Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Towards reliable ab initio sublimation pressures for organic molecular crystals – Are we there yet?

Supporting Information

Ctirad Červinka [†,*], *Gregory Beran* [‡]

[†] Department of Physical Chemistry, University of Chemistry and Technology Prague, Technická 5, CZ-166 28 Prague 6, Czech Republic

[‡] Department of Chemistry, University of California, Riverside, California 92521, United States

*Corresponding author: cervinkc@vscht.cz

TABLE S1

Experimental and optimized crystal structures used as input for all first-principles calculations in this work. Unit-cell parameters given in Å and degrees.

Molecule	*T* (K)	Data set	*a*	*b*	*c*	*β*
Ethane	85[a]	Exp.	4.226	5.623	5.845	90.41
	0	DFT@DFT[b]	3.99	6.89	5.19	70.1
	85	HMBI(C,A)@DFT[c]	4.15	7.18	5.39	69.8
	85	HMBI(C,H)@DFT[d]	4.21	7.30	5.45	69.5
	0	HMBI(M,A)@HMBI[e]	4.05	5.47	5.76	91.1
	85	HMBI(C,A)@HMBI[f]	4.11	5.53	5.96	91.2
	85	HMBI(C,H)@HMBI[g]	4.14	5.56	6.12	91.3
Methanol	122[a]	Exp.	4.647	4.929	9.040	90.00
	0	DFT@DFT[b]	5.03	4.42	9.08	90.0
	122	HMBI(C,A)@DFT[c]	4.96	4.41	8.99	90.0
	122	HMBI(C,H)@DFT[d]	4.97	4.41	9.00	90.0
	0	HMBI(M,A)@HMBI[e]	4.82	4.50	8.90	90.0
	122	HMBI(C,A)@HMBI[f]	4.85	4.52	8.98	90.0
	122	HMBI(C,H)@HMBI[g]	5.00	4.55	9.14	90.0
Benzene	298[a]	Exp.	7.287	9.200	6.688	90.00
	0	DFT@DFT[b]	7.34	9.33	6.72	90.0
	298	HMBI(C,A)@DFT[c]	7.49	9.52	6.88	90.0
	298	HMBI(C,H)@DFT[d]	7.72	9.85	7.10	90.0
Imidazole	298[a]	Exp.	7.326	4.997	9.556	122.68
	0	DFT@DFT[b]	7.35	5.17	9.64	119.1
	298	HMBI(C,A)@DFT[c]	7.53	5.34	9.74	116.7
	298	HMBI(C,H)@DFT[d]	7.66	5.53	9.78	113.3

[a] Temperature at which the experiment was performed.

[b] Structure optimized with respect to static cohesive energy only, obtained at the PBE-D3(BJ)/PAW level.

[c] Structure optimized with respect to quasi-harmonic Helmholtz energy, obtained for PBE-D3(BJ)/PAW geometries and phonons, CCSD(T)/CBS+Amoeba HMBI refinement of the cohesive energy.

[d] Structure optimized with respect to quasi-harmonic Helmholtz energy, obtained for PBE-D3(BJ)/PAW geometries and phonons, CCSD(T)/CBS+pHF HMBI refinement of the cohesive energy.

[e] Structure optimized with respect to static cohesive energy only, obtained at the HMBI MP2/avtz+Amoeba level.

[f] Structure optimized with respect to quasi-harmonic Helmholtz energy, obtained for MP2/avtz+Amoeba HMBI geometries and phonons, with CCSD(T)/CBS+Amoeba HMBI refinement of the cohesive energy.

[g] Structure optimized with respect to quasi-harmonic Helmholtz energy, obtained for MP2/avtz+Amoeba HMBI geometries and phonons, with CCSD(T)/CBS+pHF HMBI refinement of the cohesive energy.

FIGURE S1

Comparison of percentage deviations of calculated vibrational frequencies for crystalline ethane – lattice modes (left) and intramolecular modes (right) calculated at various levels of theory. Experimental frequencies measured at 20 K culled from refs.[1, 2] Diamonds stand for quasi-harmonic frequencies calculated at the predicted unit-cell volumes at 20 K, circles stand for quasi-harmonic frequencies calculated at the experimental unit-cell volumes at 20 K, and squares stand for harmonic frequencies calculated for the unit-cell optimized with respect to its electronic energy only. Various shades of blue and red are used only to highlight the differences among the individual data sets.

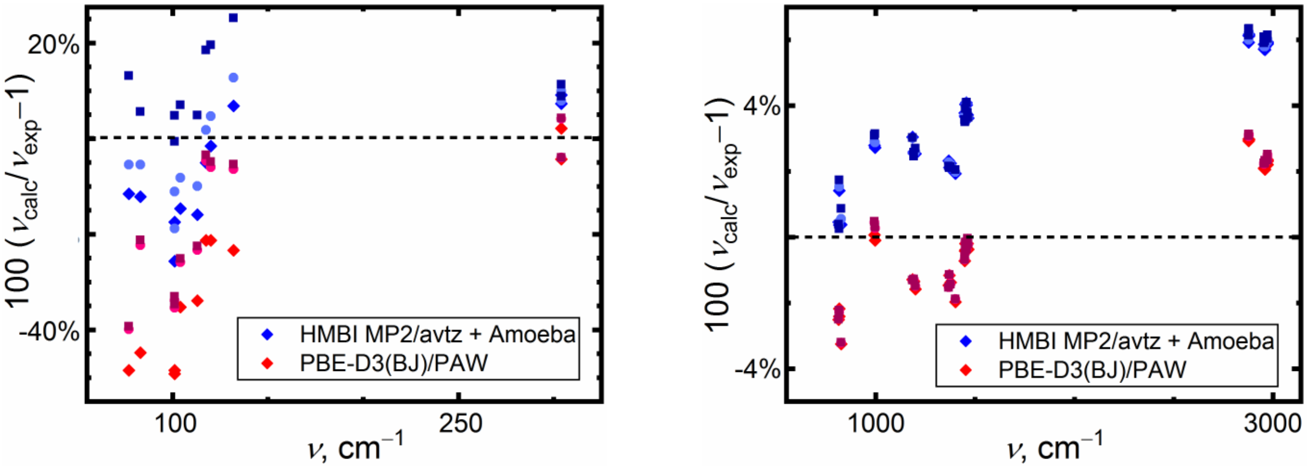


FIGURE S2

Comparison of molar volumes (left) and isobaric heat capacities (right) calculated at various levels of theory for crystalline ethane. Data based on PBE-D3(BJ) geometries/phonons and Amoeba embedding unless stated otherwise. Experimental V_m and C_p culled from refs. [1, 2] and ref. [3, 4], respectively.

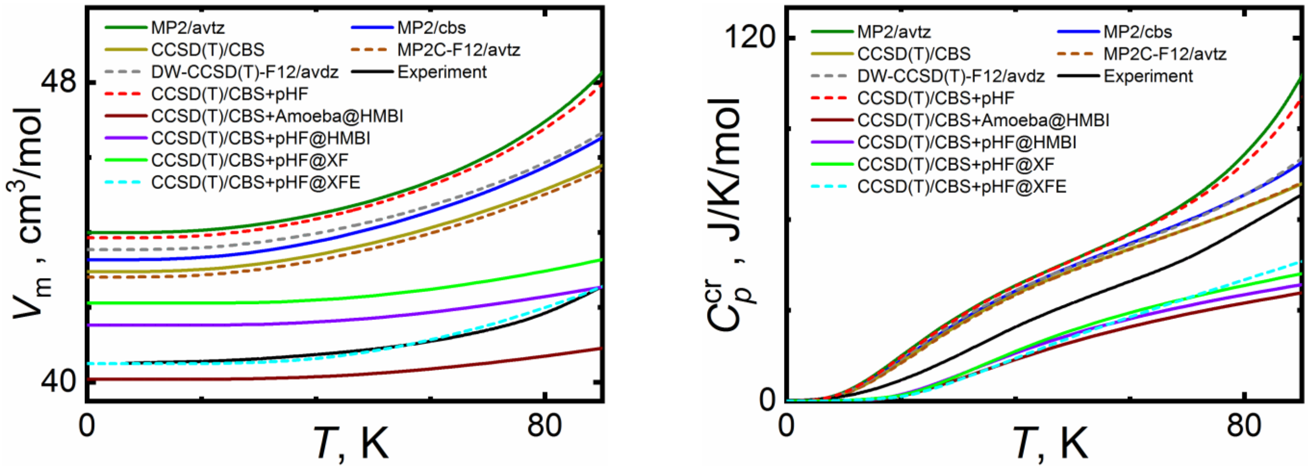


FIGURE S3

Comparison of percentage deviations of calculated vibrational frequencies for crystalline methanol – lattice modes (left) and intramolecular modes (right) calculated at various levels of theory. Experimental frequencies measured at 20 K culled from refs.[5, 6] Diamonds stand for quasi-harmonic frequencies calculated at the predicted unit-cell volumes at 20 K, circles stand for quasi-harmonic frequencies calculated at the experimental unit-cell volumes at 20 K, and squares stand for harmonic frequencies calculated for the unit-cell optimized with respect to its electronic energy only. See our previous work[7] for more details. Various shades of blue and red are used only to highlight the differences among the individual data sets.

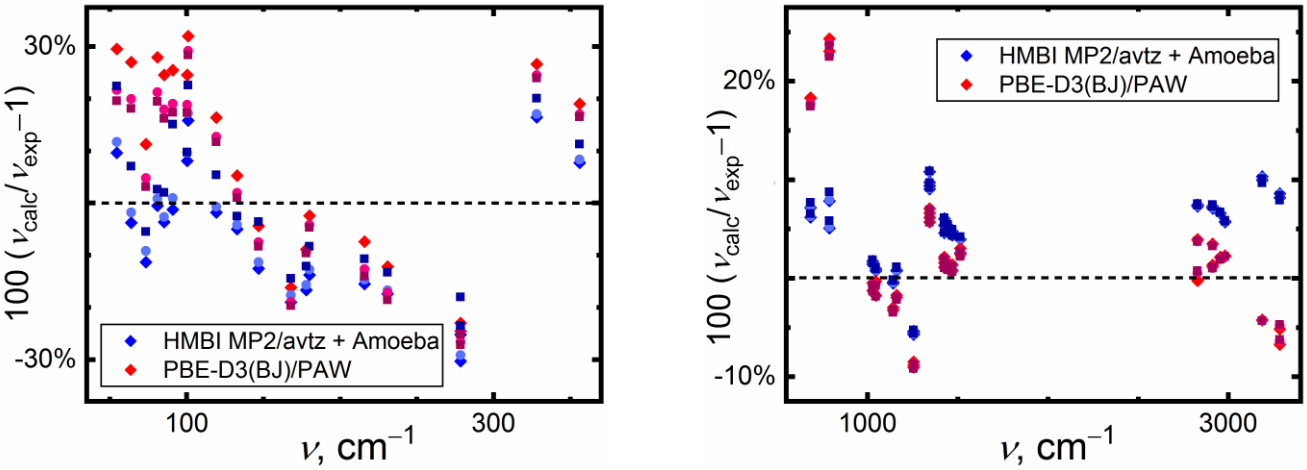


FIGURE S4

Comparison of molar volumes (left) and isobaric heat capacities (right) calculated at various levels of theory for crystalline methanol. Data based on PBE-D3(BJ) geometries/phonons and Amoeba embedding unless stated otherwise. Experimental V_m and C_p culled from refs.[8-12] and ref. [13], respectively.

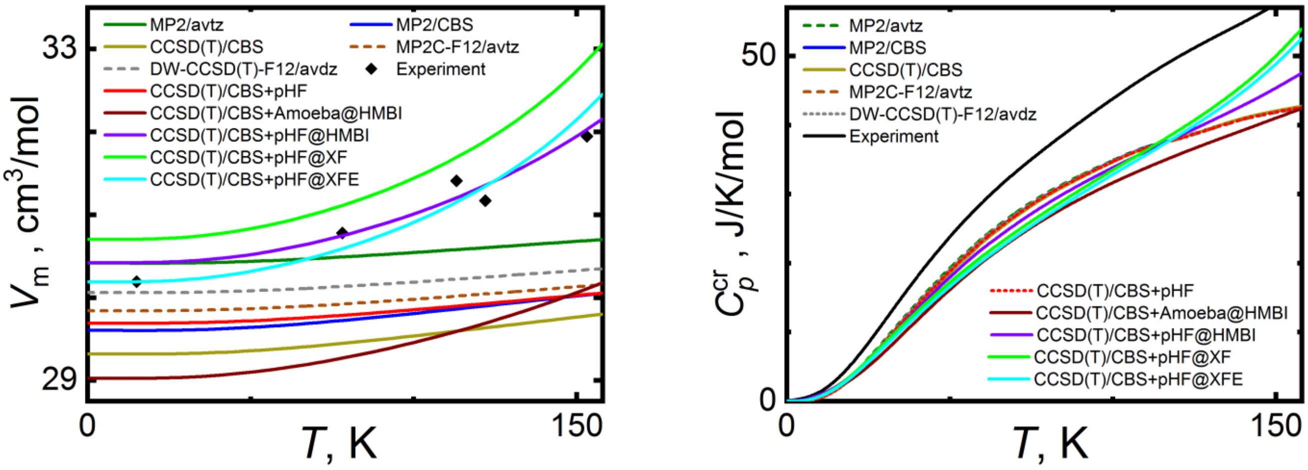


FIGURE S5

Comparison of percentage deviations of calculated vibrational frequencies for crystalline benzene – lattice modes (left) and intramolecular modes (right) calculated at various levels of theory. Experimental frequencies culled from refs.[14-16]

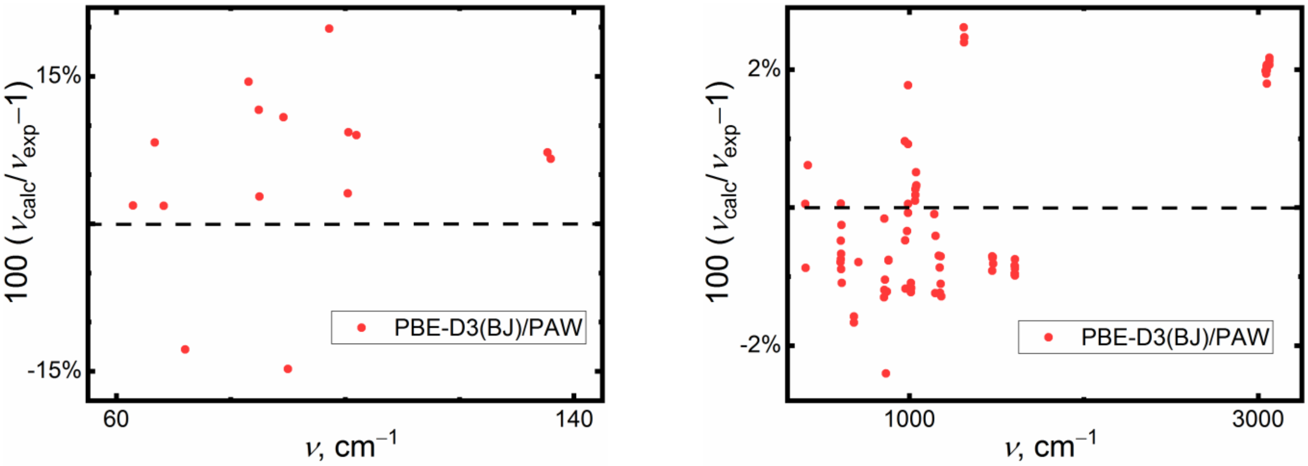


FIGURE S6

Comparison of molar volumes (left) and isobaric heat capacities (right) calculated at various levels of theory for crystalline benzene. Data based on PBE-D3(BJ) geometries and Amoeba embedding unless stated otherwise. Experimental V_m and C_p culled from refs.[17-22] and ref. [23], respectively.

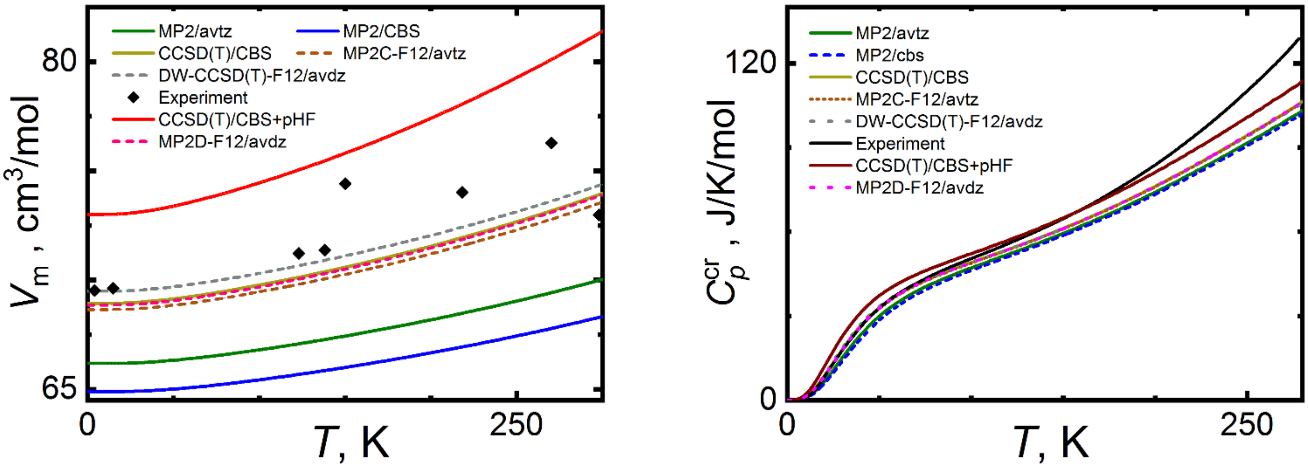


FIGURE S7

Comparison of percentage deviations of calculated vibrational frequencies for crystalline imidazole – lattice modes (left) and intramolecular modes (right) calculated at various levels of theory. Experimental frequencies culled from refs.[24-26]

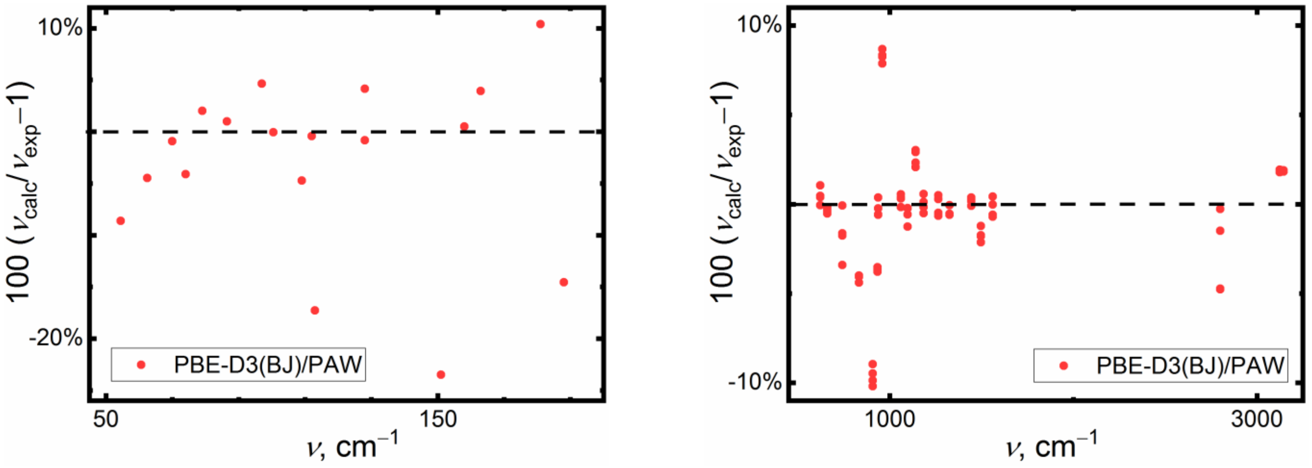
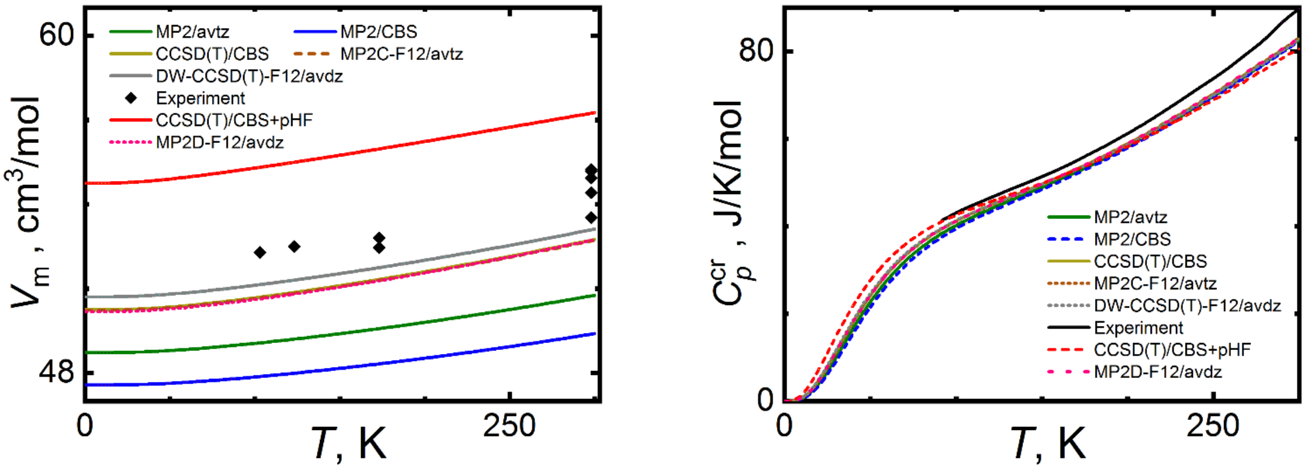


FIGURE S8

Comparison of molar volumes (left) and isobaric heat capacities (right) calculated at various levels of theory for crystalline imidazole. Data based on PBE-D3(BJ) geometries and Amoeba embedding unless stated otherwise. Experimental V_m and C_p culled from refs.[27-32] and ref. [33], respectively.



References for the SI

1. N. A. Klimenko, N. N. Gal'tsov and A. I. Prokhvatilov, *Low Temp. Phys.*, 2008, **34**, 1038-1043.
2. G. J. H. van Nes and A. Vos, *Acta Crystallogr. B*, 1978, **34**, 1947-1956.
3. R. K. Witt and J. D. Kemp, *J. Am. Chem. Soc.*, 1937, **59**, 273-276.
4. A. Tooru and C. Hideaki, *Chem. Lett.*, 1976, **5**, 683-688.
5. O. Galvez, B. Mate, B. Martin-Llorente, V. J. Herrero and R. Escribano, *J. Phys. Chem. A*, 2009, **113**, 3321-3329.

6. A. Anderson, B. Andrews, E. M. Meiering and B. H. Torrie, *J. Raman Spectrosc.*, 1988, **19**, 85-89.
7. C. Červinka and G. J. O. Beran, *Phys. Chem. Chem. Phys.*, 2017, **19**, 29940-29953.
8. W. Biltz, W. Fischer and E. Wunnenberg, *Z. Phys. Chem. A*, 1930, **151**, 13-55.
9. M. Riembauer, L. Schulte and A. Wurflinger, *Z. Phys. Chem. Neue Fol.*, 1990, **166**, 53-61.
10. K. J. Tauer and W. N. Lipscomb, *Acta Crystallogr.*, 1952, **5**, 606-612.
11. B. H. Torrie, O. S. Binbrek, M. Strauss and I. P. Swainson, *J. Solid State Chem.*, 2002, **166**, 415-420.
12. B. H. Torrie, S. X. Weng and B. M. Powell, *Mol. Phys.*, 1989, **67**, 575-581.
13. H. G. Carlson and E. F. Westrum, *J. Chem. Phys.*, 1971, **54**, 1464-&.
14. E. R. Bernstein, *J. Chem. Phys.*, 1970, **52**, 4701-4716.
15. G. Taddei, H. Bonadeo, M. P. Marzocchi and S. Califano, *J. Chem. Phys.*, 1973, **58**, 966-978.
16. J. P. Pinan, R. Ouillon, P. Ranson, M. Becucci and S. Califano, *Journal of Chemical Physics*, 1998, **109**, 5469-5480.
17. S. K. Nayak, R. Sathishkumar and T. N. G. Row, *Crystengcomm*, 2010, **12**, 3112-3118.
18. W. I. F. David, R. M. Ibberson, G. A. Jeffrey and J. R. Ruble, *Physica B*, 1992, **180**, 597-600.
19. G. A. Jeffrey, J. R. Ruble, R. K. McMullan and J. A. Pople, *Proc. Royal Soc. Lond. A*, 1987, **414**, 47-57.
20. E. G. Cox, D. W. J. Cruickshank and J. A. S. Smith, *Proc. Royal Soc. Lond. A*, 1958, **247**, 1-21.
21. G. E. Bacon, N. A. Curry and S. A. Wilson, *Proc. Royal Soc. Lond. A*, 1964, **279**, 98-+.
22. A. Budzianowski and A. Katrusiak, *Acta Crystallogr. B*, 2006, **62**, 94-101.
23. G. D. Oliver, M. Eaton and H. M. Huffman, *J. Am. Chem. Soc.*, 1948, **70**, 1502-1505.
24. P. W. Loeffen, R. F. Pettifer, F. Fillaux and G. J. Kearley, *J. Chem. Phys.*, 1995, **103**, 8444-8455.
25. C. Perchard and A. Novak, *J. Chem. Phys.*, 1968, **48**, 3079-3084.
26. M. Majoube and G. Vergoten, *J. Chem. Phys.*, 1982, **76**, 2838-2847.
27. G. Will, *Z. Kristallogr. Cryst. Mater.*, 1969, **129**, 211-&.
28. R. K. McMullan, J. Epstein, J. R. Ruble and B. M. Craven, *Acta Crystallogr. B*, 1979, **35**, 688-691.
29. J. Epstein, J. R. Ruble and B. M. Craven, *Acta Crystallogr. B*, 1982, **38**, 140-149.
30. B. M. Craven, R. K. McMullan, J. D. Bell and H. C. Freeman, *Acta Crystallogr. B*, 1977, **33**, 2585-2589.
31. Y. A. Omelchenko and Kondrash.Yd, *Sov. Phys. Crystallogr.*, 1971, **16**, 88-+.
32. D. Paliwoda, K. F. Dziubek and A. Katrusiak, *Cryst. Growth Des.*, 2012, **12**, 4302-4305.
33. H. G. M. De Wit, C. G. De Kruif and J. C. Van Miltenburg, *J. Chem. Thermodyn.*, 1983, **15**, 891-902.