Molecular symmetry, melting temperatures and melting enthalpies of substituted benzenes and naphthalenes

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Thermodynamic parameters of melting for mono- and di-substituted benzenes and naphthalenes have been examined. Correlations with molecular structural parameters are discussed. With very few exceptions, *ortho*- and *meta*-disubstituted benzenes melt at lower temperatures than *para*-isomers, an enthalpic effect related to crystal cohesion. However, no significant correlation was found between melting temperature and crystal density or packing energy. The concept of molecular shape and symmetry is discussed in connection with the stability of crystal packing.

A very old rule of thumb[1] says that symmetrical molecules pack in a three-dimensional periodic lattice more easily than less symmetrical ones, and hence form more stable, higher-melting and less soluble crystals. No strict definition of symmetry in this context has ever been given, nor has any theoretical justification ever been found for this concept, which is most often verified by empirical inspection of several pieces of experimental evidence, but has never been embodied in a molecular theory of the organic solid state. In fact, while it is obvious that structure determines the properties of molecules and crystals, no theory or relationship has ever been proposed to link molecular properties to melting points with a reasonable predictive power.

The internal cohesion of an organic crystal is a complex function of intermolecular forces, depending on molecular polarity and polarizability, and driving the spatial arrangement of molecules. The total lattice energy can be experimentally determined by measuring the sublimation enthalpy,[2] or can be calculated by empirical methods,[3] if the crystal structure is known; much more problematic is a pertinent definition of molecular symmetry and shape.

A very inexpensive indicator of crystal cohesion is the melting temperature, T_M; however, when a crystal melts the cohesive forces are only partially destroyed, and survive to a large extent in the liquid, which can be partially structured; conversely, the solid may be already partially disordered before melting. In fact, T_M is sensitive to entropic factors, which are even more difficult to assess than enthalpic ones (melting enthalpies can be measured rather easily and are available in reasonable numbers in the literature).

We present here a study of a large collection of melting temperatures over a sample of crystals with controlled structural variability. Two types of compound have been considered: the mono- and di-substituted benzenes, and the mono- (and, partially, di-) substituted naphthalenes, the aim being mainly to examine the relationships between molecular symmetry, shape, polarity, or hydrogen bonding ability, and crystal structure and cohesion.

Data collection and selection

Melting temperatures are readily available from standard repertories.[4] Differences of a few degrees appear in different sources, but these are uninfluential for our purposes. The higher value was anyway accepted, also in those very few cases where the existence of polymorphs is explicitly mentioned. Melting temperatures of volatile substances are seldom, if ever, reported; freezing temperatures, sometimes reported, were discarded, being critically sensitive to environment and purity and often significantly lower than melting temperatures. For the substances here considered, it can be safely assumed that when no melting temperature is reported the substance is liquid at ordinary temperature. Boiling temperatures, T_B, were also collected.

Much less abundant are melting enthalpies, ΔH_M.[5] Reported values were considered to be equilibrium ones, on the assumption that they had been measured at T_M, or that their temperature dependence is weak (liquid–solid ΔC_P usually being small).

For each substituent group, the following indicators were assigned: the polarity and hydrogen bonding donor and acceptor ability, each on an arbitrary scale from 0 to 4; and the number of internal degrees of freedom (essentially, rotations about single bonds). Table 1 shows these data, while Table S1 (deposited)† collects all the thermochemical data here used.

Results

In an attempt to correlate crystal cohesion with the nature of substituents, the following cohesive ability function was defined for a benzene molecule with two substituents, i and j [eqn. (1)],

$$\mathrm{CA} = 0.4M_r + 3(P_i + P_j) - 4(F_i + F_j) + 7\textstyle\sum_{i,j}(D_iA_j) \quad (1)$$

where M_r is the molecular weight, and, for each substituent, P is the polarity index, F is the number of degrees of freedom, and D and A are the donor and acceptor abilities (Table 1). Fig. 1 shows the correlation between CA and T_M for mono- or *para*-di-substituted benzenes. The result is not entirely unsatisfactory, considering the empirical nature of the P, D and A parameters, and of the numerical coefficients in the definition of CA; the terms in the above expression are just crude representations of the quantitative parameters on which crystal cohesion depends, that is, essentially, multipole moments, polarizability and hydrogen bonding.

Fig. 2(*a*) shows the difference in melting temperature, ΔT_M, between *para*- and *ortho*-disubstituted benzenes, while Fig. 2(*b*) shows the corresponding differences in boiling temperatures, ΔT_B. Fig. 2(*c*) shows ΔT_M between *para*- and *meta*-disubstituted benzenes. *para*-Compounds have higher melting temperatures than their *meta*- and *ortho*-counterparts, and this is a true solid-state effect—either enthalpic or entropic—and not an intrinsic,

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† Deposited under the Supplementary Publications Scheme. For details, see 'Instructions for Authors (1995)', *J. Chem. Soc., Perkin Trans. 2*, 1995, issue 1 [Supp. Pub. No. 57093 (8 pp.)].

Table 1 Substituent groups

Code number	Formula	Polarity index	Degrees of freedom	i_{don}, i_{acc} [a]	Name
1	CH_3	0	0	0 0	Methyl
2	CH_2CH_3	0	1	0 0	Ethyl
3	$CH_2CH_2CH_3$	0	2	0 0	*n*-Propyl
4	$CH(CH_3)_2$	0	1	0 0	Isopropyl
5	$C(CH_3)_3$	0	2	0 0	*tert*-Butyl
6	C_6H_5	0.5	1	1 0	Phenyl
7	$CH{=}CH_2$	0.5	1	1 0	Vinyl
8	CCH	1	0	2 0	
10	H	0	0	0 0	
21	F	4	0	0 4	Fluoro
22	Cl	3	0	0 3	Chloro
23	Br	2	0	0 2	Bromo
24	I	1	0	0 1	Iodo
25	CH_2Cl	3	1	0 3	Benzyl chloride
26	CH_2Br	2	1	0 2	Benzyl bromide
27	CH_2I	1	1	0 1	Benzyl iodide
28	COCl	4	1	0 4	Acid chloride
31	OH	2	0	3 2	Hydroxy (phenol)
32	CHO	3	1	1 3	Aldehyde
33	COOH	4	0	4 3	Acid (benzoic)
34	$COOCH_3$	3	1	0 3	Methyl benzoate
35	$OCOCH_3$	3	2	0 3	Acetate (phenyl)
36	OCH_3	2	1	0 2	Methoxy (anisole)
37	OCH_2CH_3	2	2	0 2	Ethoxy (phenetole)
38	NO_2	4	0	0 4	Nitro
39	CH_2OH	2	1	2 2	Benzyl alcohol
40	$COOCH_2CH_3$	3	2	0 2	Ethyl benzoate
41	$CH{=}CHCOOCH_3$	3	3	1 3	Methyl cinnamate
42	$CH{=}CHCOOC_2H_5$	3	4	1 2	Ethyl cinnamate
43	$COCH_3$	3	1	0 3	Methyl ketone
44	CH_2COOH	4	2	4 3	Benzyl acid
51	NH_2	2	0	3 1	Amino (aniline)
52	$NHCH_3$	2	1	3 0	Methylamino
53	$N(CH_3)_2$	1	1	0 1	Dimethylamino
54	CN	3	0	0 4	Cyano
55	CH_2CN	3	1	0 4	Benzyl cyanide
56	$NHCOCH_3$	2	2	3 3	Acetanilide
57	$CH{=}NOH$	3	2	2 2	Oxime (aldehyde)
58	$CCH_3{=}NOH$	3	2	2 2	Oxime (methyl ethyl ketone)
59	$CONH_2$	3	1	3 3	Amide
60	$NHCONH_2$	4	3	4 3	Urea

[a] Hydrogen-bond donor and acceptor ability.

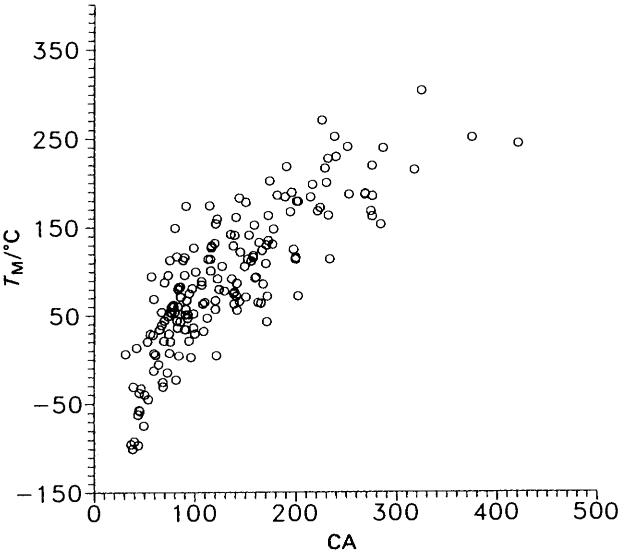


Fig. 1 Melting temperature against cohesive ability function (see text) for mono- and *para*-disubstituted benzenes

molecular effect, since the ΔT_B values are very small. These results are further corroborated by the numerous instances (not appearing) in which T_M is reported only for the *para*-derivative, other isomers being low-melting.

The few exceptions in Fig. 2(*a*)—*ortho* melting higher than *para*—deserve a comment. Some of these outliers represent chemically or structurally homogeneous sequences: for some phenol and benzyl alcohol derivatives, for example, a cyclic intramolecular hydrogen bond can be formed, so that the *ortho*-derivative acquires a compact, naphthalene-like shape, in some cases even preserving an intermolecular hydrogen bonding ability [1–4; numbers in parentheses are ΔT_M(*para*–*ortho*)]. Structure **4** is found in anthranilic (*o*-aminobenzoic) acid,[6] which is polymorphic but apparently transforms into the high-temperature monoclinic form before melting.[7] The T_M of monoclinic anthranilic acid (145 °C) is anyway significantly lower than that of its *para*-counterpart (188 °C), which is also polymorphic[8] (unfortunately, even in this clearly critical case, the authors of the structural papers do not quote the T_M of their materials). As a further confirmation of the effectiveness of this 'naphthalene-like' pattern, it may be noted that *ortho*-isomers of dihalogen or dialkyl derivatives usually have higher melting temperatures than their *meta* counterparts.

The large inversion found between *para*- (T_M = 2) and *ortho*-methoxybenzaldehyde (T_M = 38 °C) may also be tentatively explained by an intramolecular hydrogen bond (**5**). The attitude of *ortho*-aldehyde groups to act as donors in such cases is

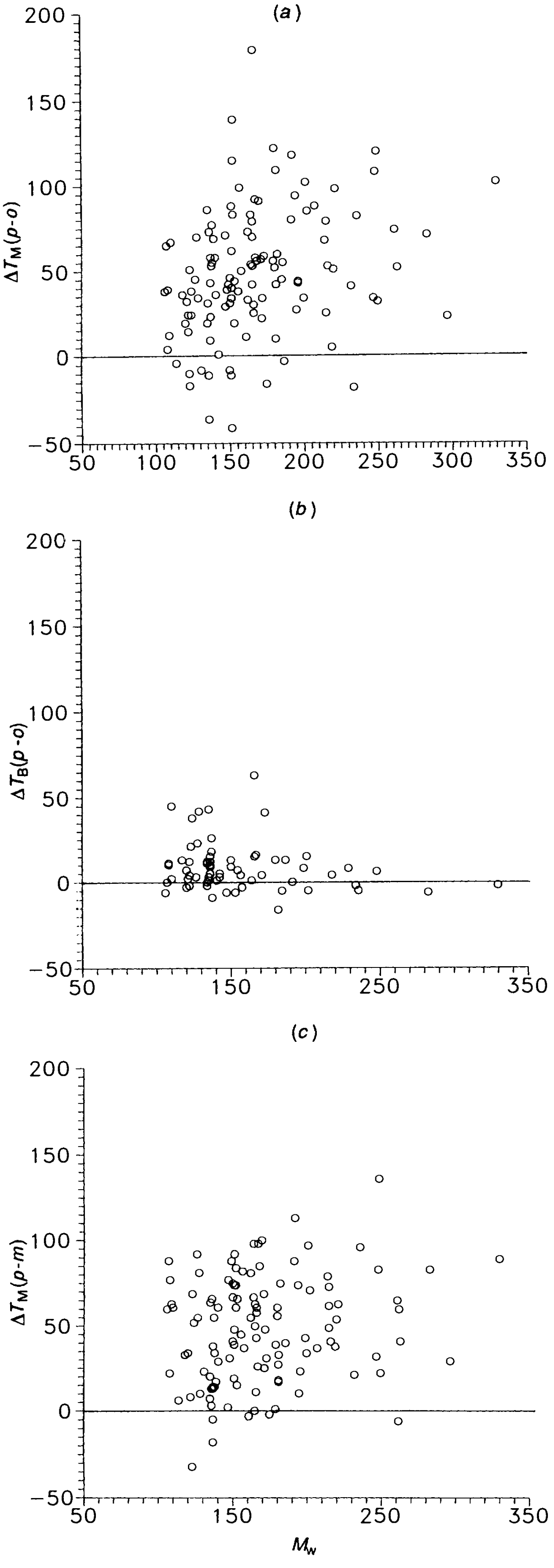
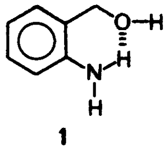


Fig. 2 (*a*) Differences in melting temperature between *para*- and *ortho*-disubstituted benzenes. (*b*) Differences in boiling temperature for the same compounds. (*c*) Differences in melting temperature between *para*- and *meta*-disubstituted benzenes. The abscissa is molecular weight.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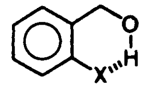
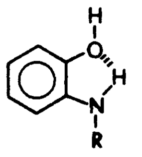
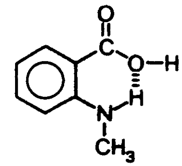
1


X = Cl (1)
X = Br (−3)
X = I (−18)

2


R = CH_3 (−10)
R = $COCH_3$ (−41)

3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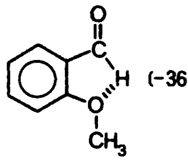
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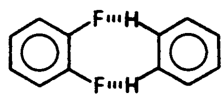
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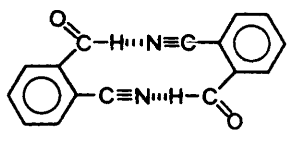
(−7)

7

witnessed by *o*-nitrobenzaldehyde[9] (although the fashion of the times prevented authors from accepting C–H ··· O interactions as hydrogen bonds), and by 1-bromo-2-naphthaldehyde.[10] The same group, understandably, acts as an acceptor in 2-hydroxy-1-naphthaldehyde.[11] Other substances may form stable intermolecular dimers only in the *ortho*-arrangement; some tentative structures are given in **6** and **7**. The case of cyanoethylbenzoate is unclear [ΔT_M(*para–ortho*) = −16]. Crystal structure determinations for these unusual cases might answer the question.

Fig. 3 shows the correlation between T_M and ΔH_M for mono- and di-substituted benzenes; it is approximately linear, although a moderate positive curvature appears. From the slope of this plot, a rough average value for the melting entropy, ΔS_M = 54 J K^{-1} mol^{-1}, is obtained (*cf.* Trouton's law, $\Delta H_B/T_B$ = 96.2 J K^{-1} mol^{-1}).

Deviations from a strict correlation in Fig. 3 must be ascribed to entropic effects. At an average ΔH_M of 17 000 J mol^{-1}, on one hand, disorder over two positions in the crystal contributes an entropy increase of $R\ln 2$ = 5.8 J K^{-1} mol^{-1}, or a T_M increase of 31 °C (with respect to the average melting entropy); on the other hand, many points in the lower part of the scatterplot are for strongly hydrogen-bonded substances, in which the partial association of the liquid reduces the melting entropy,[12] thus increasing T_M. Another, more subtle factor is the temperature dependence of the population of lattice-vibrational modes; the filling of some low-lying states may result in a fast increase of the crystal enthalpy, faster than the increase in crystal entropy, and may lower the temperature for the collapse of the crystalline edifice. An even more subtle point concerns the anharmonicity of the vibrations, which depends in an obscure way upon the spatial arrangement of molecules. The tentative nature of the above comments reflects the difficulty in bridging the gap between standard equilibrium thermodynamics and structural effects; while statistical mechanical approaches could in principle deal with the purely thermodynamic aspects of the

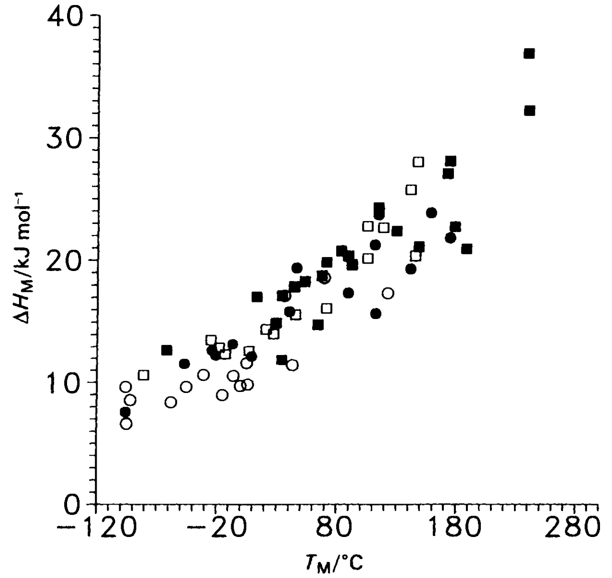

Fig. 3 Enthalpy of melting against melting temperature for mono- and di-substituted benzenes: (○), monosubstituted; (□), *ortho*-disubstituted; (●), *meta*-disubstituted; (■), *para*-disubstituted

Table 2 Differences in melting and boiling temperatures between 1- and 2-substituted naphthalenes

Substituent	ΔT_M	ΔT_B	Substituent	ΔT_M	ΔT_B
Methyl	55	−3	Amino	63	−6
Fluoro	69	—	Nitro	18	—
Chloro	81	2	OH	29	6
Bromo	53	1	$OCOCH_3$	23	—
Iodo	—	7	COOH	24	—
Methoxy	—	9	$NHCOCH_3$	−26	—
Methylamino	—	23	CH_2Cl	16	—
Ethoxy	32	4	CH_2Br	−2	—
CHO	27	—	COCl	23	7
$COCH_3$	21	0	Amide	−7	—
Oxime	6	—	CH_2OH	19	—
Cyano	30	7	$COOCH_3$	28	—

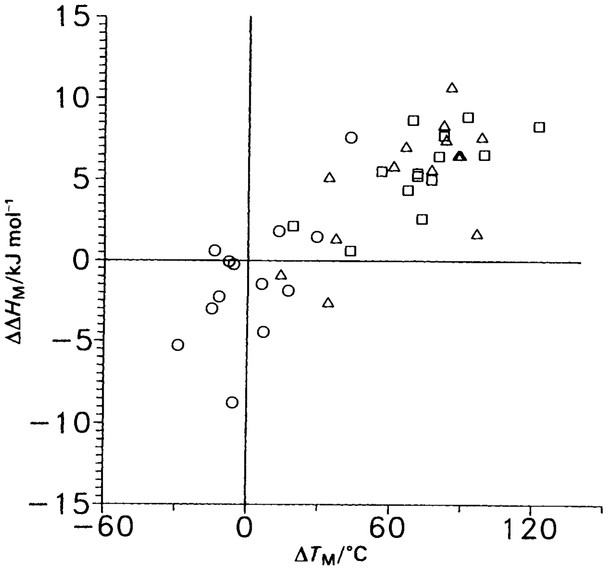

Fig. 4 Difference in melting enthalpy (kJ mol^{-1}) *vs.* difference in melting temperature: (○), *meta–ortho*; (□), *para–ortho*; (△), *para–meta*

matter, structural explanations run into the so far untamed difficulty of handling an essentially discontinuous process like melting.

Fig. 4 shows a plot of $\Delta(\Delta H_M)$ against ΔT_M between isomers: the two quantities increase roughly together. The distribution is however shifted to the right with respect to the origin of the diagram, with high ΔT_M for relatively small $\Delta(\Delta H_M)$, and even, in a few cases, to positive ΔT_M with negative $\Delta(\Delta H_M)$. In spite of this, the above results may be taken as evidence that melting is mostly enthalpy-driven, and that the melting temperature difference between isomers of disubstituted benzenes is an essentially enthalpic effect. Such a conclusion of course neglects the influence of the distribution of energy among quantum states, as discussed above.

Table 2 collects ΔT_M values between 1- and 2-substituted naphthalenes. Comparison with the corresponding ΔT_B demonstrates that the higher melting temperatures of 2-derivatives is a true solid-state effect (as in the above discussion on the results in Fig. 2).

A general analysis of disubstituted naphthalenes, with their many substitution patterns, is an overwhelming task. A few data on homodisubstituted compounds have therefore been selected, and Fig. 5(*a*) shows the trend in T_M as a function of the substitution pattern for non-hydrogen bonded crystals. Compounds on the right side of this figure—as well as *para*- against *ortho*-disubstituted benzenes—have a more regular shape, although what is actually meant by 'regular shape' is not strictly definable. In any case, the 2,6-derivative invariably is the highest-melting one, and the increase in T_M with increasingly regular molecular shape is evident. The increase in T_M with increasing polarizability of valence electrons appears on considering the halo-disubstituted series, and the increase in T_M with increasing polarity on considering the nitro- and cyano-derivatives against the less polar hydrocarbons or halohydrocarbons. Expected dips appear for vicinal derivatives with bulky substituents, as distortions from planarity presumably lead to a more awkward molecular shape.

When the same plot was drawn for hydrogen-bonded derivatives [Fig. 5(*b*)] more erratic results were obtained. Diacids and dialcohols show predictable dips for vicinal substitution patterns, as above, but the diamino derivatives do not. Hydrogen bonding is clearly structure-defining, and subtler shape effects are swept out. Interestingly, some diacids (as well as many benzoic and naphthoic tri- and tetra-acids) decompose before melting; one gets here to the paradox of a molecular crystal whose intermolecular bonds are stronger than some of the intramolecular bonds.

Crystal structures

The Cambridge Structural Database (CSD)[13] was searched for crystal structures of disubstituted benzenes determined at room temperature, with the aim of comparing the densities, packing coefficients and lattice energies of different isomers. These last quantities were calculated using empirical formulations.[3] The results appear in Table 3.

Besides a rather obvious covariance of density and packing coefficient, it is difficult to extract consistent trends from these data. The benzamides show higher densities for *para*- than for *ortho*-isomers, consistently with T_M differences, but the benzoic acids do not. Density fluctuations among polymorphs of the same substance are of the same order of magnitude as density differences between isomers. Besides, bad crystal quality or low resolution in the X-ray work can affect the cell volume to a point where its significance in structure-stability matters is obscured. Packing energy calculations suffer from the same drawback, since different levels of accuracy and refinement of the crystal structures may bring about differences in calculated packing energy of the same order of magnitude as differences between

Table 3 Crystal properties of disubstituted benzenes[a]

	Density/g cm^{-3}			Packing energy[b]			Packing coeff.[c]		
Substituents	*o*	*m*	*p*	*o*	*m*	*p*	*o*	*m*	*p*
NH_2, COOH	1.387	—	1.366	101.3	—	107.5	0.728	—	0.716
F, COOH	1.530	1.466	1.439	72.0	91.2	90.0	0.721	0.698	0.686
Cl, COOH	1.538	1.510	1.537	102.9	100.4	100.4	0.729	0.718	0.728
Br, COOH	1.925	1.828	1.851	105.0	99.6	102.1	0.755	0.715	0.728
I, COOH	2.244	2.166	2.182	107.9	105.9	105.0	0.755	0.727	0.732
NO_2, COOH	1.565	1.517[d]	1.610	117.2	104.6	123.0	0.719	0.700	0.742
		1.493[e]			112.9			0.687	
OCH_3, COOH	1.384	—	1.382	80.3	—	107.1	0.732	—	0.730
F, $CONH_2$	1.393	—	1.364	94.6	—	—	0.692	—	0.678
Cl, $CONH_2$	1.355[f]	—	1.430[h]	—	—	103.3	0.664	—	0.701
	1.371[g]	—	1.456[i]	—	—	95.0	0.673	—	0.719
Br, $CONH_2$	1.704	1.735	1.768	—	93.3	107.1	0.694	0.693	0.713
I, $CONH_2$	2.054	2.021	2.098	108.9	108.9	100.4	0.712	0.704	0.731
NO_2, $CONH_2$	1.439	1.473	1.540	120.5	90.8	106.7	0.698	0.703	0.737
NH_2, $CONH_2$	1.284	—	1.374	80.3	—	94.6	0.688	—	0.738
I, CN	2.077	—	2.106	68.6	—	68.6	0.722	—	0.732
NO_2, NO_2	1.572	1.574	1.617	96.2	97.1	100.4	0.698	0.685	0.709

[a] See CSD refcodes in Table S2 (Deposited). [b] kJ mol^{-1}. [c] Kitaigorodski packing coefficient, or ratio of molecular volume to cell volume. [d] First monoclinic phase ($P2_1/c$). [e] Second monoclinic phase ($P2_1/n$), with same space group but different structure. [f] Monoclinic phase. [g] Orthorhombic phase. [h] Triclinic phase. [i] Monoclinic phase.

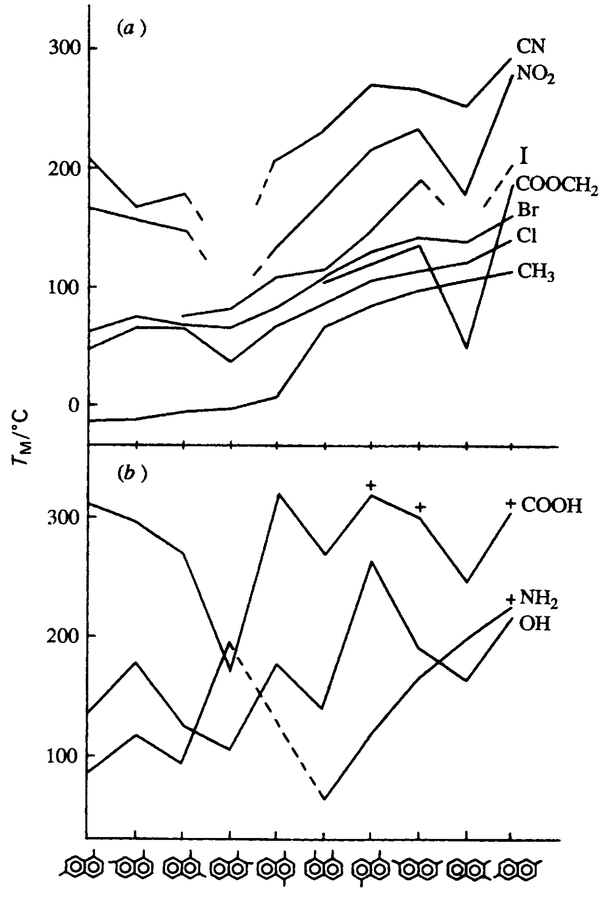

Fig. 5 Melting temperature of disubstituted naphthalenes as a function of substitution pattern (shape 'regularity' increasing from left to right). Dotted lines show guessed trends when data points are missing (when the melting point is not reported in the literature, the compound is usually low-melting). A plus sign indicates decomposition before melting.

isomers. The melting temperature is, in this respect, orders of magnitude more significant than density or packing energy.

Further remarks and conclusions

No proper theory of melting on a molecular basis exists to date and this paper reports just an examination of a large body of data from a semiempirical viewpoint, in an attempt toward systematization. Elementary (*e.g.* Lindemann) theories relate melting temperatures with Debye temperatures; in simple words, this amounts to stating that melting occurs when the amplitude of molecular thermal oscillation is a fixed fraction of intermolecular distance. Most of the assumptions in these theories, and indeed their ultimate premises, stem from consideration of simple (ideally, cubic and monoatomic) solids. Extension to molecular systems, for which many of the key concepts of such theories lose some of their meaning, is dubious. The heat capacities of organic solids do not show as much dramatic change as melting points do. An illuminating discussion of the point has been given (see ref. 12, pp. 28–39).

An attempt systematically to discuss melting properties against molecular shape is in a 1974 paper.[14] The authors synthesized all dimethyl-substituted acenaphthenes, with various point-group symmetries, and determined their melting temperatures, melting enthalpies and crystal cell volumes. The conclusion was that there is no safe ground for ordering thermodynamic values against well established molecular shape parameters. Our analysis confirms that point-group symmetry is not relevant in the description of molecular shape of evenness in connection with crystal packing efficiency.

We demonstrate that (with very few exceptions) *para*-isomers melt higher than *ortho-* or *meta*-isomers no matter what the substituents are, that is, also for heterosubstituted derivatives and for branched and unsymmetrical substituents; this last clause means that this effect depends not on the chemical nature of the substituents, but on the way they are distributed in space, a molecular attribute only loosely connected with true point-group symmetry, even if it is conceded that substituents of similar bulk and shape (*e.g.*, methyl and chlorine) be considered as symmetry-equivalent. *para*-Isomers melt higher even for polar or hydrogen-bonded substances; this finding is of special importance, since it extends the concept of 'regular shape' to molecules with strongly directional intermolecular binding properties, and does away with the usual objection to shape-cohesion arguments—that they hold only for hydrocarbons.

The *para*-substitution pattern then favours the establishment of stronger and easier intermolecular (including hydrogen) bonds, but the reasons for this preference are far from clear. Molecular centrosymmetry is not relevant either, since the rule holds also for hetero-disubstituted compounds. True point-group centrosymmetry seems to be replaced by a sort of pseudosymmetry, according to which the structure of the substituent is blurred and what counts is just bulk, or a broad distribution of bulk in space. Two blobs aligned with the centre of the phenyl ring are better suited for packing than two blobs along directions forming a 120° or 60° angle at the centre of the phenyl ring. How and why this observation is related to the various contributions of the intermolecular forces involved, and to their consequences on crystal structure adoption, is a question that still awaits an answer.

The results on the naphthalene derivatives lead to similar conclusions, although the symmetry-shape argument is even more awkward. We note only that the 2,6-isomer, the highest-melting, is centrosymmetric (in a strict sense, since only homosubstituted derivatives were considered), but so is the 1,5-isomer, which often melts far lower than non-centrosymmetric counterparts.

Finally, our results prove that molecules with a strong electrical dipole need not pack in more compact and more stable crystals. *para*-Substitution in benzenes and 2,6-substitution in naphthalenes are the least favourable for the development of such a dipole in homosubstituted derivatives or when the two substituents have the same polarity, and yet our results prove that *para*-disubstituted benzenes and 2,6-naphthalenes have higher melting temperatures and melting enthalpies than the other isomers, regardless of the nature of the substituents.

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