $\lambda = 0.71073$ Å, T = 120(2)K, $2\theta_{max} = 55.0^\circ$, 6953 reflections collected, 2646 unique (R_{int} = 0.0221). The structure was solved and refined using the programs SHELXS-97 (Sheldrick, 1990) and SHELXL-97 (Sheldrick, 1997) respectively. The program X-Seed (Barbour, 1999) was used as an interface to the SHELX programs, and X-Seed (Barbour, 2017) was used to prepare the figures. Final *GooF* = 1.056, R1 = 0.0616, wR2 = 0.1454, R indices based on 2126 reflections with I >2sigma(I) (refinement on F^2), 145 parameters, 0 restraints. Lp and absorption corrections applied, $\mu = 0.078$ mm⁻¹.

2.3 Crystal data of 1 at 140 K

C₁₄H₁₈O₂, M = 218.28, colorless block, $0.38 \times 0.19 \times 0.10$ mm³, monoclinic, space group $P2_1/n$ (No. 14), a = 7.1163(6), b = 11.9960(11), c = 14.4685(13) Å, $\beta = 97.4920(10)^\circ$, V = 1224.59(19) Å³, Z = 4, $D_c = 1.184$ g/cm³, $F_{000} = 472$, Bruker APEX-II CCD, MoK_a radiation, $\lambda = 0.71073$ Å, T = 140(2)K, $2\theta_{max} = 54.9^\circ$, 6954 reflections collected, 2650 unique (R_{int} = 0.0226). The structure was solved and refined using the programs SHELXS-97 (Sheldrick, 1990) and SHELXL-97 (Sheldrick, 1997) respectively. The program X-Seed (Barbour, 1999) was used as an interface to the SHELX programs, and X-Seed (Barbour, 2017) was used to prepare the figures. Final *GooF* = 1.081, RI = 0.0581, wR2 = 0.1449, R indices based on 2103 reflections with I >2sigma(I) (refinement on F^2), 145 parameters, 0 restraints. Lp and absorption corrections applied, $\mu = 0.077$ mm⁻¹.

2.4 Crystal data of 1 at 160 K

C₁₄H₁₈O₂, M = 218.28, colorless block, $0.38 \times 0.19 \times 0.10$ mm³, monoclinic, space group $P2_1/n$ (No. 14), a = 7.1120(6), b = 12.0123(11), c = 14.5000(13) Å, $\beta = 97.5580(10)^{\circ}$, V = 1227.99(19) Å³, Z = 4, $D_c = 1.181$ g/cm³, $F_{000} = 472$, Bruker APEX-II CCD, MoK_a radiation, $\lambda = 0.71073$ Å, T = 160(2)K, $2\theta_{max} = 54.9^{\circ}$, 6977 reflections collected, 2652 unique (R_{int} = 0.0215). The structure was solved and refined using the programs SHELXS-97 (Sheldrick, 1990) and SHELXL-97 (Sheldrick, 1997) respectively. The program X-Seed (Barbour, 1999) was used as an interface to the SHELX programs, and X-Seed (Barbour, 2017) was used to prepare the figures. Final *GooF* = 1.064, *R1* = 0.0572, *wR2* = 0.1458, *R* indices based on 2063 reflections with I >2sigma(I) (refinement on F^2), 145 parameters, 0 restraints. Lp and absorption corrections applied, $\mu = 0.077$ mm⁻¹.

2.5 Crystal data of 1 at 180 K

C₁₄H₁₈O₂, M = 218.28, colorless block, $0.38 \times 0.19 \times 0.10 \text{ mm}^3$, monoclinic, space group $P2_1/n$ (No. 14), a = 7.0911(7), b = 12.0408(11), c = 14.5761(13) Å, $\beta = 97.5520(10)^\circ$, V = 1233.7(2) Å³, Z = 4, $D_c = 1.175$ g/cm³, $F_{000} = 472$, Bruker APEX-II CCD, MoK_a radiation, $\lambda = 0.71073$ Å, T = 180(2)K, $2\theta_{max} = 55.1^\circ$, 7017 reflections collected, 2670 unique (R_{int} = 0.0222). The structure was solved and refined using the programs SHELXS-97 (Sheldrick, 1990) and SHELXL-97 (Sheldrick, 1997) respectively. The program X-Seed (Barbour, 1999) was used as an interface to the SHELX programs, and X-Seed (Barbour, 2017) was used to prepare the figures.Final *GooF* = 1.075, R1 = 0.0566, wR2 = 0.1467, R indices based on 2028 reflections with I >2sigma(I) (refinement on F^2), 145 parameters, 0 restraints. Lp and absorption corrections applied, $\mu = 0.077$ mm⁻¹.

2.6 Crystal data of 1 at 200 K

C₁₄H₁₈O₂, M = 218.28, colorless block, $0.38 \times 0.19 \times 0.10 \text{ mm}^3$, monoclinic, space group $P2_1/n$ (No. 14), a = 7.0671(7), b = 12.0636(11), c = 14.6451(13) Å, $\beta = 97.5340(10)^\circ$, V = 1237.8(2) Å³, Z = 4, $D_c = 1.171 \text{ g/cm}^3$, $F_{000} = 472$, Bruker APEX-II CCD, MoK_{α} radiation, $\lambda = 0.71073$ Å, T = 200(2)K, $2\theta_{\text{max}} = 55.1^\circ$, 7058 reflections collected, 2692 unique (R_{int} = 0.0215). The structure was solved and refined using the programs SHELXS-97 (Sheldrick, 1990) and SHELXL-97 (Sheldrick, 1997) respectively. The program X-Seed (Barbour, 1999) was used as an interface to the SHELX programs, and X-Seed (Barbour, 2017) was used to prepare the figures.Final *GooF* = 1.062, R1 = 0.0560, wR2 = 0.1467, R indices based on 1995 reflections

with I >2sigma(I) (refinement on F^2), 145 parameters, 0 restraints. Lp and absorption corrections applied, $\mu = 0.077 \text{ mm}^{-1}$.

2.7 Crystal data of 1 at 220 K

C₁₄H₁₈O₂, M = 218.28, colorless block, $0.38 \times 0.19 \times 0.10 \text{ mm}^3$, monoclinic, space group $P2_1/n$ (No. 14), a = 7.0442(7), b = 12.0864(11), c = 14.7091(14) Å, $\beta = 97.5090(10)^\circ$, V = 1241.6(2) Å³, Z = 4, $D_c = 1.168$ g/cm³, $F_{000} = 472$, Bruker APEX-II CCD, MoK_a radiation, $\lambda = 0.71073$ Å, T = 220(2)K, $2\theta_{\text{max}} = 54.9^\circ$, 7063 reflections collected, 2695 unique (R_{int} = 0.0227). The structure was solved and refined using the programs SHELXS-97 (Sheldrick, 1990) and SHELXL-97 (Sheldrick, 1997) respectively. The program X-Seed (Barbour, 1999) was used as an interface to the SHELX programs, and X-Seed (Barbour, 2017) was used to prepare the figures.Final *GooF* = 1.063, R1 = 0.0569, wR2 = 0.1474, R indices based on 1937 reflections with I >2sigma(I) (refinement on F^2), 145 parameters, 0 restraints. Lp and absorption corrections applied, $\mu = 0.076$ mm⁻¹.

2.8 Crystal data of 1 at 240 K

C₁₄H₁₈O₂, M = 218.28, colorless block, $0.38 \times 0.19 \times 0.10 \text{ mm}^3$, monoclinic, space group $P2_1/n$ (No. 14), a = 7.0251(8), b = 12.1145(13), c = 14.7700(16) Å, $\beta = 97.488(2)^\circ$, V = 1246.3(2) Å³, Z = 4, $D_c = 1.163$ g/cm³, $F_{000} = 472$, Bruker APEX-II CCD, MoK_a radiation, $\lambda = 0.71073$ Å, T = 240(2)K, $2\theta_{\text{max}} = 55.0^\circ$, 7102 reflections collected, 2707 unique (R_{int} = 0.0226). The structure was solved and refined using the programs SHELXS-97 (Sheldrick, 1990) and SHELXL-97 (Sheldrick, 1997) respectively. The program X-Seed (Barbour, 1999) was used as an interface to the SHELX programs, and X-Seed (Barbour, 2017) was used to prepare the figures.Final *GooF* = 1.062, R1 = 0.0562, wR2 = 0.1499, R indices based on 1853 reflections with I >2sigma(I) (refinement on F^2), 145 parameters, 0 restraints. Lp and absorption corrections applied, $\mu = 0.076$ mm⁻¹.

2.9 Crystal data of 1 at 260 K

C₁₄H₁₈O₂, M = 218.28, colorless block, $0.38 \times 0.19 \times 0.10 \text{ mm}^3$, monoclinic, space group $P2_1/n$ (No. 14), a = 7.0076(8), b = 12.1420(15), c = 14.8216(18) Å, $\beta = 97.481(2)^\circ$, V = 1250.4(3) Å³, Z = 4, $D_c = 1.160 \text{ g/cm}^3$, $F_{000} = 472$, Bruker APEX-II CCD, MoK_a radiation, $\lambda = 0.71073$ Å, T = 260(2)K, $2\theta_{\text{max}} = 54.9^\circ$, 7111 reflections collected, 2709 unique (R_{int} = 0.0229). The structure was solved and refined using the programs SHELXS-97 (Sheldrick, 1990) and SHELXL-97 (Sheldrick, 1997) respectively. The program X-Seed (Barbour, 1999) was used as an interface to the SHELX programs, and X-Seed (Barbour, 2017) was used to prepare the figures.Final *GooF* = 1.056, R1 = 0.0562, wR2 = 0.1541, R indices based on 1781 reflections with I >2sigma(I) (refinement on F^2), 145 parameters, 0 restraints. Lp and absorption corrections applied, $\mu = 0.076$ mm⁻¹.

2.10 Crystal data of 1 at 280 K

C₁₄H₁₈O₂, M = 218.28, colorless block, $0.38 \times 0.19 \times 0.10$ mm³, monoclinic, space group $P2_1/n$ (No. 14), a = 6.9930(8), b = 12.1747(14), c = 14.8694(18) Å, $\beta = 97.493(2)^{\circ}$, V = 1255.1(3) Å³, Z = 4, $D_c = 1.155$ g/cm³, $F_{000} = 472$, Bruker APEX-II CCD, MoK_a radiation, $\lambda = 0.71073$ Å, T = 280(2)K, $2\theta_{max} = 54.9^{\circ}$, 7154 reflections collected, 2719 unique (R_{int} = 0.0234). The structure was solved and refined using the programs SHELXS-97 (Sheldrick, 1990) and SHELXL-97 (Sheldrick, 1997) respectively. The program X-Seed (Barbour, 1999) was used as an interface to the SHELX programs, and X-Seed (Barbour, 2017) was used to prepare the figures.Final *GooF* = 1.058, R1 = 0.0579, wR2 = 0.1624, R indices based on 1706 reflections with I >2sigma(I) (refinement on F^2), 145 parameters, 0 restraints. Lp and absorption corrections applied, $\mu = 0.076$ mm⁻¹.

2.11 Crystal data of 1 at 300 K

C₁₄H₁₈O₂, M = 218.28, colorless block, $0.38 \times 0.19 \times 0.10 \text{ mm}^3$, monoclinic, space group $P2_1/n$ (No. 14), a = 6.9814(12), b = 12.218(2), c = 14.914(3) Å, $\beta = 97.532(3)^\circ$, V = 1261.2(4) Å³, Z = 4, $D_c = 1.150 \text{ g/cm}^3$, $F_{000} = 472$, Bruker APEX-II CCD, MoK_{α} radiation, $\lambda = 0.71073$ Å, T = 300(2)K, $2\theta_{\text{max}} = 54.9^\circ$, 7189 reflections collected, 2733 unique (R_{int} = 0.0244). The structure was solved and refined using the programs SHELXS-97 (Sheldrick, 1990) and SHELXL-97 (Sheldrick, 1997) respectively. The program X-Seed (Barbour, 1999) was used as an interface to the SHELX programs, and X-Seed (Barbour, 2017) was used to prepare the

figures.Final *GooF* = 1.064, *R1* = 0.0598, *wR2* = 0.1769, *R* indices based on 1625 reflections with I >2sigma(I) (refinement on F^2), 145 parameters, 0 restraints. Lp and absorption corrections applied, μ = 0.075 mm⁻¹.

2.12 Crystal data of 1 at 320 K

C₁₄H₁₈O₂, M = 218.28, colorless block, $0.38 \times 0.19 \times 0.10$ mm³, monoclinic, space group $P2_1/n$ (No. 14), a = 6.9670(14), b = 12.261(2), c = 14.960(3) Å, $\beta = 97.580(3)^\circ$, V = 1266.8(4) Å³, Z = 4, $D_c = 1.145$ g/cm³, $F_{000} = 472$, Bruker APEX-II CCD, MoK_a radiation, $\lambda = 0.71073$ Å, T = 320(2)K, $2\theta_{max} = 54.9^\circ$, 7217 reflections collected, 2746 unique (R_{int} = 0.0284). The structure was solved and refined using the programs SHELXS-97 (Sheldrick, 1990) and SHELXL-97 (Sheldrick, 1997) respectively. The program X-Seed (Barbour, 1999) was used as an interface to the SHELX programs, and X-Seed (Barbour, 2017) was used to prepare the figures.Final *GooF* = 1.078, R1 = 0.0618, wR2 = 0.1913, R indices based on 1504 reflections with I >2sigma(I) (refinement on F^2), 145 parameters, 0 restraints. Lp and absorption corrections applied, $\mu = 0.075$ mm⁻¹.

2.13 Crystal data of 1 at 340 K

C₁₄H₁₈O₂, M = 218.28, colorless block, $0.38 \times 0.19 \times 0.10 \text{ mm}^3$, monoclinic, space group $P2_1/n$ (No. 14), a = 6.9574(10), b = 12.3167(17), c = 14.993(2) Å, $\beta = 97.665(2)^\circ$, V = 1273.3(3) Å³, Z = 4, $D_c = 1.139 \text{ g/cm}^3$, $F_{000} = 472$, Bruker APEX-II CCD, MoK_a radiation, $\lambda = 0.71073$ Å, T = 340(2)K, $2\theta_{\text{max}} = 54.9^\circ$, 7272 reflections collected, 2768 unique (R_{int} = 0.0279). The structure was solved and refined using the programs SHELXS-97 (Sheldrick, 1990) and SHELXL-97 (Sheldrick, 1997) respectively. The program X-Seed (Barbour, 1999) was used as an interface to the SHELX programs, and X-Seed (Barbour, 2017) was used to prepare the figures.Final *GooF* = 1.055, R1 = 0.0646, wR2 = 0.1972, R indices based on 1444 reflections with I >2sigma(I) (refinement on F^2), 145 parameters, 0 restraints. Lp and absorption corrections applied, $\mu = 0.075 \text{ mm}^{-1}$.

3. DSC thermogram



Figure S1. DSC thermogram of as-synthesized material of 1 showing no phase transformation before melting. The sample was heated from 30 °C to 150 °C at the rate of 2 °C min⁻¹ and then cooled at the rate of 2 °C min⁻¹ to 30 °C, then heated till melting.

4. Photomicrographs of a crystal at different temperatures:



100K

140K

160K

180K



300K320K340K360KFigure S2. Photomicrographs of the single crystal used in variable temperature X-raydiffraction study

5. Thermal ellipsoid plot:





Figure S3. Thermal ellipsoid plots of **1** at different temperatures. Atoms are shown with 50% probability thermal ellipsoids.



6. Fingerprint plot at different temperatures



Figure S4. Fingerprint plots generated from Hirshfeld surfaces of **1** at different temperatures.^{2b} Long spikes indicate $O-H\cdots O$ hydrogen bonding and other portion of the plot indicate van der Waals interaction. Finger print plots at different temperature show no significant changes in intermolecular interactions in the crystal structure with the change of temperature.

7. Table S1. Quantification of intermolecular interactions (Calculated by Crysta	al
Explorer, Version 3.1)	

Temperature (K)	O-H (%)	C-H (%)	H-H (%)
100	10.9	24.4	64.7
120	10.8	24.4	64.8
140	10.8	24.4	64.8
160	10.8	24.4	64.8
180	10.8	24.3	64.9
200	10.8	24.2	65.0
220	10.8	24.1	65.1
240	10.8	24.1	65.1

260	10.8	24.0	65.2
280	10.8	23.9	65.3
300	10.8	23.8	65.4
320	10.8	23.7	65.5
340	10.8	23.6	65.6

8. Table S2 C–C–C angles in the C–C=C–C=C–C spine at different temperatures:

Temperature (K)	C1-C6-C7	C6-C7-C8	C7-C8-C9	C8-C9-C10
100	175.50	177.88	176.87	178.04
120	175.80	177.75	176.93	178.27
140	175.98	177.83	176.91	178.44
160	176.00	178.08	176.98	178.32
180	176.06	178.16	176.84	178.37
200	175.95	178.27	176.80	178.45
220	175.94	178.45	176.73	178.62
240	176.06	178.30	176.96	178.27
260	176.19	178.18	177.01	178.59
280	176.27	178.19	177.08	178.53
300	176.43	178.03	177.15	178.40
320	176.37	178.25	177.12	178.32
340	176.40	178.30	176.78	178.66

9. Table S3 Change of different torsion angles in the molecule of compound 1

Temperature	C2-C3-	C6-C1-C2-	C6-C1-	C9-C10-	C9-C10-	C11-C12-
(K)	C4-C5 (°)	C3 (°)	C5-C4 (°)	C14-C13 (°)	C11-C12 (°)	C13-C14
						(°)
100	16.5	162.8	-153.9	-149.6	157.8	14.0
120	16.8	162.4	-153.4	-150.1	158.2	13.7
140	17.0	161.8	-152.8	-150.7	158.5	13.7
160	17.4	161.5	-152.2	-151.9	158.9	12.2
180	18.2	160.8	-151.2	-151.9	158.4	11.5
200	18.9	160.4	-150.1	-151.9	158.1	10.6
220	19.2	159.7	-149.5	-152.0	157.8	9.6
240	19.6	159.1	-148.6	-152.3	157.5	8.9
260	19.7	158.4	-147.8	-152.4	157.2	8.0
280	19.8	157.9	-147.3	-152.3	156.6	7.2
300	19.6	157.0	-146.5	-152.7	156.4	6.4
320	19.3	156.1	-145.7	-152.6	155.9	5.8
340	19.5	155.0	-144.5	-152.5	155.4	5.0

10. Table S4. Hydrogen bonding Geometry

	Temperature (K)	O–H···O (1) Å	O…O (1) Å	O−H···O (2) Å	O…O (2) Å
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100	1.82	2.686(2)	1.80	2.762(2)
120	1.83	2.692(2)	1.80	2.762(2)
140	1.84	2.699(2)	1.80	2.763(2)
160	1.86	2.706(2)	1.81	2.763(2)
180	1.85	2.710(2)	1.81	2.770(2)
200	1.85	2.717(2)	1.81	2.775(2)
220	1.85	2.722(2)	1.81	2.778(2)
240	1.85	2.727(2)	1.82	2.783(2)
260	1.85	2.731(2)	1.82	2.788(2)
280	1.86	2.738(2)	1.83	2.793(2)
300	1.86	2.744(2)	1.83	2.797(2)
320	1.87	2.752(2)	1.84	2.804(3)
340	1.88	2.759(3)	1.85	2.808(3)

11. Table S5. Unit cell parameters of 1 and calculation of tilt angle (θ) at dif	ferent
temperatures:	

Temp (K)	<i>a</i> axis (Å)	<i>b</i> axis (Å)	c axis (Å)	β / °	Volume (Å ³)	Tilt angle
						(θ)
100	7.1352(6)	11.9641(10)	14.4049(12)	97.37(1)	1219.5(2)	46.50
120	7.1268(7)	11.9819(11)	14.4375(13)	97.43(1)	1222.5(2)	46.56
140	7.1163(6)	11.9960(11)	14.4685(13)	97.49(1)	1224.6(2)	46.66
160	7.1120(6)	12.0123(11)	14.5000(13)	97.56(1)	1228.0(2)	46.65
180	7.0911(7)	12.0408(11)	14.5761(13)	97.55(1)	1233.7(2)	46.91
200	7.0671(7)	12.0636(11)	14.6451(13)	97.53(1)	1237.8(2)	47.16
220	7.0442(7)	12.0864(11)	14.7091(14)	97.51(1)	1241.6(2)	47.40
240	7.0251(8)	12.1145(13)	14.7700(16)	97.49(1)	1246.3(2)	47.61
260	7.0076(8)	12.1420(15)	14.8216(18)	97.48(1)	1250.4(3)	47.81
280	6.9930(8)	12.1747(14)	14.8694(18)	97.49(1)	1255.1(3)	48.01
300	6.9814(12)	12.218(2)	14.914(3)	97.53(1)	1261.2(4)	48.17
320	6.9670(14)	12.261(2)	14.960(3)	97.58(1)	1266.8(4)	48.37
340	6.9574(10)	12.3167(17)	14.993(2)	97.67(1)	1273.3(3)	48.62



Figure S5. Calculation of tilt angle θ with respect to *a* axis

12. Stacking of molecules at different temperatures







320K

Figure S6. Stacking of molecules of 1 along [100] direction

13. Calculation of Thermal Expansion co-efficient by PAScal programme³:

Output

				Direction	
Axes	α(MK ⁻¹)	σα (MK ⁻¹)	a	b	с
\mathbf{X}_1	-116.0346	3.3053	-0.9988	0.0000	-0.0492
\mathbf{X}_2	118.0179	7.5862	-0.0000	1.0000	-0.0000
X 3	184.2117	4.8437	0.0586	-0.0000	0.9983
V	185.2159	6.9190			

Expansivity Indicatrix



Plots





% change in length

Т \mathbf{X}_1 \mathbf{X}_2 **X**3 X1,calc X2,calc X3,calc 100.0000 0.0000 0.0000 0.0000 0.1319 -0.2340 -0.1731 120.0000 -0.1361 0.1488 0.2297 -0.1002 0.0020 0.1954 140.0000 -0.2990 0.2666 0.4470 -0.3322 0.2380 0.5638 160.0000 -0.3792 0.4029 0.6705 -0.5643 0.4741 0.9322 180.0000 -0.6614 0.6411 1.1896 -0.7964 0.7101 1.3006 200.0000 -0.9926 0.8317 1.6677 -1.0284 0.9462 1.6690 220.0000 -1.3102 1.0222 2.1145 -1.2605 1.1822 2.0375 240.0000 -1.5765 1.2571 2.5407 -1.4926 1.4182 2.4059 260.0000 -1.8228 1.4869 2.9016 -1.7246 1.6543 2.7743 280.0000 - 2.0312 1.7603 3.2345 - 1.9567 1.8903 3.1427 300.0000 -2.2015 2.1222 3.5431 -2.1888 2.1263 3.5112 320.0000 -2.4128 2.4816 3.8612 -2.4209 2.3624 3.8796 340.0000 -2.5634 2.9472 4.0870 -2.6529 2.5984 4.2480

Volume

TV (Å3)Vlin (Å3)100.00001219.54411216.0307120.00001222.49861220.5483140.00001224.59011225.0659160.00001227.99441229.5834180.00001233.74891234.1010200.00001237.78461238.6186220.00001241.57891243.1362

```
240.0000 1246.2898 1247.6538
260.0000 1250.3803 1252.1713
280.0000 1255.1360 1256.6889
300.0000 1261.1692 1261.2065
320.0000 1266.7520 1265.7241
340.0000 1273.3036 1270.2417
```

Input

Т	σT	a	В	С	α	β	γ
100	2	7.1352	11.9641	14.4049	90.0000	97.3660	90.0000
120	2	7.1268	11.9819	14.4375	90.0000	97.4320	90.0000
140	2	7.1163	11.9960	14.4685	90.0000	97.4920	90.0000
160	2	7.1120	12.0123	14.5000	90.0000	97.5580	90.0000
180	2	7.0911	12.0408	14.5761	90.0000	97.5520	90.0000
200	2	7.0671	12.0636	14.6451	90.0000	97.5340	90.0000
220	2	7.0442	12.0864	14.7091	90.0000	97.5090	90.0000
240	2	7.0251	12.1145	14.7700	90.0000	97.488	90.0000
260	2	7.0076	12.1420	14.8216	90.0000	97.481	90.0000
280	2	6.9930	12.1747	14.8694	90.0000	97.493	90.0000
300	2	6.9814	12.218	14.914	90.0000	97.532	90.0000
320	2	6.9670	12.261	14.960	90.0000	97.580	90.0000
340	2	6.9574	12.3167	14.993	90.0000	97.665	90.0000

14. Description of animation

Video S1 prepared from the images shown in Figure S6. Cyclopentyl groups at each terminal of C-C=C-C=C-C spine rotates as the temperature increases to adjust steric hindrance.

15. References

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- 3. M. J. Cliffe, A. L. Goodwin, J. Appl. Cryst., 2012, 45, 1321.