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Empirical Intermolecular Potentials for Organic Crystals: the '6-exp' Approximation Revisited

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Abstract

Empirical intermolecular potentials have been developed for organic crystals containing C, H, N, O, Cl and S atoms without hydrogen bonds, using atom–atom radial functions in the form $E = A\exp(-BR) - CR^{-6}$. The number of disposable parameters is thus reduced to a minimum, there is no need to evaluate atomic or site charges, and convergence problems connected with the use of Coulombic R^{-1} terms are avoided. The optimization of the potential parameters A, B, C for each pair of atomic species has been carried out using as observables the distribution of atom–atom distances in 1846 organic crystals, the heats of sublimation of 122 compounds, and the structural data (rigid-body positional parameters and cell dimensions) for 217 crystals. On average, the agreement with sublimation heats is better than 2 kcal mol^{-1}, and the observed crystal structures are stable, under the action of the postulated potentials, within small displacements. Calculated harmonic lattice vibration frequencies compare favourably with available measured frequencies, and are quite reasonable in general. The potentials are transferable and successful in the description of some essential crystal properties; their simple formulation may substantially reduce the computing times in large-scale molecular dynamics or molecular recognition applications, or in crystal structure prediction studies where they can be used for a first screening of a very large number of trial structures.

Strategy

A simple but reliable procedure for the calculation of the intermolecular potential energy in organic crystals is highly desirable, both from a theoretical and from a practical point of view. Many properties of these crystals can be obtained from such calculations, and eventually the crystal structure might become predictable from molecular structure alone. A great computational simplification is achieved in the so-called atom–atom approximation (Pertsin & Kitaigorodski, 1987), by which the total lattice energy is a sum of two-body interactions only. Each of these is in turn a sum of terms which are supposed to represent the various interactions between atoms of different molecules in crystals. The number and type of these terms may vary, and, as is usually the case in empirical formulations, their one-to-one correspondence to physical effects is questionable. Unless separate evidence or first-principles calculations are available, a better philosophical and practical attitude is to consider all the parameters as disposable instruments for the overall fit to a selection of geometrical, physical or thermodynamic crystal properties.

A question of economy then arises, as the value of an empirical scheme increases with the ratio of the number of properties it is able to predict to the number of parameters it must use. In this age of superfast and relatively inexpensive computers, the trend in the calibration of empirical force fields is to increase the number of disposable parameters. Commonly encountered in both intra- and intermolecular fields are atomic (or site) charges, derived by fitting the molecular electrostatic potential (Merz, 1992; Williams, 1991) and used in the calculation of Coulombic contributions to interaction energies. To ensure the reliability of the molecular wavefunction, a high-quality *ab initio* molecular orbital calculation must be carried out, and this is still problematic for very large organic molecules. If a low-quality wavefunction is accepted, then the derived atomic or site charges must be regarded as no more than supplementary disposable parameters, with the further disadvantage of being non-transferable. It has been shown that these charges also depend on molecular conformation (Stouch & Williams, 1992). Today, computer simulations of condensed phases or crystal structure prediction (Gavezzotti, 1991*a*; Gdanitz, 1992) require the survey of multidimensional phase spaces, where the intermolecular potentials are to be recalculated a very large number of times. Simpler potentials and the removal of the convergence problem connected with the R^{-1} terms may save a considerable amount of computer time (Perlstein, 1992). Therefore, in the present work we have reconsidered the optimization of empirical parametric functions in

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the simplest form, the so-called '6-exp' potential:

$$E_{ij} = A\exp(-BR_{ij}) - CR_{ij}^{-6}$$

where the double index designates any couple of atoms in different molecules, at a distance R_{ij}. A, B and C are parameters established for each $X\cdots Y$ interaction, X or Y being C, H, N, O, S or Cl, and the total packing energy is a lattice sum over i and j. The following expressions convey the dependence upon the well depth ε, the interatomic separation at the minimum R^0, and the steepness parameter λ:

$$A = 6\varepsilon(\exp\lambda)/(\lambda-6); \quad B = \lambda/R^0; \quad C = \varepsilon\lambda(R^0)^6/(\lambda-6).$$

A considerable amount of work has been devoted in the past to the development of 6-exp potentials, and a comprehensive review (Pertsin & Kitaigorodski, 1987) is available.

The crystal properties of the elemental compounds have often been used to calibrate the potential between atoms of the same kind, relying on averaging rules for cross interactions. A key role has thus been played by N_2, O_2, Cl_2, CO_2, or S_8; but these molecules, and their crystals, are radically different from the molecules and the crystals of everyday organic chemistry. Even when the crystal properties of larger molecules were used for the calibration, the parameters for mixed interactions were often constrained to some sort of average, to reduce the number of parameters in view of the small number of available experimental data. Since a very large amount of structural data, and a substantial amount of thermochemical and vibrational data, are now available for organic crystals, the separate optimization of $X\cdots X$, $Y\cdots Y$ and $X\cdots Y$ parameters is a cornerstone of our procedure. In particular, a careful optimization with an increase of the well-depth parameter for the cross interactions simulates the missing electrostatic attraction terms (Pertsin & Kitaigorodski, 1987, p. 74).

Clearly, the peculiar features of the hydrogen bond are beyond the reach of such a simple formulation, which can nevertheless be considered as the ideal starting point for the extension to the treatment of X—H$\cdots Y$ interactions (X and Y being oxygen or nitrogen).

Preparation of the database

Crystal structures

Samples of organic crystal structures were extracted from the Cambridge Structural Database (CSD; Allen *et al.*, 1979), according to the following general principles: (i) no $X—H\cdots Y$ interactions with X, Y = N, O are present (*i.e.* no fully developed hydrogen bonds); (ii) the molecular size and composition is comparable to that of usual organic compounds (no molecules smaller than, say, benzene); (iii) room-temperature structures and crystal properties are preferred; (iv) the composition of each sample is established in order to single out the contributions of each kind of $X\cdots Y$ interaction.

The samples which have been selected are as follows:

(i) Hydrocarbons (C and H atoms only) (Gavezzotti, 1989): test for C···C, C···H and H···H interactions; 391 crystal structures. The potentials optimized for this sample have been assumed to be transferable to the hydrocarbon part of the other samples.

(ii) Oxahydrocarbons (C, H and O atoms) (Gavezzotti, 1991*b*): test for H···O, C···O and O···O interactions; 590 crystal structures.

(iii) Azahydrocarbons (C, H and N atoms) (Gavezzotti & Filippini, 1992): test for H···N, C···N and N···N interactions; 458 crystal structures.

(iv) Chlorohydrocarbons (C, H and Cl atoms): test for Cl···Cl, C···Cl and H···Cl interactions; 103 crystal structures.

(v) Sulfohydrocarbons (C, H and S atoms): test for S···S, S···C and S···H interactions; 210 crystal structures.

(vi) Nitro compounds (C, H atoms and NO or NO_2 groups): mainly test for O···O and N···O interactions; 41 crystal structures.

(vii) Sulfones and sulfoxides (C, H atoms and SO or SO_2 groups): mainly test for S···O functions; 53 crystal structures.

The samples cover most of the functional groups commonly encountered in organic compounds. As usual when dealing with X-ray results, experimental H-atom positions may be unreliable, and the H atoms were always located by standard geometrical procedures (Gavezzotti, 1989, 1991*b*).

Sublimation heat data

Substances for which a complete X-ray crystal structure and an experimental heat of sublimation are available were collected, in order to compare the calculated packing energy (PE) with ΔH_s (see Tables 1–4 and Figs. 1–4). Experimental values were retrieved from a compilation (Chickos, 1987) of data available before 1984, but a survey of the primary literature was also conducted. It is very difficult to judge the reliability and consistency of ΔH_s values, since many different methods are employed for their determination (Chickos, 1987; Knauth & Sabbah, 1990), with different accuracies. Besides, many compounds are polymorphic, and there is no guarantee that the same crystalline material has been used for the X-ray and for the thermochemical work [although the heats of sublimation of polymorphs are known to differ by only a few percent (Chickos, Annunziata, Ladon, Hyman & Liebman, 1986)].

Table 1. *Experimental heats of sublimation, calculated packing energies and range of calculated lattice-vibration frequencies for hydrocarbons*

See Fig. 1 for the less obvious structural formulae. Energies are in kcal mol^{-1}. Calculated PE is the packing energy at 10 Å cut-off divided by 0.95. Labels: *U*, unified functions, present work (Table 8); others as in Table 5. <0 means imaginary calculated frequencies. 1 cal = 4.184 J.

				Calculated PE[c]			ν (cm^{-1})
Crystal[a]	CSD refcodes	ΔH_s[b]	T (K)	*U*	*W*	*M*	*U*
Benzene (218 K)	BENZEN	10.6	298	10.7	11.0	10.2	33–124
Naphthalene (239 K)	NAPHTHA10	17.3[d]	298	17.4	18.0	16.2	47–131
Anthracene	ANTCEN07	25.0	298	24.0	24.7	21.6	36–144
Triphenylene	TRIPHE11	30.2	298	29.6	30.5	27.1	30–122
Phenanthrene	PHENAN12	22.7	303	22.4	23.0	20.2	26–119
Chrysene	CRYSEN	31.3	298	29.9	30.7	26.6	25–124
Pyrene	PYRENE02	23.9[e]	298	24.9	25.8	22.4	19–115
Perylene	PERLEN01	34.7[f]	298	33.1	34.2	30.0	28–116
Picene	ZZZOYC01	33.5	456	36.5	37.3	32.1	35–124
1,2,5,6-Dibenzoanthracene	DBNTHR02[g]	35.6[f,i]	449	34.5	35.4	30.4	25–115
	DBNTHR10[h]	—	—	32.6	34.0	30.1	19–132
Coronene	CORONE	35.1	473	37.9	39.0	33.8	36–100
Ovalene	OVALEN01	50.6	600	51.3	52.6	45.5	36–103
Acenaphthene	ACENAP03	20.7	303	20.3	21.0	18.8	27–141
Fluorene	FLUREN02	21.1	303	21.6	22.5	20.0	23–121
Fluoranthrene	FLUANT	20.2	303	24.9	25.5	22.0	11–121
Diphenylmethane (203 K)	ZZZMKS01	19.7	*U*	21.6	22.3	20.5	25–99
Tetraphenylmethane	TEPHME11	36.0	298	34.4	35.7	32.5	40–85[j]
Biphenyl	BIPHEN04	19.5[k]	298	21.1	21.7	19.2	39–97
trans-Stilbene	TSTILB02	24.1	298	24.3	24.9	22.3	31–127
Diphenylacetylene	DPHACT02	21.4	311	22.5	23.0	20.2	29–124
9,10-Diphenylanthracene	DPANTR	35.9	316	35.9	37.0	32.9	30–83
9,10-Dihydroanthracene	DITBOX	22.5	298	22.7	23.6	21.6	36–95
Toluene (165 K)	TOLUEN	10.3	298	12.2	12.7	12.2	15–127
Durene	DURENE05	17.8[l]	298	17.2	17.9	17.4	13–122
2,6-Dimethylnaphthalene	DMNPTL	20.1	291	20.6	21.2	19.2	<0
1,8-Dimethylnaphthalene	DMNAPH	19.8	298	19.6	20.3	18.5	23–111
1,4,5,8-Tetramethylnaphthalene	CEKREP	23.9	298	22.8	24.2	23.7	50–139
9-Methylanthracene	MANTHR02	23.6	*U*	24.6	25.4	23.0	19–117
9,10-Dimethylanthracene	DMANTR	24.7	*U*	26.5	27.4	24.5	43–122
4,5-Dimethylphenanthrene	FEWWEJ	25.0	*U*	24.3	25.2	23.0	28–112
Cyclohexane (195 K)	CYCHEX01	11.1	186	10.7	11.6	13.2	54–137
Cubane	CUBANE	19.2	298	15.6	16.2	15.6	74,94[m]
Bullvalene	BULVAL02	17.2	*U*	16.7	17.7	17.2	23–135
Hexane	HEXANE	12.1	178	11.6	12.4	14.1	59, 66, 103[m]
Heptane (100 K)	HEPTAN01	13.8	183	13.1	14.0	16.0	21–97
Octane	OCTANE10	16.3	216	15.2	16.1	17.6	42, 57, 74[m]
Cyclotetradecane (116 K)	CYTDEC	23.5[n]	298	20.8	22.6	23.4	68, 85, 93[m]

Notes: (*a*) room-temperature X-ray structure, unless otherwise stated; (*b*) as reported by Chickos (1987), unless otherwise stated, with the temperature of the determination (*U* means *T* unspecified; when a *T* range was given, the midpoint has been assumed); (*c*) refer to Tables 5 and 8 for the potential parameters; (*d*) Sinke (1974); (*e*) Smith, Stewart, Osborn & Scott (1980); (*f*) phase of ΔH_s unknown; (*g*) orthorhombic structure; (*h*) monoclinic structure; (*i*) De Kruif (1980); (*j*) but see Filippini & Gramaccioli (1986); (*k*) see discussion in Chirico, Knipmeyer, Nguyen & Steele (1989); (*l*) Colomina, Jimenez, Roux & Turrion (1989); (*m*) complete frequency set given instead of frequency range (one molecule per unit cell); (*n*) Chickos, Hesse *et al.* (1992).

Table 2. *Experimental heats of sublimation, calculated packing energies and range of calculated lattice-vibration frequencies for oxahydrocarbons*

See Fig. 2 for less obvious structural formulae. Energies are in kcal mol^{-1}. Calculated PE is the packing energy at 10 Å cut-off divided by 0.95. 1 cal = 4.184 J.

				Calculated PE		ν (cm^{-1})
Crystal	CSD refcodes	ΔH_s	T (K)	*U*	*M*	*U*
Trioxane	TROXAN	13.4	298	14.4	10.8	28–111
Dioxane	CUKCIU10	11.6[a]	255	13.0	10.8	<0
Tetroxocane	TOXOCN	19.0	298	18.6	14.2	15–81
Pentoxocane	PTOXEC	21.0	298	21.1	16.5	27–138
Maleic anhydride	MLEICA	16.8	274	13.3	9.6	22–118
Succinic anhydride	SUCANH	19.6	302	14.8	11.1	19–125
Diglycolic anhydride	DLGYAH	20.1[b]	294	16.4	12.1	19–121
Phthalic anhydride	PHTHAO	21.1	318	21.2	15.5	32–115
Norbornene anhydride	NBORAN10	23.2	298	21.6	16.3	22–95
Pyromellitic dianhydride	PYMDAN	24.0	559	24.4	18.5	26–154
1,4-Benzoquinone	BNZQUI	16.4	262	14.8	10.3	7–114
2,5-Dimethylbenzoquinone	DMEBQU01	18.4	283	19.6	15.6	29–100
1,4-Naphthoquinone	NAPHQU	21.7	313	23.2	17.6	33–113
9,10-Anthraquinone	ANTQUO07	27.1[c]	298	29.8	24.5	26–109
9,10-Phenanthrenequinone	ZZZIYE01	25.8[c]	298	27.8	22.3	<0
1,4-Cyclohexanedione	CYHEXO01	20.1	298	16.2	13.3	44–180
2,2,4,4-Tetramethylcyclobutane-1,3-dione	DMKETD02	17.0	*U*	17.6	14.7	37, 47, 86
Benzil	BENZIL02	23.5	329	26.5	20.8	17–73
Benzophenone	BPHENO10	22.0	298	23.6	19.8	25–92
Dimethyl oxalate	DMEOXA	16.5[a]	298	16.9	12.6	13–96
Dimethyl terephthalate	DMTPAL	21.1	393	28.1	22.2	9–124
Phenyl benzoate	PHBENZ	23.7	298	26.3	22.0	31–106
Dibenzoyl peroxide	DBEZPO	22.4	300	32.0	23.9	16–80
Dicyclohexylperoxydicarbonate	SEGROL	24.0[d]	303	37.0	31.5	32–101
Coumarin	COUMAR10	20.6	323	22.0	17.0	26–108
Ethylene carbonate	ETHCAR	18.8	*U*	13.6	10.4	<0

Notes: (*a*) sum of ΔH_{fus} and ΔH_{vap} from *CRC Handbook of Chemistry and Physics* (1983–84); (*b*) DeWit, Van Miltenburg & De Kruif (1983); (*c*) see discussion in Ribeiro Da Silva *et al.* (1989); (*d*) not included in the comparison with calculated packing energy, see text.

Table 3. *Experimental heats of sublimation, calculated packing energies and range of calculated lattice-vibration frequencies for azahydrocarbons*

See Fig. 3 for less obvious structural formulae. Energies are in kcal mol^{-1}. Calculated PE is packing energy at 10 Å cut-off divided by 0.95. 1 cal = 4.184 J.

				Calculated PE			ν (cm^{-1})
Crystal	CSD refcodes	ΔH_s	T (K)	U	G	M	U
1,3,5-Triazine	TRIZIN01	13.9	222	15.3	13.8	8.4	20–97
Pyrazine	PYRAZI	13.5	U	13.7	12.7	8.8	< 0
Pyrimidine (271 K)	PRMDIN	11.7[a]	U	13.6	12.6	8.8	< 0[b]
Phenazine	PHENAZ02	23.2	290	26.4	24.9	20.8	44–115
Acridine	ACRDIN01	21.9	290	25.6	25.0	21.4	23–142
Phenanthridine	PHENAT	22.6	308	23.8	23.3	20.0	26–87
2,3-Diazanaphthalene	DAZNAP	23.1	U	19.3	18.0	13.6	< 0
N-Methyl carbazole	NMCABZ	22.8[c]	298	22.6	22.4	19.6	20–123
trans-Azobenzene	AZOBEN01	22.9	308	25.6	24.3	21.0	32–127
cis-Azobenzene	AZBENC01	22.2	328	23.9	23.0	18.7	< 0
Triethylendiamine	TETDAM03	14.8	338	17.0	16.6	15.3	36–102
Hexamethylenetetramine	HXMTAM	18.8	316	19.7	18.7	16.3	67
Bicyclo[3.2.2]azanonane	ZBCNON	13.8	298	15.6	15.7	16.1	9–89
Cyanogen	CYNGEN	7.7	224	8.3	7.4	3.5	17–131
Malononitrile	MALONT	18.9	268	11.0	10.3	5.5	20–148
Fumaronitrile	BISJIW	16.4	298	12.8	11.6	6.8	31–147
Tetracyanomethane	TCYMET	14.6	298	14.2	14.1	5.3	27–168
Tetracyanoethylene	TCYETY[d]	20.1[f]	302	17.6	15.4	7.9	20–130
	TCYETY01[e]	—	—	19.1	16.5	8.6	52–122
4-Cyanopyridine	CYAPYR	17.5[g]	298	16.2	15.3	10.1	< 0
1,4-Dicyanobenzene	TEPNIT11	21.2	298	20.0	18.4	12.7	59, 79, 89
Mesitonitrile	MESITN	18.6[h]	298	17.8	17.6	15.3	11–135
7,7,8,8-Tetracyanoquinodimethane	TCYQME	30.1	413	28.3	25.5	15.8	36–105

Notes: (*a*) Nabavian, Sabbah, Chestel & Laffite (1977); (*b*) calculated frequencies for the low-temperature crystal structure are real (Table 9); (*c*) Jimenez, Roux & Turrion (1990); (*d*) cubic phase; (*e*) monoclinic phase; (*f*) crystal phase of ΔH_s unknown; (*g*) Bickerton, Pilcher & Al-Takhin (1984); (*h*) Meier, Dogan, Beckhaus & Rüchardt (1987).

Table 4. *Experimental heats of sublimation, calculated packing energies and range of calculated lattice-vibration frequencies for chloro, sulfur and nitro compounds*

See Fig. 4 for less obvious structural formulae. Energies are in kcal mol^{-1}. Calculated PE is packing energy at 10 Å cut-off divided by 0.95. 1 cal = 4.184 J.

				Calculated PE		ν (cm^{-1})
Crystal	CSD refcodes	ΔH_s	T (K)	U	BB	U
α-Hexachlorocyclohexane	AHCHEX01	22.2	334	20.7	20.4	< 0
β-Hexachlorocyclohexane	HCCYHB	24.6	379	22.4	21.7	30–56
γ-Hexachlorocyclohexane	HCCYHG02	21.7[a]	303	20.1	19.4	22–78
δ-Hexachlorocyclohexane	HCCYHD	23.3	343	21.1	20.4	19–73
Chloromethane (148 K)	CLMETH	6.7	U	5.9	5.8	54–134
DDT	CPTCET10	28.2	303	29.6	29.1	7–70
p-Dichlorobenzene	DCLBEN05[b]	15.5[c]	303	16.0	15.7	43, 50, 99
2,2′-Dichlorobiphenyl	DCLBIP	23.0	298	22.2	22.0	16–83
4,4′-Dichlorobiphenyl	DCLBIQ10	26.0	298	25.0	25.0	14–114
Hexachlorobenzene	HCLBNZ11	21.6[d]	298	22.7	21.6	18–47
Hexachloroethane	HEXCET02	11.7[e]	382	14.2	13.8	18–42
1,2,3-Trichlorobenzene	TCBENZ	15.7	296	17.4	16.9	14–95
1,3,5-Trichlorobenzene	TCHLBZ	13.5	291	17.8	17.4	17–59
1,2,3,5-Tetrachlorobenzene	TCLBZN	19.0[d]	298	19.2	18.6	< 0
Pentachlorobenzene	PNCLBZ	20.8[d]	298	20.6	19.7	14–61
				U	RP	
Tetrathiafulvalene	BDTOLE10	22.4	348	27.0	23.6	30–77
Dibenzothiophene	DBZTPH	22.3[f]	298	24.8	24.2	23–115
1,4-Dithiane	DITHAN	17.3	268	16.8	14.7	37–93
1,3,5-Trithiane	TRITAN10	22.4	298	18.2	14.5	35-109
5-Phenyl-1,2-dithiole-3-thione	FABPON10	29.5	298	27.0	23.5	20–108
Diphenyl disulfide	PHENSS01	22.7	U	27.2	25.8	20–90
Thianthrene	THIANT02	23.8[g]	353	28.0	26.4	30–121
1,3-Dithiolan-2-thione (163 K)	DTOLTO	19.6	298	17.8	14.7	15–103
				U	M	
Dimethyl sulfone	DMSULO	18.4	U	14.2	11.3	45–123
Methyl phenyl sulfone	MPSUFO	22.0	U	20.4	15.7	27–97
Prop-1-enyl *p*-tolyl sulfone	PRYLTS	20.0	U	25.4	20.8	21–105
				U	M	
1,4-Dinitrosopiperazine	CUVJUY	24.2	343	22.6	14.8	32–118
N,*N*-Dimethyl-*p*-nitroaniline	DIMNAN	23.6	355	25.1	19.0	26–110
o-Dinitrobenzene	ZZZFYW01	21.0	298	24.2	15.8	30–93
m-Dinitrobenzene	DNBENZ10	20.8	298	24.4	16.0	11–94
p-Dinitrobenzene	DNITBZ11	23.0	298	25.3	16.3	45–110
4,4′-Dinitrobiphenyl	DNTDPH	25.0[h]	420	35.0	24.3	28–95
p-Nitrotoluene	NITOLU	18.9	298	20.6	14.7	13–109
1,3,5-Trinitrobenzene	TNBENZ10	25.6	298	25.0	17.1	12–116
2,4,6-Trinitro-*m*-xylene	TNOXYL	31.0	365	31.4	21.4	26–116
2,4,6-Trinitrophenetole	TNPHNT	28.8	298	28.4	20.2	17–106
2,4,6-Trinitrotoluene	ZZZMUC01	27.1	298	28.7	19.6	15–114
2,6-Dichlorobenzoquinone	DCLBQN	16.7	295	15.1	12.3	< 0
Tetrachlorobenzoquinone	TCBENQ01	23.6	344	16.8	15.2	18–119

Notes: (*a*) Sabbah & Xu (1991*a*); (*b*) triclinic phase; (*c*) crystal phase of ΔH_s unknown; (*d*) Sabbah & Xu (1991*b*); (*e*) the crystal has several phase transitions; (*f*) Chirico, Knipmeyer, Nguyen & Steele (1991); (*g*) Sabbah & El Watik (1989); (*h*) not included in the comparison with calculated packing energies, see text.

Whenever more than one experimental value was available, sometimes more recent values were preferred; in other cases, higher values were selected, since experimental inaccuracies are more likely to produce lower-than-true values (Bondi, 1963).

The comparison of calculated packing energies (PE) with observed ΔH_s values assumes that the molecule has the same conformation in the solid and in the gaseous state. If not, the heat of sublimation must be smaller than the calculated PE by an amount equivalent to the gain in conformational energy on going from the crystal to the gas-phase molecule.

Distribution of intermolecular contacts

One of the most revealing techniques in the study of intermolecular interactions is the analysis of the distribution of intermolecular distances in real crystals. Calling N the number of distances in each interval, and M the number of molecules in each sample, the following density function is calculated for each $X\cdots Y$ pair

$$D(R) = (N/M)/(4\pi R^2 \mathrm{d}R).$$

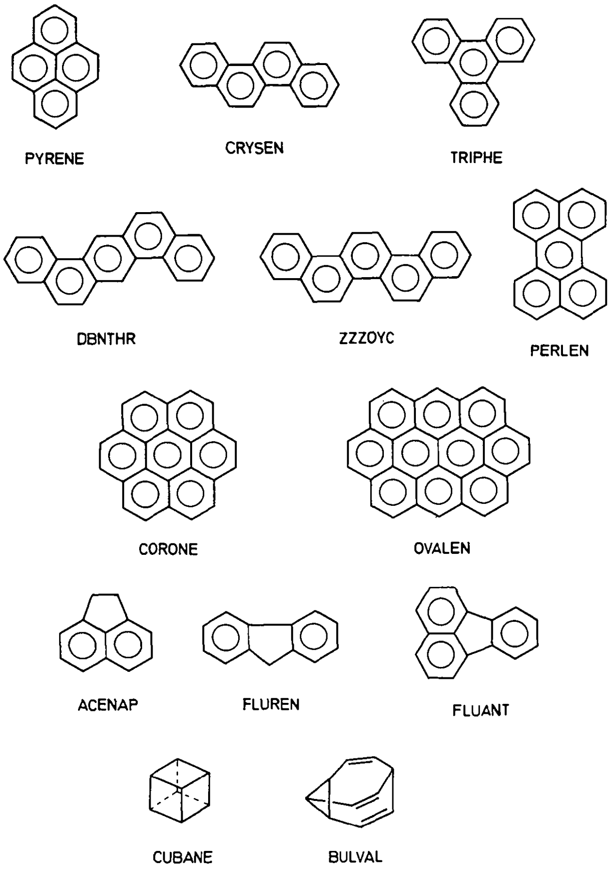

Fig. 1. Structural formulae of some of the hydrocarbons studied.

The results are shown in Figs. 5–7. $D(R)$ is the density of distances between R and $R + \mathrm{d}R$ ($\mathrm{d}R$ = 0.1 Å) in a spherical shell, over all the molecules in the sample. This density is not, however, normalized with regard to stoichiometry; for example, in pure hydrocarbons the densities are higher because these are binary compounds, while in nitro derivatives the N···O density is very low because these are quaternary compounds. The higher densities for oxahydrocarbons than for azahydrocarbons may reflect a higher O/(C + H) than N/(C + H) ratio within our samples.

We assume van der Waals radii as C, 1.75; H, 1.17; N, 1.5; O, 1.4; S, 1.8; Cl, 1.77 Å. In hydrocarbons and oxa- or azahydrocarbons, for C···C, O···O, N···N and N···O the sum of these radii defines an empirical limit, below which almost no contacts are observed in crystals. The same holds for H···H distances, allowance being made for the calculated positions of these atoms (methyl H atoms are especially

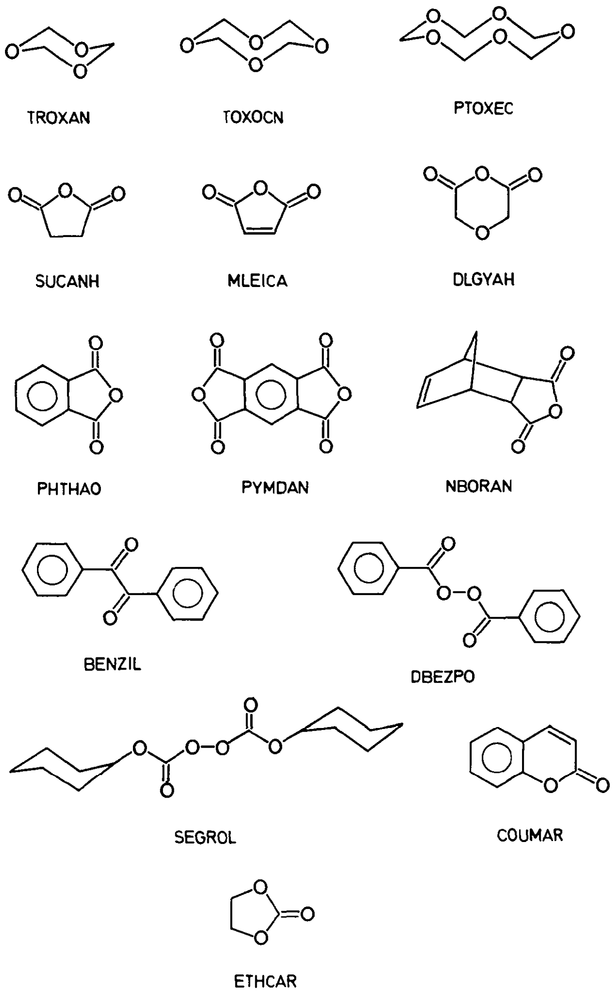

Fig. 2. Structural formulae of some of the oxahydrocarbons studied.

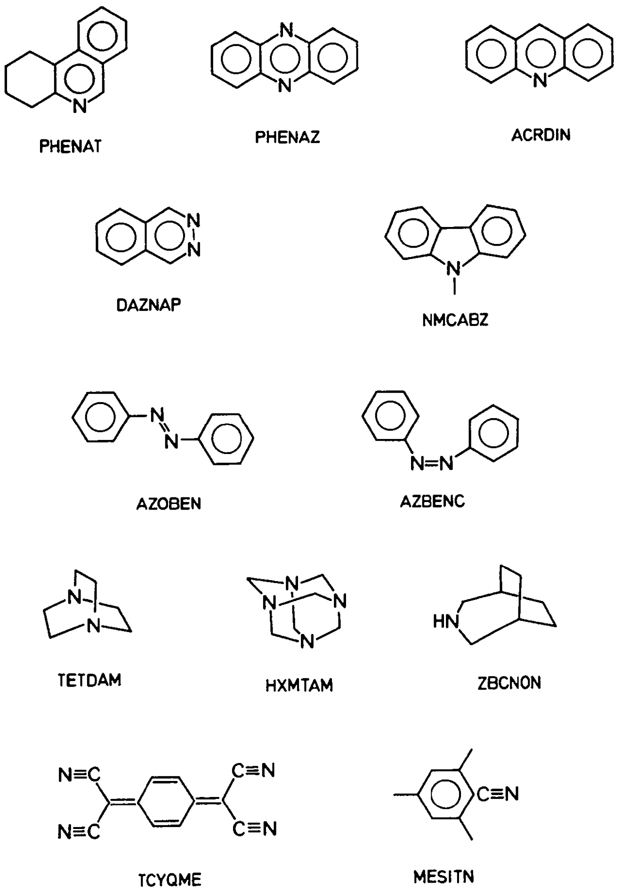

Fig. 3. Structural formulae of some of the azahydrocarbons studied.

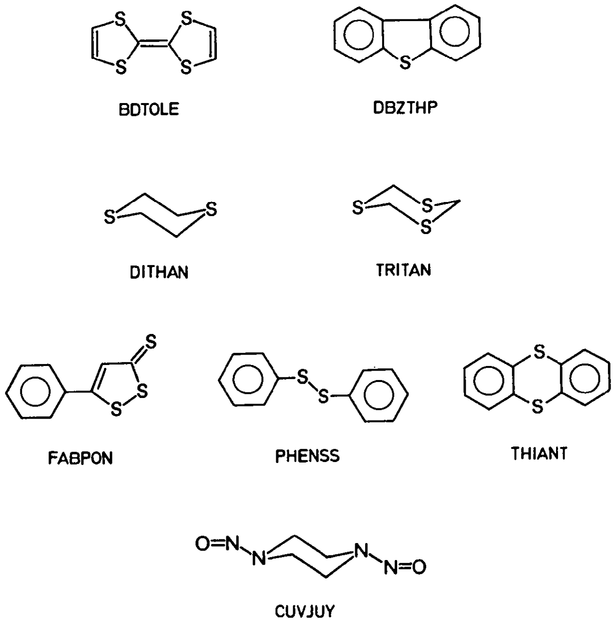

Fig. 4. Structural formulae of some of the chloro, sulfur and nitro compounds studied.

critical). This rule does not always hold for mixed interactions, between atoms of different electronegativity and in different chemical environments. Special attractions may arise from electrostatic effects; thus, short contacts are found, for example, between carbonyl O atoms and acyl C atoms in carboxylic acid anhydrides [see Gavezzotti (1991*b*) for a discussion, with quotations from the literature]; a consistent number of short C—H···O and C—H···N contacts appear – they are now recognized as C—H···*X* 'hydrogen bonds' (Desiraju, 1991, and references therein). Even the distribution of C···H distances reveals a number of short contacts. Con-

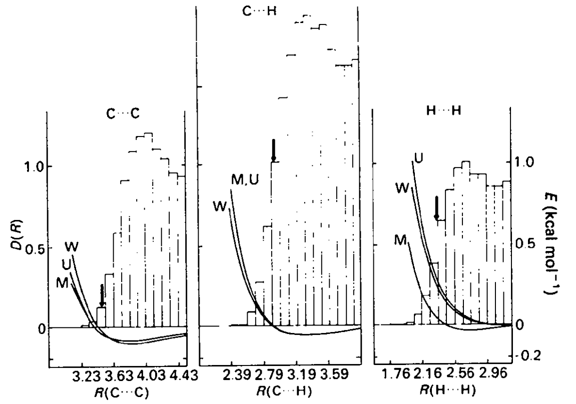

Fig. 5. Intermolecular contact density (left ordinate) for hydrocarbon crystals. Also plotted are the corresponding potential energy curves (right ordinate): W = Williams, M = Mirsky functions (see Table 5); U = unified functions, present work (see Table 8). The vertical arrows mark the sums of the pertinent van der Waals radii. 1 cal = 4.184 J.

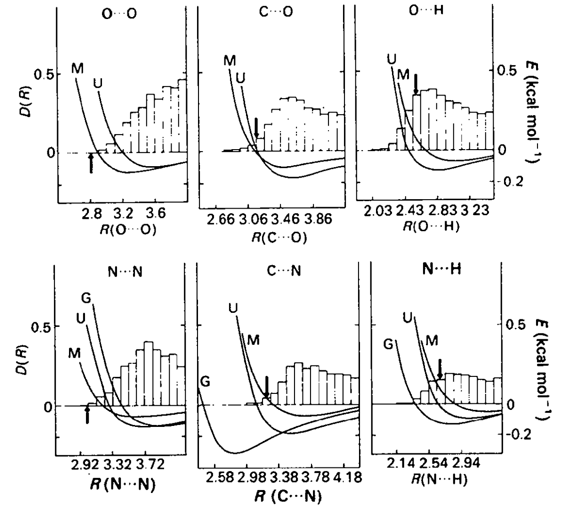

Fig. 6. Intermolecular contact density (left ordinate) for oxa- and azahydrocarbon crystals. Also plotted are the corresponding potential energy curves (right ordinate): G = Govers, W = Williams, M = Mirksy functions (see Table 5); U = unified functions, present work (see Table 8). The vertical arrows mark the sums of the pertinent van der Waals radii. 1 cal = 4.184 J.

tacts shorter than standard packing radii appear for the highly polarizable chlorine atoms, in a confirmation of the so-called 'chloro effect' (see Desiraju, 1989, Chapter VI).

The distance distributions are used in the following way. First we consider it unreasonable to have a large number of repulsive atom–atom interactions in crystals, so that an appropriate atom–atom potential should become repulsive only after the $D(R)$ has fallen below a certain threshold; the reason being that in non-hydrogen-bonded organic crystals there are no strong attractive forces to compensate any steeply increasing repulsion at short distances. Second, the minimum of the interatomic potential curve should be located approximately where the contact density reaches its first peak – the most frequent contacts at the shortest possible distance. Thus, the observed distributions provide a basic indication of the location of R^0 and of the beginning of the repulsive branch of the potential curve. These arguments do not hold for H···H interactions (see *Discussion*).

A qualitative hint for the calibration of the well depth, ε, comes from the recognition of short interatomic contacts between atoms of different electronegativity, implying attractive interactions other than pure dispersion. As discussed before, to reproduce this effect within the limitations of the 6-exp potential form, the well depth is increased.

The parameter λ controls the curvature at the minimum and the steepness of the repulsion branch. Since actual crystals are always in the attractive regime, there is little information on this parameter in observed crystal structures. It does however influence the lattice vibration frequencies, which increase with λ.

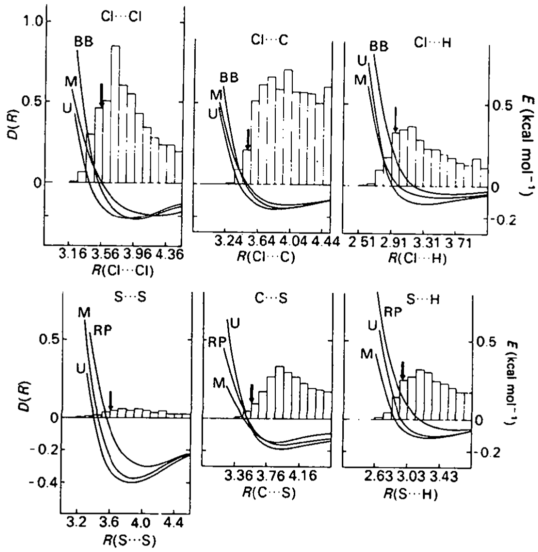

Fig. 7. Intermolecular contact density (left ordinate) for chloro- and sulfohydrocarbon crystals. Also plotted are the corresponding potential energy curves (right ordinate): *BB* = Bates–Busing, *RP* = Rinaldi–Pawley, *M* = Mirsky functions (see Table 5); *U* = unified functions, present work (see Table 8). The vertical arrows mark the sums of the pertinent van der Waals radii. 1 cal = 4.184 J.

Discrepancy indices

Calculated packing energies are matched with the N observed ΔH_s, and the following energetic discrepancy factors are calculated

$$F_1 = \sum(1/N)100|\Delta H_s - \mathrm{PE}|/\Delta H_s$$

$$F_2 = \sum(1/N)|\Delta H_s - \mathrm{PE}|,$$

where PE is the packing energy at 10 Å cut off, divided by 0.95 to account for the lack of convergence. F_2 is probably more reliable, since the expected error in each ΔH_s is likely to be constant, so that smaller values are affected by much larger percentage errors. A third index

$$F_3 = \sum(\Delta H_s - \mathrm{PE})$$

is useful for global rescaling, since it is negative if the potential underestimates the heats of sublimation, and *vice versa*.

Even when ΔH_s is not available, each observed crystal structure provides a test for the potentials, since in principle it should be at the absolute minimum in the packing-energy hypersurface (neglecting entropy contributions). A selected sample of most representative crystal structures were relaxed under the action of the potentials, with respect to cell parameters and the allowed rigid-body translational and rotational displacements. The program *PCK*83 (Williams, 1983) was used, and the observed crystal structure was input as a starting point, preserving all elements of crystal and molecular symmetry. For each structure, a discrepancy factor, F, is calculated (Williams, 1983),

$$F = (\Delta\theta/2)^2 + (10\Delta x)^2 + (100\Delta a/a)^2 + (100\Delta b/b)^2 + (100\Delta c/c)^2 + \Delta\alpha^2 + \Delta\beta^2 + \Delta\gamma^2,$$

where $\Delta\theta$ is the total rigid-body rotational displacement after the minimization (°), Δx is the total rigid-body translational displacement (Å), and the other six terms depend on the changes in cell parameters (Å and °; the empirical factors $\frac{1}{2}$, 10 and 100 bring the contributions from the different displacements to a comparable scale).

Averages were then taken as

$$F_s = (1/N)\sum_i F_i$$

$$F_D = (1/N_D)\sum_i F_i,$$

where N is the total number of structures, and N_D is the total number of degrees of freedom in each data set.

For all crystal structures for which sublimation heats were available, the lattice vibration frequencies were also calculated (Filippini & Gramaccioli, 1986). Prior to the lattice-dynamical calculation, the structure was relaxed with respect to the rigid-body degrees of freedom only; if the potential functions are inadequate, trouble in the optimization procedure or imaginary calculated frequencies result. A few detailed comparisons between calculated and observed lattice-vibration frequencies were carried out; this is a very critical test of the potential functions, but is seldom applicable, because of the scarcity of experimental data.

Optimization of the potentials

The performance of several literature potential functions, all in the 6-exp form (see Table 5), was tested first. The functions are plotted against the corresponding $D(R)$ in Figs. 5–7. For hydrocarbons, the best results were obtained using the Williams parameter set (Williams, 1967; set *W*, with the C—H bond length constrained to 1.08 Å in our calculations). For oxahydrocarbons, the parameter set given by Mirsky (Mirsky, 1978; set *M*) in her compilation is acceptable for less polar compounds, but fails, for example, for quinones or anhydrides, where special interactions are present (Gavezzotti, 1991*b*). For azahydrocarbons, the parameter set derived by Govers (Govers, 1975; set *G*) proved adequate for the calculations of lattice energies, but produced substantial cell shrinkages, mainly because the R^0 values are too small for N···H and N···C interactions (see Fig. 6). The *M* parameter set for azahydrocarbons gave poor results, especially for nitrile compounds (see also Gavezzotti & Filippini, 1992). For chlorohydrocarbons, the Bates–Busing set (Bates & Busing, 1974; set *BB*) lacks a Cl···H potential, having been developed for perchloro compounds. For sulfur compounds, the Rinaldi–Pawley scheme (Rinaldi & Pawley, 1975; set *RP*) provides only an S···S interaction potential. Mirsky (1978) has collected a full set of parameters for chloro and sulfur compounds also.

In a first round of optimization, the R^0 and ε values were readjusted, starting from the most promising literature potential sets, following the guidelines described in the previous sections. When unavoidable, the usual mixing rule

$$A_{xy} = (A_{xx}A_{yy})^{1/2}; \quad B_{xy} = \tfrac{1}{2}(B_{xx} + B_{yy});$$
$$C_{xy} = (C_{xx}C_{yy})^{1/2}$$

was applied (for example, to supply Cl···H potentials for the *BB* set, or S···C and S···H potentials for the *RP* set). The optimization was conducted by a trial-and-error procedure, since no algorithm for automatic optimization could be applied here; the definition of a global discrepancy index is not straightforward, since it must convolute several heterogeneous indices, whose dependence upon the potential parameters is quite indirect. Besides, even with present-day computers, a few cycles of calculation of first and second derivatives on such a hypothetical discrepancy index, over our very large database, would lead to exceedingly long computing times.

Table 5. *Literature functions*

Atom–atom potential parameters in the form: $E_{ij} = A\exp(-BR_{ij}) - CR_{ij}^{-6}$. A in kcal mol^{-1}, B in Å^{-1} and C in kcal mol^{-1} Å^{-6}. 1 cal = 4.184 J. See text for potential-set labels and references.

Interaction	*A*	*B*	*C*	ε	R^0	λ	Label
C···C	83630	3.60	568.0	0.095	3.88	14.0	*W*
C···H	8766	3.67	125.0	0.049	3.30	12.1	
H···H	2654	3.74	27.3	0.010	3.37	12.6	
C···C	71600	3.68	421.0	0.079	3.80	14.0	*M*
C···H	18600	3.94	118.0	0.049	3.30	13.0	
H···H	4900	4.29	29.0	0.030	2.80	12.0	
O···O	77700	4.18	259.4	0.122	3.25	13.6	
O···C	75700	3.91	339.4	0.098	3.52	13.8	
O···H	19500	4.23	88.0	0.060	3.02	12.8	
N···N	42000	3.78	259.0	0.067	3.60	13.6	
N···C	55300	3.73	331.4	0.073	3.70	13.8	
N···H	14400	4.00	91.0	0.045	3.20	12.8	
O···N	57900	3.97	262.9	0.090	3.42	13.6	
Cl···Cl	4580	2.262	2980.0	0.197	4.21	9.5	
Cl···C	16700	2.94	1055.0	0.127	3.99	11.7	
Cl···H	4560	3.07	322.0	0.077	3.50	10.8	
S···S	235000	3.49	2346.0	0.378	3.90	13.6	
S···C	99400	3.54	847.0	0.141	3.88	13.6	
S···H	33934	3.89	260.0	0.106	3.35	12.8	
N···N	105400	3.60	760.0	0.133	3.85	13.9	*G*[c]
N···C	11480	3.60	375.0	0.298	2.84	10.2	
N···H	4833	3.67	143.0	0.131	2.77	10.1	
Cl···Cl	185710	3.52	1495.0	0.224	3.95	13.9	*BB*
Cl···C[a]	124391	3.56	923.0	0.146	3.92	14.0	
Cl···H[b]	22201	3.63	202.0	0.047	3.66	13.2	
S···S	41182	2.90	2761.0	0.299	4.07	11.8	*RP*
S···C[a]	58686	3.25	1252.0	0.174	3.96	12.9	
S···H[b]	10455	3.32	275.0	0.059	3.64	12.1	

Notes: (*a*) average with Williams (*W*) C···C; (*b*) average with Williams H···H; (*c*) uses Williams for the C, H part.

Considerable improvement was obtained in this way, but the results were not deemed satisfactory. In keeping with the arguments discussed previously, the λ parameters were particularly ill defined. In a second optimization stage, the R^0 values were all placed at or about the distance of the maximum in the $D(R)$ histograms (except for H···H), and then were optimized within small variations, together with rescaling of the ε parameters, always by careful trial and error. As expected, F_s gave mostly indications on R^0, while F_{1-3} were useful for ε. The λ parameter was set at an average value for all interactions; two values, 12.5 and 13.5, were tested. Further attempts to optimize this parameter, using lattice-vibration frequencies as a test, gave rather inconclusive results, besides the expected increasing trend for all frequencies on increasing λ. The final choice was $\lambda = 13.5$; the match between calculated and observed lattice frequencies (see below) shows at least that our choice has no adverse consequences on the lattice dynamics. A partial test of the repulsive branch of the potential is provided by calculations of the rotational barriers for molecules in crystals, where large displacements from the minima occur. Table 6 gives some results which are considered satisfactory, since calculated values are upper limits, as a rigid environment is assumed.

Heats of sublimation are compared with calculated energies in Tables 1–4. Table 7* collects the values of all the discrepancy indices, while Table 8 collects the final parameters of the unified (U) potential set, and the potential curves are plotted in Figs. 5–7, against the corresponding $D(R)$. Table 9 gives some comparisons between calculated and observed lattice-vibrational frequencies.

Discussion

Equilibrium distances

The ratio of the optimized R^0 values to the sum of the corresponding van der Waals radii ranges from 1.07 to 1.29. Kitaigorodski (1973) estimated that this ratio should be about 1.15. This result is a useful guideline for further parametric studies of intermolecular potentials, although its interpretation in terms of physical effects in crystals is not clear-cut (but see the paragraph below on crystal structure relaxation). The H···H potential is an exception since its minimum is very shallow and is not sharply defined. The potential function is actually repulsive for a wide range of observed H···H distances. This could be related to the very small polarizability of the H atoms.

Sublimation heats

The performance of the potentials in reproducing heats of sublimation is outstanding. The average absolute discrepancy is only 1.8 kcal mol^{-1} whereas it has been estimated (Pertsin & Kitaigorodski, 1987, pp. 79–80) that, in view of the approximations in the calculation and of the inaccuracies in the experiments, the expected deviation may be as high as 3–4 kcal mol^{-1}.

In hydrocarbons (Table 1) the maximum deviation is 4.7 kcal mol^{-1} (for fluoranthrene). In oxahydrocarbons (Table 2) ΔH_s is underestimated for anhydrides, and this can be understood (Gavezzotti, 1991*b*) in terms of incompletely reproduced electrostatic contributions. Less obvious is the interpretation of the sometimes large overestimation of the ΔH_s of esters. Note that for dimethyl oxalate a ΔH_s of 11.4 kcal mol^{-1} was reported (Anthoney, Carson,

Table 6. *Barriers to in-plane rotation* (kcal mol^{-1}) *for molecules in their crystals*

See Gavezzotti & Desiraju (1988) for a discussion of the method of calculation and of the experimental values. 1 cal = 4.184 J.

			Calculated	
Molecule	Experimental	M	U (λ = 12.5)	U (λ = 13.5)
Benzene	4.0	3.4	3.6	5.0
Naphthalene	21.7	38.4	36.5	55.5
Pyrene	14.6	58.7	47.2	73.7
Coronene	6.0	3.2	3.8	5.7
Hexachlorobenzene	—	7.1	11.6	15.4

Table 7. *Overall discrepancy indices for the performance of various potential-parameter sets*

See text for the description of each index. The CSD refcodes for the crystal structures included in each data set can be found in the supplementary material.

	Structural				Energetic			
	N	N_D	F_s	F_D	N	F_1	F_2	F_3
Hydrocarbons								
W	50	430	66	8	38	5.8	1.3	33
M			131	15		8.5	2.0	−49
U			59	7		5.4	1.2	0
Oxahydrocarbons								
M	42	345	100	12	25	21.8	4.3	−102
U			67	8		12.1	2.4	12
Azahydrocarbons								
G	41	310	150	20	23	11.7	2.3	−27
M			105	14		32.6	5.9	−131
U			66	9		10.8	2.0	−3
Nitro compounds								
M	11	99	104	12	10	28.0	6.9	−69
U			36	4		7.5	1.7	12
Chlorohydrocarbons								
BB	34	306	36	4	15	15.6	2.9	−34
M			38	4		10.6	1.8	−9
U			54	6		8.7	1.5	2
Sulfohydrocarbons								
RP	27	233	52	6	8	16.8	3.8	−13
M			85	10		12.7	2.9	−23
U			47	5		13.8	3.2	14
Sulfones and sulfoxides								
M	12	106	53	6	3	23.9	4.8	−13
U			36	4		18.9	3.7	0
Overall								
M	217	1829	94	11	122	18.3	3.7	−396
U			57	7		9.3	1.9	37

Table 8. *Unified* (U) *functions*

Atom–atom potential parameters in the form: $E = A\exp(-BR_{ij}) - CR_{ij}^{-6}$. λ = 13.5 in all cases. See also heading to Table 5.

Interaction	A	B	C	ε	R^0
H···H	5774	4.01	26.1	0.010	3.36
H···C	28870	4.10	113.0	0.049	3.29
H···N	54560	4.52	120.0	0.094	2.99
H···O	70610	4.82	105.0	0.121	2.80
H···S	64190	4.03	279.0	0.110	3.35
H···Cl	70020	4.09	279.0	0.120	3.30
C···C	54050	3.47	578.0	0.093	3.89
C···N	117470	3.86	667.0	0.201	3.50
C···O	93950	3.74	641.0	0.161	3.61
C···S	126460	3.41	1504.0	0.217	3.96
C···Cl	93370	3.52	923.0	0.160	3.83
N···N	87300	3.65	691.0	0.150	3.70
N···O	64190	3.86	364.0	0.110	3.50
O···O	46680	3.74	319.0	0.080	3.61
O···S	110160	3.63	906.0	0.189	3.72
O···Cl[a]	80855	3.63	665.0	0.139	3.72
S···S	259960	3.52	2571.0	0.445	3.83
Cl···Cl	140050	3.52	1385.0	0.240	3.83

Notes: (*a*) Average of O···O and Cl···Cl parameters.

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* A list of CSD refcodes and literature references for 217 crystal structures in Table 7 has been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55999 (20 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 9. *Calculated (observed) lattice-vibration frequencies* (cm^{-1}) *for selected compounds*

Refcode		Frequencies						
PHENAN12[a]	A	35 (32)	53 (47)	66 (61)	85 (97)	119 (108)		
	B	26 (32)	52 (36)	81 (60)	104 (99)			
PYRENE02[b]	A_g	19 (30)	40 (46)	48 (56)	67 (76)	95 (92)	109 (127)	
	B_g	26 (30)	38 (41)	47 (56)	72 (67)	96 (93)	113 (126)	
HEPTANE[c]	A_g	35 (31)	46 (38)	57 (52)	61 (62)	71 (78)	97 (–)	
HEXANE[c]	A_g	59 (53)	66 (74)	103 (87)				
CUBANE[d]	A_g	94 (63)		E_g 74 (85)				
DURENE05[e, f]	A_g	40 (39)	91 (75)	122 (105)				
	B_g	13 (32)	92 (72)	113 (103)				
ANTQUO07[g, h]	A_u	32 (32)	68 (72)		B_u 48 (36)			
	A_g	26 (27)	63 (51)	104 (66)				
	B_g	59 (–)	81 (57)	109 (82)				
DMEOXA[i]	A_g	58 (63)	73 (88)	96 (108.5)				
	B_g	51 (70)	84 (98)	89 (113.5)				
SUCANH[j]	A	28 (37)	42 (42.5)	51 (49.5)	63 (75.5)	81 (88)	118 (111)	
	B_1	40 (48)	62 (65)	88 (75)	92 (95)	125 (142)		
	B_2	19 (32)	57 (59)	66 (70)	96 (90)	117 (128)		
	B_3	54 (–)	63 (57)	73 (73)	82 (88.5)	100 (133)		
PHTHAO[k]	A_1	32 (35)	41 (52)	65 (90)	83 (113)	101 (135)		
	B_1	37 (54)	49 (68)	63 (84)	76 (114)	112 (125)		
	A_2	42 (54)	49 (69)	71 (84)	78 (112)	96 (125)	115 (135)	
	B_2	40 (36)	48 (53)	63 (82)	89 (89)	98 (112)		
TETDAM03[l]	E_{1g}	61 (70)		E_{2g} 36 (47)				
	A_g	63 (59)		B_g 102 (–)				
	E_{2u}	38 (42)		B_u 57 (53)				
TCYETY[m]	A_g	64 (65)	83 (76)	130 (100)				
(monoclinic)	B_g	31 (29)	77 (88)	118 (113)				
	A_u	20 (–)	110 (–)		B_u 61 (–)			
TCYETY01[m]	T_g	52 (70)	92 (84)	122 (131)				
(cubic)	T_u	76 (–)	119 (–)					
TCYQME[n]								
	Raman	42 (41)	59 (65)	66 (80)	76 (102)	87 (109)	103 (134)	105
	IR	36 (–)	66 (–)	67 (–)				
PRMDIN[o]	A_1	44 (–)	68 (–)	70 (67)	117 (88)	118 (94)		
	A_2	9 (–)	46 (–)	56 (–)	64 (–)	91 (–)	121 (–)	
	B_1	18 (34)	68 (50)	77 (63)	88 (–)	136 (99)		
	B_2	18 (–)	54 (–)	75 (–)	78 (–)	118 (77)		
HXMTAM[p]	T	67 (63)						
DCLBEN05[q]	A_g	43 (44)	50 (56)		B_g 99 (82)			
HCLBNZ11[r]	A_u	31 (–)	40 (51)		B_u 18 (–)			
	A_g	18 (21)	34 (45)	47 (56)				
	B_g	20 (25)	32 (38)	46 (54)				
HEXCET02[s]	A_g	18 (21)	23 (28.5)	28 (34)		B_{1g} 19 (29.5)	41 (–)	42 (–)
	B_{2g}	20 (–)	27 (37)	36 (55)		B_{3g} 22 (30)	32 (46)	39 (–)
TRITAN10[t]	A_1	38 (60)	109 (92)		A_2 35 (50)	78 (–)	103 (96)	
	B_1	56 (–)	88 (78)		B_2 85 (83)	89 (–)		
DMSULO[u]	A_u	87 (–)		B_{2u} 112 (92)		B_{3u} 65 (87)		
	A_g	98 (105)		B_{1g} 45 (68)	101 (102)			
	B_{2g}	123 (103)		B_{3g} 55 (110)	123 (130)			
TCBENQ01[v]	A_u	21 (37)	92 (62)		B_u 55 (61)			
	A_g	18 (31)	41 (43)	119 (78)				
	B_g	24 (16)	58 (47)	101 (78)				

References: (*a*) Colombo (1977); (*b*) Bree, Kydd, Misra & Vilkos (1971); (*c*) Brunel & Dows (1974); (*d*) Dalterio & Owens (1988); (*e*) Kurshunov & Mamizerova (1972); (*f*) Sanquer & Meinnel (1972); (*g*) Wyncke, Brehat, Hadni, Miyazaki & Ito (1973); (*h*) Miyazaki & Ito (1973); (*i*) Landry, Nash & Tinti (1976) (Raman measurements at 77 K); (*j*) Bougeard, Righini & Califano (1979); (*k*) Colombo, Kirin, Volovsek & Long (1988); (*l*) Hedoux, Sauvajol & More (1988); (*m*) Chaplot, Mierzejewski & Pawley (1985); (*n*) Carlone, Cyr & Jandl (1982); (*o*) Gamba & Bonadeo (1981) (X-ray structure at 107 K); (*p*) Dolling & Powell (1970); (*q*) Podogrigora, Shabanov & Remizov (1983); (*r*) Bates, Thomas, Bandy & Lippincott (1971); (*s*) Woost & Bougeard (1986); (*t*) Thomas (1977); (*u*) Machida, Kuroda & Hanai (1979); (*v*) Rey-Lafon (1978).

Laye & Yurekli, 1976); we have used instead the sum of the vaporization and fusion enthalpies, or 16.5 kcal mol^{-1}. A redetermination of ΔH_s (Chickos & Sabbah, 1992) gave a preliminary value of 18.0 kcal mol^{-1}; this case stands as an extreme example of the oscillations in experimental values, and confirms that caution should be used in discussing single compounds. The sublimation heat of dimethylterephthalate has recently been redetermined (Chickos & Hosseini, 1992) as 25.5 kcal mol^{-1} at 358 K, a value much closer to our calculated one. The measured heat of sublimation for DBEZPO is suspiciously low; that for SEGROL is so low that this compound has been excluded from the averages.

In azahydrocarbons (Table 3) ΔH_s is underestimated for nitrile compounds, especially malononitrile and fumaronitrile, presumably due to incompletely reproduced electrostatic effects – although several other nitrile crystals are accurately described by the U functions. ΔH_s is also underestimated for diazanaphthalene; aromatic aza compounds are further discussed in the paragraph dealing with crystal structure relaxation. The ΔH_s's of the dinitrobenzene derivatives are consistently overestimated, while those of the trinitro derivatives are well reproduced. The ΔH_s of p,p'-dinitrobiphenyl has been reported [as mentioned in the review by Chickos (1987)] as 25.0 kcal mol^{-1} at 420 K, but, even considering the high temperature of the determination, this value seems pathologically low, against a calculated lattice energy of 35.0 kcal mol^{-1}. We concluded that the experimental value was unreliable, and discarded this structure from our averages. In fact, for all compounds for which our calculated lattice energy is substantially higher than the observed one a redetermination of ΔH_s would be desirable.

The results are somewhat less satisfactory for sulfur compounds, with a substantial overestimation of ΔH_s for compounds with S atoms in cyclic aromatic systems, and an underestimation for trithiane. The derivation of better potentials for sulfur compounds may require a more sophisticated functional form; in any case, a larger thermochemical database is needed if further optimizations are to be attempted.

Fig. 8 shows a graphic comparison of observed and calculated heats of sublimation. The literature parameter sets show a systematic underestimation of the lattice energies of polar compounds, while the outstanding performance of the U set is clearly visible.

Crystal structures

The degrees of freedom in each crystal structure are in principle six cell parameters (but some may be constrained by lattice symmetry), three rigid-body molecular translations and three rotations (but some may also be constrained according to the site symmetry). Most structures, when relaxed under the action of the potentials, quickly reached a stable minimum, although in some cases the starting structure was calculated to be in a saddle point (non-positive-definite Hessian). This indicates that the PE hypersurface may have several neighbouring subminima, as already noted in previous work (Gavezzotti, 1991*a*), and warns that the final result may be somewhat sensitive to the starting point and to the details of the optimization procedure. Also, non-rigid molecules have been treated in fact as rigid bodies, but the detailed analysis of the internal degrees of freedom would have been an overwhelming task.

The U potentials produce an F_s of 57 per molecule, and an F_D of 7 per degree of freedom. However, the total discrepancy is never equally apportioned over the various degrees of freedom; most of the deviation usually comes from an unavoidable cell-shrinkage effect, which presumably has to do with the neglect of molecular libration. An F_D of 7 corresponds to $\Delta x = 0.26$ Å, or $\Delta\theta = 5°$, or $\Delta a = 2.5\%$, or $\Delta\alpha = 2.5°$. Since cell edges are frequently off by as much as 5%, Δx's and $\Delta\theta$'s are usually well below the averages shown above.

A very high F value was calculated for a few crystals. For coronene ($F = 831$), ovalene (615), and, to a much lesser extent, triphenylene (97), the optimization led to shortening of one cell edge to about 4 Å, with a corresponding increase of the other cell edges. The potential thus reorients the molecules into parallel layers, probably as a result of an underestimation of the attraction between a large π system and the H atoms. Indeed, it has been shown (Williams & Starr, 1977) that the inclusion of explicit electrostatic terms in the potential (at the expense of an increase in the number of parameters) removes this pitfall. Interestingly, our potentials do not predict such a structure reorganization for benzene ($F = 22$). Other large F values, mainly because of rotational displacements, result for anhydrides and quinones: maleic anhydride ($F = 190$, $\Delta\theta = 15°$), *p*-benzoquinone (206, 21°), dimethylbenzoquinone (214, 12°). This may be because of an imperfect representation of the C—H···O hydrogen bonds; succinic anhydride, the H atoms of which are less acidic, shows a rotational displacement of only 6°. Large F values result for 2,3-diazanapthalene, triazine and tetrazine. There is no simple structural explanation for this, but the difficulties of dealing with aromatic aza compounds using empirical potentials are well known (Pertsin & Kitaigorodski, 1987, pp. 93–105; Stone & Price, 1988, and references therein). A few nitrile compounds also show some structural instability under the action of our optimized potentials.

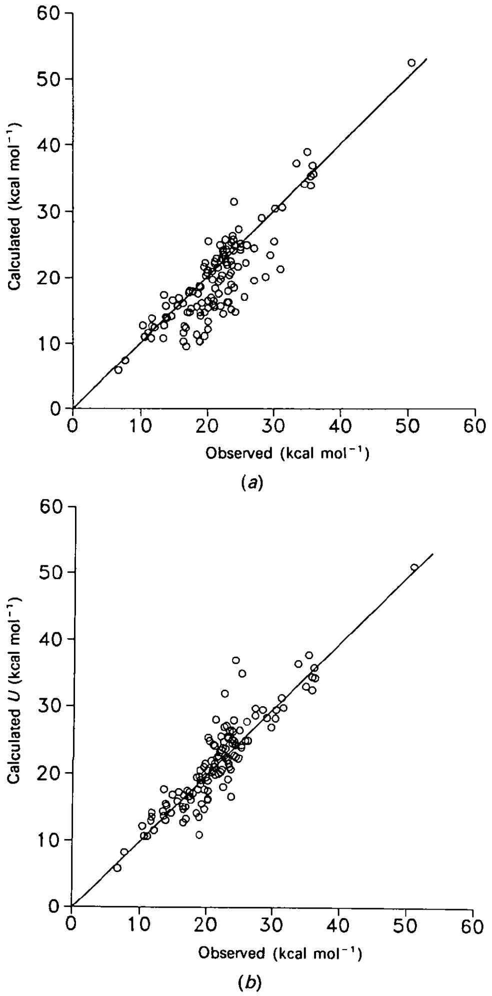

Fig. 8. Observed *versus* calculated heats of sublimation for 122 crystals: (*a*) potentials obtained from literature (Mirsky compilation), see Table 5; (*b*) potentials developed in this work.

Lattice vibration frequencies

The calculated frequency ranges (Tables 1–4) are very good for hydrocarbons; the new functions do not, however, give a dramatic improvement over previous calculations (Filippini, Gramaccioli, Simonetta & Suffritti, 1973). For the other classes of compounds considered here the general agreement is encouraging, apart from a few cases of imaginary frequencies. Calculated frequencies are matched to the observed ones for the crystals in Table 9. It should be remembered that for non-rigid molecules the possibility of mixing of internal and external modes arises and a comprehensive treatment of both modes (Filippini & Gramaccioli, 1986) would be required to accurately reproduce the experimental spectrum.

The results for standard molecules (benzene, naphthalene and anthracene) are not presented in detail, since they are not significantly different from those obtained using Williams' potential (Filippini *et al.*, 1973). The results for phenanthrene and pyrene are also satisfactory. Discrepancies for durene and hexane are possibly as a result of mixing with internal modes. For cubane, the experimental A_g and E_g frequencies appear to have been interchanged. For anthraquinone, agreement for IR is good, while a mismatch in the Raman frequencies appears; it could arise from one missing observed frequency, especially for B_g. The agreement is generally good for succinic anhydride and dimethyl oxalate also, while for phthalic anhydride all calculated frequencies are lower than those observed.

A very good agreement is obtained for hexamethylenetetraamine and triethylenediamine; for nitrile compound, the results are satisfactory in the case of tetracyanoethylene, less so for TCNQ. For pyrimidine, one imaginary frequency appears using the high-temperature crystal structure, while using the 107 K structure the agreement is satisfactory. The results for chloro compounds are quite resonable, and even for trithiane, the calculated PE of which does not compare favourably with ΔH_s, the agreement is acceptable.

Concluding remarks

A new set of empirical atom–atom intermolecular potential functions for organic crystals without hydrogen bonds has been derived in a consistent manner. The separate optimization of parameters for each couple of atomic species, together with the use of a large body of experimental data encompassing all the building blocks of organic chemical compounds, ensures an acceptable accuracy and transferability even using the simple 6-exp functional form. The strong point of the formulation is its adherence to simple and basic structural requirements, especially in the consistent location of R^0 against the distribution of distances in real crystals.

The good results obtained in the calculation of many crystal properties for many different compounds demonstrate that simple and relatively inexpensive force fields can still find useful applications. They can be used to describe the non-hydrogen-bonded part of complex interacting systems, presumably without significant loss in accuracy with respect to more sophisticated force fields.

Building upon these results, the development of a more complete force field for organic crystals including hydrogen-bonded systems is in progress.

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C—H···O Packing Motifs in Some Cyclopenta[*a*]phenanthrenes

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Abstract

An analysis has been made of the C—H···O interactions in cyclopenta[*a*]phenanthrenes, for which structural data on fifteen 15,16-dihydrocyclopenta[*a*]phenanthren-17-ones are available. These compounds mostly contain only one O atom, a carbonyl group at the 17-position, and therefore the only groups available for interactions are C—H groups. In addition, the crystal structure of a second polymorph of the 11-ethyl derivative is described. $M_r = 260.33$, *Pbca*, $a = 17.012\ (2)$, $b = 21.042\ (2)$, $c = 7.6465\ (6)$ Å, $V = 2737.2\ (4)$ Å^3, $Z = 8$, $D_x = 1.264$ Mg m^{-3}, Cu $K\alpha$, $\lambda = 1.5418$ Å, $\mu = 0.56$ mm^{-1}, $F(000) = 1104$, $T = 295$ K, final $R = 0.090$ for 1669 reflections above $2\sigma(F)$. The conformation of the ethyl group is *gauche* [C(12)—C(11)—C(18)—C(19) = 75.8 (7)°], differing from the *cis* value of $-1.3\ (5)°$ for the *Pnaa* form. The molecular distortion in the *Pbca* polymorph is also larger than that in the *Pnaa* polymorph; this distortion is evidenced by torsion angles (13–20°) in the bay region and by an out-of-plane displacement (0.8 Å) of the C atom of the methylene portion of the ethyl group [the C atom attached to C(11)]. Packing diagrams and intermolecular distances were analyzed for all the dihydrocyclopenta[*a*]phenanthrenes for which structural data are available. There appear to be three types of packing. The first type consists of a dimer herringbone formed by the interactions of two molecules by way of the ketone group and the C—H of C(12) of the adjacent ring. The second type of packing also involves a dimer but involves C—H and O═C groups at either ends of the molecule. The third type is a layer structure and involves com-

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