Altona, Buys & Havinga, 1969) (see the relevant torsion angles in Table 4) and an isopropyl group does not lead to efficient crystal packing in the β-mode. Another significant conclusion emerging from these studies is that the role of chlorine as a universal steering group is not applicable to all molecular frameworks, especially if it is significantly non-planar.

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Molecular Packing of Crystalline Azahydrocarbons

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Abstract

The crystal structures of 458 azahydrocarbons, that is, organic molecules containing C, H and N atoms without N—H···N hydrogen bonding, have been retrieved from the Cambridge Structural Database. Statistical analyses of molecular and crystal parameters were performed, and the results compared with hydrocarbons and oxygen-containing compounds. Average atomic contributions to molecular volumes, surfaces and packing energies were obtained. Packing coefficients are just slightly lower than for hydrocarbons, showing no clear sign of breakdown of close packing, while the crystal density increases with increasing nitrogen content as expected. Some evidence of weak C—H···N hydrogen bonding appears, especially with nitrile N atoms, while no unusually short C···N intermolecular distances are observed.

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Lattice energies calculated with several sets of literature parameters were compared with sublimation heats, and lattice vibration frequencies were calculated. Schemes for the prediction of sublimation energies are given.

Introduction

In previous work, some structural properties of crystalline organic compounds were analyzed using samples of 391 hydrocarbon crystal structures (Gavezzotti, 1989, 1990*a*) and 590 oxahydrocarbon crystal structures (Gavezzotti, 1991) retrieved from the Cambridge Structural Database (CSD) (Allen, Kennard & Taylor, 1983). The obvious extension of that work is to consider the analogous nitrogen-containing compounds, and this paper describes a statistical analysis of the crystal properties of azahydrocarbons not forming hydrogen bonds [a restricted sample of mononitriles has already been studied (Gavezzotti, 1990*b*)]. The geometrical and energetic trends among crystal structures in the three data sets will be the starting point for the formulation of a generalized force field for intermolecular interactions in non-hydrogen-bonded organic crystals.

Molecular and crystal properties

The CSD was searched for crystal structures containing C, H, N atoms with crystal coordinates for all non-H atoms, at room temperature, without disorder or unresolved ambiguities. Compounds with N—H bonds, charged residues, solvate or clathrate molecules, were excluded; crystal structures with more than one molecule in the asymmetric unit were not considered, since they pose small technical problems in the calculations, and the choice among other structures was already a wide one. H-atom positions were assigned as previously described (Gavezzotti, 1991). The final data set consisted of 458 crystal structures; Table 1(deposited)* contains the CSD refcodes. Table 2 summarizes the size and stoichiometry of the compounds.

Molecular and crystal properties (Gavezzotti, 1989, 1990*a*, 1991) were calculated for each compound. The *Appendix* gives a summary. The crystal-packing energies were calculated using empirical atom–atom potentials (Mirsky, 1978; see also Mirskaya & Nauchitel, 1972) of the 6-exp type (see *Appendix*), without explicit Coulombic (that is, R^{-1}) terms. We call this scheme Mirsky-7 (M7), or Mirsky-10 (M10), according to the value of the cutoff imposed in the lattice sums, 7 or 10 Å. A more accurate formulation has been proposed for a restricted set of azahydrocarbons by Williams & Cox (1984), including Coulomb terms and accelerated convergence of lattice sums (we call this scheme Coulomb-convergent Williams, or CCW). As for oxahydrocarbons, this parametrization is not readily transferable, and is not applicable to larger molecules, since atomic charges must be evaluated for each molecule from high-quality *ab initio* wavefunctions. Another parameter set of the 6-exp form for nitrogen-containing crystals has been proposed by Govers (1975); we call this scheme G10. Unless otherwise stated, the statistical results in the following sections refer to M7 calculations, which are suitable for application to moderately polar substances – the large majority within our data set. A section of this paper will be devoted to a comparison of the different data sets, and to an analysis of short N···H interactions.

Table 2. *Averages and ranges of some molecular properties within the database* (*see Appendix for the definition of symbols*)

Property	Average	Range
W_m (Da)	265	51–706
S_m (Å^2)	292	76–793
V_m (Å^3)	256	53–702
$N_{\rm atoms}$	38	5–108
Z_p	0.217	0.033–2.000

Correlations

The calculated packing potential energy, PPE, correlates with the usual molecular size descriptors (Table 3); the correlation parameters are quite similar to those for hydrocarbons and oxahydrocarbons. The heat of sublimation can be estimated (Gavezzotti, 1989) from these correlations as $\Delta H_{\rm sub} \simeq$ PE(7 Å)/0.8 (where PE = $\frac{1}{2}$PPE is the packing energy), since a 7 Å cutoff produces about 80% of the total lattice energy. Fig. 1 shows molecules for which both the crystal structure and experimental sublimation heat are available; Fig. 2 shows compounds for which only the latter is available.

Table 4 shows the fair agreement obtained between the sublimation heats estimated from the correlations and the experimental values. Estimating the packing energy using the total number of valence electrons in the molecule implies that differences in polarizability are neglected. Table 4 shows that the sublimation energies are underestimated for nitrile compounds, and less so for compounds containing aromatic or tertiary N atoms. The sublimation energy is on the other hand often overestimated for small-size globular molecules, where the crystal may

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* A list of CSD refcodes for the compounds considered has been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54955 (4 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Parameters for the linear regression* $PPE = aX + b$ *or* $PPE = aX + bY + c$ (kJ mol^{-1})

PPE at 7 Å cutoff; root-mean-square deviations are between 5.8 and 6.2. See *Appendix* for the definition of symbols.

X or X, Y	a	b	c
$N_{\text{non-H}}$	6.49	48.1	
W_m	0.50	46.4	-
Z_v	1.301	47.3	
V_m	0.494	51.9	-
S_m	0.464	42.7	-
S_{250}	0.489	4.1	
S_{250}, C_s	0.519	56.1	−27.2
S_{250}, Z_p	0.444	−52.3	31.8

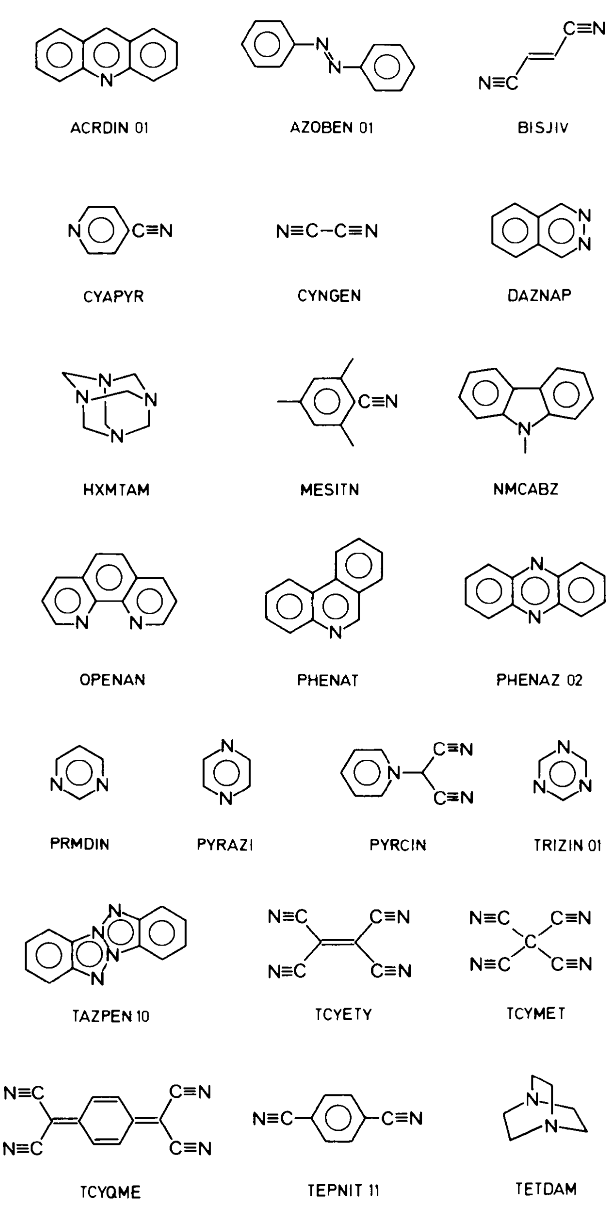

Fig. 1. Molecules for which both the crystal structure and experimental sublimation heat are available.

be perturbed by large-amplitude molecular rotations (some of the cage compounds in Fig. 2 are known to form plastic crystals). For PYRCYN, the large underestimation of ΔH_{sub} may arise from the fact that the compound is a zwitterion or carries fully-developed charges; however, for TAZPEN10, the experimental ΔH_{sub} seems too low from comparison of several values for similar compounds (see footnote *n*, Table 4).

Table 5 reports the observed crystal densities and other packing parameters for azahydrocarbons. As for oxahydrocarbons, the crystal density increases with increasing heteroatom content, as described by Z_p (Fig. 3); the lower threshold for the crystal density is $D_c = 0.42Z_p + 0.92$ Mg m^{-3}. Apparently, the packing coefficient also increases with increasing nitrogen content, although the effect is barely significant.

Table 6 shows the results of a principal-component analysis on molecular and crystal properties. D_c and D_{el} represent crystal compactness, W_m and Z_v represent molecular size, Z_p describes the heteroatom content and the other variables describe molecular shape. For hydrocarbons and azahydrocarbons, molecular size, molecular shape and crystal compactness descriptors mix in the first two eigenvectors, while for oxahydrocarbons the correlation to crystal compactness is mostly absorbed by Z_p.

Table 7 reports average atomic increments to molecular volume and surface, as well as the average atomic contributions to PPE, E_i (see *Appendix*). These data allow an estimation of the molecular volume, molecular surface and packing energy for any C,H,N-containing molecule, by summing the appropriate atomic contributions.

N···H and N···C contacts in azahydrocarbons

Fig. 4 shows histograms for the E_i of the three types of N atom (M7 parameterization). In this figure, the dashed areas refer to atoms having repulsive contacts

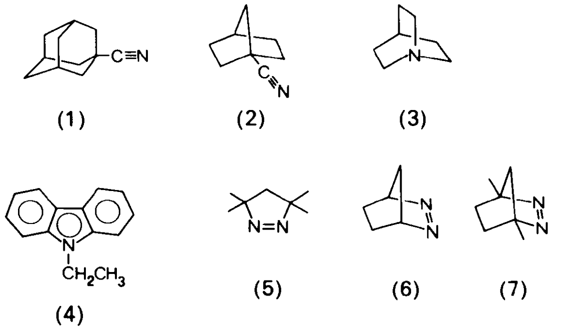

Fig. 2. Molecules for which only the experimental sublimation heat is available.

Table 4. *Heats of sublimation: experimental values and estimated values from the correlations in Table* 3 (kJ mol^{-1})

	$\Delta H_{\rm sub}$(exp)	From S_{250}	From Z_v
ACRDIN01	90.8^a, 94.6^b	82.0	83.3
AZOBEN01^c	92.0	81.2	84.9
BISJIW^d	69.5	56.9	52.3
CYAPYR^e	73.2	61.1	60.2
CYNGEN^f	36.4	43.9	44.4
DAZNAP^g	96.7	65.3	68.6
HXMTAM	74.9^f, 78.7^d	61.1	74.9
MESITN^h	77.8	79.5	74.9
NMCABZ^i	95.4	77.4	84.9
OPENAN^k	98.3	71.1	83.3
PHENAT	94.6^f, 108^k	82.0	83.3
PHENAZ02	90.4^a, 100^l	81.2	83.3
PRMDIN^f	48.9	49.0	54.0
PYRAZI^f	60.7	48.5	54.0
PYRCYN^m	125.5	77.0	72.0
TAZPEN10^n	70.3	88.7	91.2
TCYETY	86.2^f, 84.1^d	77.4	65.3
TCYMET^o	61.1	73.2	61.9
TCYQME^p	105.8	105.	88.3
TEPNIT11^q	88.7	73.2	66.9
TETDAM03^t	63.6	56.5	66.9
TRIZIN01	54.4^r, 58.2^d	48.5	54.0
(1)^{h,s}	76.1	–	81.6
(2)^h	61.9		68.6
(3)^t	50.6		66.9
(4)^t	99.2		89.5
(5)^u	61.5	–	72.0
(6)^u	55.2	–	60.2
(7)^u	72.0	–	70.3

References: (*a*) McEachern, Sandoval & Iniguez (1975), (*b*) Steele, Chirico, Hossenlopp, Nguyen, Smith & Gammon (1989), (*c*) Bouwstra, Oonk, Blok & De Kruif (1984), (*d*) De Wit, Van Miltenburg & De Kruif (1983), (*e*) Bickerton, Pilcher & Al-Takhin (1984), (*f*) as quoted in Williams & Cox (1984), (*g*) Mills (1973), (*h*) Meier, Dogan, Beckhaus & Ruechardt (1987), (*i*) Jimenez, Roux & Turrion (1990), (*j*) McEachern, Iniguez & Ornelas (1975), (*k*) see the discussion in reference at footnote *b* of this table, (*l*) Arshadi (1980), (*m*) Cox & Pilcher (1970), (*n*) Chia & Simmons (1967), (*o*) Barnes, Mortimer & Mayer (1973), (*p*) Kersten & Oppermann (1984), (*q*) Sato-Toshima, Sakiyama & Seki (1980), (*r*) Bystrom (1982), (*s*) crystal structure not available for (1)–(7), (*t*) Westrum, Wong & Morawetz (1970), (*u*) Engel, Melaugh, Mansson, Timberlake, Garner & Rossini (1976). For a review on heats of sublimation for organic compounds, see Chickos (1987).

in the first coordination shell, mostly originating from short N···H contacts. Nitrile nitrogens have the largest number of these interactions, but quite a few also appear for =N— nitrogens. There are none in tertiary N atoms.

Fig. 5 shows the distribution of intermolecular N···H and N···C contacts in azahydrocarbons, together with the Mirsky and Govers potential-energy curves. Using the former potentials, the population of N···H contacts with repulsive energies > 0.8 kJ mol^{-1} is rather high, although apparently smaller than it was in oxahydrocarbons for O···H contacts (Gavezzotti, 1991). Since most of these apparently repulsive contacts appear for nitrile and aromatic nitrogens, near which more readily accessible regions of high electron density can be found, we conclude that the repulsions are due to a shortcoming of the M7 scheme, which fails to recognize what are in fact attractive interactions of broadly electrostatic character (a perhaps more intuitive representation could be as attractions between partial atom charges, although these are ill-defined quantities). The results of Figs. 4 and 5 therefore demonstrate the existence of weak or moderate C—H···N hydrogen bonds. A definition of the type of H atoms involved in such short contacts was not attempted, since this effect is a complex function of the chemical environment. The C—H···N hydrogen bond spans the region 2.25 < R(N···H) < 2.60 Å (slightly longer than the C—H···O bond). Fig. 6 shows the scatterplot for the C—H···N angle as a function of the N···H distance; the directional selectivity appears to be very weak, interactions being limited only by the N···C distance of closest approach (about 3.25 Å, as for the sum of standard van der Waals radii).

Table 5. *Parameters of crystal compactness*

HYD hydrocarbons, OXA oxahydrocarbons, AZA azahydrocarbons. See *Appendix* for the definition of symbols.

Z_p range	No. of crystals	D_c	$D_{\rm el}$	C_k
0.0–0.2	287	1.193	0.387	0.709
0.2–0.4	114	1.271	0.403	0.717
0.4–0.6	37	1.306	0.413	0.720
0.6–0.8	9	1.408	0.435	0.737
> 0.8	12	1.485	0.462	0.730
All AZA	458	1.231	0.394	0.711
All HYD	391	1.198	0.387	0.717
All OXA	590	1.297	0.416	0.696

Short C···N contacts are sparse in azahydrocarbons, and the number of contacts giving repulsive interactions according to Mirsky potentials is negligible or, at least, not distinguishable from the noise

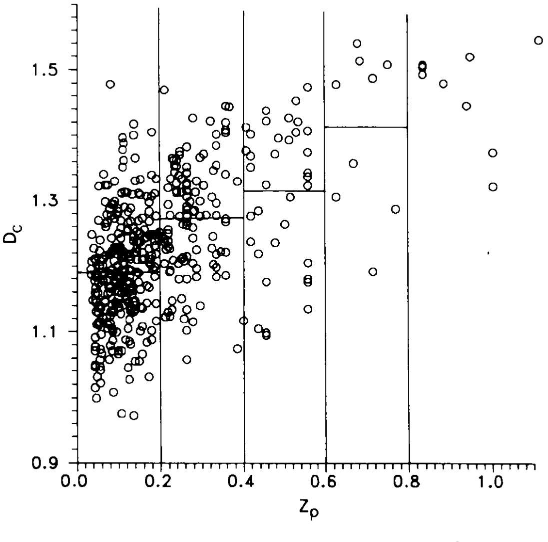

Fig. 3. A scatterplot of the crystal density (Mg m^{-3}) against Z_p (see *Appendix* for definition). Horizontal bars mark the average value for each section.

Table 6. *Principal-component analysis*

		Factor components							
	Eigenvalue	D_c	D_{el}	W_m	Z_v	C_s	F_c	R_s	Z_p
HYD	3.23	0.61	0.57	0.92	0.89	−0.49	−0.33	0.74	
OXA	3.09	–	–	0.95	0.95	−0.75	0.11	0.83	0.13
AZA	3.95	−0.63	−0.62	0.85	0.87	−0.76	−0.11	0.78	−0.69
HYD	1.35	−0.77	−0.80	0.24	0.30	−0.51	0.22	0.36	
OXA	2.49	0.96	0.97	–				–	0.78
AZA	1.89	0.75	0.75	0.45	0.40	–	−0.32	0.43	0.32
HYD	1.06	–		0.15	0.15	0.52	0.86	0.26	
OXA	1.15	0.10	–			0.34	0.94	0.33	−0.15
AZA	1.04		–	0.12	0.11	0.30	0.92	0.27	–

Table 7. *Average volumes and surfaces for atoms in molecules, and atomic contribution to the* M7 *PPE* (*for the central atom in each scheme*)

				E_i (kJ mol^{-1})		
	No. of hits†	V (Å^3)	S (Å^2)	OXA	HYD	AZA
H	7984	2.3	6.52	2.68	2.80	2.64
N atoms						
C≡N	337	9.9	17.8	–	–	5.94
N*C*C‡	193	7.9	10.8	–		5.77
N=N—N	30	9.2	12.0		–	6.15
C=N—C	300	6.2	9.1	–	–	5.52
(CC)N(N)	92	4.2	3.6			4.94
(CC)N(C)	315	2.9	2.9	–	–	4.23
C atoms						
(CC)C(C)	1033	8.2	5.2	5.94	5.52	5.61
(O,N)C(H_3)	172	16.8	12.3	9.20	–	7.99
(C)C(H_3)	497	15.3	11.5	7.87	7.28	7.20
(CC)C(H_2)	695	11.9	6.9	6.86	7.07	6.74
(CCC)C(H)	342	8.6	3.3	5.52	5.52	5.15
(CCCC)C	157	5.1	1.0	4.31	4.02	4.02

† In azahydrocarbons.

‡ Asterisks denote any type of bond.

resulting from inaccurate geometrical data. While in oxahydrocarbons directional C···O forces clearly appeared, there is no evidence of special C···N interactions in our data. This fact can be explained simply in terms of electronegativity differences.

Comparison of crystal potentials for azahydrocarbons

Fig. 7 shows the Mirsky and Govers potential-energy curves for N···H. A deep attractive well is evident in the Govers curve, the minimum being at an N···H distance (2.75 Å) where a substantial population of N···H contacts appears in the existing crystal structures (Fig. 5*a*). The function accounts in a satisfactory way for the short N···H interactions. Fig. 8 shows the same for C···N potentials; the Govers minimum is located at about 2.7 Å, where our histogram of the density of intermolecular contacts (Fig. 5*b*) shows no population. The position of this minimum is therefore unrealistic and, while it is unharmful when the potential is used for calculation of the energy of known crystal structures, it could prove dangerous if the potential were used for crystal structure prediction. We have applied a correction, shifting the minimum to the extreme region of observed C···N contacts (3.0 Å): this correction obviously does not alter the energy calculated for experimental structures. Table 8 gathers together the values for all potential parameters.

To test the potential functions thoroughly, we have calculated a number of crystal properties for the compounds in Fig. 1, as well as for other compounds (Fig. 9) used either in the calibration of CCW parameters, or in which the nitrile groups presumably play a major role in the crystal packing. Table 9 shows the results. The calculations include structure optimization under the action of the specified potentials; for the M10 and G10 calculations, only the rigid-body librational and translational degrees of freedom have been relaxed, while the CCW procedure also includes the optimization of cell parameters. We have checked that the difference between 10 Å cutoff and full convergence is insignificant.

Table 9 also shows the range of lattice-vibration frequencies calculated by a method described previously (Filippini & Gramaccioli, 1989, and references therein), within the harmonic approximation.

Discussion

For nitrogen-containing compounds without N—H···N hydrogen bonds, the crystal density increases as expected with increasing nitrogen content and close packing is not affected by the presence of the heteroatoms, as demonstrated by the value of the packing coefficients. The M10 potential-energy scheme is acceptable for molecules with a small nitrogen content or weak bond polarity, but proves quite inaccurate, for example, for crystals containing nitrile groups or even aromatic N atoms, where the packing is complicated by electrostatic effects and interactions of the hydrogen-bond type. Their presence is revealed when a statistical survey of appropriately partitioned energies is carried out (see Fig. 5). C—H···N attractive interactions are widespread, and, like C—H···O interactions (Desiraju, 1991), may be structure defining.

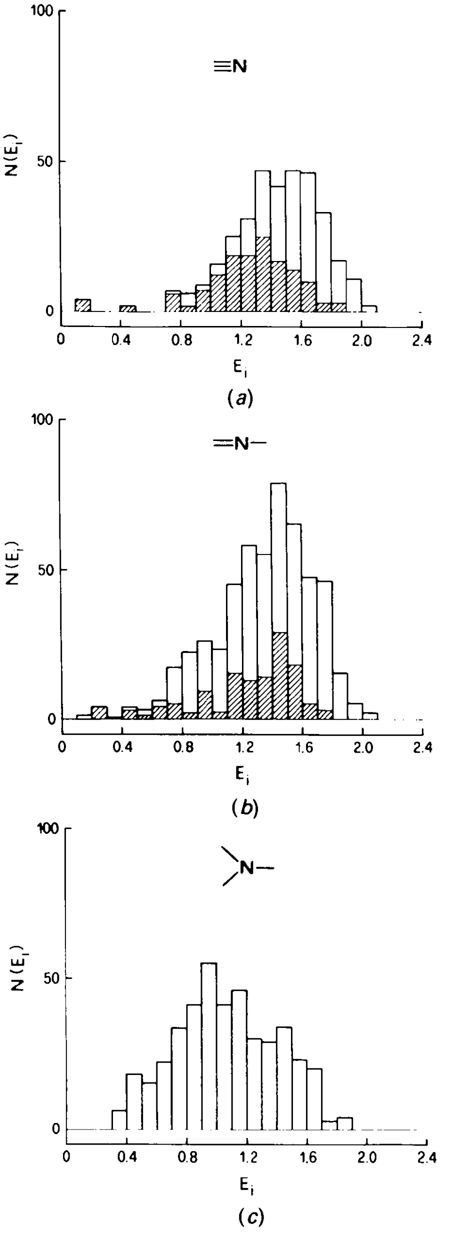

Fig. 4. Histogram of the N-atom contributions to PPE (E_i, see *Appendix*) for (*a*) ≡N, (*b*) =N—, and (*c*) >N—. Dashed areas: cases in which repulsive contacts in the 2 to 3 Å shell around the atom are present, although the overall contribution is still attractive.

The comparison between calculated and experimental sublimation heats (Table 9) shows that the CCW scheme is the most accurate, but the G10 scheme is almost as accurate. The average percentage deviation, |(obs. − calc.)|/obs., is 7.1 for CCW and 9.3 for G10, for the eight crystals for which this comparison is possible. The average deviation for G10 increases to 10.4 over 20 compounds (Table 9; TAZPEN10 and PYRCYN, however, were excluded

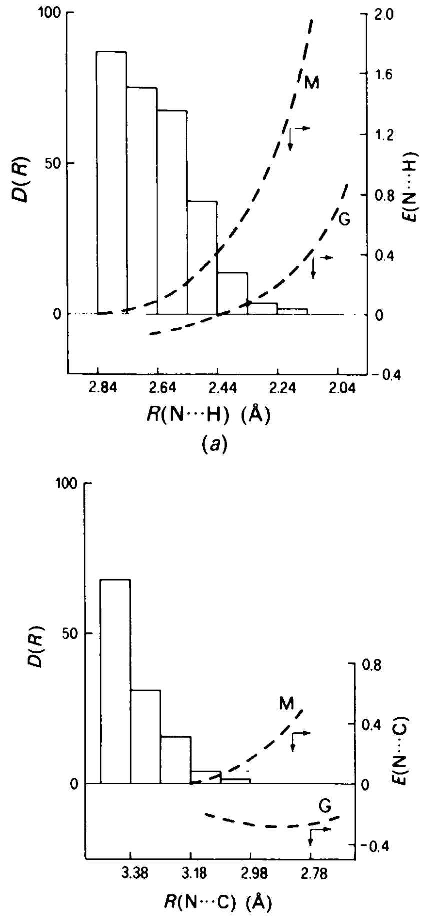

Fig. 5. Radial density of (*a*) N···H and (*b*) N···C intermolecular contacts in the azahydrocarbon sample; the curve is the pertinent Mirsky 6-exp nonbonded potential (energy scale on the right; units are kcal mol^{-1}; 1 kcal = 4.184 kJ). $D(R) = N_{\text{contacts}}/(4\pi R^2 dR)$.

for the reasons discussed previously). The performance of the G10 scheme is therefore remarkable in spite of it being of the simple 6-exp form, without the need for *ad hoc* site charges to be determined for each molecule. This result demonstrates that electrostatic interactions can be incorporated to a large extent into simple 6-exp potential functions, at least for the calculation of packing energies.

All major discrepancies between calculated packing energies and observed heats of sublimation, with the exception of DAZNAP, are for nitrile compounds, another result that points to the very special interactions that must be present in such crystals. Nevertheless, the sublimation heats for TCYMET and TCYQME are well reproduced.

The calculation of lattice-vibration frequencies and of thermodynamic functions and atomic displacement parameters is more critical than the simple calculation of the packing energy, since it must rely on the second derivatives of the potential functions. Unfortunately, comparison with the Raman and IR experimental frequencies is seldom possible, due to the lack of experimental data, but calculated frequency ranges of 20–130 cm^{-1} can be considered a reasonable result and a preliminary validation of the potential functions used in the calculations. Conversely, imaginary calculated frequencies reveal shortcomings of the potential functions and/or anharmonicity of the molecular motion in the crystal. It is symptomatic that imaginary frequencies or inability to optimize the rotational and translational degrees of freedom usually go together with disagreement between the calculated packing energy and the observed sublimation enthalpy.

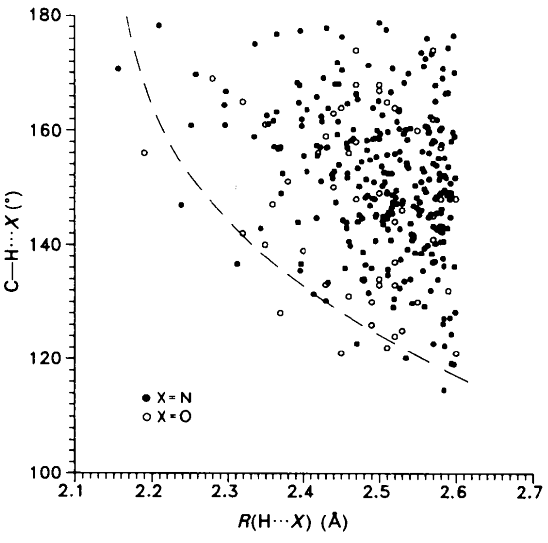

Fig. 6. A scattergram of $X\cdots$H—C angles *versus* $X\cdots$H distance (unique contacts only) for oxa- and azahydrocarbons. The curve denotes points at which the C and X atoms are in contact [$R(\mathrm{C}\cdots X) = 3.25$ Å].

Table 8. *Atom–atom potential function parameters of the form*: $E = A\exp(-BR_{ij}) - CR_{ij}^{-6}$ (*where the units are* kJ mol^{-1} *and* Å)

		A	*B*	*C*
Mirsky	N···N	175728	3.78	1084
	C···N	231375	3.73	1387
	N···H	60250	4.00	381
Govers	N···N	440994	3.60	3180
	N···C	48032	3.60	1569
	N···H	20221	3.67	598
Modified	N···C	64095	3.60	1715

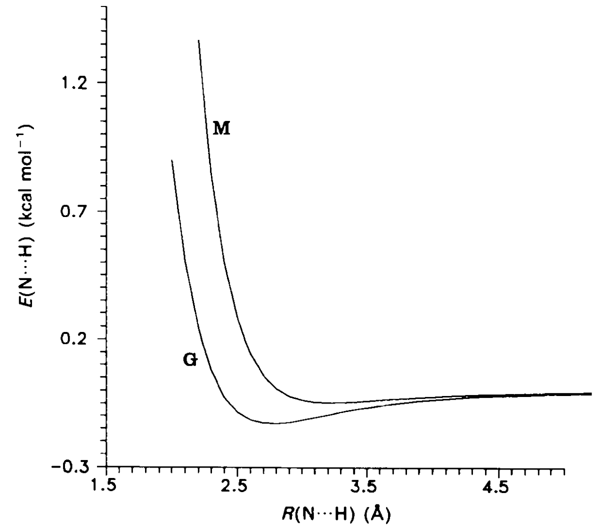

Fig. 7. Mirsky (M) and Govers (G) 6-exp N···H non-bonded curve.

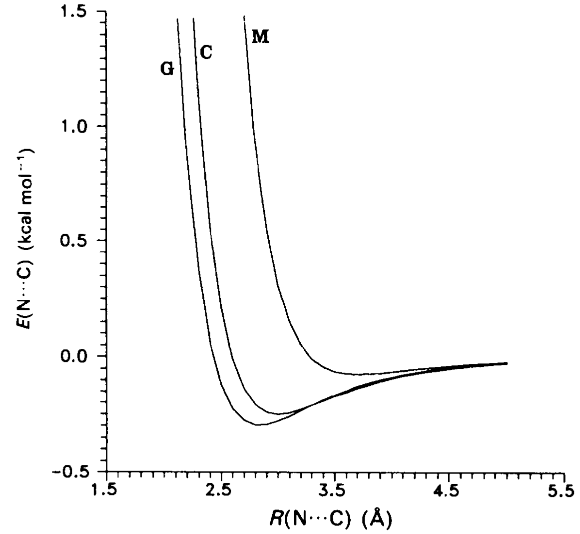

Fig. 8. Mirsky (M), Govers (G) and modified (C) 6-exp N···C non-bonded curves.

Table 9. *Heats of sublimation, calculated packing energies* (kJ mol^{-1}) *and lattice frequencies* (cm^{-1})

	ΔH_{sub} (exp)	M10	G10	CCW[a]	Frequencies[b] M10	Frequencies[b] G10
ACRDIN01	92.9	85.8	100.4	–	21–118	19–125
AZOBEN01	92.0	84.1	97.9	–	29–96	28–112
BISJIW	69.5	29.7	47.7	–	25–104	17–75
CYAPYR	73.2	40.2	61.9	–		
CYNGEN	36.4	14.6	29.7	35.1		
DAZNAP	96.7	55.6	73.6	–	8–91	
HXMTAM	77.0	64.4	75.7	80.8	52	51
MESITN	77.8	61.1	71.1	–	1–123	15–129
NMCABZ	95.4	79.1	90.4	–	16–102	18–110
OPENAN	98.3	75.3	94.1	–	15–103	15–109
PHENAT	100.8	79.9	93.7		18–72	20–80
PHENAZ02	95.4	82.8	100.4	103.3	35–85	35–99
PRMDIN	48.9	36.8	51.5	56.5	17–100	16–79
PYRAZI	60.7	35.1	51.9	53.6		
PYRCYN	125.5		89.5	–		15–68
TAZPEN10	70.3	90.0	121.8		18–96	21–102
TCYETY[c]	85.4[e]	33.5	64.8	–		18–73
TCYETY01[d]		33.9	65.8	90.8	31–93	43–110
TCYMET	61.1	29.3	56.9	–	13–124	38–143
TCYQME	105.8	65.3	104.2	–	25–94	27–88
TEPNIT11	88.7	51.5	75.3	–	48–75	43–68
TETDAM03	63.6	60.7	66.9	66.9	32–80	25–80
TRIZIN01	56.1	33.1	56.1	55.2		25–70
BUGKIX	–	31.8	62.8	–	31–95	26–93
CAACTY		20.1	35.6	–		
FAJXUJ	–	88.7	114.6		24–72	19–76
FITSEG	–	39.3	70.3	–		
TCNCBT	–	44.8	92.0	–	35–112	23–79
TCYCPR	–	39.7	75.7	96.2	19–99	23–95
TETRAZ		29.3	53.6	61.1	33–107	37–132

Notes: (*a*) From Williams & Cox (1984). (*b*) No entry means inconsistencies in the optimization of rigid-body motion parameters, or imaginary frequencies. (*c*) Cubic phase. (*d*) Experimental sublimation heat without specification of the crystal phase.

It is encouraging to see that in most cases the atom–atom potentials derived from purely static crystal properties may be used to describe the lattice dynamics. This supports the view that the atom–atom potentials are not merely phenomenological functions used to fit experimental data, but indeed simulate the actual intermolecular potential (Pertsin & Kitaigorodskii, 1987). However, 23% of the structures considered here showed inconsistency in the lattice-dynamical calculations, either during minimization of the packing energy, or in the derivation of lattice frequencies (at least one negative eigenvalue, see Table 9). A detailed analysis of these cases, and attempts to further improve the design of the potentials in this respect, are beyond the scope of the present paper.

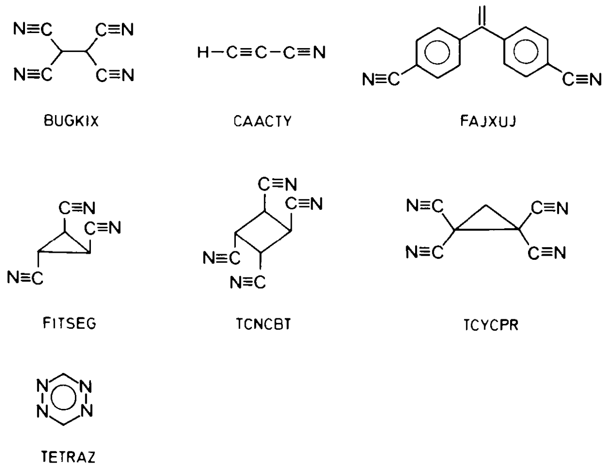

Fig. 9. Other compounds (in addition to those in Fig. 1) used to test the potential functions (see text).

The results shown in Figs. 5, 7 and 8 illustrate how fruitful a survey of purely geometrical data can be, as can the distribution of intermolecular distances. Such a survey clarifies the meaning of the so-called van der Waals radii, which, following Kitaigorodskii's early intuition, provides a measure of the threshold separation below which no contacts are observed in organic crystals, unless supplementary attractive interactions exist. In addition, it provides a guide to the location of minima in potential-energy curves; since sublimation energies provide a check of the well depth, and lattice vibrations or cell-parameter variations help in modelling the repulsive part of the potential, the results so far collected along these lines for hydrocarbons, oxahydrocarbons and azahydrocarbons promise a large improvement in the presently available potential functions for C-, H-, N-, O-containing crystals for comparatively little effort. The derivation of comprehensive and transferable empirical potentials for such compounds, without hydrogen bonds, is currently being pursued (Filippini & Gavezzotti, work in progress). Nothing forbids application of the same strategy to hydrogen-bonded crystals.

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APPENDIX

Definition of symbols

(1) 6-exp potentials: the interaction between atoms i and j in the crystal is

$$E = A\exp(-BR_{ij}) - CR_{ij}^{\;6},$$

where A, B and C are paremeters to be specified for each couple of atomic species; the lattice energy is obtained by appropriate double summations over i and j, and is always a negative number, although in the tables the minus sign is omitted for brevity.

(2) W_m is the molecular weight, S_m the molecular van der Waals surface, V_m the molecular van der Waals volume; N_{atoms} is the total number of atoms, Z_v the total number of valence electrons in the molecule. S_{250} is the molecular surface obtained by ignoring H atoms and setting all other atomic radii to 2.5 Å (a type of available outer surface). C_s is the self-packing coefficient, or the ratio of the molecular volume to the volume of the parallelepiped containing the molecule. Z_p is the ratio of the number of valence electrons for N atoms to the number of those for C and H atoms (an index of nitrogen content).

(3) D_c is the crystal density, D_{el} is the total number of electrons in the cell divided by the cell volume, C_k is the Kitaigorodskii packing coefficient, or total molecular volume in the cell divided by the cell volume.

(4) F_c is the cylindrical index, or $0.5(M_1 + M_2)/M_3$, the M's denoting the moments of inertia in descending order, R_s is a sphericity index defined as the difference between $\frac{1}{3}$ of an average molecular radius and the volume/surface ratio; since this ratio is just $R/3$ for a sphere, deviations of R_s from zero are deviations from sphericity.

(5) E_i is the part of PPE that is ascribed to atom i in the molecule, as obtained by an appropriate breakdown of the double sums in the lattice energy. Unless otherwise stated, it is a negative number, although in the figures and tables the minus sign is omitted.

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