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Theoretical Evaluation of the Intermolecular Interaction Energy of a Crystal: Application to the Analysis of Crystal Geometry

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Simple formulae for the interaction energy between two molecules have been used for writing a program which evaluates the total interaction energy of the molecules in a crystal. These formulae appear as sums of atom–atom and, eventually, atom–bond and bond–bond contributions. The non-additivity of the polarization energy is taken into account, and a rough estimate of the third-order non-additive terms ('triple dipole') is introduced. A suitable modification of the formulae for short interatomic distances allows us to treat hydrogen-bond interactions as well. We present results for the crystals of CH_4, CO_2, C_6H_6, and $C_6H_5NO_2$. The energies calculated for the experimental geometry are in good agreement with experiment. For CO_2 and $C_6H_5NO_2$ minimizations of the computed energy (with respect to unit cell parameters and orientation and position of one molecule in the cell) were performed and it was found that the experimental configuration actually was very close to a minimum. The configurations of neighbour molecules in the crystal are compared with the optimal configuration of a binary complex, and it appears that, for non-hydrogen-bonded molecules, significant differences between these configurations may occur. Finally, for nitrobenzene several local minima seem to exist on the energy hypersurface; the minimum corresponding to the known experimental geometry appears to be the lowest, but only by a small amount.

1. Introduction

An extensive compilation of the stacking patterns observed in the crystalline state for nucleic bases, either isolated or in combined form (nucleosides and nucleotides) was recently given by Bugg, Thomas, Sundaralingam & Rao (1971). Stacked configurations of the purine or pyrimidine rings appear in all these crystals, but the overlap is almost always partial. Trying to explain this partial stacking in terms of binary interactions only (*i.e.* the interaction between the two partially stacked bases), Bugg *et al.* were led to suggest that these partially stacked patterns could be understood only in terms of the polarization contribution [indeed, by using the dipole approximation (see *e.g.* Claverie & Rein, 1969) for the electrostatic and dispersion energy, they found that these two contributions could not explain the observed pattern]. However, when actual computations of the various contributions to the intermolecular interaction energy are performed, the polarization contribution never appears as the prominent one [as concerns stacked configurations, see *e.g.* Claverie, Pullman & Caillet (1966) (stacked purines and pyrimidines); Caillet & Pullman (1968) (tetramethyl uric acid and aromatic hydrocarbons); Mantione (1968, 1969 *a,b*) (charge transfer complexes: tetracyanoethylene and aromatic hydrocarbons)]. In all these cases several stacked configurations were tried (by moving the molecules in parallel planes) in order to explore roughly the energy surface: not only the *absolute magnitude* of the polarization contribution appeared markedly smaller than the magnitude of the other contributions, but the same property appeared to hold also for the *variations* of the different contributions: therefore, it may not be argued that the polarization term, although small by itself, could play a prominent role (by its variation) in the determination of the minimum-energy configuration.

Two other features, relevant for the present problem, appeared in these calculations of binary complexes:

(1) The simplest long-range formulae (based upon the dipole–dipole approximation) cannot be used safely in the equilibrium region (3 to 4 Å between the closest atoms for organic molecules); for stacked molecules, the variation of the electrostatic energy, when one of the molecules is translated in its own plane, is incorrectly described by the dipole–dipole approximation: the dipole–dipole energy decrease when the molecules depart from the stacked configuration corresponding to dipoles antiparallel to each other, while the more correct monopole approximation (interaction between atomic net charges) does not behave in such a simple way: small decreases or *increases* of the electrostatic interaction occur for displacements of 1 Å from the position corresponding to antiparallel stacked dipoles. This situation actually occurs for two adenine molecules (Caillet & Claverie, 1974). As a consequence, as concerns the electrostatic energy, it may not be argued that a completely stacked configuration is markedly preferred: this is true for the dipole–dipole approximation (which is not reliable in the range of equilibrium distances), but not for the more exact monopole–monopole approximation.

(2) If we now consider the total interaction energy, a somewhat analogous situation appears to hold: with the long-range formulae (dipole–dipole, dipole–induced dipole, London formula for the dispersion energy*), a minimum corresponding to the stacking of the antiparallel dipoles is obtained (because all energies have their minima for this position); on the contrary, with more refined approximations suited for the distances of interest, no deep minimum occurs: the energy surface (corresponding to the two-dimensional displacements of one molecule in a plane parallel to the other) is rather flat in a region extending to at least 1 Å around a position of complete stacking; it is even possible that several small minima occur in this region. It may also happen that the energy varies very little with respect to angular variables [benzene, which is reported in §3(*C*) below, is a striking example].

The consequences of such a situation concerning the configuration of molecules in crystals are clear: if the minimum of the interaction energy (with respect to displacements of the molecules around the configuration of the binary minimum) is flat instead of deep, the position of the minimum will be highly sensitive to any external perturbation, for example the presence of neighbour molecules in the crystal. Therefore, no direct contradiction *a priori* exists between the existence of partially stacked configurations in crystals and more completely stacked configurations in binary complexes; a quantitative study appears necessary to clear up the point.

More recently, Motherwell & Isaacs (1972) attempted to make some intermolecular energy calculations relevant to this problem. They were interested in crystals of various purine nucleosides, but they made their calculations for *columns* of molecules only (and not for a real three-dimensional lattice).

Essentially, they found that, in such columns, the bases alone stack more completely than the nucleosides, and they concluded that the partial stacking was due to the presence of the ribose. But as we have pointed out previously (Caillet & Claverie, 1974) this cannot be the unique cause of partial stacking since it is also observed in three-dimensional crystals of nucleic acid bases.

In this previous work, we reported a detailed study for the case of adenine and showed how different stacking patterns appeared in binary complexes and columns on the one hand, and in the crystal on the other. In the present work, we shall describe in detail our method for calculating the intermolecular interaction energy of a crystal and we shall present some applications to crystals of ordinary molecules (methane, carbon dioxide, benzene, nitrobenzene); among other results, it will be made clear that the differences between configurations in binary complexes and in crystals are a rather general phenomenon, by no means special to the molecules of biochemical interest like those considered by Bugg *et al.* (1971).

2. Method

(*a*) *Basic formulae*

We evaluate the interaction energy as the sum of three long-range contributions (electrostatic, polarization and dispersion) and a short-range repulsive contribution.

Information about these formulae may be found in previous papers (Huron & Claverie, 1969, 1972, 1974; Claverie, 1973). Here we shall briefly describe the formulae and parameter values as used in the present work for molecules close to each other. For molecules separated by a distance rather large with respect to their own dimensions (this case evidently occurs in the case of crystals), simplified formulae may be safely used (the exponentially decreasing short-range term is neglected and the long-range terms are evaluated according to the dipole approximation).

(*a*) *Electrostatic energy*

For the calculation of this term, we need net atomic charges of the two interacting molecules. This energy is given by

$$E_{\varrho\varrho}=\sum_i{}^{(1)}\sum_j{}^{(2)}\frac{\varrho_i\varrho_j}{R_{ij}}\,. \qquad (1)$$

We note that $\sum_i^{(m)}$ extends to all objects i (here the atoms) belonging to molecule m; ϱ_i and ϱ_j are the net charges of atoms i and j of molecules (1) and (2).

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* $E_{\rm disp}=-\frac{3}{2}\frac{U_1U_2}{U_1+U_2}\frac{\alpha_1\alpha_2}{R^6}$ where R is the distance between the two molecules (for example between the two points where the dipoles are placed).

The net charges: The net charges on the different atoms of a molecule are calculated with the Del Re (1958) method for the σ charges and with the Hückel method for the π charges (Berthod & Pullman, 1965); when the charges are evaluated by a different method, this is indicated in §3 for the molecule studied.

(*b*) *Polarization energy*

(α) *Bond polarizabilities*

When we consider two molecules, the polarization of molecule (1) by molecule (2) is given by

$$E_{\mathrm{pol}(2\to 1)} = -\tfrac{1}{2}\sum_u {}^{(1)}\mathscr{E}_u^{(2)}\mathrm{b}_u\mathscr{E}_u^{(2)} \qquad (2)$$

where $\mathscr{E}_u^{(2)}$ is the electric field induced by molecule (2) at some fixed point[*] of the bond u of molecule (1). For the calculation of $\mathscr{E}_u^{(2)}$, molecule (2) is represented by the same set of charges (and eventually dipoles) which is used for the calculation of the electrostatic energy. b_u is the polarizability tensor of the bond u of molecule (1), and in a local coordinate system whose x axis is directed along the bond, it is of the diagonal form

$$\mathrm{b} = \begin{pmatrix} b_L & 0 & 0 \\ 0 & b_T & 0 \\ 0 & 0 & b_V \end{pmatrix} \qquad (3)$$

where b_L, b_T and b_V are the principal polarizabilities of the bond; for most bonds, $b_T = b_V$ (see *e.g.* LeFèvre, 1965) and when the two polarizabilities are not equal, we replaced them by their mean value in order to simplify the calculations.

(β) *Atom polarizabilities*

The calculation of the polarization energy as a sum of bond contributions gives rise to a purely practical problem, namely a substantial increase in computation time, due to the fact that it is necessary to compute all intermolecular atom–bond distances besides the atom–atom distances which are, in any case, necessary for the calculation of the electrostatic energy. Owing to the large number of intermolecular interactions which are to be calculated for the evaluation of the crystal energy, it becomes essential that the computation time of each interaction is reduced as much as possible. To achieve this, it would be interesting to make use of the atom–atom distances only. As concerns the polarization energy, this means that the polarization energy of a molecule will be calculated as a sum of atom polarization contributions:

$$E_{\mathrm{pol}}(1) = -\tfrac{1}{2}\sum_i \alpha_i(\mathscr{E}_i)^2$$

where $\mathscr{E}_i$ is the electric field created at the atom i of molecule (1) by all other molecules [only molecule (2) in the case of a binary complex], and α_i is the mean polarizability attributed to atom i. $\mathscr{E}_i$ is calculated as indicated in §(α) above. As concerns the atomic polarizabilities, we have not tried to use directly a systematic of increments because it has been recognized for a long time that such atomic polarizability increments are much less transferable (from one molecule to another) than bond increments. We therefore continue to use these bond polarizabilities, and, for each molecule, we calculate from them atomic polarizabilities according to the following procedure:

Let u be the bond between atoms i and j, and α_u the *mean* polarizability of this bond [$\alpha_u = (b_{uL} + b_{uT} + b_{uV})/3$]. We divide this polarizability α_u into two parts $\alpha_{u,i}$ and $\alpha_{u,j}$ which will be attributed respectively to atoms i and j. This partition is done according to weights attributed to atoms, these weights being obtained from the number of electrons in the following way: let N_u be the number of electrons involved in the bond u (2 for a C–C bond, 4 for a C–C bond, 3 for a C$\overset{\cdots}{-}$C bond in benzene; more complicated π systems will be treated below; let N_i^c (or N_j^c) be the numbers of electrons of atoms i (or j) which are not involved in bonds, the two 1s electrons being excluded (thus, for second-row atoms: C, N, O, F, N_i^c would be equal to the number of lone-pair electrons; see below for the case of heavier atoms); and let v_i (or v_j) be the number of atoms bonded to the atom i (or j). We consider that the N_i^c electrons are equally distributed between the v_i bonds† starting from i (and similarly from j), and we share equally the N_u bonding electrons between i and j: thus, for the bond u, we attribute to atom i

$$n_{u,i} = N_u/2 + N_i^c/v_i$$

electrons, and similarly $n_{u,j}$ electrons to atom j:

$$n_{u,j} = N_u/2 + N_j^c/v_j\,.$$

Then, the mean bond polarizability α_u is shared between atoms i and j according to the weights $n_{u,i}$ and $n_{u,j}$, so that we obtain the atomic polarizability increments due to the bond u:

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[*] In all our previous work about molecular interactions, we used the middle of the bond. In the present work, we also used a tentatively refined choice: for every bond, we consider the number n_b of 'bonding electrons' (two for a single bond, four for a double bond, ...) and the numbers n_{c1}, n_{c2} of 'non-bonding electrons' from the bonded atoms (1 and 2) that we attribute to the bond. n_{c1} is defined in the following way: we take the total number N_1 of 'non-bonding electrons' of atom 1 (core+lone pairs) and we share equally this number between the v bonds starting from this atom: $n_{c1} = N_1/v_1$ for each of these bonds. Then, noting A_1 and A_2 the points where the atoms 1 and 2 are placed, we consider the middle M of A_1A_2, the middle P_1 of A_1M and the middle P_2 of MA_2; we now define the centre of mass P of M, P_1 and P_2 with the respective weights n_b, n_{c1} and n_{c2}. We may use this point P for calculating the electric field which will polarize the bond. For atoms beyond the first row, however, this choice may overestimate the contribution of the core electrons, which become more and more numerous; it would therefore be more cautious to use a reduced 'effective' number of core electrons instead of the true one.

[*] We use here the word 'bond' with the meaning 'pair of bonded atoms', *i.e.* whether the *chemical* bond is single, double, triple, aromatic, we count it as one bond.

$$\alpha_{i,u}=\frac{n_{u,i}}{n_{u,i}+n_{u,j}}\alpha_u$$

$$\alpha_{j,u}=\frac{n_{u,j}}{n_{u,i}+n_{u,j}}\alpha_u\,.$$

Then the total atomic polarizability of each atom is obtained by summing the increments thus obtained from the bonds which start from the atom considered:

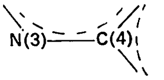
$$\alpha_i=\sum_{u\in i}\alpha_{i,u}$$

where $u\in i$ means that the summation is extended to the bonds starting from the atom i.

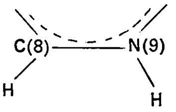
Remark 1. *Evaluation of the number* N_u *of bonding electrons in the case of conjugated systems* (*delocalized* π *bonds*)

There is no problem for the σ bond, which contributes $N_u^\sigma=2$ electrons to N_u. For getting N_u^π, we proceed in the same way as we did for the non-bonded electrons, *i.e.* we take the number N_i^π (or N_j^π) of π electrons that atom i (or j) gives to the 'pool' of the π system, and we share this number equally between the v_i^π π *bonds* which start from atom i (and similarly for atom j). We obtain in this way for the bond u between i and j:

$$N_u=N_u^\sigma+N_u^\pi=N_u^\sigma+(N_i^\pi/v_i^\pi+N_j^\pi/v_j^\pi)\,.$$

Examples: (*a*) bond  in adenine $N_3^\pi=1$, $v_3^\pi=2$; $N_4^\pi=1$, $v_4^\pi=3$; $N_{(34)}^\pi=\frac{1}{2}+\frac{1}{3}=0{\cdot}833\ldots$

As concerns the other numbers implied in the calculation of the atomic polarizabilities, we have $N_{(34)}^\sigma=2$, $N_3^c=2$, $v_3=2$, $N_4^c=0$, $v_4=3$, hence $N_u=2{\cdot}833\ldots$, $n_{(34),3}=1{\cdot}4166\ldots+1$ and $n_{(34),4}=1{\cdot}41666\ldots$ (*b*) bond



in adenine

$$N_8^\pi=1,\ v_8^\pi=2;\ N_9^\pi=2,\ v_9^\pi=2$$
$$N_{(89)}^\pi=\tfrac{1}{2}+\tfrac{2}{2}=1{\cdot}5;\ N_{(89)}=3{\cdot}5$$
$$N_8^c=0,\ v_8=3;\ N_9^c=0,\ v_9=3$$
$$n_{(89),8}=n_{(89),9}=N_{(89)}/2=1{\cdot}75\,.$$

Of course, more refined choices could be made: thus, for the numbers N_i^π, atomic π electronic populations, or, for the numbers N_u^π, bond π electronic populations (Diner, 1967) could be used. But the simple procedure given above appears sufficient in practice, because the final weights are rather insensitive to slight modifications of the π population. In the case of the $-NO_2$ group of nitrobenzene, for example, we used $N_N^\pi=1$ and $N_O^\pi=1{\cdot}5$, but the use of the more standard numbers $N_N^\pi=2$ and $N_O^\pi=1$ does not lead to widely different final results.

Remark 2. *'Effective' number of electrons for the atoms beyond the second-row*

For such atoms (S, P and the halogen atoms Cl, Br, I) some caution is necessary in order to define an effective number N^c of non-bonded electrons. To consider only the non-bonded valence electrons seems in sufficient, since all halogen atoms, for example, would then receive the same number N^c; but to consider all non-bonded electrons except the 1*s* would give too high values of N^c, because the inner-shell electrons certainly contribute less to the polarizability than those of the outer shell. The following recipe may be proposed: for analogous bonds, the atomic contribution to the polarizability will be supposed constant; thus, in the series of bonds C–H, C–Cl, C–Br, C–I, the atomic contribution for C will be, according to the previous rules, $\alpha_C=\alpha_{C-H}/2$; then we shall use $a_X=\alpha_{C-X}-\alpha_C$ (where X = Cl, Br or I). Similarly, C–S may be considered analogous to C–O and C–P to C–N. In the applications that we have made up to now, such heavier atoms were not involved, so that the proposed recipe has not been checked. Further work will be necessary to decide whether or not it is satisfactory.

For a binary complex, the total polarization energy is

$$E_{\text{pol}}=E_{\text{pol}(1\to2)}+E_{\text{pol}(2\to1)}$$

where $E_{\text{pol}(2\to1)}$ is the polarization energy of molecule (1) by molecule (2).

(*c*) *Dispersion and repulsion energy*

In previous work involving calculations of intermolecular interaction energies (Huron & Claverie, 1969, 1971; Mantione & Daudey, 1970) we used two kinds of approximate formulae for the evaluation of the dispersion term:

(1) a sum of bond–bond interactions (each calculated by a London-type formula using bond polarizabilities).

(2) a sum of atom–atom $1/R^6$ terms, according to the semi-empirical formula proposed by Kitaigorodskii (1961*a*). Several improvements were brought to these formulae, involving comparison both with experimental results and with values calculated from the London-type formula (Huron & Claverie, 1969, 1972, 1974).

The Kitaigorodskii formula also involves a repulsion energy calculated as a sum of atom–atom terms, and from preliminary calculation of the sublimation energy of some crystals [methane, carbon dioxide, benzene, nitrobenzene: see §III-2(*a*) below] it appeared that this repulsion energy was better fitted to the corresponding (atom–atom) evaluation of the dispersion energy than to the bond–bond formula (it must be appreciated that the number of close contacts in crystals makes the results rather sensitive to a correct fitting of the various contributions to the interaction energy). To derive a correctly fitted dispersion–repulsion formula on the basis of the bond–bond formula (for the dispersion) implies further research (a possibility would be to define atom–atom terms, starting from bond–bond interactions, in such a way that these atom–atom terms give at long-distance results asymptotically equal to those of the bond–bond interactions). In the present work, we content ourselves with the Kitaigorodskii-type improved formula; indeed, we shall deal with molecules involving only H and first-row atoms (C, N, O), and the parameters that we have for them appear sufficiently reliable for obtaining useful results.

This formula appears as a sum of atom–atom interactions:

$$E^{\rm KIT}=\sum_i{}^{(1)}\sum_j{}^{(2)}E(i,j) \tag{4}$$

where each atom–atom contribution $E(i,j)$ is the sum of a dispersion and a repulsion term:

$$E(i,j)=k_ik_j\left[-\frac{A}{z^6}+C\exp\left(-\alpha z\right)\right] \tag{5}$$

where

$$z=R_{ij}/R^{0\prime}_{ij} \tag{6}$$

and

$$R^{0\prime}_{ij}=\sqrt{(2R^W_i)(2R^W_j)} \tag{7}$$

where R^W_i and R^W_j are the van der Waals radii of atoms i and j (generally taken from Bondi, 1964). In the present work, we used the values:

$$R^W_{\rm H}=1{\cdot}2\ \text{Å}\ \ R^W_{\rm C(aliphatic)}=1{\cdot}7\ \text{Å}\ \ R^W_{\rm C(aromatic)}=1{\cdot}77\ \text{Å}$$
$$R^W_{\rm N(aromatic)}=1{\cdot}60\ \text{Å}\ \ R^W_{\rm O(aromatic)}=1{\cdot}50\ \text{Å}\ .$$

As concerns the use of the geometric mean (7) instead of the arithmetic mean $(2R^W_i+2R^W_j)/2=R^W_i+R^W_j$, see Huron & Claverie (1969). The ratio A/C is fixed by the condition that the minimum of (5) (as a function of R) occurs for $R=R^0_{ij}=\frac{13}{11}R^{0\prime}_{ij}$ (see Huron & Claverie, 1969).

The parameters α, A and C are kept independent of the atomic species i and j. The values that we use presently are (Huron & Claverie, 1972)

$$A=0{\cdot}214\quad C=47\times10^3\quad \alpha=12{\cdot}35\ . \tag{8}$$

They slightly differ from those (Huron & Claverie, 1969) corresponding to the original value of Kitaigorodskii (1961 *a,b*), because there was an error in the calculations upon which these original values were based (Huron & Claverie, 1972; Kitaigorodskii & Mirskaya, 1964).

The parameters k_i depend on the atomic species; they are necessary to allow the energy minimum to have different values according to the atomic species involved (Kitaigorodskii, Mirskaya & Nauchitel, 1970; Huron & Claverie, 1974). The values used in the present work are

$$k_{\rm H}=1\quad k_{\rm C}=1\quad k_{\rm N}=1{\cdot}18\quad k_{\rm O}=1{\cdot}36\ . \tag{9}$$

Finally, we took into account the effect of variable electronic population on the repulsive contribution (*cf.* Murrell, Kettle & Tedder, 1965; pp. 339–340): we introduced, for every atom–atom repulsive term, the multiplicative factor $(1-\varrho_i/N^{\rm Val}_i)\,(1-\varrho_j/N^{\rm Val}_j)$, where $N^{\rm Val}_i$ is the number of valence electrons of the atom i and ϱ_i its net charge (thus the factor is 1 for a neutral atom). We therefore have

$$E_{\rm rep}(i,j)=(1-\varrho_i/N^{\rm Val}_i)\,(1-\varrho_j/N^{\rm Val}_j)k_ik_jC \times\exp\left(-\alpha R_{ij}/R^{0\prime}_{ij}\right)\ . \tag{10}$$

This correction is rather small in most cases; it actually becomes noticeable for H atoms bonded to O or N atoms because they have a non-negligible positive net charge, while $N^{\rm Val}=1$.

(*d*) *Case of the hydrogen bond*

The effect just described above decreases the repulsion in the case of a hydrogen bond since the H atom has a positive non-negligible charge. This is not yet sufficient, however, to make the equilibrium distance short enough; a possible explanation of this situation is that the charge-transfer contribution becomes significant at distances shorter than the usual equilibrium distances. Now, this contribution varies exponentially with distance and is attractive (negative sign). In order to represent this, we used at short distances (for the hydrogen–heavy atom interactions) a reduced repulsive term defined in the following way: we choose two distances $R_m<R_M$; for $R>R_M$, we use the normal constants A,C,α; for $R<R_m$, we use modified constants A',C',α'; and for $R_m<R<R_M$ we use interpolated values defined by

$$K(x)=\frac{K+K'}{2}+\frac{K-K'}{2}\cdot(0{\cdot}375x^5-1{\cdot}25x^3+1{\cdot}875x) \tag{11}$$

where

$$x=\left(R-\frac{R_m+R_M}{2}\right)\bigg/\left(\frac{R_M-R_m}{2}\right)\ ;$$

the polynomial $P(x)=0{\cdot}375x^5-1{\cdot}25x^3+1{\cdot}875x$ has been chosen so as to have vanishing first and second derivatives for $x=\pm1$ and to take the values $P(-1)=-1$, $P(1)=1$ [so that $K(R)$ and its first and second derivatives are continuous, which is a convenient feature if minimization procedures involving derivatives are to be employed]. In (11), K represents one of the symbols A, C or α. The values used in the present work are

$$R_m=1{\cdot}8\ \text{Å}\quad R_M=2{\cdot}6\ \text{Å}$$
$$A'={\rm A}/5\qquad C'={\rm C}/2{\cdot}7\qquad \alpha'=13{\cdot}8\ . \tag{12}$$

These values were fitted to reproduce correctly the equilibrium distance and energy for the hydrogen bond between water molecules and between formamide molecules. It must be emphasized that the parameter A for the dispersion energy had to be reduced, too; this is in agreement with the theoretical analysis of Murell & Teixeira-Dias (1971), according to which the $1/R^6$ formula overestimates the dispersion term at short distances [owing to the penetration part of the intermolecular integrals, which reduces their value with respect to their $1/R^3$ (dipole–dipole) approximation].

(*B*) *Interaction energy for a crystal*

(*a*) *Formulae*

For a crystalline array containing N molecules, the total interaction energy is

$$E=\sum_{p<q}^{N}\sum^{N} u_{pq}^{\text{add}}+\sum_{p}^{N} u_{p}^{\text{pol}} \tag{13}$$

where u_{pq}^{add} represents the sum of the pairwise additive interactions (electrostatic, dispersion, repulsion) between the molecules p and q, and u_{p}^{pol} represents the polarization energy of the molecule p in the electric field of all surrounding molecules (*i.e.* the polarization energy of each bond of the molecule p is calculated from the total electric field created by all other molecules on this bond). Now:

$$\sum_{p<q}^{N}\sum^{N} u_{pq}^{\text{add}}=\tfrac{1}{2}\sum_{q\neq p}^{N}\sum^{N} u_{pq}^{\text{add}}\,.$$

When N becomes very large, the boundary effects may be neglected and, owing to the equivalence of all molecules in a crystal, $\sum\limits_{q\neq p} u_{pq}^{\text{add}}$ is the same for all molecules i, and the same property holds for u_{p}^{pol}. Hence, if we note that

$$U^{\text{add}}=\sum_{q\neq p} U_{pq}^{\text{add}} \qquad U^{\text{pol}}=u_{p}^{\text{pol}}, \tag{14}$$

we get

$$E=\frac{N}{2}\,U^{\text{add}}+NU^{\text{pol}}$$

and the energy per molecule is

$$E/N=\tfrac{1}{2}U^{\text{add}}+U^{\text{pol}}\,. \tag{15}$$

Remark: *The non-additive terms beyond second order of perturbation*

These terms are not completely negligible, but simplified formulae for them have not been worked out as thoroughly as for the first and second-order terms. Most works have dealt only with *non-polar* molecules, for which non-additive terms (similar to the second-order dispersion term) appear at the third perturbation order only (Axilrod, 1951; Kihara 1958; Kestner & Sinanoglu, 1963). In the present work, we have used the results of Kestner & Sinanoglu (1963) who evaluated this third-order non-additive term for a condensed phase (liquid or solid) and found a positive (destabilizing) contribution equal to 7% of the absolute value of the (second-order) dispersion term in the case of methane. For polar molecules, the polarization term is the only non-additive term up to the second order, and its correct value is easily obtained, as indicated above, by using for each molecule the total electric field created by all other molecules (see Pullman, Claverie & Caillet, 1966, 1967). But there are also new terms at higher orders, and they will be, at least partially, non-additive. Unfortunately, such terms beyond the second order have been studied systematically only very recently (Stogryn, 1971), and no simplified formulae have been yet devised for them. We therefore did not attempt to evaluate them in the present work, and this introduces a slight supplementary uncertainty of the results in the case of molecules with non-negligible net charges.

(*b*) *Practical procedure for computation*

The crystal is built from a central cell in which the molecules are deduced one from another from the symmetry elements and the coordinates given in the literature. The building of the crystal is obtained by translations of the central cell along the three crystal axes so as to form a finite crystal which is approximately a cube with the original cell at its centre. This is achieved by choosing some maximum number of layers in the crystallographic direction corresponding to the smallest edge of the unit cell and calculating the number of layers in the two other directions so as to get approximately a cube. Layers are added until the convergence of the energy is obtained to a prescribed accuracy (the accuracy is defined as the ratio of the energy difference due to the last layer added divided by the total interaction energy). An accuracy of 10^{-3} was obtained with four or five layers for all the crystals considered in this work.

There are N_c molecules in the central cell. For the experimental crystal structure, all molecules are equivalent, thus it would be sufficient to compute U^{add} and U^{pol} for one of these N_c molecules; but when some molecules are displaced (for investigating the variation of the energy) the equivalence may cease to be rigorous. In the present work, we therefore computed U^{add} and U^{pol} for all N_c molecules of the central cell and took the arithmetic mean.

When molecule q is not very close to molecule p, it becomes legitimate to use the simplified formulae for the long-range interactions (based upon the so-called dipole approximation) and omit the calculation of the repulsion contribution (which becomes completely negligible as soon as the atoms are not in close contact). The electrostatic energy then reduces to the interaction between the molecular dipoles (we put the dipole at the middle of the segment joining the 'centre of mass' of the positive atomic net charges and the centre of mass of the negative ones; we shall call this point the 'centre of force'). The dispersion energy is approximated by replacing all atom$\cdots$atom distances R_{ij} by the distance R joining the 'centres of force' of the two molecules, thus

$$E_{\text{disp}}=-\frac{A}{R^{6}}\sum_{i}^{(p)}\sum_{j}^{(q)} k_i k_j (R_{ij}^{0'})^{6} \tag{16}$$

and the quantity

$$\sum_{i}^{(p)}\sum_{j}^{(q)} k_i k_j (R_{ij}^{0'})^{6}=\sum_{i}^{(p)}\sum_{j}^{(q)} k_i k_j (4R_i^{w}R_j^{w})^{3}$$

may be calculated once for all.

Finally, as concerns the polarization energy, we calculate only the electric field created by the dipole of molecule q at the centre of force of molecule p, and we use this electric field for all the bonds of molecule p.

The use of these simplified long-range formulae results in considerable saving of computing time, especially because the molecules lying far from a given molecule p are much more numerous than those lying close to it.

Our computer program calculates the energies u_{pq} from both sets of formulae (complete and simplified) and compares, for every new molecule q, the difference Δu_{pq} of these two values of u_{pq} to the current total interaction energy U_{tot}. As soon as $|\Delta u_{pq}/U_{\text{tot}}|$ is smaller than a prescribed threshold ε for all molecules q of a cell, the distance D of the centre of this cell to the centre of the central cell is taken as a 'cutting distance', which means that, for every molecule q belonging to a cell whose distance to the central cell is larger than or equal to D, only the simplified long-range formulae are used.

In practice, for a threshold $\varepsilon=0{\cdot}5\times10^{-2}$, the long-range formulae were used in the second layer for the crystals considered.

(*c*) *Variation of the crystal geometry and minimization procedure*

One of the main interests of a program computing the intermolecular energy of a crystal is, of course, the possibility of modifying the crystal geometry and searching energy minima. We have six parameters for the unit cell (a,b,c; α,β,γ) and six parameters for each molecule of the unit cell in the general case (three Euler angles defining the orientation of the molecule with respect to some centre chosen in the molecule, and the three coordinates of this centre).

In the applications reported in §3, we did not leave all these parameters arbitrary, because this would have involved prohibitively long computation times: we left free at most the six unit cell parameters and the six parameters of *one* molecule in the unit cell, the other molecules of this cell being obtained according to symmetry operations of the space group (experimentally known in all the cases that we considered).

As the centre of the molecule, we chose the 'centre of mass' of the atoms, each atom receiving a weight equal to its *atomic number* (and not its true mass, so that our centre is slightly different from the true centre of gravity).

For the Euler angles (φ,θ,ψ), we used the choice of Kemble (1937); let us denote $Oxyz$ the initial coordinate system and $OXYZ$ the final system, and let us introduce the notation $\mathscr{R}(\alpha,\overrightarrow{Ov})$ for the rotation by an angle α around an axis $\overrightarrow{Ov}$; we first perform on $Oxyz$ the rotation $\mathscr{R}(\varphi,\overrightarrow{Oz})$, which transforms $\overrightarrow{Oy}$ into $\overrightarrow{Ou}$, which will be the node line (intersection of the planes $x\overrightarrow{Oy}$ and XOY) and $\overrightarrow{Ox}$ into $\overrightarrow{Ox'}$; then the rotation $\mathscr{R}(\theta,\overrightarrow{Ou})$ which transforms $\overrightarrow{Oz}$ into $\overrightarrow{OZ}$ and $\overrightarrow{Ox'}$ into $\overrightarrow{Ox''}$; and finally the rotation $\mathscr{R}(\psi,\overrightarrow{OZ})$ which transforms $\overrightarrow{Ou}$ into $\overrightarrow{OY}$ and $\overrightarrow{Ox''}$ into $\overrightarrow{OX}$. To sum up (the rotations are performed in the order from right to left):

$$OXYZ=\mathscr{C}[Oxyx]$$

with

$$\mathscr{C}=\mathscr{R}(\psi,\overrightarrow{OZ})\mathscr{R}(\theta,\overrightarrow{Ou})\mathscr{R}(\varphi,\overrightarrow{Oz})$$

and

$$\overrightarrow{Ou}=\mathscr{R}(\varphi,\overrightarrow{Oz})\overrightarrow{Oy},\quad \overrightarrow{OZ}=\mathscr{R}(\theta,\overrightarrow{Ou})\overrightarrow{Oz}\,.$$

When the rotations are considered in the reverse order, the alternative expression is obtained:

$$\mathscr{C}=\mathscr{R}(\varphi,\overrightarrow{Oz})\mathscr{R}(\theta,\overrightarrow{Oy})\mathscr{R}(\psi,\overrightarrow{Oz})\,.$$

This expression may also be useful because it contains only rotations around the fixed axes of the initial coordinate system.

The minimizations were performed with the program *STEPIT* written by J. P. Chandler, available under Number Q.C.P.E. 66 from the Quantum Chemistry Program Exchange (Chemistry Department, Room 204, Indiana University, Bloomington, Indiana 47401, U.S.A.).

3. Results and discussion

The purpose of our study was twofold. First, it was necessary to check the validity of our formulae for the calculation of the intermolecular energy: this implied the computation of energy for crystals of which not only the structure but also the internal energy (sublimation energy) were known. We took methane, carbon dioxide, benzene and nitrobenzene. For the last, we could not find an experimental value of the sublimation energy, but a catalogue of molecular structure increments (Bondi, 1963) allows an evaluation. Actually nitrobenzene was treated mainly in connexion with our second purpose, namely to compare the relative configurations of molecules in binary complexes on the one hand and in crystals on the other: being highly polar, nitrobenzene was a useful complement to benzene, and it supplied a structure (parallel layers of almost coplanar molecules) much more similar to that of the adenine crystal than benzene does; thus some general features could be expected to appear from a comparison between nitrobenzene and adenine.

According to the remark in § 2-(*B*)-(*a*) above, we did not attempt to evaluate the third-order terms for the polar molecules (CO_2 and $C_6H_5NO_2$). This was done for methane, which is a favourable case (practically no net charge and spherically symmetric) where only the so-called 'triple dipole' term, analogous to the second-order dispersion (Axilrod, 1951; Kihara, 1958: Kestner & Sinanoglu, 1963), needs to be calculated. Benzene will be discussed below in §(*C*).

(*A*) *Crystal of methane*

The analysis of solid methane gives a face-centred cubic lattice, with $a=5{\cdot}89$ Å. There are four molecules in the central cell, with their C atoms at the points (0; 0; 0); (*a*/2; *a*/2; 0); (0; *a*/2; *a*/2); (*a*/2; 0; *a*/2). Since the exact orientations of the molecules are not well known (Kitaigorodskii, 1961 *a,b*; see however Kihara & Koba, 1959), we tried several orientations; we give the results for the most favourable. The fractional coordinates for the first molecule are: C(1) (0; 0; 0); H(1) (0; 0; 0·1834); H(2) (0; 0·1730; −0·0604); H(3) (0·1497; −0·0864; −0·0604); H(4) (−0·1497; −0·0864; −0·0604). The three other molecules are deduced from the first by symmetry with respect to the points (0; *a*/4; *a*/4); (*a*/4; 0; *a*/4); (*a*/4; *a*/4; 0). We took a net charge equal to 0·02 on each H atom and −0·08 on the C. These charges may be too small (a calculation according to Del Re's method gives values twice as large: 0·04 on H and −0·16 on C). Moreover, if we take $4·5\times10^{-34}$ esu cm^2 for the octopole moment of CH_4, according to Stogryn & Stogryn (1966), and C–H = 1·09 Å, it will be necessary to put a charge 0·376 on the H atoms (and −1·504 on C) in order to reproduce this octopole moment: these values are too high and simply show that the octopole moment must not be reproduced from the net charges only. Anyway, the electrostatic and polarization energies are completely negligible in the case of methane: we found an electrostatic energy $0·25\times10^{-4}$ kcal/mole and a polarization energy $-0·14\times10^{-2}$ kcal/mole (thus, even with a value multiplied by 10 for the net charges, *i.e.* electrostatic and polarization energies multiplied by 10^2, we would still obtain respectively only $0·25\times10^{-2}$ and −0·14 kcal/mole).

The three-body contribution (third-order term in the perturbation theory of intermolecular forces), repulsive in this case, was assumed equal to 7% of the dispersion energy (Kestner & Sinanoglu, 1963). The experimental value of the sublimation energy (−2·51 kcal/mole) was corrected by taking into account the zero-point energy evaluated by Kihara & Koba (1959) to be 0·48 kcal/mole, hence the value −2·99 for the minimum of the potential curve.

The different energies are collected below for the crystal of methane:

experimental	–2·99 kcal/mole
calculated to second order	–3·15 kcal/mole
calculated to third order	–2·87 kcal/mole .

The agreement between calculation and experiment is quite satisfactory for checking the program of calculation of energies.

We have also tried to use this program to find the best position for the methane molecule, which is not known exactly. For this trial, we first start from the initial position obtained by performing a rotation (+45° around *Oy*) on the molecule defined at the beginning of the present section. The total energy (up to the second order) obtained for this initial position is –2·95 kcal/mole, a value which is not very far from the energy obtained previously (–3·15 kcal/mole). When the minimum is reached, we get an energy of –3·177 kcal/mole, very close to the value –3·15 kcal/mole, although the position is clearly different: coordinates of the first molecule: C(1) (0·0001; −0·0001; 0); H(1) (0·0681; 0·1558; 0·0683); H(2) (−0·1802; −0·0063; 0·0316); H(3) (0·0311; −0·0058; −0·1801); H(4) (0·0815; −0·1422; 0·0815).

We also performed a minimization with the position defined at the beginning of this section as the initial position. We obtain a minimum energy of –3·20 kcal/mole (up to the second order), for a position still different from the previous ones: coordinates of the first molecule: C(1) (0; 0·0270; 0·0187); H(1) (0·0405; 0·0270; 0·1976); H(2) (−0·0134; 0·2; −0·0402); H(3) (0·1326; −0·0594; −0·0733); H(4) (−0·1594; −0·0594; −0·0071).

The energy minima obtained by the calculations are very close, and we can deduce that it is difficult to know the exact position of the molecule in the cell. This agrees with experiment (see *e.g.* Kitaigorodskii, 1961*b*): the molecules undergo almost free rotation already at very low temperatures, so that the experimental data give only the position of the centre of the molecule and no special orientation.

(*B*) *Crystal of carbon dioxide*

This crystal has a face-centred cubic lattice [*cf.* Kihara & Koba (1959) for indications about the detailed structure]; *a* = 5·54 Å (extrapolation at 0°K according to Kitaigorodskii, Mirskaya & Nauchitel (1970). We used the net charges 0·6652 on the C and −0·3326 on each O, which reproduce the experimental quadrupole moment $Q=4·1\times10^{-26}$ esu. cm^2 (Kitaigorodskii *et al.*, 1970; Stogryn & Stogryn, 1966). For the experimental sublimation energy, Giauque & Egan (1937) give –6·44 kcal/mole (evaluated for 0°K) (–6·03 measured at 195° K).

(1) *Experimental configuration*

We obtained for the total energy and its various components the values given in Table 1. As generally found, the atom–atom formula gives better results (relative error of −10%) than the bond–bond formula, essentially because the dispersion term is larger. We have not tried to evaluate the third-order terms.

Table 1. *The total energy and its components*

	Electrostatic	Polarization	Dispersion	Repulsion	Total
Atoms	−2·51	−0·21	−8·78	5·70	−5·80
Bonds	−2·51	−0·32	−8·04	5·70	−5·17

(2) *Minimization trials*

We shall now give the results (using atom–atom formulae) of several partial minimizations.

In all cases, only molecule (1) (whose C atom lies at the origin) is moved freely; the other molecules (2,3,4) are deduced from (1) by the symmetry operations of the crystal.

(I) The lattice lengths (a,b,c) vary, while (α,β,γ) and the molecule at the origin are kept fixed.

(II) The cell angles (α,β,γ) vary while (a,b,c) and molecule at the origin are kept fixed.

(III) With the cell parameters fixed, molecule (1) is displaced from its crystalline position (ternary axis of the cubic cell): it is placed along Oz and then left free to move in the cell.

(IV) (a, b, c), (α, β, γ), (φ, θ, η) kept fixed, (T_1, T_2, T_3) left free.

The results of these different trials are given in Table 2 with the different variable parameters and their values before and after minimization.

When we observe the results of the different calculations, the striking character is the great stability of the crystalline geometry: so, when the molecule is placed very far from the crystalline orientation the minimization procedure brings it to this observed orientation and it seems that this minimum is the only one because the variation of the different parameters of the cell is not very important and the same minimum energy is reached in the different cases studied.

Thus the crystal of carbon dioxide has a very stable geometry and the minimization procedure actually seems to give the experimental cell parameters and crystalline position whatever the values initially chosen.

It is interesting to note that our absolute minimum (−6·18 kcal/mole, obtained for $a=5{\cdot}66$ Å, slightly larger than the experimental value $a=5{\cdot}54$ Å) is significantly closer to the experimental value (−6·44 kcal/mole) than the value obtained directly for the experimental $a=5{\cdot}54$ Å, namely −5·99 kcal/mole: the relative error reduces from −7% to −4%.

(*C*) *Crystal of benzene*

The crystal structure was taken from Cox (1958). It is interesting to note the difference between the cell dimensions at two different temperatures. For the calculations, we took the cell parameters at −3°C: $a=7{\cdot}460$, $b=9{\cdot}666$, $c=7{\cdot}034$ Å in an orthorhombic crystal where $\alpha=\beta=\gamma=90°$.

As concerns the atomic net charges we took −0·1 for C and +0·1 for H. The Del Re method gives respectively −0·053 and +0·053, but the anisotropy of the C atoms (the Slater exponent of the p_π orbital is smaller than that of the p_σ orbitals, which expresses that the p_π orbitals are more diffuse than the p_σ ones in benzene) gives rise to supplementary atomic quadrupole moments on these atoms, and the sum of these moments as evaluated by Mantione (1969 *a,b*) is of the same order of magnitude as the quadrupole moment of the Del Re charges (namely 3×10^{-26} esu cm^2). Hence the total resulting moment (6×10^{-26} esu cm^2) may be reproduced by approximately doubled charges. The experimental values of the quadrupole moment of benzene are, unfortunately, very different according to the method used (Mantione, 1971, part 2, chap. III, §1, p. 69): their absolute values vary from $3{\cdot}6\times10^{-26}$ esu cm^2 (microwave line broadening: Hill & Smith, 1951; Smith, 1956) to 34·86 esu cm^2 (diamagnetic anisotropy: Daiby, 1963) with intermediate values of 12 to 16×10^{-26} esu cm^2 (analysis of virial coefficients: De Rocco & Spurling, 1967). Stogryn & Stogryn (1966) give only the smallest value.

The heat of sublimation (enthalpy) is about 10·3 kcal/mole in the temperature range −58 to −30°C (Hamilton Jones, 1960). If we accept that $\Delta(PV)=RT$ (=0·426 kcal/mole at −58°C and 0·482 kcal/mole at −30°C) we obtain the experimental sublimation energy $\Delta E=\Delta H-\Delta(PV)$ in the range 9·82 to 9·87 kcal/mole.

The calculation of the crystalline energy gives −12·1 kcal/mole at second order, and −11·15 kcal/mole when adding a third-order term evaluated as 7% of the dispersion energy (with the polarization and dispersion energies calculated from bond contributions instead of atom contributions, these values become respectively −9·57 and −8·75). These results are in satisfactory agreement with experiment.

For comparison, we also calculated binary interactions in various geometries. We have obtained by various geometric transformations four positions for which we have calculated the different interaction energies.

The first benzene molecule is placed as indicated in Fig. 1. The second molecule was obtained by rotating the first molecule in some definite manner (four types of rotations were tried) and then translating the rotated

Table 2. *Crystalline energies in carbon dioxide and variations of the different veriables used for the minimizations (carbon dioxide)*

	Energy (kcal/mole)	a	b	c	α	β	γ	φ	θ	ψ	T_1	T_2	T_3
I	−5·99	5·54	5·54	5·54	90	90	90	0	0	0	0	0	0
	−6·18	5·66	5·66	5·64									
II	−5·99	5·54	5·54	5·54	90	90	90	0	0	0	0	0	0
	−5·99				90	90	90						
III	−3·98	5·54	5·54	5·54	90	90	90	0	−54·73*	−45*	0	0	0
	−5·99							0	0	0			
IV	−5·99	5·54	5·54	5·54	90	90	90	0	0	0	0	0	0
	−6·00										0·008	0·008	0·008

* These values of θ and ψ correspond to the molecule collinear with Oz ($54{\cdot}73=\arccos 1/\sqrt{3}$ is the angle of the ternary axis with Oz; φ remains arbitrary since the molecule is linear).

molecule; all combinations of the following translations were used:

along *Ox* (Å): 0·0 0·5 1·0 1·5
along *Oy* (Å): 0·0 0·5 1·0 1·5
along *Oz* (Å): 4·8 5·0 5·2 5·4 .

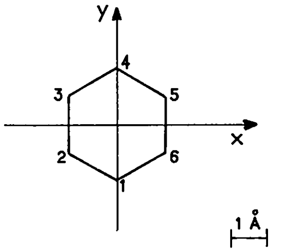
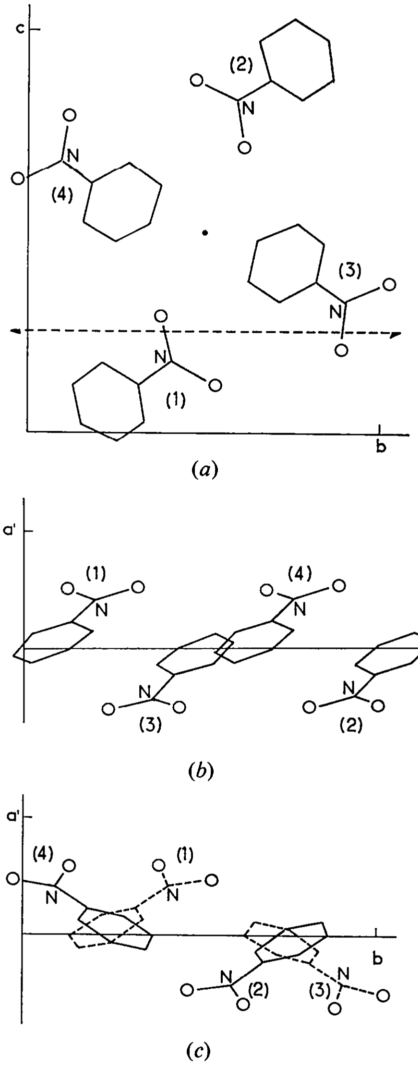


Fig. 1. Geometry and atom numbering of the benzene molecule.



(*a*)

(*b*)

(*c*)

Fig. 2. Geometry of the four molecules in the cell of the nitrobenzene crystal. (*a*) Orthogonal projection on the *bc* plane. (*b*) Orthogonal projection on the *ac* plane. (*c*) Orthogonal projection on the *ab* plane.

The four types of relative orientations that we considered were:

(I) no rotation at all; in this case the translations along *Oz* vary from 3·2 to 5·4 Å with an interval of 0·2 Å.

(II) rotation by 90° with respect to *Oy* [this makes the two bonds (2′,3′) and (5′,6′) of the second molecule parallel to *Oy* (1,4) of the first].

(III) rotation by 90° with respect to *Ox* [this makes (1′,4′) of the second molecule perpendicular to the plane *xOy* of the first, the plane of the second molecule being parallel to *Oy* (1,4)].

(IV) the same rotation as (III) followed by a rotation by 90° with respect to *Oz* [(1′,4′) is still perpendicular to *xOy*, but now the plane of the second molecule is parallel to *Ox*].

In Table 3, we give, for each of these orientations, the lowest energy value and the translation for which it was obtained.

Table 3. *Energies of the binary interactions and crystalline energy of benzene*

Angle of rotation and axis	Translation along *Ox*	along *Oy*	along *Oz*	Minimum value (kcal/mole)
I 0°	1·5	1·5	3·4	−2·45
II 90°/*Oy*	0	1	4·8	−2·47
III 90°/*Ox*	0	0	5	−2·95
IV (90°/*Ox*) followed by (90°/*Oz*)	0	0	5	−2·25
Crystal: interaction between molecules (1) and (4) (90°/*Oy*)	0	1·1	4·99	−2·31

These energy values are not very far from one another. The lowest one is not obtained when the two molecules are parallel (orientation I), but when one of the two molecules is perpendicular to the other with an H atom directed towards the plane of the first molecule (orientation III).

The crystalline geometry corresponds closely to another orientation (II): molecule (4) (Cox, 1958) has its plane perpendicular to that of molecule (1), with a bond parallel to it, and its centre has coordinates (0; 1·1; 4·99) in the coordinate system attached to molecule (1) (according to Fig. 1).

It is interesting to note that in the crystal, the molecules are in a relative position not very far from position (III) (absolute minimum). It seems possible that before crystallization a binary complex (III) is formed: when different molecules come around this group, their influence on the first complex makes the second molecule turn around its axis by 30°. This is not an important rotation and we may consider benzene as somewhat similar to adenine in the sense that the crystalline configurations are all different from that of the binary minimum but at least one of them is not very far from it.

Anyway, the minimum values obtained for the different binary complexes do not give a very sharp minimum and a real minimization would be necessary in this case in order to obtain the exact configuration of the minimum (but this information would not be very interesting owing to the shallowness of this minimum).

(*D*) *Crystal of nitrobenzene*

The crystal structure (Fig. 2) was taken from Trotter (1959); it corresponds to the temperature −30°C. We could not find an experimental value of the sublimation enthalpy (or energy); Hamilton Jones (1960) gives about 20 kcal/mole for ΔH of the three isomers of dinitrobenzene (*ortho*: 20·7; *meta*: 19·4; *para*: 21·2). Bondi (1963) gives a catalogue of molecular structure increments; with $\Delta H(C_6H_5) \simeq 9$ and $\Delta H(.NO_2) = 6{\cdot}8$, we get $\Delta H \simeq 15{\cdot}8$ kcal/mole hence $\Delta E \simeq 15{\cdot}3$ kcal/mole.

The atomic net charges [Del Re method for σ charges, Hückel method for π charges, see section 2(*A*) (*a*) above] are [we label C(1) the atom bonded to N]: C(1) (0·172); C(2) and C(6) (−0·006); C(3) and C(5) (−0·053); C(4) (−0·023); N (−0·006); O (−0·146) each; H(2) and H(6) (+0·054); H(3), H(5) and H(4) (+0·053). With the atomic coordinates of the crystal (see below), these charges give a dipole moment $\mu = 0{\cdot}796$ e Å = 3·82 Debye, in good agreement with the experimental value $\mu = 3{\cdot}93$ Debye (McClellan, 1963).

(*a*) The crystalline parameters for nitrobenzene at −30 °C (Trotter, 1959) are $a = 3{\cdot}86$, $b = 11{\cdot}65$, $c = 13{\cdot}24$ Å, $\beta = 95°35$.

The calculation of the total energy of the crystal gives the following contributions:

electrostatic	−1·95	kcal/mole
polarization	−0·42	
dispersion	−20·40	
repulsion	+6·66	
total	−16·11	

(total + third order (−7% of dispersion): −14·69).

(*b*) It is interesting to note that the molecules are almost parallel in the crystal: so we have made calculations of binary complexes where the molecules are exactly parallel. When one molecule is translated over the other, the minimum value of the energy is obtained when the two molecules are in the relative position indicated in Fig. 3 and with a vertical distance of about 3·4 Å. This position is the best with respect to the electrostatic energy, because the dipoles are antiparallel. The rings are not superimposed because of the electrostatic energy.

The different contributions are:

electrostatic	−1·47
polarization	−0·35
dispersion	−7·86
repulsion	+2·92
total	−6·76 kcal/mole.

(*c*) In order to compare the configurations in the crystal with the binary complex just considered, we give in Table 4 the interactions of a molecule [(2) of cell 0,0,0] with all neighbour molecules in the same plane (cells 0,0,0; 0,1,0; 0,1,1; 0,0,1) and in the planes above (cells 1,0,0; 1,1,0; 1,1,1; 1,0,1) and below (cells −1,0,0; −1,1,0; −1,1,1; −1,0,1). We give the electrostatic term and the total energy with polarization energy excluded (because it is not pair-additive). We see that all these interactions reach at most about one half of the energy corresponding to the binary minimum described in (*b*); it must be emphasized that the superimposed molecules [(2) in cells 0,0,0 and 1,0,0 or −1,0,0] being deduced one from the other by a translation, have their dipoles parallel (and a repulsive electrostatic energy); thus, even for them, the configuration is very different from that of the binary minimum (*b*). We may conclude that, in the case of nitrobenzene, the requirement of having a minimum energy for the crystal results in rather close pair energies, *all of them* markedly smaller than the energy of the binary minimum energy. This situation is similar to that encountered for the cytosine crystal, as mentioned by Caillet & Claverie (1974), and contrasts with that for adenine (Caillet & Claverie, 1974) and for benzene, for which *one* of the pair configurations found in the crystal is not very different from the configuration of a binary minimum.

(*d*) Finally, we have performed minimization calculations with a modified crystal where the first molecule lies exactly in the plane *yOz*. In all these minimization calculations, molecules (2,3,4) were always deduced from the first by the symmetry transformations of the crystal.

In Table 5 we give for each case two lines of results: on the first the value of the energy and the different parameters before minimization, and on the second the corresponding values after the minimization (when a parameter is kept constant no value is given on the second line).

The crystal position is taken as reference position, so the Euler angles are given with respect to this posi-

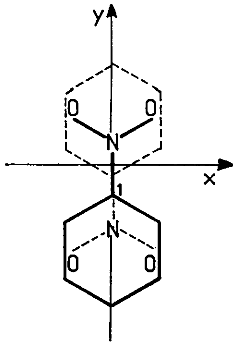


Fig. 3. Geometry of the minimum energy configuration for the binary complex of nitrobenzene.

tion; the molecule placed exactly in the yOz plane corresponds to

$$\varphi=283\cdot51^\circ \quad \theta=21\cdot40^\circ \quad \psi=98\cdot07^\circ.$$

We performed the following minimizations:

(I) Variation of the cell parameter a (the three angles are equal to 90°)

(II) Variation of a and β.

(III) Variation of a, b and c.

(IV) Variation of a and φ, θ, ψ (the Euler angles of the molecule).

(V) A complete minimization by using as initial values of the parameters those obtained from the previous minimization (IV).

In minimization IV (a, ψ, θ, φ variable) the energy obtained after minimization is relatively low and corresponds to molecules not parallel as in the preceding minimizations. The electrostatic energy is better in this case and it is probably the reason why the molecules are twisted out of the yOz plane in the real crystal.

When all the variables of the cell and of the molecule are left free (case V) the minimization procedure results in a minimum energy slightly lower than the crystalline energy already calculated, although the configuration is clearly different (−16·48 up to the second order, and −14·7 with the third-order contribution evaluated as −7% of the dispersion energy).

(VI) This unexpected result makes it necessary to perform a minimization with the experimental crystalline configuration as a starting point: this actually gives a minimum for a very slight displacement, and the value of this minimum (−16·65 kcal/mole, and −14·97 with the third-order correction) is actually lower than the previous one.

(VII) Finally, starting from the experimental values of the cell parameters and molecule (1) in the plane yOz

Table 4. *Energies of interaction of molecule* (2) *of the central cell* (0,0,0) *of a crystal of nitrobenzene* (*Fig.* 2) *with different molecules taken in the cells around the central cell*

In each cell, molecule (1) corresponds to the coordinates given by Trotter (1959) in his Table 2. Molecule (2) is deduced from (1) by an inversion with respect to the point $(0,\frac{1}{2},\frac{1}{2})$. Molecule (3) is deduced from (1) by a screw transformation (rotation 180° around the binary axis parallel to **b** and passing at point $(0,0,\frac{1}{4})$, followed by a translation $\frac{1}{2}$ along this axis. Molecule (4) is deduced from (3) by the same inversion as above [center $(0,\frac{1}{2},\frac{1}{2})$]. All energies are expressed in kcal/mole.

Molecule (2) of the cell (0,0,0) with							
Cell		(0,0,0)		(0,1,0)	(0,1,1)	(0,0,1)	
Molecule		(4)	(3)	(4)	(1)	(3)	(1)
Electrostatic energy		−0·70	−0·07	−0·7	−0·46	−0·07	−1·12
Total energy without polarization		−1·76	−1·36	−1·76	−1·13	−1·36	−3·21
Cell	(1,0,0)			(1,1,0)	(1,1,1)	(1,0,1)	
Molecule	(2)	(4)	(3)	(4)	(1)	(3)	(1)
Electrostatic energy	+1·14	−0·11	+0·008	−0·11	+0·45	−0·70	−0·33
Total energy without polarization	−3·53	−0·225	−0·167	−0·225	−0·274	−1·67	−0·67
Cell	(−1,0,0)			(−1,1,0)	(−1,1,1)	(−1,0,1)	
Molecule	(2)	(4)	(3)	(4)	(1)	(3)	(1)
Electrostatic energy	+1·14	−0·78	−0·70	−0·78	−0·05	+0·008	−1·29
Total energy without polarization	−3·53	−1·98	−1·67	−1·98	−0·11	−0·167	−2·56

Sum of the different total energies without polarization	−29·33
$\frac{1}{2}$ sum corresponding to the energy for one molecule	−14·66

Total energy for the crystal with the different contributions:

Electrostatic	Polarization	Dispersion	Repulsion	Total
−1·95	−0·42	−20·40	+6·66	−16·11

Table 5. *Energies obtained for the different minimizations performed with nitrobenzene*

	Energy (kcal/mole)	a (Å)	b (Å)	c (Å)	α	β	γ	φ	θ	ψ	T_1	T_2	T_3
I	+15·36	3·86	11·65	13·24	90	90	90	283·51	21·40	98·07	0	0	0
	+13·22	3·35											
II	+15·36	3·86	11·65	13·24	90	90	90	283·51	21·40	98·07	0	0	0
	+10·97	3·45				69·98							
III	+15·36	3·86	11·65	13·24	90	90	90	283·51	21·40	98·07	0	0	0
	−10·52	3·40	12·38	14·20									
IV	+15·36	3·86	11·65	13·24	90	90	90	283·51	21·40	98·07	0	0	0
	−14·11	3·73						333·25	8·13	73·85			
V	−14·11	3·73	11·65	13·24	90	90	90	333·25	8·13	73·85	0	0	0
	−16·48	3·80	11·42	13·64	90	112·65	90	333·79	8·13	73·85	0·1885	0	0
VI	−16·10	3·86	11·65	13·24	90	95·58	90	0	0	0	0	0	0
	−16·65	3·80	11·42	12·85	90	93·41	90	0	0	0	0·0443	0	0·1287
VII	+15·25	3·86	11·65	13·24	90	95·58	90	283·51	21·40	98·07	0	0	0
	−15·21					106			0·47		0·24	0·14	0·01

a minimization was performed with respect to β and the parameters (φ, θ, ψ; T_1, T_2, T_3 of molecule (1). The resulting orientation of molecule (1) is still quite different from those found previously (V and VI); true enough, the parameters a, b, c, α, γ were not allowed to vary, but the previous results [compare the partial minimization (IV) with the complete one (V)] make it unlikely that important changes of the orientation of molecule (1) would occur by leaving the parameters a, b, c, α, γ free to vary. Thus, minimization VII strongly suggests the existence of a third local minimum.

4. Conclusion

The first purpose of this work was to check whether the simple formulae developed in our laboratory for the calculation of the interaction energy between two molecules could be applied with sufficient reliability to the study of crystals. The results in §3 which concern four rather different molecules (CH_4, CO_2, C_6H_6, $C_6H_5NO_2$) seem to indicate that this is actually the case:

(1) The energies calculated for the experimental crystalline configuration are in satisfactory agreement with experimental values of the sublimation energy.

(2) When a minimization has been performed by starting from the experimental position (this we did for CO_2 and $C_6H_5NO_2$), a minimum very close to this position has been obtained. This result indicates that the method may be useful not only for getting energy values but also for analysing the geometry of the crystal (orientations of the molecules with respect to each other).

A second purpose was a comparison between the relative orientation of two molecules in the crystal and in the binary complex. A thorough analysis has been given in a previous paper for adenine (Caillet & Claverie, 1974). The results of the present work confirm the previous ones: in the case of stacking interactions, which have a weakly specific geometry, there is no strict relationship between the relative configurations of two molecules in the crystal and in the binary complex. In some cases (adenine) there exists in the crystal one binary configuration not too different from that of the binary complex; but in other cases (cytosine, nitrobenzene) there is no such configuration to be found in the crystal. As concerns benzene, its binary minimum configuration is not well defined (very shallow minimum) so that the problem of comparing binary configurations for two molecules and for the crystal practically loses its meaning.

Finally, the present study supports the view that, at least for not too simple molecules, several local minima may exist on the energy hypersurface besides the one corresponding to the experimental configuration (we found a single minimum for CO_2, but two and probably three for $C_6H_5NO_2$). A similar result has been reported by Ahmed & Kitaigorodskii (1972) who found two minima in their study of the crystal structure of 3,6-diphenyl-*s*-tetrazine.

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Univalent (Monodentate) Substitution on Convex Polyhedra

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Pólya's enumeration theorem has been used to evaluate, by computer, the numbers N of distinct configurations (= positional isomers) produced by univalent (monodentate) substitution at the vertices of convex polyhedra of crystallographic or stereochemical interest. The values of N are tabulated for a large variety of polyhedra of up to $V = 120$ vertices and for up to V kinds of structureless substituents. The N have been evaluated not only for the maximum point-group symmetry of each polyhedron but also, for $V \leq 24$, for *all* the subgroup symmetries of the maximum point group. For $V > 24$ only polyhedra of cubic and icosahedral symmetries are included. An example shows how the tables of N can be used to enumerate pairs of enantiomorphs. The effect of symmetry on N for large values of V is examined.

Symbols and abbreviations

a	axial digyre (see text)
$\mathscr{A}$	Archimedean polyhedron (isogonal)
$\mathscr{A}^*$	Catalan polyhedron (dual to $\mathscr{A}$, isohedral)
$\mathscr{C}_1$	number of all non-isomorphic convex polyhedra of maximum p.g. symmetry C_1 and a given V
d	diagonal digyre (see text)
$\mathscr{D}$	dual polyhedron
E	number of edges
F	number of faces
i	centre of symmetry; inversion
$\mathscr{K}a$	Kasper polyhedron
m	mirror plane
ma	axial mirror plane (also in combinations maa and mad; see text)
md	diagonal mirror plane (also in mdd; see text)
mh	horizontal mirror plane (also in combinations mha and mhd; see text)
N	number of distinct configurations
$\mathscr{N}$	number of all non-isomorphic convex polyhedra of a given V
$p(\mathbf{G})$	order of the point group $\mathbf{G}$
p.g.	point group
$\mathscr{P}\ell$	Platonic polyhedron
v', v''	nonequivalent (vertical) mirror planes
V	number of vertices
$\mathscr{V}$	vertex-figure derivative
Z	cycle index
$\mathscr{Z}$	number of Z-isomorphic classes
Δ	deltahedron (Freudenthal & van der Waerden, 1947)
Π	partition
8–2	running number of polyhedron of $V = 8$ and maximum p. g. symmetry in Table 5
8–2 (*20*)	running number of polyhedron of $V = 8$ obtained from, or related to, **8–2** by lowering the p.g. symmetry from the maximum possible for **8–2**, *32*, to *20*
45, *109*	running number of a p.g. in Table 3

A problem of some importance in various branches of science is the determination of the number N of distinct‡ positional isomers that can be obtained by

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‡ Distinct positional isomers are not congruent with respect to rotation.