High-pressure differential thermal analysis study of the phase behaviour in some *tert*-butyl compounds: pivalic acid, 2-methylpropane-2-thiol and *tert*-butylamine

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Pressure–temperature phase diagrams of the *tert*-butyl compounds (Bu^{t}X) pivalic acid (X = CO$_2$H), 2-methylpropane-2-thiol (X = SH) and *tert*-butylamine (X = NH$_2$) have been determined at temperatures between 100 K and the melting curve and up to 300 MPa with the aid of differential thermal analysis (DTA) under pressure. New normal as well as high-pressure induced phases have been found for 2-methylpropane-2-thiol and *tert*-butylamine. The results for the studied compounds are compared to those previously obtained for compounds belonging to the same *tert*-butyl family (*i.e.* X = Cl, Br, CH$_2$OH, NO$_2$, Me and CN) in order to establish similar trends in the phase behaviour as well as in the thermodynamic properties of the phase transitions. For the related *tert*-butyl compounds, with the exception of the X = CN compound, the average of the slopes (dT/dp) of the melting and the II to I transition curves have been determined to be (0.64 ± 0.14) and (0.27 ± 0.13) K MPa^{-1} respectively.

tert-Butyl compounds Bu^{t}X (X = Cl, Br, NO$_2$, SH, NH$_2$, CO$_2$H, Me, CH$_2$OH, CN *etc.*) are typical representatives of plastic crystals, due to their almost globular shape.[1] Such compounds display a rich polymorphism that has stimulated a large number of experimental investigations as well as theoretical studies in order to rationalize the thermodynamic properties and molecular dynamics of the various solid phases.[2–12] Guthrie and McCullough[13,14] have tried to derive the entropies of transition from symmetry and steric considerations. They assumed ten distinguishable orientations for *tert*-butyl compounds in the high-temperature phase corresponding to ΔS = Rln10 in approximate accordance with the experimental entropy change of the transition from the ordered low-temperature phase into the plastic phase. The method of finding the number of orientations used by Guthrie and McCullough, however, was heavily questioned by Clark *et al.*[15] Also, the volume-dependent part of the entropy change has to be taken into consideration, as has been shown in a recent paper.[16] Furthermore, the orientational disorder is not necessarily characterised by a discrete number of distinguishable orientations (Frenkel model). Results from incoherent quasi-elastic neutron scattering suggested an (almost) isotropic tumbling motion for many molecules in their plastic phases.[5,17,18] Also, computer simulations discount the Frenkel model in many cases.[19]

It is interesting to note that there are many substances which exhibit pressure-induced disordered phases. Examples can also be given for *tert*-butyl compounds, *e.g.* in *tert*-butyl chloride (X = Cl).[20–22]

The pressure–temperature behaviour of plastic crystals can qualitatively be explained by the Pople–Karasz theory,[23] which was later extended by Amzel and Becka.[24] The essential parameter of this theory is the ratio of two energy barriers: $v = E_r/E_d$, E_r and E_d being the barriers against reorientation and diffusion, respectively. The values of such a parameter in a homologous series would be a measure for the variation of the anisotropy of the molecular shape. From this point of view a comparison of the polymorphism for similar plastic crystals can elucidate the nature of the phase situation.

Here we report on the pressure dependence of the phase behaviour of some selected *tert*-butyl compounds Bu^{t}X established with the aid of differential thermal analysis under pressure; particularly, we have studied the compounds X =

CO$_2$H (pivalic acid, PA), X = SH (2-methylpropane-2-thiol, TBT) and X = NH$_2$ (*tert*-butylamine, TBA). The results will be analysed in comparison with the previous findings for similar compounds such as X = Cl (*tert*-butyl chloride, TBC),[21] X = Br (*tert*-butyl bromide, TBB),[25] X = NO$_2$ (2-methyl-2-nitropropane, TBN),[16,26] and X = CH$_2$OH (neopentyl alcohol, NPA),[27] as well as some results obtained from the literature for X = Me (neopentane, NP) and X = CN (*tert*-butyl cyanide, TBCN).[28]

Experimental

Differential thermal analysis

The experimental device used for the high-pressure differential thermal analysis (DTA) measurements has been described elsewhere.[29,30] The measurements were performed in closed indium capsules.

The limit of experimental error for the transition temperatures determined from the DTA curves (usually on heating runs at a rate of 1 K min^{-1}) is less than 0.5 K. The error for the pressure, generated by compressed argon and measured by using Bourdon gauges, is expected to be less than 0.5 MPa.

Materials

Pivalic acid, obtained from Aldrich (99%), was distillated under reduced pressure and dried with molecular sieves. A sample with purity higher than 99.85% (GC) was attained. 2-Methylpropane-2-thiol and *tert*-butylamine were purchased from Aldrich and Fluka with purities higher than 99 and 99.5%, respectively. The substances were used without further purification.

Results

Common features

The details of the measurements on particular substances can be found in the thesis of Reuter[31] for TBN, TBT, TBA, the thesis of Wilmers[32] for TBC, the thesis of Kreul[33] for TBB and NPA and in the diploma thesis of Büsing[34] for PA.

Enthalpy changes at atmospheric pressure were calculated from the peak areas of the DTA curves whenever they were not available from the literature.

The transition temperatures, determined at the half height of the DTA peaks after the onset of the phase transition as a function of pressure, were fitted by polynomials. Volume changes were derived from the enthalpy changes and the slopes of the transition lines using the Clausius–Clapeyron equation. This set of thermodynamic values together with the associated entropy changes are collected in Table 1. Fig. 1 contains the pressure–temperature phase diagrams of the compounds studied in this work (PA, TBT and TBA), together with those obtained in recent years (TBC, TBB, NPA and TBN) as well as those obtained from the literature (NP and TBCN).

Pivalic acid (Bu^{t}CO$_2$H)

Pivalic acid is a well-known plastic crystal which has been thoroughly studied by means of several techniques such as quasielastic neutron scattering,[35] (QNS),[39] NMR,[40–45] X-ray diffraction,[46] dielectric methods[47] and Raman spectroscopy.[48]

At atmospheric pressure PA melts at 308.3 K from the orientationally disordered phase (I). Below 279.8 K it transforms into an ordered solid form. In phase I the molecules which are known to form dimers display overall molecular tumbling, while in phase II two types of motions are present: methyl group reorientations about the methyl axes (C_3) and reorientations of the tert-butyl groups about the C–CO$_2$H axis (C_3').[40,41,45,46]

The pressure–temperature phase diagram of PA derived from DTA measurements[34] is shown in Fig. 1(f). The slope of the melting transition line (0.78 K MPa^{-1}) differs significantly from that given in the previous work of Hasebe et al. (0.45 K MPa^{-1}),[45] who used NMR under pressure. Nevertheless, the value for the slope of the coexistence line of

Table 1 Thermodynamic properties of the *tert*-butyl compounds

		compound Bu^{t}X								
parameter	phase transition	PA (X=CO$_2$H)	TBT (X=SH)	TBA (X=NH$_2$)	TBC (X=Cl)	TBB (X=Br)	NPA (X=CH$_2$OH)	TBN (X=NO$_2$)	NP (X=Me)	TBCN (X=CN)
T/K	I→ℓ	308.7	274.4^a	205.2	248.4^c	256.2^c	331.4^f	299.2^g	257^i	292.1^k
	II→I	279.8	199.4^a	201.3	219.4^c	231.5^c	236.2^f	260.1^g	140^i	232.7^k
	III→II		157.0^a	197.5	183.1^c	208.7^c		215.3^g		213.0^k
	IV→III		151.6^a	148.3						
ΔH/kJ mol^{-1}	I→ℓ	2.1	2.5^a	0.9^b	2.0^c	2.0^c	3.9^f	2.6^g	3.3^i	9.3^k
	II→I	8.6	1.0^a	5.6	5.7^c	1.1^c	4.0^f	4.7^g	2.6^i	1.9^k
	III→II		0.7^a	~0.45	1.9^c	5.7^c		4.2^g		0.2^k
	IV→III		4.1^a	~0.45						
ΔS/J mol^{-1} K^{-1}	I→ℓ	6.8	9.0^a	4.3^b	8.0^c	7.5^c	11.8^f	8.7^g	12.7^i	31.8^k
	II→I	30.7	4.9^a	27.8	25.8^c	4.6^c	16.9^f	17.9^g	18.4^i	7.8^k
	III→II		4.1^a	~2.3	10.2^c	27.2^c		19.6^g		1.1^k
	IV→III		26.8^a	~3.0						
ΔV/cm^3 mol^{-1}	I→ℓ	5.4	5.9	2.6	4.6^d	3.9^e	7.9^f	5.0^h	9.9^j	11.5^l
	II→I	8.8	1.8	5.2	4.4^d	1.8^e	4.0^f	2.5^h	5.5^j	
	III→II			1.0	1.8^d	5.4^e		5.0^h		
	IV→III			2.7						
(dT/dp)/K MPa^{-1}	I→ℓ	0.78	0.65	0.61	0.57^d	0.51^e	0.67^f	0.57^h	0.78^i	0.36^i
	II→I	0.35	0.37	0.18	0.17^d	0.40^e	0.24^f	0.14^h	0.30^i	
	III→II		0.21	0.17	~0.18^d	0.20^e		0.26^h		
	IV→III		0.10	0.20						

^{a}Ref. 13. ^{b}Ref. 35. ^{c}Ref. 36. ^{d}Refs. 21 and 22. ^{e}Ref. 25. ^{f}Ref. 27. ^{g}Ref. 37. ^{h}Refs. 16 and 26. ^{i}Ref. 28. ^{j}Calculated from ref. 28. ^{k}Ref. 38. ^{l}Calculated from refs. 28 and 38.
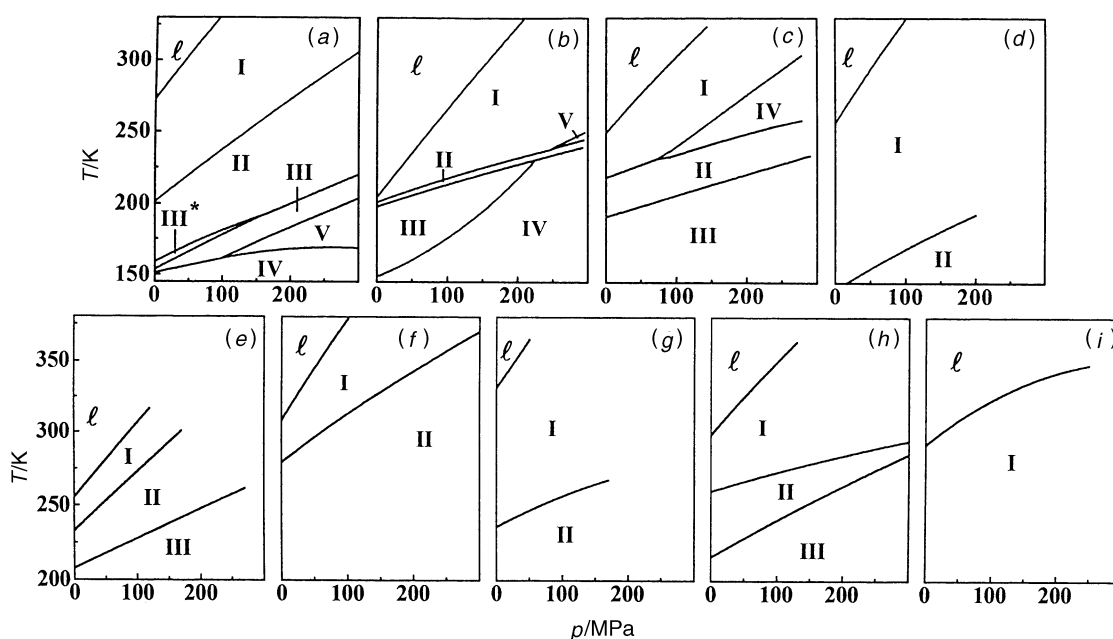

Fig. 1 Pressure–temperature phase diagrams of selected *tert*-butyl compounds: (a) TBT (X=SH), (b) TBA (X=NH$_2$), (c) TBC (X=Cl), (d) NP (X=Me), (e) TBB (X=Br), (f) PA (X=CO$_2$H), (g) NPA (X=CH$_2$OH), (h) TBN (X=NO$_2$) and (i) TBCN (X=CN)

Table 2 Transition temperatures of PA ($X=CO_2H$) as a function of pressure [$T/K = a + b \times (p/MPa) + c \times (p/MPa)^2$]

transition	a/K	$b/K\ MPa^{-1}$	$c/10^4\ K\ MPa^{-2}$
II–I	279.7 ± 0.8	0.347 ± 0.015	1.53 ± 0.56
I–ℓ	308.1 ± 0.9	0.784 ± 0.044	8.21 ± 4.15

phases II and I (0.35 K MPa^{-1}) is closer to the previous value (0.31 K MPa^{-1}).[45] The coefficients of the fitted polynomials for the transition lines of PA are shown in Table 2. The temperature range of phase I is enlarged with increasing pressure, a result that is known to be the normal behaviour of plastic crystals.

2-Methylpropane-2-thiol (Bu^{t}SH)

It has been shown earlier[49] that TBT displays three solid–solid phase transitions at about 152, 157 and 199 K in addition to the melting process at 274 K. On decreasing temperature there are then four different solid phases, denoted as solid I, II, III and IV. The dominant motions are overall molecular tumbling in the liquid phases I, II and III and reorientation of the *tert*-butyl group in solid phase IV.[50–53]

Normal pressure measurements. The DTA traces of TBT at normal pressure (0.1 MPa) for a heating run clearly show the mentioned sequence of the phases from IV to liquid. On the other hand, as has been previously reported in the literature, the above sequence is not observed on cooling, where phase II transforms directly to phase IV.

High pressure measurements. The pressure–temperature phase diagram of TBT [Fig. 1(*a*)] shows two new high-pressure induced phases (III* and V). The temperature ranges of the plastic phases II and I increase with increasing pressure as was observed in the case of pivalic acid (PA). For values of pressure higher than 75 MPa, a peak is observed in the thermograms that indicates the transition from phase III to phase III* (Fig. 2), while at a lower pressure the transition III–III* is not observed, which means that phase IV transforms directly into phase III*, which transforms into phase II at higher temperature. In order to obtain the phase III* at pressures lower than 75 MPa the transition line IV–III/III* must be crossed at pressures higher than 75 MPa and then the pressure has to be diminished in phase III until the desired value is reached. Such a detour process allows the determination of the coexistence line of the phases III and III* in the low pressure region. Unfortunately, we did not succeed in obtaining the III–III* transition at normal pressure due to the narrow temperature region of phase III at such low pressures [see Fig. 1(*a*)]. Fig. 3 displays two thermograms of measurements at 50 MPa (with and without detour) which demonstrate the described behaviour.

For pressures higher than 200 MPa the IV–V transition is obtained by means of a detour consisting of (i) diminution of
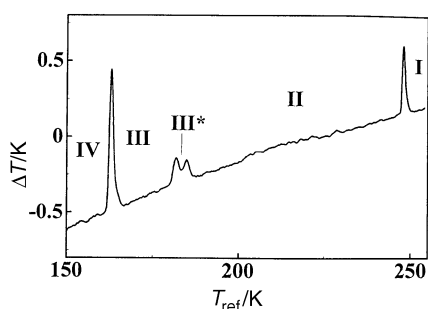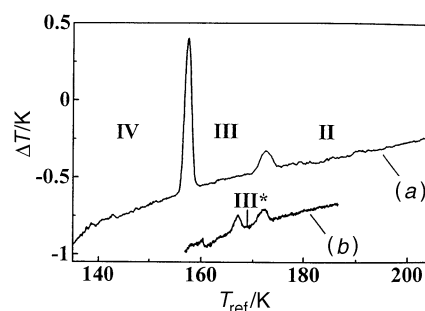
Fig. 2 DTA trace for TBT ($X=SH$) at 110 MPa

Fig. 3 DTA traces for TBT ($X=SH$) at 50 MPa (*a*) without and (*b*) with detour showing the transitions III–III* and III*–II (see text)

the pressure to values lower than 150 MPa, (ii) cooling to temperatures lower than 140 K and (iii) increasing the pressure again. It should be mentioned that it seems probable that phase V should also be obtainable at pressures above 200 MPa by increasing the annealing time appropriately.

Table 3 summarizes the determined coexistence lines for the different transitions, their pressure ranges as well as the coefficients of the fitted polynomials. According to the obtained results two triple points appear in the phase diagram: (i) III–III*–II at (160 ± 5) MPa and (192 ± 1) K and (ii) III–IV–V at (99 ± 5) MPa and (161 ± 1) K.

tert-Butylamine (Bu^{t}NH$_2$)

So far, the phase behaviour of TBA has been the subject of not more than two studies.[35,54] Finke *et al.*,[35] who measured the heat capacities of TBA between 12 and 340 K in an adiabatic calorimetry study, found two solid–solid transitions. The first transition, at 91.30 K, was described by the authors as a second-order or lambda transition. The second solid–solid transition, being of first order, was found at 202.27 K ($\Delta S = 29.9$ J mol^{-1} K^{-1}) and the melting transition was detected at a temperature of 206.19 K ($\Delta S = 4.28$ J mol^{-1} K^{-1}). In a dielectric study, no evidence for the existence of a plastic phase was found,[54] probably due to the use of temperature intervals of about 10 K, while phase I extends over only 3.9 K.

Normal pressure measurements. The second-order transition at 91.3 K was not detected in our measurements, due to the limited sensitivity of the equipment. Fig. 4 shows a DTA thermogram of TBA, that was measured at normal pressure.

The first peak, at 197.5 K, belongs to a transition that was not mentioned in the work of Finke *et al.*[35] We designate the respective transition as III–II. The second intense peak is due to transition II–I and is detected at 201.3 K. The melting takes place at 205.2 K. Comparing the determined melting temperature with the value given by Finke *et al.*, the calorimetric purity of the sample can be calculated using the van't Hoff equation as being >99.75%. On cooling, only two transitions show up in the DTA curves, the freezing at about 203.5 K and transition I–III near 193 K.

High pressure measurements. The phase behaviour of *tert*-butylamine was examined in the pressure range from 0.1 to 300 MPa. Fig. 1(*b*) shows the pressure–temperature phase diagram that resulted from these measurements. Two new phases, IV and V [Fig. 1(*b*)], were discovered in the high-pressure measurements. The transition from phase IV to phase III was not detected at low pressures; it appeared for the first time in the DTA thermograms at a pressure of about 190 MPa. Obviously, phase IV crystallises (in the timescale of the DTA measurements) only if phase III is cooled down to pressures between 190 and 220 MPa. To obtain the coexistence line at lower pressure, it is therefore necessary to pressurize phase III to about 200–220 MPa and to cool down to achieve the III–IV

Table 3 Transition temperatures as a function of pressure $[T/K = a + b \times (p/\text{MPa}) + c \times (p/\text{MPa})^2]$ and pressure ranges for the transition lines of TBT (X=SH)

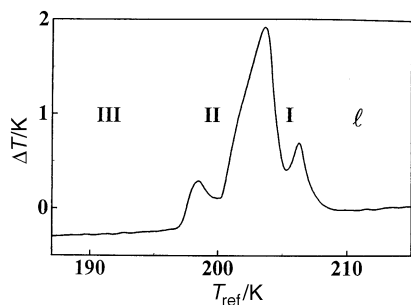| transition	pressure range/MPa	a/K	b/K MPa^{-1}	c/10^4 K MPa^{-2}
I–ℓ	$0 < p < 100$	272.3 ± 0.3	0.650 ± 0.018	4.44 ± 1.38
II–I	$0 < p < 300$	201.5 ± 0.4	0.368 ± 0.006	0.65 ± 0.21
III–II	$p > 160$	158.3 ± 7.9	0.213 ± 0.075	0.23 ± 1.75
III*–II	$p < 160$	159.2 ± 0.7	0.236 ± 0.023	1.84 ± 1.58
III–III*	$0 < p < 160$	153.7 ± 0.4	0.241 ± 0.004	—
V–III	$p > 99$	140.3 ± 1.6	0.212 ± 0.008	—
IV–III	$p < 99$	151.3 ± 0.2	0.099 ± 0.003	—
IV–V	$p > 99$	149.6 ± 2.7	0.149 ± 0.031	2.92 ± 0.81

Fig. 4 DTA thermogram of TBA (X=NH$_2$) at normal pressure

transition. Afterwards, the pressure can be reduced down to the desired value, at which the measurement of the IV–III transition can be performed. The result of this detour is depicted in Fig. 5. The upper thermogram [Fig. 5(a)] is the result of a 'normal' measurement (i.e., the pressure was kept the same on cooling as well as on heating), whereas the lower thermogram [Fig. 5(b)] was obtained after performing the described detour process. Unlike the III–III* transition of TBT, the IV–III transition of TBA could be measured—by using the described detour process—even at normal pressure.

The second high-pressure induced phase V appears in the thermograms at pressures above ca. 250 MPa. Fig. 6 contains the DTA curves of two measurements performed at different pressures. In the upper thermogram, obtained at about
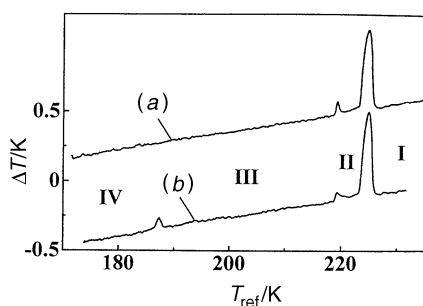

Fig. 5 Thermograms for TBA (X=NH$_2$) at about 135 MPa (a) without and (b) with detour
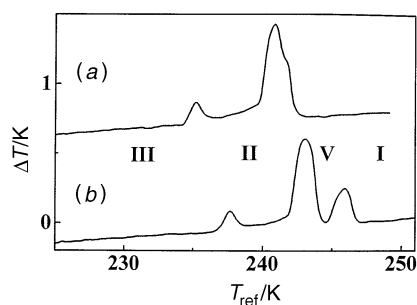

Fig. 6 Thermograms of TBA (X=NH$_2$) at (a) ca. 256 MPa and (b) ca. 274 MPa

256 MPa, the peak of the II–I transition already exhibits a shoulder on its high temperature side. In the lower thermogram, obtained at ca. 274 MPa, the two peaks, originating from the phase transitions II–V and V–I, are clearly separated.

The seven coexistence lines that appear in the pressure–temperature phase diagram of TBA [Fig. 1(b)], have been fitted to polynomials, the coefficients of which are shown in Table 4. From these polynomials the coordinates of the triple points can be calculated: (i) II–III–IV at (224 ± 3) MPa and (230.5 ± 0.5) K, (ii) I–II–V at (247 ± 2) MPa and (238.5 ± 0.5) K.

The slopes of the phase transition lines dT/dp at normal pressure can be used to calculate the volume changes of the transitions via the Clausius–Clapeyron equation. In addition to the slopes, the enthalpy changes are needed. The work of Finke et al.[35] contains accurate values of the transition enthalpies, but it is rather difficult to attach these values to the transitions that were detected in our measurements. It is questionable whether the enthalpy change of the transition from 'crystals II' to 'crystals I', as designated by Finke et al., corresponds to the enthalpy change of 'our' transition II–I or to the sum of the enthalpy changes of the transitions III–II and II–I. Assuming the latter, the two transition enthalpies can be estimated by comparing the areas of the two corresponding DTA peaks. The transition enthalpies and volumes obtained in this way are combined in Table 5. If the enthalpy change measured by Finke et al.[35] is fully assigned to the II to I transition, a volume variation of (5.24 ± 0.09) cm^3 mol^{-1} is obtained.

Discussion

A theory of fusion of molecular crystals that takes into account orientational as well as positional disorder was developed by Pople and Karasz[23] on the basis of the Lennard–Jones–

Table 4 Transition temperatures of TBA (X=NH$_2$) as a function of pressure $[T/K = a + b \times (p/\text{MPa}) + c \times (p/\text{MPa})^2]$

transition	a/K	b/K MPa^{-1}	c/10^4 K MPa^{-2}
I–ℓ	205.1 ± 0.8	0.608 ± 0.021	0.22 ± 1.10
II–I	201.2 ± 0.2	0.175 ± 0.003	1.02 ± 0.12
III–II	197.8 ± 0.3	0.167 ± 0.006	0.98 ± 0.25
IV–III	148.5 ± 1.2	0.197 ± 0.024	$-(7.47 \pm 1.04)$
IV–II	198.7 ± 1.0	0.142 ± 0.037	—
II–V	205.7 ± 3.2	0.133 ± 0.012	—
V–I	180.2 ± 8.8	0.236 ± 0.032	—

Table 5 Enthalpy and volume changes for the transitions of TBA (X=NH$_2$)

transition	ΔH/J mol^{-1}	ΔV/cm^3 mol^{-1}
I–ℓ	882.0 ± 0.8^a	2.6 ± 0.1
II–I	5600 ± 100	4.9 ± 0.2
III–II	450 ± 100	0.4 ± 0.1

^{a}Ref. 35.

Devonshire approach.[55] Amzel and Becka[24] extended the model of Pople and Karasz by introducing the existence of more than two possible positions of minimum orientational energy in the crystal in addition to the fact that molecules can occupy either α or β sites, *i.e.* one of two interpenetrating lattices. In both theories the authors defined a non-dimensional parameter v (temperature and volume independent), characteristic of the molecular crystal, as the ratio between the energy barriers for the reorientation and diffusion of the molecules. Both energy barriers can be obtained by several experimental techniques such as NMR or dielectric methods. Nevertheless, after a careful and detailed search in the literature for the compounds mentioned in this paper, the energy barriers were either not found or the scatter in the values reported by different groups (even with similar techniques) was considerable. Nevertheless, some results of the model can be analysed in terms of different correlations.

The slopes (dT/dp) for the melting process are quite similar for the related compounds, except for TBCN (X=CN), the behaviour of which does not obey the general rules that can be derived for the other compounds.

Fig. 7 displays the volume change as a function of the entropy change at the melting and at the II–I processes for the collected compounds. The slope of the line relating the melting values, which runs through the origin, corresponds to the average of the experimental slopes (dT/dp) for all the compounds (except for TBCN) and it can be considered as the 'normal slope' for *tert*-butyl compounds. The average value was determined to be (0.64 ± 0.14) K MPa^{-1} (the error being calculated in order to cover all the known values for the compounds studied so far). It should be mentioned that this correlation between ΔS_m and ΔV_m was predicted by the model of Amzel and Becka.[24] However, the correlation was derived on the basis of a common value of D, *i.e.* the number of the positions of minimum orientational energy in the crystal; in other words, the number of distinguishable orientations of the molecule in the lattice. It is obvious that this number varies from one *tert*-butyl compound to another, due to the fact that the substituent groups in the Bu^{t}X molecules (X=SH, NO$_2$, Me *etc.*) can generate additional distinguishable orientations for each one of the tetrahedral orientations. Moreover, it must be taken into account that the entropy change of the melting (and also for the solid–solid phase transitions) is not only a result of the change in the number of orientations but also of the volume change, as has been proved recently from the pVT data of TBN (X=NO$_2$).[16] With regard to the line joining the II–I transition values, the correlation is relatively more scattered. This fact is a direct consequence of the differences of the disorder in phases II of the related compounds. The obtained average value for the experimental slopes is determined as (0.27 ± 0.13) K MPa^{-1}. In this context it should be mentioned that Schneider[56] found as an experimental evidence that very different phase transitions (solid–solid, solid–smectic, smectic–smectic, smectic–nematic, nematic–isotropic liquid, *etc.*) exhibit
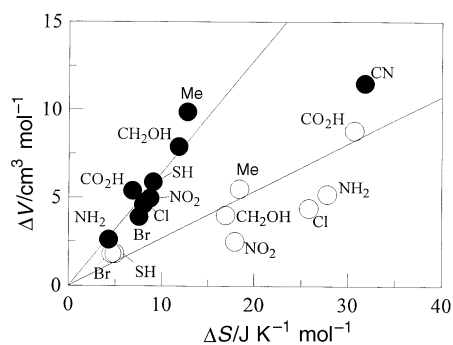
rather similar slopes, the given average value being *ca.* 0.35 K MPa^{-1}.

The entropy and volume changes at the melting transitions of the considered compounds can be compared by using a reduced temperature defined as the ratio between the solid–solid phase transition temperature (II to I) and the melting temperature (T_t/T_m). In such a way, Fig. 8 and 9 display the entropy and volume changes at the melting transitions as a function of the defined reduced temperature. Both indicate that the further the solid–plastic phase transition is away from the plastic–liquid transition, the more the plastic phase differs from the liquid phase thermodynamically. This relationship seems to be independent of the shapes and sizes of the molecules. For example, the volumes of the Cl atom and of the Me group are very close; that means that the asymmetry factor (defined as the ratio of the distance from the central carbon to the van der Waals envelope of the Me groups and from the same central carbon atom to the X substituent[57]) for molecules like TBC (X=Cl) and NP (X=Me) is almost the same (*ca.* 1), but the temperature range of the orientationally disordered phase is very different, as is clearly seen from the T_t/T_m values (0.883 and 0.545, respectively). Moreover, compounds which display a similar temperature range for phase I, like TBN (X=NO$_2$) and TBC (X=Cl) (the T_t/T_m values of which are 0.872 and 0.883, respectively) have clearly different behaviour when their molecular shapes are compared; in the former the asymmetry factor is 1.07, whilst for the latter it is 1.00. Secondly, the mentioned result seems also to be independent of the intermolecular interactions present in the orientationally disordered phase. This is clearly seen if one compares *tert*-butyl compounds which exhibit intermolecular interactions by means of hydrogen bonds such as PA (X= CO$_2$H)[45,47,58] and NPA (X=CH$_2$OH).[27] The temperature domain of the plastic phase is in these cases very different (T_t/T_m values are 0.908 and 0.714 for PA and NPA, respectively).

The entropy and volume changes at the II–I transition as a function of T_t/T_m does not give a reasonable correlation. This is not surprising if one assumes that the thermodynamic
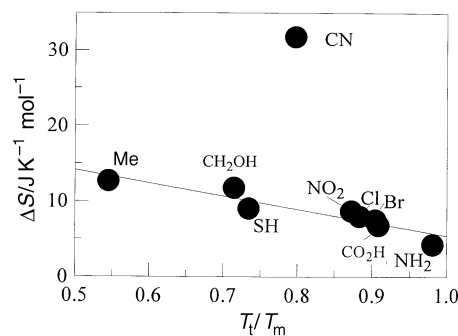

Fig. 8 Entropy change (ΔS_m) at the melting transition as a function of the reduced temperature T_t/T_m

Fig. 7 Volume change (ΔV) as a function of entropy change (ΔS) for the melting (●) and II–I transition processes (○)
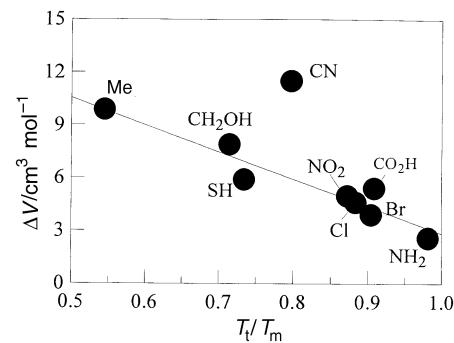

Fig. 9 Volume change (ΔV_m) at the melting transition as a function of the reduced temperature T_t/T_m

properties of phase II (with considerably different characteristics for the *tert*-butyl compounds) cannot be related to the temperature domain stability (given by T_t/T_m values) of the disordered forms.

It was mentioned in the preceding discussion that TBCN (X = CN) behaves differently than the other *tert*-butyl compounds in spite of the shape and size similarities of the molecules. For this compound it has been shown that in phase II the molecules undergo rapid reorientational motions about their C–CN axes.[5] These motions are quite similar to those found for TBC (X = Cl)[59] and TBB (X = Br)[18] in phase III. In the high-temperature phase I of TBCN the molecules possess a large degree of freedom of motion along the dipole axes, but only small fluctuations (librational motions) of these axes occur (about 10–15°)[18,60] as in the case of phase II of TBC (X = Cl). However, in phase II of TBB (X = Br) the molecules appear to have large fluctuations of the dipole axes (about 60° from their mean direction).[18] On the basis of dielectric measurements[22] the high-pressure phase IV of TBC (X = Cl) [Fig. 1(c)] appeared to be more closely related to phase II of TBB (X = Br) than the phase II of TBC (X = Cl) according to the static permittivity. This conclusion was strengthened by comparing the entropy change of the II–I transition for TBB (X = Br) (4.60 kJ mol^{-1}) and for TBC (X = Cl) (25.8 kJ mol^{-1}). In this context, phase I of TBCN (X = CN) should not be considered as an orientationally disordered phase; strictly speaking, this phase should be reported as a librational phase, much like phase II of TBB (X = Br) and TBN (X = NO$_2$).

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