After heating of the sealed NMR tube at 130 °C for 10 min, all of the **24** had gone to **25** and the hydrazine **45** remained unchanged, even after an additional 2 h at 130 °C.

Heating **26** with benzpinacol for 20 min afforded products **27** and **48** in the 5:1 ratio according to ^{1}H NMR. The amount of **48** decreased on longer heating, reaching an undetectable level after 10 h. In contrast, bis(azoalkane) **28** showed **29** as the only product, even when thermolysis was interrupted after 20 min.

Flash Photolysis. The rate constant for quenching of benzhydryl radicals by ATB was determined by laser flash photolysis using 540-nm light to monitor the radical. A nitrogen-purged solution of 3.35×10^{-5} M benzophenone and 0.066 M triethylamine[13] in hexane and a solution of 2.83×10^{-4} M phenylbenzoin[18] was irradiated at 266 nm. Similarly, a 5×10^{-3} M solution of phenylbenzoin was irradiated at 355 nm. Addition of ATB shortened the decay lifetime, although vaporization of the quencher during purging causing scatter in the calculated k_q values. It was clear, however, that k_q was at least 10^8 M^{-1} s^{-1}.

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Statistical Analysis of Some Structural Properties of Solid Hydrocarbons

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Abstract: The crystal structures of 391 hydrocarbon molecules, comprising 18 249 atoms, retrieved from the Cambridge Structural Database, have been examined. Centrosymmetric space groups occur more frequently than in general organic compounds. Tables of atomic volume and surface increments are given. Averages of various packing indices are calculated. Molecular size is correlated to the packing energy, as computed by empirical potentials; methods to estimate accurately sublimation energies are developed, and trends in groups of compounds are discussed in terms of molecular structural properties. These trends survive changes in the potential energy parameters. It is found that flat, rigid, unsaturated molecules have the best chances to form a compact crystal, while alkyl substituents are strong perturbing factors. Bulk moduli and thermal conductivities are estimated, and it is found that the modulus is a convenient index of packing efficiency and correlates to molecular shape and symmetry effects. A principal-component analysis reveals three main factors, which can be interpreted as size, packing score, and packing "failure" coordinates; the shape effect cannot yet be deconvoluted from these factors. The analysis of the distribution of atomic contributions to the cohesion energy allows a verification of the homomeric principle and reveals the intramolecular screening factors that diminish the cohesion at certain atoms, as opposed to the effects of irregular molecular shape, which diminish the cohesion more uniformly at all atoms. Cylindric molecules pack in such a way that their elongation axes are very nearly parallel in the solid state. Future uses of the packing analysis hydrocarbon files are sketched.

X-ray crystallography has been, in the last 30 years or so, at the forefront of organic physical chemistry, providing an invaluable help in understanding chemical properties in terms of structure. As a result of this massive effort, all the basic information a chemist may need on molecular geometry is by now, or will be in the next few years, stored in the Cambridge Structural Database[1a,b] (CSD), from which exhaustive catalogs of molecular dimensions have already been produced.[1c]

It has been less widely recognized, let alone exploited, that another kind of expertise is made available by X-ray studies of organic crystals, that is, a detailed knowledge of the molecular packing. This intermolecular information is stored in the CSD as well, and, although so far considered as a fringe benefit of crystal studies, it is now very much in demand for use in materials science and drug design. It appears then well worth trying to tap this source of chemical knowledge; among the previous efforts in this direction we may mention studies of H bonding[2a-b] and of

Table I. Geometrical Rules for Automatic Classification of C Atom Types and Assignment of Hydrogen Atoms[a]

no. of bonds to other C atoms	test procedure	classification (H atoms assigned)
3	$R_1 + R_2 + R_3 < 4.44$	aromatic (none)
	>4.44	aliphatic (one, methine)
2	$R_1 + R_2 < 2.65$	acetylenic or allenic (none)
	$2.65 < R_1 + R_2 < 2.96$	aromatic (one H atom)
	$R_1 + R_2 > 2.96$	methylenic (two H atoms)
1	$R < 1.48$	ad hoc procedures
	$R > 1.48$	methylic (three H atoms)

[a] R_i's are the distances (Å) from other C atoms.

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(1) (a) Data were retrieved from the 1986 release. Programs used are described in: Allen, F. H.; Bellard, S.; Brice, M. D.; Cartwright, G. A.; Doubleday, A.; Higgs, H.; Hummelink, T.; Hummelink-Peters, B. J.; Kennard, O.; Motherwell, W. D. S.; Rodgers, J. R.; Watson, D. G. *Acta Crystallogr.* **1979**, *B35*, 2331. (b) *Molecular Structures and Dimensions*; Kennard, O., Watson, D. G., Allen, F. H., Bellard, S. A., Eds.; Reidel: Dordrecht, The Netherlands, 1984; Vol. 15, and continuing series. (c) Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc., Perkin Trans. 2* **1987**, S1.

0002-7863/89/1511-1835$01.50/0

some special intermolecular approach distances.[2c-e]

We have developed a number of methodologies for the classification of the intermolecular properties of organic crystals,[3] and, to some extent, of their dynamic behavior.[4] This paper is devoted to a statistical analysis of these properties, using 391 (nearly all the fully characterized) crystal structures of hydrocarbons in the CSD.

Retrieval from the CSD and Placement of Hydrogen Atoms. Automatic generation of input files for the program OPEC[3b] from the output of the bibliographic search programs[1a] was performed; hydrogen atoms, whose positions were inaccurately determined by X-ray studies, were assigned on the basis of C atom connectivity. Table I shows how; the large number of exceptions (taken care of separately) for conjugated sp and sp^2 C atoms illustrates the difficulty of coding the valence shell of carbon in terms of geometry only. Details on the procedures for data retrieval and H atom positioning are given in the Appendix.

The final data set contained 391 crystal structures of hydrocarbons, virtually all the well-characterized, disorder-free X-ray (with some neutron) determinations for such compounds, as of 1986. Table II (in the supplementary material) contains the CSD refcodes. The presence in the CSD of both independent and symmetry-related atom coordinates was of enormous help, as was the provision of crystal symmetry information in the convenient form of repetition matrices and vectors, even for nonstandard choices of origin or space group. Incidentally, it should be noted that molecules made of more than one asymmetric unit introduce nonindependent data in the averages of some atomic intermolecular properties. This is tantamount to giving multiple weight to some atoms, and we thought it appropriate to retain this weighting since our analysis is focused on properties of entire molecules.

The files so generated are thus standardized in the choice of the appropriate symmetry subgroups (a technical problem) and in the location of H atoms (an important methodological problem in packing analysis). Since they are ready for access by OPEC and many other packing energy or lattice dynamics programs, they can be used to probe a number of crystal chemistry topics. The CSD OPEC interface computer programs are available for distribution upon request to the author.

Subdivision into Main Groups. The classification of compounds in groups or classes of distinct molecular properties is a difficult but essential task. We are satisfied at this stage with an a priori partitioning based on gross structural features. A posteriori, when all the molecular and crystal properties of each compound are known, a cluster analysis could fruitfully be applied. The preliminary screening into structural groups was done as follows. AR-PLANAR (23 compounds): sp^2 C atoms only, in condensed ring systems (planar or nearly planar shape). AROM (20 compounds): sp^2 C atoms only, all involved in aromatic ring structures. AR-ETHYL (18 compounds): sp^2 C atoms only, aromatic rings and ethylenic systems. CLPHN (39 compounds): cyclophanes and molecules with aromatic rings held face to face. HELIC (24 compounds): helicenes and twisted polyaromatic compounds. GEM-PHE (25 compounds): compounds with *gem*-polyphenyl substitution, forcing propeller-like arrangements. ANNUL (15 compounds): annulenic ring structures, bridged or not. ALIPH (19 compounds): sp^3 C atoms only, rings with no less than six C atoms. STRING (105 compounds): rings with less than six C atoms, and cage structures, spiro compounds, rotanes and propellanes. YNES (18 compounds): all molecules with at least one sp C atom, plus allenes and cumulenes. GENERAL (85 compounds): all compounds obeying none of the above conditions. These include, for instance, alkyl-substituted aromatics.

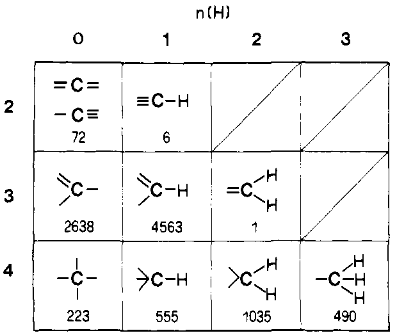

Figure 1. Types and number of carbon atoms in the data set, by coordination number (top to bottom) and number of hydrogens (left to right).

The above classification is often subjective, as many compounds belong, strictly speaking, to more than one of these groups. Further sorting, on the basis of more specific requirements, was then performed for special purposes.

Calculation of Molecular and Crystal Properties. (a) Molecular Properties (See Reference 3 for Details). These include the following: atomic connectivity and labeling of each atom according to its coordination sphere (see Figure 1); W_m = molecular mass; N_C and N_H = number of C and H atoms; M_1, M_2, and M_3 = moments of inertia in decreasing order and direction cosines of inertial axes in the crystal; Z_v = number of valence electrons; S_m and V_m = molecular van der Waals surface and volume; S_i, V_i = contribution of atom i to these; S_r, V_r = contribution of all atoms of species r.

(b) Crystal Properties. These include the following: D_c and D_{el} = density in g/cm^3 and number of electrons per unit volume in the cell; C_k = Kitaigorodski packing coefficient or ratio of occupied to total volume of the cell; PE, packing energy computed as a sum of atom–atom terms of the 6-exp (Buckingham) type, within a 7-Å cutoff. This can be partitioned over atoms, giving E_i (also called energetic relevance[3a]), over atomic species, giving E_{rs}, or over molecules, giving E_{1j}. The following holds

$$\sum_j E_{1j} = \sum_i E_i = \sum_{r,s} E_{rs} = \text{PE}$$

where i runs over atoms, j over molecules in the crystal, and r and s over atomic species (C or H). R_{1j} is the distance of the center of mass of molecule 1 to that of molecule j in the crystal.

Discussion of the Parametrization. We consider as parameters in our model the following quantities: (i) the atomic radii, which influence S_m and V_m, (ii) bond distances and angles involving H atoms, and (iii) the functional form and the coefficients of the nonbonded energy potentials.

The choice of atomic radii has already been discussed, and it was found that volumes and surfaces are insensitive to small variations of the radii.[3b-c] Even smaller is the sensitivity to slight changes of geometry at the H atoms. Standardization of the C–H distance at 1.08 Å is consistent with the practice followed in the optimization of the potential energy functions we are using. We have checked that calculated PE's are only marginally influenced by variations of this parameter within a few hundredths of an angstrom or by changes in bond angles.

The choice of the potential functions deserves further comment. PE is computed as a sum of atom–atom terms, as has been done successfully for decades.[5] We have settled, at the beginning of our work on packing analysis,[3a] on a comprehensive set of parameters[6a-b] for carbon-, hydrogen-, and heteroatom-containing

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(3) (a) Gavezzotti, A. *Nouv. J. Chim.* **1982**, *6*, 443. (b) Gavezzotti, A. *J. Am. Chem. Soc.* **1983**, *105*, 5220. (c) Gavezzotti, A. *J. Am. Chem. Soc.* **1985**, *107*, 962. (d) Gavezzotti, A.; Desiraju, G. R. *Acta Crystallogr.* **1988**, *B44*, 427.

(4) Gavezzotti, A.; Simonetta, M. *Acta Crystallogr.* **1975**, *A31*, 645. (b) Gavezzotti, A.; Simonetta, M. *Acta Crystallogr.* **1976**, *A32*, 997. (c) Filippini, G.; Gavezzotti, A.; Simonetta, M.; Mason, R. *Nouv. J. Chim.* **1981**, *5*, 211.

(5) Pertsin, A. J.; Kitaigorodsky, A. I. *The Atom–Atom Potential Method*; Springer-Verlag: Berlin, 1987.

Table III. Space Group Frequencies (%)

space group	hydrocarbons[a]	general organic compounds[b]
$P2_1/c$	42.4	36.0
$P\bar{1}$	14.9	13.7
$C2/c$	10.3	6.6
$Pbca$	7.7	4.3
$P2_12_12_1$	4.6	11.6
$P2_1$	4.4	6.7
others	15.7	21.1

[a] This work; 391 structures. [b] Reference 10; 29 059 compounds.

molecules. It reproduces sublimation energies[6a,3d] and the equilibrium positions of molecules in the crystal: in this, however, it is not superior to other formulations. More specialized parameter sets have appeared since, mostly through the work of Williams and collaborators.[6c–g] One undesirable feature of these last parametrizations, for our present purposes, is the explicit presence of coulombic terms over site charges, which do not always reside on atomic nuclei: this impedes all our energy-partitioning schemes.

The question of explicit electrostatic contributions in packing theories becomes more and more relevant on going to crystals of heteroatom-containing molecules. It has been proposed[7a] that plausible potential functions without coulombic terms can be developed also for moderately polar substances, electrostatic interactions being partly embodied in the 6-exp expansion. The straightforward interpretation of the r^{-1} terms as "coulombic" terms has been criticized[7b] along the same line of thought. With the proviso that one is losing accuracy in the calculation of some crystal properties if these terms are missing, we endorse these opinions; for example, for the calculation of lattice vibrations or of the energy of hydrogen bonds,[8] accurately calibrated parameters must be used. In our perspective, however, absolute values of lattice energies are not the most important part of the theory. Thus we use simpler functions and shift the emphasis on structural properties, like molecular shape, available space in the crystal, or the mutual orientation of elongation axes or of molecular dipoles. Properties like molecular reorientation or crystal reactivity are such that long-range, slowly varying electrostatic contributions are either spectator forces[9a] or can be described by simpler terms than extensive lattice sums.[4b] In fact, chemically significant, if not quantitative, results have been obtained in this way even for polar molecules (see ref 3a–c and 9b and references therein).

We may conclude that our parametrization is well suited for the problems we want to discuss, and, from experience gathered during its development, we also conclude (see further sections) that reasonable changes in the parameters do not affect the trends on which our packing analysis is founded.

Overall Statistics. The data set contains 78, 7202, and 2303 C atoms with coordination 2–4, respectively, and 8666 H atoms. On the average, therefore, the C/H ratio is 1.11, and the ratio of 3- to 4-coordinated C atoms is 3.13. sp-Hybridized and allenic C atoms are a rarity. The average W_m, S_m, and V_m are 299 Da, 323 Å^2, and 296 Å^3, respectively. Thus, the data set contains mainly medium-size molecular objects. Crystal cohesion energies are substantial, confirming that, barring more subtle questions such as the overlooking of localized disorder or the use of lower symmetry space groups, no gross mistaking of spatial symmetry has ever occurred in the X-ray structure analyses.

Table IV. Averages (σ) of Packing Coefficients, C_k, and Densities for Groups of Compounds

group symbol	no. of entries	C_k	D_c, g/cm^3	D_{el}, e/Å^3
AR-PLANAR	23	0.749 (28)	1.340 (111)	0.423 (32)
HELIC	24	0.723 (13)	1.287 (47)	0.407 (12)
AROM	20	0.724 (22)	1.256 (65)	0.398 (19)
AR-ETHYL	18	0.725 (15)	1.232 (47)	0.392 (13)
CLPHN	39	0.737 (26)	1.240 (62)	0.400 (19)
ANNUL	15	0.733 (13)	1.219 (59)	0.392 (16)
YNES	18	0.717 (25)	1.162 (85)	0.372 (22)
STRING	105	0.703 (32)	1.193 (85)	0.388 (23)
GENERAL	85	0.711 (20)	1.155 (88)	0.375 (23)
GEM-PHE	25	0.707 (18)	1.166 (41)	0.375 (11)
ALIPH	19	0.708 (24)	1.010 (64)	0.346 (20)
all	391	0.717 (28)	1.198 (102)	0.387 (26)

Table V. Parameters a_1 and a_2 for PE = $a_1S_M + a_2$ (kcal·mol^{-1}; 7-Å Cutoff) for Various Groups or Classes of Hydrocarbon Compounds[a]

group or class	a_1	a_2	S
AR-PLANAR	0.2442 0.2839[b]	−13.10 −16.25[b]	4.69
AROM	0.1256	11.40	11.33
AR-ETHYL	0.1518	4.99	4.43
methylated planar aromatics	0.1627	2.00	3.89
alkyl-substituted planar aromatics	0.1493	3.42	4.90
ANNUL	0.1648	2.24	2.54
HELIC	0.1064	19.03	3.97
GEM-PHE	0.0764	25.55	6.40
ALIPH	0.1159 0.1101[b]	11.33 9.57[b]	
all	0.1125 (0.0036)	14.29 (1.22)	7.16

[a] σ's are 0.01–0.02 for a_1 and 1–5 for a_2. They are given explicitly for the regression on all hydrocarbons (in parentheses). S is the rms deviation. [b] Using potential energy parameters from Williams: Williams, D. E. *J. Chem. Phys.* **1967**, *47*, 4680.

The distribution of the crystal structures among space groups is given in Table III, which reveals a noticeable increase of the frequency of centrosymmetric space groups with respect to general organic compounds,[10] with a consistent trend over all six most populated space groups. This may indicate that, packing forces in hydrocarbons being feebler than in polar compounds, the help of the center of symmetry in producing a compact packing is sought more often. This result may also depend on the distribution of molecular symmetries and chiralities within the sample.

Table IV collects averages of some packing indices. The AR-PLANAR group stands out as significantly more compact; the close-packing principle is more strictly obeyed in this group. A progressively looser packing is observed in groups that contain flexible molecules, like the alkanes, or the HELIC or GEM-PHE groups, where the irregular shape impedes a regular occupation of the available space. This table is important in that it provides standards by which the compactness of any crystal or material made of hydrocarbon molecules can be measured and to some extent predicted.

Packing Energy Dissection and Statistics. A detailed study of the convergence behavior of the lattice sums for PE was conducted on a sample of 60 widely different crystal structures. A cutoff of 7 Å produces 86% of the PE at 15-Å cutoff, on the average; this being known[11] to be convergent within 1%, $^1/_2$PE at 7 Å can be taken as 85% of the total sublimation energy (the overall accuracy does not warrant a discussion of zero-point energies).

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(6) (a) Mirsky, K. V. *Acta Crystallogr.* **1976**, *A32*, 199. (b) Mirsky, K. V. In *Computing in Crystallography. Proceedings of an International School on Crystallographic Computing*; Delft University Press: Twente, The Netherlands, 1978; pp 169–182. (c) Williams, D. E. *Acta Crystallogr.* **1974**, *A30*, 71. (d) Williams, D. E.; Cox, S. R. *Acta Crystallogr.* **1984**, *B40*, 404. (e) Cox, S. R.; Hsu, L. Y.; Williams, D. E. *Acta Crystallogr.* **1981**, *A37*, 293. (f) Hsu, L. Y.; Williams, D. E. *Acta Crystallogr.* **1980**, *A36*, 277. (g) Williams, D. E.; Houpt, D. J. *Acta Crystallogr.* **1986**, *B42*, 286.

(7) (a) Reference 5, pp 74 and 75, and passim. (b) Ramdas, S.; Thomas, N. W. In *Organic Solid State Chemistry*; Desiraju, G. R., Ed.; Elsevier: Amsterdam, The Netherlands, **1987**; p 438.

(8) Tang, C. P.; Chang, H. C.; Popovitz-Biro, R.; Frolow, F.; Lahav, M.; Leiserowitz, L.; MacMullan, R. K. *J. Am. Chem. Soc.* **1985**, *107*, 4058, and references therein. Especially: Lifson, S.; Hagler, A. T.; Dauber, P. *J. Am. Chem. Soc.* **1979**, *101*, 5131.

(9) (a) Gavezzotti, A. *Acta Crystallogr.* **1987**, *B43*, 559. (b) Gavezzotti, A. *Tetrahedron* **1987**, *43*, 1241. See: Kearsley, S. K.; McBride, J. M. *Mol. Cryst. Liq. Cryst.* **1988**, *156*, 109. They use parameters from ref 6c and 6e.

(10) Mighell, A. D.; Himes, V. L.; Rodgers, J. R. *Acta Crystallogr.* **1983**, *A39*, 737.

(11) Kitaigorodsky, A. I. *Molecular Crystals and Molecules*; Academic Press: New York, 1973; p 167.

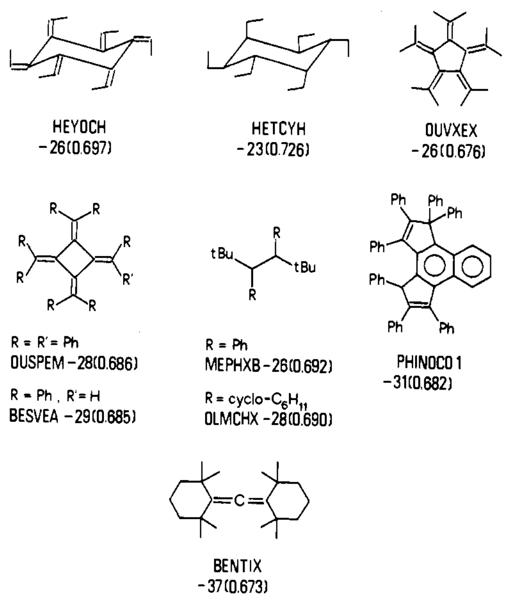

Figure 2. Compounds with $S_M > 160$, not belonging to the AR-PLANAR group, which deviate by more than 25% from the S_M/PE correlation. Refcode, percent deviation, and packing coefficient (in parentheses) are given. Optimization of methyl hydrogen positions slightly reduces some deviations.

Table VI. Averages of Atomic Properties (σ's of the Distribution in Parentheses)[a]

atom	no. of entries	$\bar{S}$, Å^2	$\bar{E}$, kcal·mol^{-1}
hydrogen	8666	6.48 (65)	0.67 (16)
sp carbon	78		1.57 (35)
sp^2 carbon	7202		1.60 (40)
sp^3 carbon	2303		1.54 (41)

[a] No average surface for C atoms, since the distribution is multimodal (see text and Tables VII and VIII).

Comparisons with the few available experimental values confirm this.

The PE is a function of molecular size and shape. For example, when the melting points of very uniform classes of substances are plotted against molecular size, rigid and unfolded molecules show steeper rates of increase than flexible and folded ones.[12] In the context of condensed phases, size can be conveniently represented by the molecular surface, while there is no simple and safe index of molecular shape (although some possibilities will be explored later in this paper).

Table V reports the regression parameters for PE versus S_m data. The AR-PLANAR group stands out with the largest slope by far; then come the rigid bridged annulenes, the aromatics, and at the end the curled and flexible GEM-PHE and HELIC molecules. Particularly striking is the decrease in slope upon introduction of alkyl substituents on the rigid aromatic cores. One can see from Table V that the use of different PE functions only marginally changes the absolute values and does not alter the trends in slopes or the conclusions on the dependence of packing efficiency on structure.

The regression on all hydrocarbons systematically overestimates PE for $S_m < 150$. On the contrary, PE is underestimated for molecules containing large planar aromatic fragments, as discussed before. Aside from this, the calculated PE is lower than the estimate by more than 25% in only the few cases illustrated in Figure 2. For some, an explanation can be attempted on the basis of molecular structure (see below), but the occasional misinterpretation of the structure in terms of disorder or of missed solvate molecules cannot be ruled out. Biases to the opposite side due to the low temperature of the X-ray determination are not likely, since for naphthalene, for example, the PE increases by only 1.7% on going from 239 to 92 K.

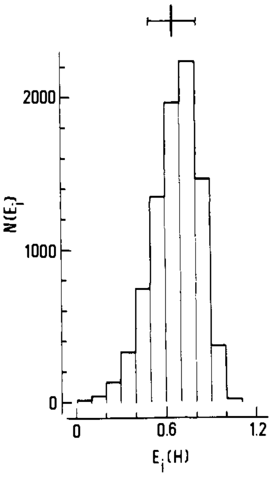

Figure 3. Histogram of atomic contributions to PE (atomic relevances) of hydrogen atoms (kcal mol^{-1}). The average and standard deviation are shown on top.

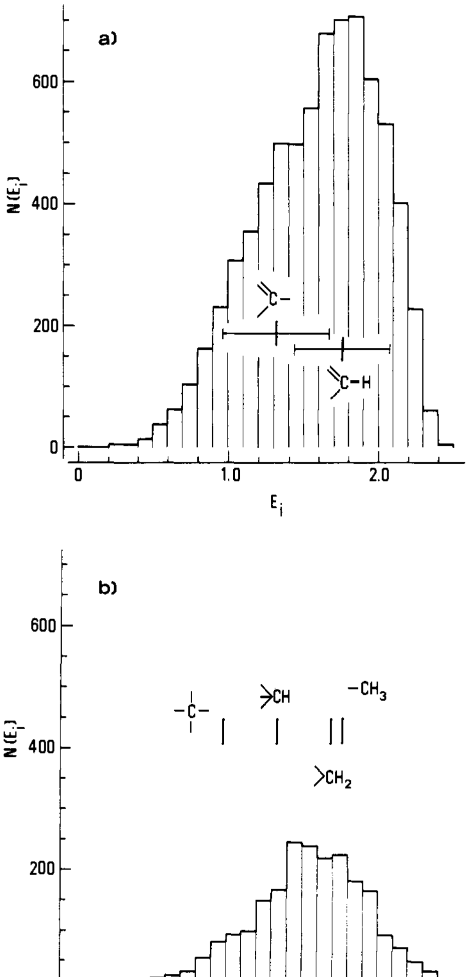

Figure 4. (a) Histogram of E_i (kcal mol^{-1}) for sp^2 carbon atoms. (b) Same for sp^3 carbon atoms. Vertical bars show the averages for each type of atom.

The correlations in Table V can be used in the predictions of sublimation energies with an accuracy comparable to that of the experimental determinations. The different slopes reveal that a molecular shape effect is involved in the packing; we feel that the

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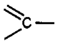
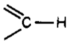
[12] Ubbelohde, A. R. *The Molten State of Matter*; Wiley: Chichester, England, 1978; pp 136 and 160.

Table VII. Averages of Atomic Properties for Aromatic Carbon Atoms[a]

						
group	n	$\bar{S}$	$\bar{E}$	n	$\bar{S}$	$\bar{E}$
AR-PLANAR	250	5.79 (12)	1.82 (17)	324	10.64 (55)	2.11 (17)
AR-ETHYL	130	5.40 (66)	1.40 (28)	322	10.42 (82)	1.89 (27)
GENERAL	562	5.27 (93)	1.36 (33)	884	10.59 (75)	1.79 (29)
HELIC	343	5.19 (114)	1.24 (29)	453	10.52 (88)	1.73 (28)
STRING	469	5.16 (118)	1.25 (33)	837	10.84 (71)	1.77 (29)
ANNUL	60	5.02 (82)	1.59 (16)	170	10.20 (74)	1.92 (16)
AROM	216	5.01 (106)	1.25 (41)	408	10.47 (85)	1.72 (33)
CLPHN	350	4.61 (79)	1.17 (22)	442	9.77 (138)	1.53 (28)
GEM-PHE	174	4.28 (128)	0.95 (35)	553	10.29 (114)	1.53 (37)
all	2638	5.12 (104)	1.32 (37)	4563	10.49 (93)	1.76 (33)

[a] n is the number of entries; units of Å^2 and kcal mol^{-1}. $\bar{S}$, average of S_i; $\bar{E}$, average of E_i.

Table VIII. Average Atomic Properties of Aliphatic C Atoms[a] and of the Acetylenic Group

	$-C(H_3)$			$>C(H_2)$			$>C(H)$			$-\overset{\vert}{\underset{\vert}{C}}-$		
group	n	$\bar{S}$	$\bar{E}$	n	$\bar{S}$	$\bar{E}$	n	$\bar{S}$	$\bar{E}$	n	$\bar{S}$	$\bar{E}$
CLPHN				216	6.84	1.84						
GEM-PHE	36	11.33	1.57							23	0.83	0.65
STRING	122	10.91	1.68	404	7.50	1.68	433	4.07	1.38	124	1.23	0.97
GENERAL	223	11.15	1.79	145	6.79	1.74	47	2.71	1.25	44	0.51	1.00
ALIPH	42	10.96	1.71	214	6.83	1.76	46	1.84	1.06			
all	490	11.08 (1.19)	1.74 (33)	1035	7.09 (1.44)	1.69 (31)	555	3.69 (1.49)	1.32 (34)	223	0.98 (1.00)	0.96 (26)

	≡C—, =C=			≡C(H)		
group	n	S	E	n	S	E
YNES	68	12.19	1.55	6	21.32	2.11

[a] See also captions to Table VII. σ's given in parentheses only for the sample of all atoms.

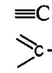
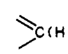
main importance of the correlations and the data of Table V is that they provide standards by which the packing efficiency of other classes of molecular morphologies can be checked.

We now turn to an analysis of the distributions of atomic properties. Figures 3 and 4 show the histograms of E_i, while Tables VI–VIII show averages over various atom types, along with averages of S_i. Table IX shows average atomic volumes, which are affected by small standard deviations, since volume is less sensitive to changes in molecular geometry than surface and also because volume is computed by a more schematic method (the volume of H atoms is constant by construction). The data in Table IX provide updates and integrations to previously published[3b–c] tables of group increments. The volumes we obtain are about 90% of those obtained by an analysis of the electron density boundaries at 0.002 au,[13] although the partitioning of volumes into atomic basins on quantum chemical grounds is quite different from our crude partitioning into spheres and caps. Trends are however similar, and the quantum chemical result confirms that atomic volume corresponds to a well-established and reproducible molecular property.

The distributions of E_i's in Figures 3 and 4 are skewed: an atom can contribute less than the average, due to various effects, but not more than what is allowed at the saturation of its intermolecular coordination sphere. The histogram for H is narrow and represents very sharply the fact that the contribution of each H atom to the PE of hydrocarbons must be nearly constant (the constancy of the C–H distance is not a bias, since small variations could equally well have opposite effects). The homomeric principle,[3a] which states that a given atomic species tends to contribute a fixed amount to the PE in any crystal, is thus strictly obeyed for H atoms, whose surfaces are most evenly exposed to intermolecular contacts.

The histograms for carbon atoms conceal a bimodal (Figure 4a) or multimodal (Figure 4b) distribution. The averages in Table VI are thus, strictly speaking, scarcely significant: remarkably, they are, however, almost exactly equal. The components can be resolved on chemical grounds, as shown in Figure 4 and detailed in Tables VII and VIII. The enforcement of the homomeric principle depends here on the definition of a species, be it a carbon atom, or each of the types of C atoms according to intramolecular coordination. Complete validation of the principle would require that standard deviations (SD) tend to zero, which could be approached, as the definition of species becomes narrower and narrower.

Table IX. Average Atomic Volumes of C Atoms (Å^3)[a]

type	no. of entries	V (this work)	V (ref 13)[b]
≡C— =C=	72	12.1 (1)	
≡C(H)	6	15.9 (2)	14.6
	2638	8.3 (2)	
	4563	11.7 (1)	
$=C\binom{H}{H}$	1	15.5	11.5
$-\overset{\vert}{\underset{\vert}{C}}-$	223	5.2 (3)	6.1
$>C(H)$	555	8.6 (2)	6.8
$>C(H_2)$	1035	11.9 (1)	7.5
$-C(H_3)$	490	15.3 (1)	8.5

[a] H atom volume is 2.3 Å^3, constant by construction; the volume of each group can be obtained by adding the value in column 3 for C plus 2.3 times the number of H atoms. [b] From electron density at 0.002-au threshold and partitioning of the density into atomic basins.

In Table VII, the AR-PLANAR group stands out again for high values of $\bar{E}$ and for the small SD's of E_i and S_i (a small SD for the S_i is indicative of structural homogeneity within the group). As before, the annulene group follows; low values of S_i appear in the GEM-PHE and CLPHN groups, for conformational reasons connected with steric strain (the relationship between S_m and molecular strain has already been discussed[14]). High values of

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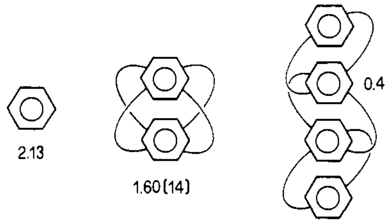
(13) Bader, R. F. W.; Carroll, M. T.; Cheeseman, J. R.; Chang, C. *J. Am. Chem. Soc.* **1987**, *109*, 7968.

(14) Bianchi, R.; Gavezzotti, A.; Simonetta, M. *THEOCHEM* **1986**, *135*, 391.

Chart I



S_i for the ring atoms appear in the STRING group, an effect which has already been noticed both on surfaces[3c] and volumes.[13] While higher $\bar{S}$ values generally correspond to higher $\bar{E}$ values, the relationship between individual S_i and E_i is much less clear. The values of S_i reflect the shielding by atoms within the bonding coordination sphere of atom i, while the intermolecular exposure may depend also on the interposition of further parts of the molecule. Thus, a direct relationship between S_i and E_i can be expected only for atoms in similar conformational environments.

Out of 9583 carbon atoms, 197 deviate by more than 70% and 247 by more than 60% from the average $\bar{E}$. It is often found that compounds that deviate from the S_m/PE correlation contain several atoms whose E_i is low; this is the result of intramolecular, rather than intermolecular, factors. Lattice stability tends to be achieved by a uniform participation of all atoms to the binding field, but intramolecular self-screening can prevent this. To exemplify, consider the following series, where the average E_i for ring C atoms bearing H atoms are reported (in parentheses, the number of samples in the average; the loose connections mean different types of cyclophane bridges; Chart I).

The structure of benzene allows interactions on both sides of the molecule, while in the other cases one or both directions are blocked from intermolecular contacts by the screening from the rest of the molecule.

On the other hand, a low PE may correspond to a general, but less drastic, decrease in all the E_i's in the molecule; then the packing is soft, and a low density is also observed. This is the result of an irregular molecular shape or may reveal the accidental overlooking of disorder or of solvate molecules. Finally, it may be thought that low E_i's result from forced repulsive intermolecular contacts, rather than from the lack of attractive ones; this type of strain is, however, very difficult to establish between C atoms in hydrocarbon crystals.

The above indicates that the E_i's can be used to trace close packing to the level of single atoms and thus to analyze at that level chemically or structurally relevant phenomena in molecular crystals. Comparisons of E_i for the same atom in different crystal phases of the same compound have been reported.[15]

Bulk Moduli and Thermal Conductivities. There has been recently a renewed interest in the calculation of surface and volume for use in empirical correlations to physical properties of the condensed phases.[16] For crystals it is also possible to obtain the number and relative orientation of nearest neighbors and to calculate the sublimation energy, given the success of the nonbonded potential method. Some mechanical and thermal properties of the crystal can then be estimated.[17] The bulk modulus at zero pressure and at 60% of the melting temperature is given by

$$K_0 = 4.18 \times 10^{7}(\Delta H_{\text{sub}}/V_{\text{m}})[31.63(D_{\text{c}}V_{\text{m}}/W_{\text{m}}) - 14.2] \text{ (dyn cm}^{-2}\text{)}$$

and the thermal conductivity by

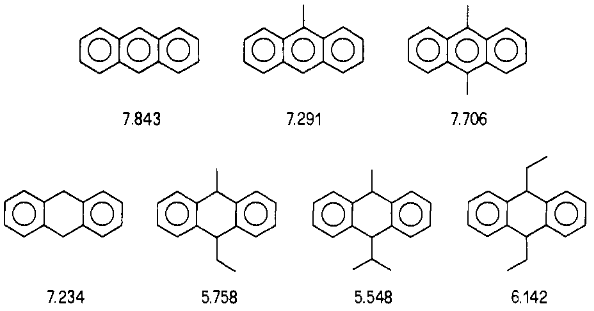
$$\lambda = 1.35 \times 10^{-4}\Delta H_{\text{sub}}^{3/2}/(W_{\text{m}}^{1/2}V_{\text{m}}^{2/3})(fT)^{-1} \text{ (cal cm}^{-1}\text{ s}^{-1}\text{ deg}^{-1}\text{)}$$

Table X. Average Zero-Pressure Bulk Modulus, K_0, and Reduced Thermal Conductivity, λfT, for Groups of Compounds[a]

group or class	K_0	λfT
AR-PLANAR	8.17	1.64
other aromatics + annulenes	6.57	1.36
planar aromatics with aliphatic substituents	6.41	1.38
HELIC	5.92	1.26
CLPHN	6.00	1.18
GEM-PHE	5.05	1.16
all hydrocarbons	6.16 (127)	1.31 (21)

[a] Units of dyn cm^{-2} and cal cm^{-1} s^{-1} deg^{-1}, respectively. σ's range from 0.69 to 1.27 and from 0.10 to 0.25, respectively. K_0 at 60% of the melting temperature.

Chart II



where f is the number of degrees of freedom in the molecule (e.g., 6 in benzene, 7 in biphenyl) and T is the temperature (K). Table X reports some results: the AR-PLANAR and GEM-PHE groups are at the extremes of the distribution, as usual. This table can be a rough guide to design a molecular structure so as to obtain a desired solid-state property.

No doubt, these equations are not yet precise instruments for the evaluation of the corresponding properties, but, if more experimental data became available, empirical formulations could be improved and could provide a solid bridge between crystal structure and physical properties of the solid state. The possibility of accurately computing lattice vibration frequencies, as well as the derivatives of the potential in any direction in space, using atom–atom potentials, opens more rigorous paths in this direction. We stress here that the contents of the Cambridge Database have a substantial potential for application to organic materials science.

K_0, even as roughly computed as above, is an overall index of packing efficiency, probably more accurate than the packing coefficient. In the series in Chart II, one can see that the alkyl substituents introduce a disturbance in the packing, which is reduced in the centrosymmetric derivatives. The analysis of the corresponding C_k values is much less clear-cut.

Crystal Packing of Cylindric Molecules. Quantification of molecular shape remains an elusive task. To try to introduce some objective criteria, we define the following indices

$$F_{\text{C}} = 0.5(M_1 + M_2)/M_3 \qquad \text{cylindric index}$$

$$F_{\text{S}} = M_1/M_3 \qquad \text{spherical index}$$

$$F_{\text{D}} = M_1/[0.5(M_2 + M_3)] \qquad \text{discoidal index}$$

where the M_i are the moments of inertia. If $M_1 \cong M_2$, F_{C} and F_{S} nearly coincide; a molecule is cylindric if F_{C} is greater than 3 and spherical if it is less than 1.5, implying $M_1 \cong M_2 \cong M_3$. A symmetric, disklike molecule like benzene or coronene will have $F_{\text{D}} = 2$. All these conditions, however, do not always coincide with classifications made by visual inspection of the molecular envelope.

One useful parameter in coding packing modes is the angle that the unique axis (minimum or maximum inertia) forms with the same axis in nearest-neighbor molecules; this was used to sort structural types in planar hydrocarbons.[3d] We now find that all aromatic rigid molecules with $F_{\text{C}} > 2.5$ pack in such a way that the angle formed by the cylinder elongation direction with its closest neighbor is very small. Figure 5 and Table XI substantiate this principle in the structural chemistry of hydrocarbon crystals,

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(15) Bar, I.; Bernstein, J. *J. Phys. Chem.* **1984**, *88*, 243.

(16) (a) Connolly, M. L. *J. Am. Chem. Soc.* **1985**, *107*, 1118. (b) Meyer, A. Y. *J. Comput. Chem.* **1988**, *9*, 18. (c) Gibson, K. D.; Scheraga, H. A. *Mol. Phys.* **1987**, *62*, 1247. (d) Valvani, S. C.; Yalkowsky, S. H.; Amidon, G. L. *J. Phys. Chem.* **1976**, *80*, 829. (e) Pascual-Ahuir, J. L.; Silla, E.; Tomasi, J.; Bonaccorsi, R. *J. Comput. Chem.* **1987**, *8*, 778.

(17) Bondi, A. *Physical Properties of Molecular Crystals, Liquids and Glasses*; Wiley: New York, 1968; Chapters 4 and 5.

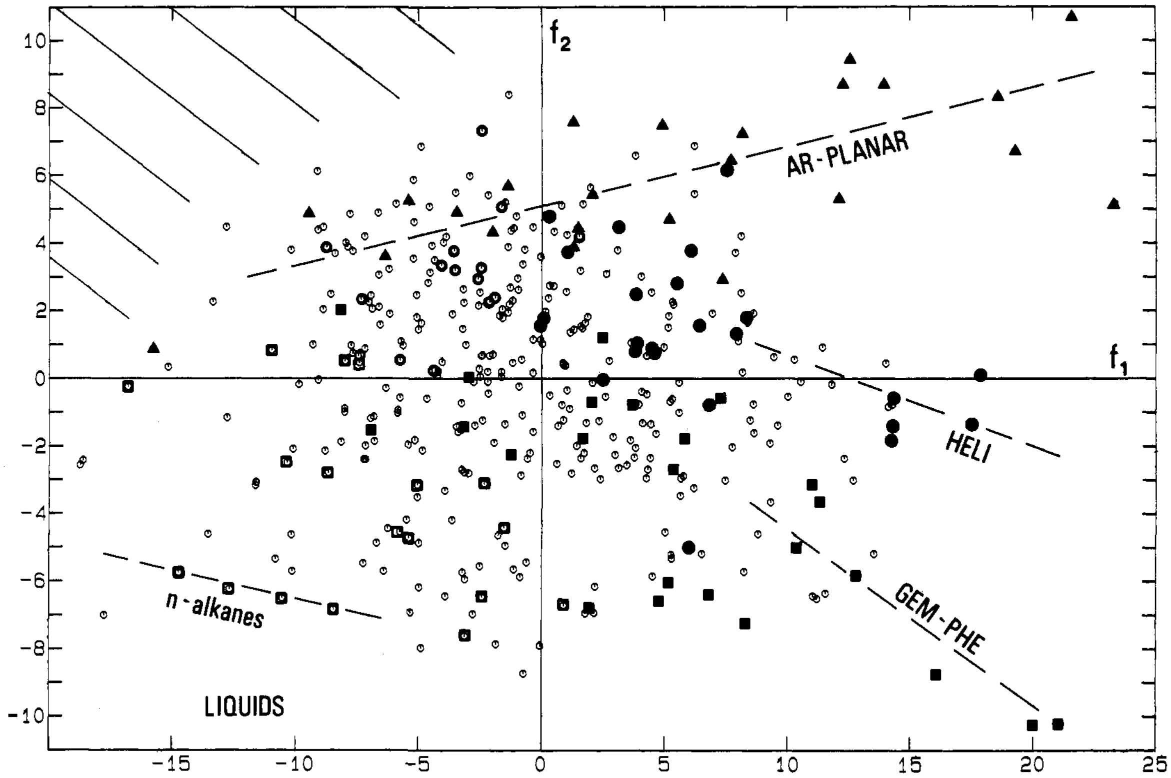

Figure 6. Scattergram of factor scores along the principal component axes f_1 and f_2 (see Table XII). Filled triangles, circles, and squares are AR-PLANAR, HELIC, and GEM-PHENYL groups, respectively. Open circles and squares are ANNUL and ALIPH groups, respectively. See text for other symbols.

stoichiometry, while the third PC, f_3, is the corresponding out-of-phase combination. Since a high carbon content favors tighter packing,[18] f_2 is a packing score moment (molecules with high f_2 use efficiently their size, shape, and composition); while f_3 is a measure of the extent to which stoichiometry and packing coefficient are discordant. Both of these PC's somewhat encode the shape factor in packing, but it is not yet possible to express it in a clear and unequivocal numerical index.

Plots of the distribution of the 391 points in the three projections show no sign of clustering: our sample spans a continuum of size and packing tightness. Figure 6 shows the f_1-f_2 projection. The upper right quadrant contains members of the flat aromatics family. The helicenes straddle the upper and lower right quadrants, while the lower right one hosts nearly the entire GEM-PHE family. Note how in these last two groups f_2 decreases on increasing f_1, size being a nuisance to close packing, due to increasingly irregular shapes.

Moving to the left (smaller sizes), one observes the close-packed, unsaturated annulenes clustered in the upper quadrant, and the pure aliphatic compounds in the lower one, bordered at the lower left by the linear alkanes. The high hydrogen content is coupled with loose packing in these compounds. Small globular molecules like bullvalene and cubane are, on the contrary, on the high f_2 side, owing to their efficient close packing.

Hydrocarbon crystals can thus be classified by computing the PC's as in Table XII and then entering the plot in Figure 6. On the upper left of this plot is a forbidden zone of small size and very high carbon content and/or close packing (it could be inhabited by molecules like the polyacetylenes at low temperature; incidentally, lowering the temperature always increases f_2). On the lower left and center is the liquid state. On the lower right, the packing is difficult, but the liquid state is not likely, due to the large molecular size. The formation of liquid crystals or the uptake of solvate molecules could be envisaged.

Figure 6 has a high classification value but still a very rough predictive value. An analogous plot obtained by using molecular properties only results in a size versus saturation (N_C/N_H) plot but completely misses the shape factor. A detailed and careful work of comparison could undoubtedly pave the way to an understanding of this so far elusive effect; alternatively, another molecular parameter, perhaps embodying molecular topology, could be devised to take this factor into charge.

Summary and Perspective. (1) When the Cambridge Structural Database was used, standardized files for packing analysis and crystal chemistry studies of hydrocarbons have been produced. They provide a statistical basis of 391 structures comprising 9583 carbon and 8666 hydrogen atoms.

(2) Statistics on the distribution among space groups reveals an increase of the occurrence of centrosymmetric ones, with respect to general organic compounds.

(3) Extant hydrocarbon crystals average a C/H ratio of 1.11, a $C(sp^2)/C(sp^3)$ ratio of 3.13, a packing coefficient of 0.717, and a density of 1.198 g/cm^3 or 0.387 e/Å^3; the effects of molecular structure or shape irregularity on crystal compactness are reflected in deviations from the last three averages.

(4) A number of indices of molecular size are correlated by linear regression to the computed packing energy. The slopes of the straight lines for groups of structurally different compounds reveal a shape factor in crystal packing, and the trends do not depend on the choice of potential energy parameters. The correlations provide standards by which the packing efficiency of any class of hydrocarbon materials can be judged, as well as a simple and reliable method for estimating sublimation energies. Deviations can be used to spot undetected disorder or solvate molecules.

(5) Tables of volume and surface increments for any type of carbon and hydrogen atoms, averaged over a very large data set, have been obtained.

(6) Rigid aromatic molecules are the best choice to obtain a compact crystal, and the introduction of alkyl substituents largely perturbs the tight packing.

(7) The enforcement of the homomeric principle (constant contribution of each atomic species) is verified for H atoms and less strictly for carbon atoms. Inter- and intramolecular factors for the occurrence of abnormally low values have been identified, the last ones having to do with partial filling of the atomic coordination sphere by intramolecular contacts.

(8) Bulk moduli and thermal conductivities of hydrocarbon crystals have been estimated, and guidelines to relate them to

molecular shape emerged. The bulk modulus is a convenient index of packing efficiency.

(9) Molecular shape is roughly coded by ratios of moments of inertia. Aromatic, rigid, cylindric molecules pack in such a way that the elongation axes are very nearly parallel.

(10) A principal-component analysis reveals three moments, which can be interpreted as a size parameter, a packing tightness parameter, and a packing failure parameter. Compounds of similar molecular shapes are grouped in moments space.

The hydrocarbon files are susceptible to many future uses: molecule-to-molecule energies and the composition of the coordination shell, with the distribution of interatomic contacts, deserve further examination; the shape factor can be coded after the analysis of the differences between molecules of the same size but with different packing energies; the packing of isomers, or of the same molecule in different crystal phases, can be examined; molecular reorientations can be studied, and the barriers can be calculated and related to molecular shape; the performance of different potential energy parameters can be tested over a much larger basis than is normally used in their derivation. Even more important as a further step is, however, the study of the influence of substituents of moderate polarity (heteroatoms in cycles, chlorine versus methyl) on the packing standards we have outlined for hydrocarbon cores and even the analysis of how groups with larger dipole moments (cyano or carbonyl groups) may perturb the geometrical features of hydrocarbon packing.

Acknowledgment. Partial financial support from Ministero della Pubblica Istruzione, Fondi 40%, is acknowledged. We thank the Servizio Italiano di Diffusione Dati Cristallografici del CNR (Parma) and Dr. T. Pilati for help in the handling of the Cambridge Files and Prof. E. Ortoleva for the use of his plotting programs.

Appendix

For the retrieval of crystal data from the Cambridge SD, classes[1b] 5 and 19–31 were considered, for substances containing only C and H atoms. Disordered structures, inclusion compounds, and solvates were excluded. When more than one determination was reported for the same compound, the most recent one, or the one nearest to room temperature, was retained. Thus, the overwhelming majority of data refer to room-temperature analyses. When more than one polymorph or optical isomer was available, all were included in the data set.

In a first step, years 1975–1986 were considered. No R factor threshold was imposed, since intermolecular properties are sensitive to the general packing pattern, and much less to details in the refinement of the structure. In a second step, the search ran over years 1930–1974, editing out structures with especially high R factor and projection structures.

To calculate the H atom positions, we have imposed a C–H distance of 1.08 Å throughout[3] and used the following protocol:

(a) For methyl groups, compute one approximate C–C–C–H torsion angle, ω, using X-ray H atom positions and use this to build a methyl group with angle C–C–H = 109.47° and torsion angles ω, $\omega + 120$, $\omega + 240$; if no X-ray hydrogens are available, use $\omega = 60°$. As a side result, it appears that in aliphatic environments ω is near to 60° in most cases, while a spread of values is observed in methyl substituents at aromatic rings.

(b) For methylene groups, use two H atoms, in the plane bisecting the C–C–C angle and perpendicular to the C–C–C plane. C–C–H angles are computed by requiring orthogonality of hybrids at carbon.[3a,4a]

(c) For methyne hydrogens, renormalize the C–H distance, starting from X-ray hydrogen positions; if these are not available, compute an approximate position with no C–C–H angles <100°.

(d) For aromatic ring or ethylenic H atoms, calculate the positions in the C–C–C plane, on the bisector of the C–C–C angle.

In a few remaining cases, ad hoc procedures were adopted, based on reasonable geometric conditions.

Supplementary Material Available: Table II, with the Cambridge Database refcodes (5 pages). Ordering information is given on any current masthead page.

Kinetics of Electron-Transfer Reactions of Hydroquinones and Ascorbic Acid with 1-Phenyl-3-pyrazolidone Radicals

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Contribution from the Paper and Reversal Chemistry Laboratory, Eastman Kodak Company, Rochester, New York 14650. *Received June 8, 1988*

Abstract: The kinetics of oxidation of four hydroquinones and ascorbic acid by 1-phenyl-3-pyrazolidone radicals have been examined in aqueous solution from pH 6.5 to 9.5. For the hydroquinones, the kinetics are markedly autocatalytic unless sulfite is present in the solutions. The autocatalysis is apparently due to accumulation of a significant quantity of semiquinone formed via reproportionation of the quinone product with unreacted hydroquinone. If present in sufficient concentration, sulfite eliminates autocatalysis by scavenging quinone, and the kinetics are first-order in each reactant. The kinetic results suggest that the electron transfer from hydroquinone to the radical to form semiquinone is rate-limiting. In the case of ascorbic acid, autocatalysis is not observed, and the kinetics are first-order in oxidant and reductant. The kinetic dependence on pH permits the resolution of bimolecular rate constants for oxidation of the fully ionized and the singly protonated reductants. The correlation of these rate constants with thermodynamic driving force is in agreement with the Marcus theory.

It is well-known that photographic developers containing a combination of a hydroquinone (H_2QX) and a 1-aryl-3-pyrazolidone (HP) exhibit development rates many times greater than is seen when either agent is used alone.[1] This so-called superadditivity has been studied extensively. It is widely accepted that superadditivity is largely due to a regeneration mechanism in which the pyrazolidone anion (P^-) is the predominant agent for reduction of silver ions and the hydroquinone serves primarily to reduce the oxidized pyrazolidone (radical) to its active form (eq 1–3, where the quinone QX is the two electron oxidation

$$\mathrm{Ag^+ + P^- \xrightarrow[\text{fast}]{} Ag^0 + P^{\bullet}} \tag{1}$$

$$\mathrm{2Ag^+ + H_2QX \xrightarrow[\text{slow}]{} 2Ag^0 + QX + 2H^+} \tag{2}$$

$$\mathrm{2P^{\bullet} + H_2QX \rightarrow 2P^- + QX + 2H^+} \tag{3}$$

product derived from H_2QX, and $P^{\bullet}$ is pyrazolidone radical).

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[1] Levenson, G. I. P. *Photogr. Sci. Eng.* **1969**, *13*, 299.

0002-7863/89/1511-1843$01.50/0