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# Some molecular packing studies of crystalline hydrocarbons.

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Packing analysis of some alkyne structures shows that short C⋯C contacts are more numerous in these than in other hydrocarbon structures, and that the structures are well described by currently used potential-energy functions. Calculations of the lattice energy of the two crystalline modifications of benzene using various proposed energy functions correctly predict that benzene I is the more stable, only when interactions arising from C–H bond polarity are included.

## Packing analysis of alkyne structures

Potential-function parameters for non-bonded interactions for molecular-packing analysis may be deduced by least-squares fitting of calculated to experimental crystal data. These are most commonly derivatives of lattice energy with respect to cell parameters or rigid-body structural parameters, which should be zero for the observed structure; other non-zero data are heats of sublimation or elastic constants, which are often of lower accuracy, but at least some of which must be included for scaling purposes (Williams, 1970, 1974). Some difficulty can arise because of parameter interaction, which in the case of hydrocarbon crystals derives particularly from the fact that the peripheral atoms of the molecule are invariably hydrogen, and consequently as short contacts between carbon atoms occur infrequently the repulsive C⋯C coefficient may not be well defined (Williams, 1970). For this reason it has been considered desirable to use data sets based on a variety of hydrocarbon types, which should include some aromatic hydrocarbons wherein the carbon atoms are relatively exposed. The structures of alkynes, particularly longer-chain poly-ynes, might be expected to be more dependent upon C⋯C interaction, and we have analysed the packing of a number of such structures to investigate this and to establish the effectiveness of currently used energy functions to describe such structures. Energy functions calculated have been both conventional lattice energy, $E$, using the potential parameters given by Williams (1974), and repulsive lattice energy, $E_R$, as defined by Williams (1969) and using the potential parameters given therein. In each calculation the molecule was defined by the observed carbon atom positions, with hydrogen atoms calculated in the expected geometry for a C–H bond length of 1·027 Å (Williams, 1965), and the cell parameters assumed as observed. Lattice energy was minimized with respect to all variable cell and rigid-body orientational parameters, and repulsive lattice energy with regard to orientational parameters only. For all structures the molecular centre is a centre of inversion, and thus there are no translational variables.

The results of these calculations are given in Table 1, wherein $\theta$ and $\theta_R$ represent the changes in molecular orientation during the two different energy refinements. For comparison, comparable results are listed for *n*-hexane, benzene and naphthalene. The types of intermolecular contacts which are shorter than the distance of the minimum of the appropriate non-bonded energy function (C⋯C 3·93; C⋯H 3·56; H⋯H 3·18 Å), *i.e.* the repulsive interactions, are listed in Table 2 for *n*-hexane, naphthalene and 1,10-diphenyldecapentayne. For the aliphatic hydrocarbon these are mainly C⋯H and H⋯H, for the aromatic hydrocarbon C⋯H predominate, but in neither structure are C⋯C interactions at all numerous. By contrast, in the poly-yne more than half the contacts are between carbon atoms. Notwithstanding this very different distribution, the lattice-energy minima for the alkyne structures correspond well with the observed structures, and the relative weighting of the terms in the potential-energy function between the different types of contact then appears to be confirmed.

As a further check, the repulsive lattice-energy space was explored more extensively by systematically varying the orientational parameters used for the starting model and minimizing from each (Williams, 1969, 1973), for 1,8-diphenyloctatetrayne and for 1,10-diphenyldecapentayne. For both a number of energy minima were located, but that corresponding to the observed structure was the global minimum, being at least 10 kJ mol⁻¹ lower than any other.

## Polarity of the C–H bond in potential-energy models

The majority of potential-energy models that have been proposed for packing studies of hydrocarbons have implicitly or explicitly assumed Coulombic interactions arising from C–H bond polarity to be negligible, but it has been shown that agreement between the calculated energy minimum and the observed structure can be markedly improved by inclusion of a Coulombic term, and for a point-charge model optimal fit was obtained with a charge separation of 0·36 e (Williams, 1974). Improvement was particularly notable for

Table 1. *Lattice-energy minima for alkyne crystal structures*

| | $E$ (kJ mol$^{-1}$) | $\theta$ (°) | $a$ (Å) $\Delta a$ | $b$ (Å) $\Delta b$ | $c$ (Å) $\Delta c$ | $\beta$ (°) $\Delta\beta$ | $E_R$ (kJ mol$^{-1}$) | $\theta_R$ (°) |
|---|---|---|---|---|---|---|---|---|
| But-2-yne[a] | −27·1 | † | 7·66 | | 6·89 | | 3·8 | † |
| | | | 0·00 | | +0·10 | | | |
| Octa-2,4,6-triyne[b] | −49·9 | † | 6·60 | | 12·66 | | 0·6 | † |
| | | | −0·22 | | +0·11 | | | |
| Diphenylacetylene[c] | −100·1 | 1·5* | 12·75 | 5·73 | 15·67 | 115·2 | 1·8 | 4·5* |
| | | 1·1* | −0·09 | −0·01 | −0·02 | 0·0 | | 4·2* |
| 1,4-Diphenylbut-1,3-diyne[d] | −122·9 | 1·5 | 6·61 | 6·04 | 14·92 | 105·0 | 3·3 | 1·7 |
| | | | +0·14 | −0·06 | −0·03 | +0·6 | | |
| 1,8-Diphenyloctatetrayne[e,f] | −144·4 | 0·4 | 17·74 | 3·99 | 10·78 | 110·5 | 3·3 | 4·3 |
| | | | −0·05 | +0·02 | 0·00 | −0·1 | | |
| 1,10-Diphenyldecapentayne[e,f] | −132·0 | 0·8 | 18·67 | 5·25 | 8·82 | 113·7 | 1·8 | 0·9 |
| | | | +0·06 | −0·05 | +0·03 | 0·0 | | |
| n-Hexane[g] | −53·3 | 3·3 | 4·17 | 4·70 | 8·57 | $\alpha$ 96·6 | | 3·0 |
| | | | +0·02 | −0·17 | +0·70 | $\beta$ 87·2 | | |
| | | | | | | $\gamma$ 105·0 | | |
| | | | | | | $\Delta\alpha$ +0·1 | | |
| | | | | | | $\Delta\beta$ −1·0 | | |
| | | | | | | $\Delta\gamma$ −1·9 | | |
| Benzene[h] | −53·8 | 3·4 | 7·39 | 9·42 | 6·81 | | 1·8 | 4·4 |
| | | | +0·10 | −0·15 | +0·11 | | | |
| Naphthalene[i] | −82·7 | 1·9 | 8·24 | 6·00 | 8·66 | 122·9 | 1·7 | 2·5 |
| | | | −0·05 | −0·15 | 0·00 | −0·9 | | |

References: (a) Pignatoro & Post (1955); (b) Jeffrey & Rollett (1952); (c) Robertson & Woodward (1938); (d) Wiebenga (1940); (e) Watanabe, Taguchi & Masaki (1959); (f) Masaki, private communication; (g) Norman & Mathisen (1961); (h) Bacon, Curry & Wilson (1964); (i) Cruickshank (1957).

\* Two independent molecules in the unit cell.
† All carbon atoms lie on a diad axis.

Table 2. *Numbers of repulsive interactions (per asymmetric unit)*

| | C···C | C···H | H···H |
|---|---|---|---|
| n-Hexane | 5 | 48 | 39 |
| Naphthalene | 13 | 51 | 12 |
| 1,10-Diphenyldecapentayne | 72 | 52 | 11 |

benzene I (the normal-pressure crystalline form) and this is illustrated by the lattice-energy-minimization calculations reported in Table 3, which were performed as described in the previous section, for the parameter set W(a) which assumes neutral atoms, and W(b) which assumes the above charge separation. Not only does parameter set W(b) describe the benzene I structure more adequately, but it also correctly predicts benzene I to be more stable than the high-pressure modification benzene II, whereas set W(a) predicts the converse (Hall & Williams, 1975).

Ramachandran (1974) has drawn attention, using benzene I as an example, to the fact that although various proposed potential functions differ significantly in form and lead to very different values for the lattice energy, they all satisfactorily predict the molecular orientation corresponding to the energy minimum. This is confirmed by the results in Table 3, where the lattice energy of the two benzene structures has been minimized using a number of potential functions, each calculation being as previously described except that the C—H bond length for the molecule was as assumed by the appropriate authors. In particular, the parameter sets K and MCMS, which respectively assume charge separations of zero and 0·015 e, represent the

benzene I structure equally effectively as does W(b). However, although all the various potential functions also describe the benzene II structure acceptably with regard to the coordinates of the minimum, it is notable that only W(b) predicts that benzene II is less stable than benzene I. For all the energy functions, the non-bonded lattice energy of the slightly more compact benzene II structure is greater (more negative); the Coulombic contribution to the lattice energy is, however, larger in the case of benzene I, −17·7 as opposed to −13·8 kJ mol$^{-1}$ assuming the point-charges of W(b), and this offsets the other. Ramachandran (1974) has observed that the inclusion of quadrapole–quadrapole interaction in the calculation of lattice energy significantly lowers the value of the global minimum relative to the lowest false minimum in the benzene I energy space, confirming that Coulombic energy can be an important component of the lattice energy of a crystalline hydrocarbon. Minimization of the lattice energy with regard to cell parameters (*i.e.* the assumption that the derivative should be zero) implies that the calculation refers to zero pressure (Hall & Williams, 1975), when any pressure–volume work term must also be zero, and when benzene I is the observed stable phase. Prediction that this is so thus provides a sensitive test of any potential-energy model to be used for molecular-packing purposes.

Table 3. *Lattice-energy minima for benzene crystal structures*

Benzene I

| | $a$ (Å) | $b$ (Å) | $c$ (Å) | | $\theta$ (°) | $E$ (kJ mol$^{-1}$) |
|---|---|---|---|---|---|---|
| Observed cell parameters | 7·39 | 9·42 | 6·81 | | | |
| Potential parameter set | $\Delta a$ | $\Delta b$ | $\Delta c$ | | $\theta$ (°) | $E$ (kJ mol$^{-1}$) |
| RS[a] | −0·43 | −0·74 | −0·76 | | 2·8 | −113·1 |
| K[b] | 0·04 | −0·03 | −0·17 | | 3·1 | −47·5 |
| MKB[c] | −0·86 | −0·24 | 0·43 | | 20·4 | −45·4 |
| MCMS[d] | 0·32 | 0·03 | −0·37 | | 3·5 | −40·2 |
| W($a$)[e] | −0·64 | 0·04 | 0·22 | | 18·7 | −43·2 |
| W($b$)[f] | 0·10 | −0·15 | 0·11 | | 3·4 | −53·8 |

Benzene II

| | $a$ (Å) | $b$ (Å) | $c$ (Å) | $\beta$ (°) | | $\theta$ (°) | $E$ (kJ mol$^{-1}$) |
|---|---|---|---|---|---|---|---|
| Observed cell parameters (25 kbar) | 5·42 | 5·38 | 7·53 | 110·0 | | | |
| Potential parameter set | $\Delta a$ | $\Delta b$ | $\Delta c$ | $\Delta\beta$ | | $\theta$ (°) | $E$ (kJ mol$^{-1}$) |
| RS | −0·30 | −0·09 | −0·83 | −5·3 | | 6·6 | −121·1 |
| K | 0·08 | 0·25 | −0·08 | −4·5 | | 5·0 | −50·5 |
| MKB | 0·02 | 0·19 | −0·20 | −2·0 | | 4·8 | −47·3 |
| MCMS | 0·12 | 0·29 | −0·12 | 5·5 | | 5·5 | −43·1 |
| W($a$) | 0·17 | 0·17 | 0·05 | −1·1 | | 3·6 | −45·3 |
| W($b$) | 0·21 | 0·19 | 0·39 | −1·9 | | 1·4 | −52·7 |

References: (*a*) Ramachandran & Sasisekharan (1968); (*b*) Kitaigorodskii (1970); (*c*) Mirskaya, Kozlova & Bereznitskaya (1974); (*d*) Momany, Carruthers, McGuire & Scheraga (1974); (*e*) set *C*, Williams (1970); (*f*) Williams (1974).

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# Book Reviews

*Works intended for notice in this column should be sent direct to the Book-Review Editor (J. H. Robertson, School of Chemistry. University of Leeds, Leeds LS2 9JT, England). As far as practicable books will be reviewed in a country different from that of publication.*

**An introduction to X-ray crystallography.** By M. M. WOOLFSON. Pp. x + 380. Cambridge University Press, 1978. Price £5·50.

This is a soft-cover reprint (with errors corrected) of the successful book originally published in hard covers in 1970; it was reviewed then by T. R. Lomer, in *Acta Cryst.* A**26**, 461.

**Solid electrolytes (Topics in applied physics. Vol. 21).** Edited by S. GELLER. Pp. xi + 244. Berlin, Heidelberg, New York: Springer, 1977. Price DM 72·00, $33.20.

A review of this book by A. T. Howe has been published in the July issue of *Acta Crystallographica*, Section A, page 640.