

Coulombic Interactions in Crystalline Hydrocarbons*

BY DONALD E. WILLIAMS

Department of Chemistry, University of Louisville, Kentucky 40208, U.S.A.

(Received 6 June 1973; accepted 31 July 1973)

Coulombic intermolecular interactions in crystalline hydrocarbons were studied by means of molecular packing analysis. A C-H charge separation parameter of 0.36 e was found by analysis of nine aromatic and nine saturated hydrocarbon crystal structures. When coulombic point charges were included in the non-bonded potential model it was found that the geometric-mean combining law held for C...H repulsions. The calculated coulombic energy of the hydrocarbons studied ranged from a negligible amount for n-hexane to a maximum contribution of 29% of the total lattice energy for crystalline benzene.

Introduction

Coulombic interactions in hydrocarbon crystals have generally been considered to be negligible in effect, compared to the London dispersion energy and the repulsive energy. For example, a review by Mason (1970) gives an estimate that less than 2% of the lattice energy of naphthalene is contributed by quadrupole-quadrupole interactions. Another review by Kitaigorodskii (1970) estimates a range of 4% down to a slightly negative contribution for this same effect in naphthalene.

These conclusions were supported by calculations based on point quadrupole-point quadrupole interaction energy formulas. However, the magnitudes and orientations of the quadrupole moments may not be well known. Also, in the crystal the distance between quadrupolar molecules is similar to the dimensions of the quadrupole (*i.e.* the molecule). Therefore, the assumption that the interquadrupole distance is large relative to the dimensions of the quadrupole is not necessarily a good one.

On the other hand, a recent monopole model calculation (Warshel & Lifson, 1970), henceforth referred to as WL, for a number of saturated hydrocarbon structures led to an electrostatic charge of 0.11 e on the hydrogen atoms, with opposite charges located on the carbon atoms. We verified that this monopole distribution contributes negligibly to the lattice energy of straight-chain hydrocarbons such as n-hexane, one of the compounds studied by WL. However, a preliminary calculation by us showed that 0.11 e on the hydrogen atoms of benzene led to a lattice energy contribution of about 6 kJ/mol, or more than 10% of the experimentally observed heat of sublimation.

We decided therefore to undertake a more general investigation of the monopole model for coulombic interactions in both saturated and aromatic hydrocarbon crystals. A goal of the investigation would be to

derive the electrostatic charge distribution in hydrocarbon crystals from experimental data by means of molecular packing analysis.

The experimental basis data

Partial lattice sums for the (6-exp) potential type were already available for a set of 18 well-determined hydrocarbon crystal structures (Williams, 1970). Half of these structures were aromatic and half were saturated hydrocarbons. Fig. 1 gives the molecular structures of these 18 compounds.

Each partial lattice sum is over a particular type of pair interaction, in this case either C...C, C...H, or H...H. The form of the pair potential is such that the attractive partial sums, $S_{6\alpha\beta}$, and the repulsive partial sums, $S_{e\alpha\beta}$, may be evaluated independently. Here the subscripts α and β refer to C or H, 6 refers to the London dispersion attraction, and e refers to an exponential repulsion. Thus, for a particular atom-pair type,

$$S_6 = -\left(\frac{1}{2}\right) \sum r^{-6}, \quad \text{and} \quad S_e = \left(\frac{1}{2}\right) \sum \exp(-C_{\alpha\beta}r),$$

where the sum is over the interactions of the reference molecule with the atoms of all surrounding molecules in the crystal.

The total lattice energy is a simple linear combination of the S summations:

$$E = A_{CC}S_{6CC} + A_{CH}S_{6CH} + A_{HH}S_{6HH} \\ + B_{CC}S_{eCC} + B_{CH}S_{eCH} + B_{HH}S_{eHH}.$$

The derivatives of E with respect to a structural parameter, p , may be obtained by differentiation of the S sums either numerically or analytically (Williams, 1972*b*). The values of $A_{\alpha\beta}$, $B_{\alpha\beta}$, and $C_{\alpha\beta}$ are assumed to be independent of the structural parameters. At equilibrium the derivatives of E with respect to any structural parameter should be zero, with any deviation from zero being caused by inadequacies in the potential model or errors in the structural parameters.

The exponent coefficients $C_{\alpha\beta}$ are difficult to derive from hydrocarbon crystal data. We have assumed a

* Supported by research grant GM16260 from the National Institutes of Health, U.S. Public Health Service.

value of 3.60 \AA^{-1} for $\text{C} \cdots \text{C}$ interactions and 3.74 \AA^{-1} for $\text{H} \cdots \text{H}$ interactions, using the average for $\text{C} \cdots \text{H}$ interactions. The value for $\text{C} \cdots \text{C}$ interactions was obtained from the crystal structure of graphite (Crowell, 1958) and the value for $\text{H} \cdots \text{H}$ interactions was obtained from a quantum-mechanical calculation of the repulsion between two hydrogen molecules (Mason & Hirschfelder, 1957; Magnasco & Musso, 1966). The calculated repulsion energy of two H_2 molecules can be fitted fairly well with a dumbbell model, provided the repulsion centers are shifted into the bond by 0.07 \AA (Williams, 1965). This shift places the repulsion center coincident with the center of spherical electron density found by Stewart, Davidson & Simpson (1965). In this work we use calculated hydrogen attraction and repulsion centers located 1.027 \AA from carbon for aromatic and 1.040 \AA from carbon for saturated hydrocarbons.

The calculated lattice energy, E , is set equal to the observed heat of sublimation of the crystal corrected for zero-point vibration. For the majority of these hydrocarbons heats of sublimation have been obtained from the observed vapor pressure through the Clausius-Clapeyron equation or some variation of it. We agree with other workers (Thomson & Douslin, 1971; Radchenko, 1971) that the heats of sublimation derived from vapor pressure data are not very reliable.

Calorimetric measurements are more reliable, but are difficult to find in the literature. Fortunately complete calorimetric data are available for benzene as a representative aromatic, and for the normal alkanes from which we have chosen n-hexane as representative. Our calculation plan is to use these two accurately known heats of sublimation to scale our potential parameters, and to use the heats of sublimation derived from vapor pressure data only for checking purposes. It is possible that in some instances our calculated heats of sublimation may be more accurate than those derived from vapor pressure data.

The details of the method of obtaining the static lattice energy from calorimetric data have been presented by WL. The experimental data required are the heats of melting and vaporization, the heat capacities of the solid and gas, and the normal modes of vibration of the solid and gas. We assume that the intramolecular vibrational modes are not changed significantly in

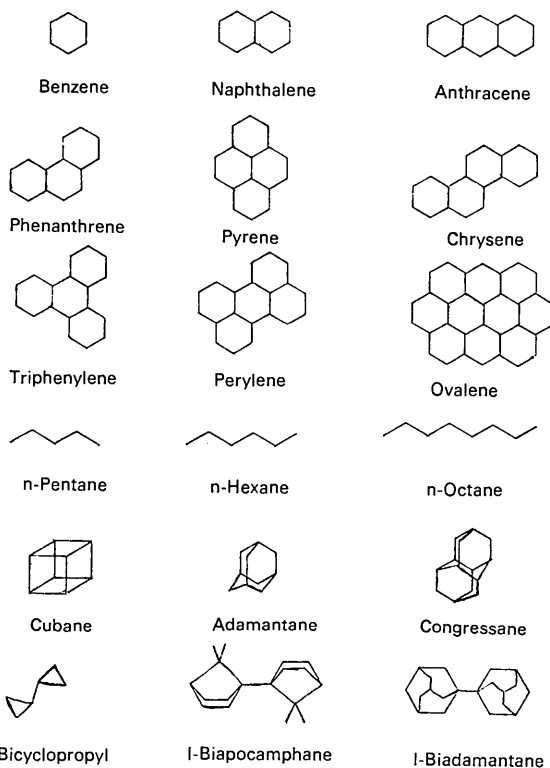


Fig. 1. The structural formulas of the compounds whose crystal structures provided the observational equations.

Table 1. *The calculated first derivatives of the lattice energy with respect to the structural parameters, based on the potential parameters of Table 2*

The units are kJ/mol, \AA , and radians.

| Compound | Reference | θ_1 | θ_2 | θ_3 | T_1 | T_2 | T_3 | a | b | c | α | β | γ |
|-----------------|------------------------------|------------|------------|------------|-------|-------|-------|-----|-----|-----|----------|---------|----------|
| Benzene | Bacon, Curry & Wilson (1964) | -2 | -5 | -1 | | | | -1 | 0 | 0 | | | |
| Naphthalene | Cruickshank (1967) | 18 | -2 | -6 | | | | 2 | 6 | 0 | | -6 | |
| Anthracene | Mason (1964) | 46 | -26 | -19 | | | | -6 | -1 | -3 | | 14 | |
| Phenanthrene | Trotter (1963) | -6 | 19 | -24 | 2 | | 2 | 1 | 7 | 1 | | 35 | |
| Pyrene | Camerman & Trotter (1965) | 25 | 24 | 0 | 3 | 10 | -11 | 0 | 1 | 3 | | 30 | |
| Chrysene | Burns & Iball (1960) | 45 | -14 | 72 | | | | -3 | 6 | 0 | | -3 | |
| Triphenylene | Ahmed & Trotter (1963) | -9 | -48 | -8 | -7 | -3 | 11 | 0 | 1 | 1 | | | |
| Perylene | Camerman & Trotter (1964) | 24 | 6 | 4 | -4 | 6 | 0 | 1 | 1 | -3 | | 33 | |
| Ovalene | Donaldson & Robertson (1953) | 22 | 5 | 22 | | | | 0 | -7 | 0 | | 28 | |
| n-Pentane | Norman & Mathisen (1964) | | 11 | | | 0 | | -6 | 2 | -1 | | | |
| n-Hexane | Norman & Mathisen (1961a) | 9 | 9 | -2 | | | | -2 | 7 | 1 | -4 | 2 | -3 |
| n-Octane | Norman & Mathisen (1961b) | 5 | 2 | -3 | | | | 0 | 11 | 2 | -5 | -1 | -8 |
| Cubane | Fleischer (1964) | | | 22 | | | | 0 | | -4 | | | |
| Adamantane | Donohue & Goodman (1967) | | | -1 | | | | -2 | | -2 | | | |
| Congressane | Karle & Karle (1965) | | | | | | | 1 | | | | | |
| Bicyclopropyl | Eraker & Rømming (1967) | 33 | | | | | | 1 | 4 | 1 | | | |
| 1-Biapocamphane | Alden, Kraut & Taylor (1968) | -9 | -7 | -1 | | | | 11 | 7 | 6 | | | |
| 1-Biadamantane | Alden, Kraut & Taylor (1968) | 3 | 0 | -8 | | | | 5 | 6 | 4 | | | |

going from the gas to the solid; WL found a small change (2.1 kJ/mol) in the intramolecular vibrational energy for n-hexane. The zero-point vibrational energies were found to be 2.78 kJ/mol for benzene (Nakamura & Miyazawa, 1969) and 2.09 kJ/mol for n-hexane (WL). The heats of sublimation at 0°K were found to be 49.52 kJ/mol (Oliver, Eaton & Huffman, 1948) for benzene and 50.51 kJ/mol (Douslin & Huffman, 1946) for n-hexane.

Our potential model is not completely consistent in that the structural derivatives must be obtained from crystals having a considerable amount of thermal motion, while the potential model does not include any account of the effects of thermal motion. At the expense of additional complexity, an approximate reckoning of the thermal effects may be included (WL; Williams, 1972a). We have not included any thermal effects in the present calculations; where possible, crystal structures determined at low temperature were used to minimize the thermal motion. Therefore, the averaged thermal effects will be incorporated into the derived potential parameters.

The coulombic monopole interactions may be included as a straightforward extension to include the sums $S_{c\alpha\beta}$ in the lattice energy. These are defined as

$$S_c = \frac{1}{2} W \sum q_j q_k r^{-1}$$

for atoms (in different molecules) with point charges q_j and q_k , separated by distance r . The factor W allows one to make some initial assumption about the distribution of the q_i and later scale this estimate up or down while maintaining the relative charge relationships.

A commonly accepted value (Barrow, 1966) for the C-H bond moment is 0.4 Debye units. For benzene, this leads to point charges of ± 0.081 e on C and H, or a charge separation in the bond of 0.162 e. If we presume a similar charge separation occurs in n-hexane, the charge on a methylene hydrogen is +0.054 and the charge on the carbon is -0.108. For a methyl group the charge on the hydrogen is +0.040 and the charge on the carbon is -0.120. These estimates are based on foreshortened C-H bond lengths (Williams, 1965) of 1.027 and 1.040 Å, which are used throughout these calculations.

The WL model is slightly different in that the charge on hydrogen is kept constant. Thus, in their model a methylene carbon would carry a charge of -0.22 e, while a methyl carbon would carry a charge of -0.33 e. We believe that the constant-charge-separation model is physically more realistic. In anticipation of the results reported later, our observed W value of 4.9 more than doubles the initial charge separation, making it look much more like the WL result in magnitude.

All lattice sums were evaluated with convergence acceleration (Williams, 1971). The convergence constant, K , was set to 0.175 for both the dispersion and electrostatic sums. The direct lattice sum was truncated at 8 Å, and the reciprocal-lattice sum was ignored. The estimated accuracy of evaluation is at least 99%.

All calculations assumed the geometric-mean combining law holds for attractions; *i.e.* $A_{CH} = (A_{CC}A_{HH})^{1/2}$.

The possible structural parameters are the three rotations and the three translations of the reference molecule (considered to be rigid) and the six lattice constants. A listing of the structural parameters is given in Table 1.

Results and discussion

The basis structural data provide 118 observational equations, plus the two equations in the lattice energy for benzene and n-hexane. These equations were fitted by least squares, minimizing the function

$$G = \sum w \left(\frac{\partial E}{\partial p} \right)^2 + \sum w' (E_c - E_o)^2,$$

where the first sum is over the 118 structural derivative equations, and the second is over the two lattice-energy equations. The weighting factors, w , were set equal to the inverse of the square of the estimated error in the first derivatives. This error was estimated as

$$\sigma \left(\frac{\partial E}{\partial p} \right) = \frac{\Delta H_s(\text{compound})}{\Delta H_s(\text{benzene})} \text{ for rotations and translations,}$$

and

$$= \frac{1}{p} \frac{\Delta H_s(\text{compound})}{\Delta H_s(\text{benzene})} \text{ for the lattice constants.}$$

Table 2. Optimum values of the nonbonded potential parameters (kJ, Å, and e) and their estimated standard deviations

| Parameter | This work | Warshel & Lifson (1970) |
|------------|-------------------------|-------------------------|
| A_{CC} | 1.88 (14) $\times 10^3$ | 5.18 $\times 10^3$ |
| A_{HH} | 1.68 (11) $\times 10^2$ | 0.65 $\times 10^2$ |
| B_{CC} | 2.99 (20) $\times 10^5$ | - |
| B_{HH} | 1.20 (5) $\times 10^4$ | - |
| Δe | 0.358 (14) | 0.33-0.44 (3-4) |
| d_{CC}^0 | 3.925 (19) | 3.616 (40) |
| E_{CC}^0 | -0.296 (30) | -0.773 (7) |
| d_{HH}^0 | 3.183 (30) | 3.548 (40) |
| E_{HH}^0 | -0.080 (10) | -0.0108 (4) |

Table 3. Trial calculations showing the relationship between the coulombic field and the geometric-mean law for repulsion, for N observational equations

| Trial | Data fitted | N | $B_{CH}/(B_{CC}B_{HH})^{1/2}$ | Δe | R |
|-------|-------------|-----|-------------------------------|------------|------|
| I | Aromatic | 72 | 0.72 | (0.00) | 4.79 |
| II | Aromatic | 72 | (1.00) | (0.00) | 5.53 |
| III | Aromatic | 72 | (1.00) | 0.388 | 3.35 |
| IV | Saturated | 46 | 1.20 | (0.000) | 2.56 |
| V | Saturated | 46 | (1.00) | (0.000) | 2.57 |
| VI | Saturated | 46 | (1.00) | 0.414 | 2.33 |
| VII | Combined | 118 | 0.67 | (0.000) | 4.54 |
| VIII | Combined | 118 | (1.00) | (0.000) | 5.21 |
| IX | Combined | 118 | (1.00) | 0.358 | 3.26 |

$$R = \left[\frac{\sum_{i=1}^N w_i \left(\frac{\partial E}{\partial p_i} \right)^2}{\sum_{i=1}^N w_i} \right]^{1/2}$$

The weights w' were set large enough to force E_c equal to E_0 within 0.01 kJ/mol; these two equations may be viewed as side conditions (Waser, 1963).

Table 1 gives the final calculated values obtained for the structural derivatives, based on the potential parameters given in Table 2. The parameters shown in Table 2 correspond to Trial IX of Table 3.

We particularly wished to investigate the relation between coulombic interactions and the geometric-mean combining law for repulsion. Earlier studies (Williams, 1966, 1967) had indicated that, in the absence of coulombic effects in the potential field, better agreement with experimental data was obtained by omitting the geometric-mean combining law for B_{CH} . Thus, B_{CH} was allowed to vary independently of B_{CC} and B_{HH} ; the observed values obtained for B_{CH} were much less than predicted by the geometric-mean law. For the presently considered data (Williams, 1970), B_{CH} was found to be only 68% of the predicted geometric-mean value.

Coulombic interactions in hydrocarbons are such that the $C \cdots C$ and $H \cdots H$ interactions are always repulsive, while $C \cdots H$ is always an attractive interaction. It can be seen that the presence of an additional attractive $C \cdots H$ interaction in the potential field, if neglected, would lead to an anomalously low value for B_{CH} . Conversely, if the $C \cdots H$ coulombic interactions were included, B_{CH} would increase in a compensatory manner to retain the observed structural parameters. Thus, in the case of the lengths of the unit-cell edges, a compensatory increase in B_{CH} would be required to offset the additional $C \cdots H$ attraction of the coulombic interaction. The effect of coulombic interactions on molecular rotation and translation in the crystal would be difficult to predict without making a detailed lattice summation calculation.

The local coulombic forces are quite significant, relative to the (exp-6) force field. In previous work it had apparently been tacitly assumed that since the coulombic contribution to the total lattice energy was negligible, therefore the local coulombic forces were also negligible. In the first place, we show here that the coulombic energy is not negligible in all hydrocarbon crystals, reaching a value of 29% of the total lattice energy of benzene. It is true, however, that the coulombic contribution to the lattice energies of n-pentane, n-hexane, and n-octane is less than 1%.

The potential parameters leading to the above conclusions show that the following forces are exerted between C and H which are 3.0 Å apart: force (exp-6) = -13.0 kJ/mole Å; force (coulombic) = +4.4 kJ/mole Å. Thus the local coulombic force is quite significant relative to the (exp-6) force. In fact, at the minimum of the (exp-6) potential, the (exp-6) force is zero, while the coulombic force is still +3.1 kJ/mole Å.

It seemed possible that the apparent failure of the geometric-mean combining law for repulsions could have been caused by the neglect of coulombic interactions. From the phenomenological or inductive

point of view, the assumption of point charges on the atoms (not necessarily physically present) could allow the geometric-mean combining law to hold, which would be very convenient for calculations in that the number of independent parameters in the force field would be reduced.

In order to test these ideas we made several least-squares fits to the observational equations. We also were concerned with the possibility that A_{CC} and/or B_{CC} might be different for aromatic and saturated carbon atoms. Table 3 shows the results obtained with various assumptions about the potential field for the aromatic, saturated, and combined data.

Trials I, IV, and VII show the results with no coulombic field and no geometric-mean assumption for B_{CH} . For the aromatic and combined data B_{CH} is 0.72 and 0.67 of the geometric-mean value, while for the saturated data B_{CH} is 1.20 of the geometric-mean value.

Trials II, V, and VIII show the effect of imposing the geometric-mean assumption. In each case the agreement becomes less good as indicated by an increase in the discrepancy index, R . The change is smallest for the saturated hydrocarbons. This decrease in agreement with the experimental data had led us to conclude previously that the geometric-mean law fails for repulsions. The small change in R for the saturated data indicates that this data subset does not define B_{CH} very well, and that the observed $B_{CH}/(B_{CC}B_{HH})^{1/2}$ ratio of 1.20 for the data subset has a large error limit.

Table 4. The observed heats of sublimation from pressure data and the calculated lattice energies and their coulombic contributions (kJ)

| Compound | ΔH_s | $-E(\text{calc.})$ | $-E(\text{coul.})$ | Reference |
|-----------------|--------------|--------------------|--------------------|-----------|
| Benzene | (52.3*) | 52.3 | 15.4 | a |
| Naphthalene | 72.4 | 79.6 | 20.0 | b |
| Anthracene | 102.1 | 108.0 | 29.2 | b |
| Phenanthrene | 86.6 | 103.7 | 27.3 | b |
| Pyrene | 100.4 | 103.3 | 18.1 | c |
| Chrysene | 118.8 | 135.6 | 37.4 | d |
| Triphenylene | 114.6 | 120.7 | 19.6 | d |
| Perylene | 129.7 | 134.1 | 20.2 | c |
| Ovalene | 211.7 | 188.2 | 13.2 | c |
| n-Pentane | 41.5† | 43.5 | 0.1 | a |
| n-Hexane | (52.6*) | 52.6 | 0.0 | a |
| n-Octane | 66.4† | 68.5 | -0.1 | a |
| Cubane | - | 57.2 | -0.1 | |
| Adamantane | 62.3 | 77.8 | 6.1 | e |
| Congressane | - | 102.6 | 14.0 | |
| Bicyclopropyl | - | 57.4 | 1.4 | |
| 1-Biapocamphane | - | 111.7 | 1.0 | |
| 1-Biadamantane | - | 135.5 | 13.5 | |

References

- (a) U.S. National Bureau of Standards (1947)
- (b) Bradley & Cleasby (1953)
- (c) Inokuchi, Shiba, Handa & Akamatsu (1952)
- (d) Hoyer & Peperle (1958)
- (e) Bratton, Szilard & Cupas (1967)

* Calorimetric result, including zero-point correction, which was fitted.

† Calorimetric result, no zero-point correction.

Trials III, VI, and IX show the effect of the coulombic field. The R values are much improved for all three data sets, even though B_{CH} was held to the geometric-mean value. Allowing B_{CH} to vary independently, in addition to allowing for the effect of the coulombic field, resulted in practically no further improvement in R . These results indicate that the (exp-6-1) potential field is more compatible with the data than the (exp-6) field with or without the assumption of the geometric-mean combining law for repulsions. Further, there is no need to relax the geometric-mean requirement for B_{CH} if coulombic effects are included.

The values found for the charge separation parameter, Δe , are remarkably similar for the three data sets, ranging from 0.358 to 0.414 e. WL, using a slightly different scheme for the charge distribution, also found a charge separation in the range 0.33–0.44 e for saturated hydrocarbons. Our results indicate that this much charge separation is also an appropriate potential field for aromatic hydrocarbons as well.

One of the most surprising results of this work is the unexpectedly large coulombic contribution to the lattice energy of hydrocarbons. All of these molecules are electrically neutral and are separated by relatively large van der Waals distances, as compared to bonded distances. Yet, the coulombic contribution ranges up to 29% of the total lattice energy. Table 4 shows the calculated coulombic energy contribution to each of the 18 crystalline hydrocarbons which were studied.

Of the compounds studied, benzene has the largest coulombic contribution to the lattice energy (29%), while the straight-chain aliphatic hydrocarbons, n-pentane, n-hexane, and n-octane, have a negligible contribution, even though they are assigned the same charge separation parameter as benzene. There seems to be a trend toward larger coulombic contributions in the aromatics. However, ovalene (an aromatic) has only

a 7% contribution, while congressane (a saturated hydrocarbon) has a 14% contribution. It appears that a detailed calculation must be made for each structure of interest to evaluate the importance of the coulombic contribution to the lattice energy.

The comparison of the calculated lattice energy, including the coulombic contribution, with the observed heats of sublimation is satisfactory. As mentioned above, heats of sublimation derived from vapor pressure data have been subject to large errors, and were not fitted in this work. In Table 4, a zero-point vibrational energy correction needs to be added to ΔH_s in column 2, which improves the agreement in every case except ovalene, for which the calculated energy is smaller than the observed ΔH_s . We think that the calculated values in Table 4 may be more accurate than observed values obtained from vapor pressure data.

The observed charge separation of this potential field leads to a C–H bond moment of 0.88D, compared to the commonly quoted value of 0.4D. We expect that interesting results will also be obtained for the charge distributions and bond moments in crystals containing molecules with nitrogen and oxygen atoms, as well as carbon and hydrogen. In particular, the method can also serve as a probe for obtaining a better potential field for coulombic interactions in hydrogen bonds.

Comparison with the WL force field

Of the many sets of nonbonded potential parameters presented in the literature (Brant, 1972), we selected the WL field as one of the best available for detailed comparison with the present results. Fig. 2 shows the ($n-6$) parts of the WL potential energy, as compared with our results. There is a rather large difference in the C...C potential curves, with the WL potential having more attraction and less repulsion than ours. We note that our potential is reasonably compatible with the interplanar spacing in graphite (Crowell, 1958) while the WL potential leads to a graphite spacing which is too small. Of course, the graphite interlayer spacing was not included as an observational quantity in either work, but it may be useful for checking purposes. Since the heat of sublimation of graphite (the interlayer energy) is not accurately known, little can be said about the depth of the C...C potential based on the graphite structure. We note that at short repulsive distances the forces (slopes) are similar. This is consistent with the observation of WL that the Williams (1967) C...C potential, which is similar to the one presently reported, satisfactorily accounted for their geometric molecular strain data involving short C...C contact distances.

Our H...H potential is slightly more repulsive, and is deeper than that of WL. Again the forces at short H...H distances are similar. We had noted in our previous work a tendency of the C...C potential to deepen and the H...H potential to become shallow (Williams, 1970). This effect was ascribed to a reduc-

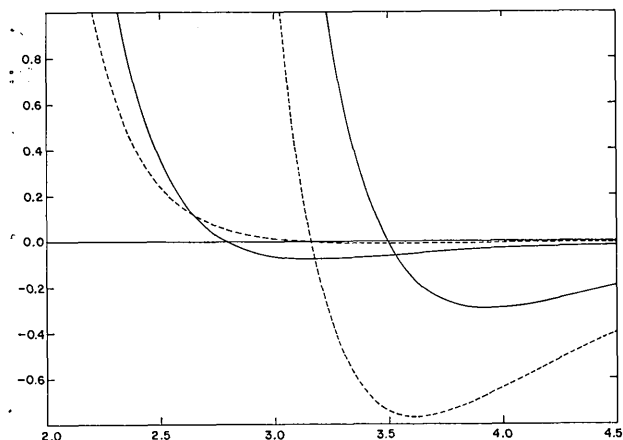


Fig. 2. The pair potential energy (kJ/mol) versus interatomic distance (Å). The two curves to the left are for H...H interactions, and the two curves to the right are for C...C interactions. The solid curves give the results of the present work, and the dashed lines give the results of Warshel & Lifson (1970).

tion in the magnitude of the second derivatives of the lattice energy which was made possible by such an energy redistribution. Our data set includes both aromatic and saturated structures; we believe that the inclusion of the aromatic structures is beneficial in contributing significant short C...C and C...H contacts which are not usually found in the saturated structures only. We have also included a wider variety of saturated structures than WL.

The inclusion of spectroscopically observed vibrational frequencies as data is permissible and desirable; unfortunately our computer programs are not presently set up to also include this data. WL found that our earlier reported (exp-6) potential (Williams, 1967) did lead to reasonable agreement with their vibrational frequency data.

We have, on the other hand, used in this work aromatic hydrocarbon data and molecular orientation information not utilized by WL. It has been pointed out frequently (Williams, 1966; Brant, 1972) that there are large correlations between individual potential parameters and one should not ascribe too much significance to differences between individual parameters. Table 2 shows for example that the differences between our set of parameters and those of WL are of the order of ten to twenty standard deviations. Yet the two sets of parameters each describe the observed structure of n-hexane with about the same accuracy.

The choice of nonbonded potential parameters is dictated by a wide variety of factors. We have used here a set of five adjustable parameters for hydrocarbons. No direct thermal or intramolecular effects were included in the observational equations or in the potential model. On the other hand, the WL potential field for hydrocarbons is specified by 23 adjustable parameters. Clearly, if one is interested in thermal and intramolecular effects a larger number of parameters are needed. If the mathematical form of the potential field is approximately correct, a larger number of adjustable parameters should lead to better agreement with the data set used. As for our five-parameter force field, there is no difficulty in principle in extending the treatment to include the observed lattice vibrational frequencies; also, an approximate method of treating thermal expansion without the introduction of addi-

tional adjustable parameters is available; and subgroup rotations may be added to our potentials by adding only one parameter per subgroup (Williams, 1972b).

A final test of the nonbonded parameter set is the calculation of the observed crystal structure by minimization of the energy (or free energy, depending on the parameterization). Table 5 shows the results obtained for n-hexane with the present parameters (shown in Table 2) and the results reported by WL. The Table also shows our results for a representative aromatic hydrocarbon structure, benzene.

There seems to be little difference between our highly simplified five-parameter potential field and the 23-parameter WL potential field, as far as the n-hexane crystal structure is concerned. For benzene, the same five-parameter potential also gives fairly good agreement, with the worst discrepancy occurring in the *b* lattice constant.

Additional columns in Table 5 show the results when the summation limit is set at 6 Å (rather than 8 Å) and the convergence constants set to 0.2 (rather than 0.175). It is interesting that the effect of chopping off the lattice sum actually improves the agreement with the observed crystal structure of benzene. WL also comment on this point in a footnote in their paper. Certainly this circumstance provides a practical argument for using the 6 Å limit (with convergence acceleration), since large amounts of computer time are thereby saved. As can be seen from the Table, the results for n-hexane are changed very little in going from the 8 Å to the 6 Å summation limit.

References

- AHMED, F. R. & TROTTER, J. (1963). *Acta Cryst.* **16**, 503–508.
 ALDEN, R. A., KRAUT, J. & TRAYLOR, T. G. (1968). *J. Amer. Chem. Soc.* **90**, 74–82.
 BACON, G. E., CURRY, N. A. & WILSON, S. A. (1964). *Proc. Roy. Soc. A* **279**, 98–110.
 BARROW, G. M. (1966). *Physical Chemistry*. New York: McGraw-Hill.
 BRADLEY, R. S. & CLEASBY, T. G. (1953). *J. Chem. Soc.* pp. 1690–1692.
 BRANT, D. A. (1972). *Ann. Rev. Biophys. Bioeng.* **1**, 369–408.

Table 5. *Parameter differences (calculated value minus observed value) between the observed structures and the models refined with the optimum nonbonded potential parameters*

ΔC_i are the distances between the observed and calculated carbon positions.

| Parameter | n-Hexane WL model | n-Hexane 8 Å limit | n-Hexane 6 Å limit | Benzene 8 Å limit | Benzene 6 Å limit |
|--------------|----------------------|-----------------------|-----------------------|----------------------|----------------------|
| <i>a</i> | 0.15 Å | 0.02 | 0.02 | 0.10 | 0.08 |
| <i>b</i> | −0.12 | −0.19 | −0.17 | −0.30 | −0.13 |
| <i>c</i> | −0.07 | 0.08 | 0.07 | 0.18 | 0.10 |
| α | −0.5° | −0.1 | 0.1 | — | — |
| β | 0.8 | 1.0 | 1.1 | — | — |
| γ | −1.9 | −1.6 | −1.8 | — | — |
| ΔC_1 | 0.04 Å | 0.11 | 0.11 | 0.12 | 0.07 |
| ΔC_2 | 0.09 | 0.02 | 0.03 | 0.07 | 0.05 |
| ΔC_3 | 0.03 | 0.04 | 0.04 | 0.12 | 0.08 |

- BRATTON, W. K., SZILARD, I. & CUPAS, C. A. (1967). *J. Org. Chem.* **32**, 2019–2021.
- BURNS, D. M. & IBALL, J. (1960). *Proc. Roy. Soc. A* **257**, 491–514.
- CAMERMAN, A. & TROTTER, J. (1964). *Proc. Roy. Soc. A* **279**, 129–146.
- CAMERMAN, A. & TROTTER, J. (1965). *Acta Cryst.* **18**, 636–643.
- CROWELL, A. D. (1958). *J. Chem. Phys.* **29**, 446–447.
- CRUICKSHANK, D. W. J. (1957). *Acta Cryst.* **10**, 504–508.
- DONALDSON, D. M. & ROBERTSON, J. M. (1953). *Proc. Roy. Soc. A* **220**, 157–170.
- DONOHUE, J. & GOODMAN, S. (1967). *Acta Cryst.* **22**, 353–354.
- DOUSLIN, D. R. & HUFFMAN, H. M. (1948). *J. Amer. Chem. Soc.* **68**, 1704–1708.
- ERAKER, J. & RØMMING, C. (1967). *Acta Chem. Scand.* **21**, 2721–2726.
- FLEISCHER, E. B. (1964). *J. Amer. Chem. Soc.* **86**, 3889–3890.
- HOYER, H. & PEPPERLE, W. (1958). *Z. Elektrochem.* **62**, 61–66.
- INOKUCHI, H., SHIBA, S., HANDA, T. & AKAMATSU, H. A. (1952). *Bull. Chem. Soc. Japan*, **25**, 299–302.
- KARLE, I. L. & KARLE, J. (1965). *J. Amer. Chem. Soc.* **87**, 918–920.
- KITAIGORODSKII, A. I. (1970). *Advanc. Struct. Res. Diff. Meth.* **3**, 173–247.
- MAGNASCO, V. & MUSSO, G. F. (1967). *J. Chem. Phys.* **46**, 4015–4025.
- MASON, E. A. & HIRSCHFELDER, J. O. (1957). *J. Chem. Phys.* **26**, 756–766.
- MASON, R. (1964). *Acta Cryst.* **17**, 547–555.
- MASON, R. (1970). *Perspect. Struct. Chem.* **3**, 59–90.
- NAKAMURA, M. & MIYAZAWA, T. (1969). *J. Chem. Phys.* **51**, 3146–3147.
- NORMAN, N. & MATHISEN, H. (1961a). *Acta Chem. Scand.* **15**, 1755–1760.
- NORMAN, N. & MATHISEN, H. (1961b). *Acta Chem. Scand.* **15**, 1747–1754.
- NORMAN, N. & MATHISEN, H. (1964). *Acta Chem. Scand.* **18**, 353–360.
- OLIVER, G. D., EATON, M. & HUFFMAN, H. M. (1948). *J. Amer. Chem. Soc.* **70**, 1502–1505.
- RADCHENKO, L. G. (1971). *Russ. J. Phys. Chem.* **45**, 747. [*Zh. Fiz. Khim.* **45**, 1310.]
- STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.
- THOMSON, G. W. & DOUSLIN, D. R. (1971). *Physical Methods of Chemistry*, edited by A. WEISSBERGER, Vol. 1, part 5, pp. 83–89.
- TROTTER, J. (1963). *Acta Cryst.* **16**, 605–608.
- U. S. NATIONAL BUREAU OF STANDARDS (1947). Circular C461, U. S. Department of Commerce.
- WARSHEL, A. & LIFSON, S. (1970). *J. Chem. Phys.* **53**, 582–594.
- WASER, J. (1963). *Acta Cryst.* **16**, 1091–1094.
- WILLIAMS, D. E. (1965). *J. Chem. Phys.* **43**, 4424–4426.
- WILLIAMS, D. E. (1966). *J. Chem. Phys.* **45**, 3770–3778.
- WILLIAMS, D. E. (1967). *J. Chem. Phys.* **47**, 4680–4684.
- WILLIAMS, D. E. (1970). *Trans. Amer. Cryst. Assoc.* **6**, 21–34.
- WILLIAMS, D. E. (1971). *Acta Cryst.* **A27**, 452–455.
- WILLIAMS, D. E. (1972a). *Acta Cryst.* **A28**, 84–88.
- WILLIAMS, D. E. (1972b). *Acta Cryst.* **A28**, 629–635.

Acta Cryst. (1974). **A30**, 77

Anisotropic Corrections of Measured Integrated Bragg Intensities for Thermal Diffuse Scattering—General Formula

BY JIMPEI HARADA

Department of Applied Physics, Nagoya University, Nagoya, Japan

AND MAKOTO SAKATA

Department of Chemistry, Tokyo University of Education, Tokyo, Japan

(Received 28 May 1973; accepted 31 July 1973)

The correction of measured integrated intensities for the first-order thermal diffuse scattering (TDS) is considered on the basis of the existing theory of X-ray thermal diffuse scattering for an elastic wave of long wave length. Generalized formula for the TDS correction α is found to be represented by a quadratic form in the Miller indices h, k, l and a tensor $\Delta\beta$, as $\alpha = \Delta\beta_{11}h^2 + \Delta\beta_{22}k^2 + \Delta\beta_{33}l^2 + 2\Delta\beta_{12}hk + 2\Delta\beta_{23}kl + 2\Delta\beta_{31}lh$. $\Delta\beta$ is a tensor introduced in this paper which characterizes the anisotropy of the TDS correction. The form of the tensor $\Delta\beta$ is shown to depend only on the crystallographic system. The relation between $\Delta\beta$ and the temperature-parameter tensor is presented.

Introduction

Recently remarkable progress has been made in the accuracy of crystal structure analysis by means of X-ray diffraction from single-crystal specimens. Even for organic crystals and minerals, if they are not too com-

plicated, it is becoming possible to investigate bonding electrons between atoms and lone-pair electrons (*e.g.* Iwata & Saito, 1972) by analysis of charge-density distributions. In such analysis the reliability of the result depends on the accuracy of the observed structure factors and a significant point in the discussion