Table 2. *Theoretical expressions for $_BR_1(I_N)$ and $_BR(I_N)$ for the related and unrelated cases for any model of a complex crystal belonging to triclinic, monoclinic and orthorhombic systems: all atoms in general positions*

Space-group category number	$_BR_1(I_n)$		$_BR(I_N)$	
	Related	Unrelated	Related	Unrelated
1	$\dfrac{2t_1+t_6}{2-C_n}$	$\dfrac{2-t_5}{2-C_n}$	$\dfrac{2t_1+t_7}{2-C_n}$	$\dfrac{2t_2-t_8}{2-C_n}$
2	$\dfrac{8t_1+3t_6}{6-3C_n}$	$\dfrac{8-3t_5}{6-3C_n}$	$\dfrac{2t_3+3t_7}{6-3C_n}$	$\dfrac{2t_4-3t_8}{6-3C_n}$
3	$\dfrac{4t_1+t_6}{4-C_n}$	$\dfrac{4-t_5}{4-C_n}$	$\dfrac{4t_1+t_7}{4-C_n}$	$\dfrac{4t_2-t_8}{4-C_n}$
4	$\dfrac{16t_1+3t_6}{12-3C_n}$	$\dfrac{16-3t_5}{12-3C_n}$	$\dfrac{4t_3+3t_7}{12-3C_n}$	$\dfrac{4t_4-3t_8}{12-3C_n}$
5	$\dfrac{8t_1+t_6}{8-C_n}$	$\dfrac{8-t_5}{8-C_n}$	$\dfrac{8t_1+t_7}{8-C_n}$	$\dfrac{8t_2-t_8}{8-C_n}$
6	$\dfrac{8t_1-t_6}{8+C_n}$	$\dfrac{8+t_5}{8+C_n}$	$\dfrac{8t_1-t_7}{8+C_n}$	$\dfrac{8t_2+t_8}{8+C_n}$
7	$\dfrac{32t_1-3t_6}{24+3C_n}$	$\dfrac{32+3t_5}{24+3C_n}$	$\dfrac{8t_3-3t_7}{24+3C_n}$	$\dfrac{8t_4+3t_8}{24+3C_n}$

$t_1 = 1 - \sigma_{1P}^2$ $t_5 = C_p + C_n$
$t_2 = 1 - \sigma_{1P}^2 + \sigma_{1P}^4$ $t_6 = (2\sigma_{1P}^2 - 1)C_p - C_n$
$t_3 = 3 - 2\sigma_{1P}^2 - \sigma_{1P}^4$ $t_7 = \sigma_{1P}^4 C_p - C_n$
$t_4 = 3 - 2\sigma_{1P}^2 + 3\sigma_{1P}^4$ $t_8 = \sigma_{1P}^4 C_p + C_n$

by studying Table 1 of FH (1963b) keeping in view (i) the forms of the geometrical structure factors for these special positions and (ii) the form of the expressions in (45). It is useful to note here that in crystals containing atoms in fixed positions, it is in general necessary to classify the reflexions into different categories and evaluate the theoretical and experimental values of the R indices for the various categories separately. The method of classifying the reflexions into categories can be understood from the illustrative examples given in FH (1963b) in connexion with the moments test for space-group determination.

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Derivation of Carbon–Nitrogen, Hydrogen–Nitrogen and Nitrogen–Nitrogen Non-Bonded Potential Parameters in Molecular Crystals*

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Potential function parameters for CN, HN, and NN non-bonded atom–atom pair interactions were derived from the heats of sublimation of cyanogen and dicyanoacetylene and from the crystal structures of cyanogen, dicyanoacetylene, tetracyanoethylene, s-tetrazine, pteridine and pyridazino[4,5-d]pyridazine. Procedure and CC, CH, and HH parameters used were those of Williams [*J. Chem. Phys.* (1967). **47**, 4680–4684]. The exponents of CN, HN, and NN repulsion terms were taken equal to those of CC, CH, and CC repulsion terms, respectively. The lattice summation was cut off at 6, 5·5 and 6 Å for the CN, HN, and NN terms, respectively. The coefficients of the attractive and repulsive terms were fitted by weighted least-squares calculations to 45 observational equations. It proved to be necessary to estimate externally the parameters of the HN attractive term. The derived parameters show rough agreement with the values found by other investigators. The experimental values of the heats of sublimation of cyanogen and dicyanoacetylene are reproduced within 4% with the calculated parameters. The parameters predict reasonable values for the heats of sublimation of tetracyanoethylene, s-tetrazine, pteridine and pyridazino[4,5-d]pyridazine. A difference of about 6 kcal mole^{-1} between the heats of sublimation of the latter two isomers was calculated.

Introduction

In order to calculate the lattice energy of molecular crystals the atom–atom approximation has proved to

be a valuable tool (Williams, 1966, 1967, 1974; Kitaigorodskii, 1973). In all these calculations lattice energy is treated, completely or for the greater part, as a limited summation of interatomic potentials between the atoms of a molecule chosen as central and the atoms of a limited number of neighbouring molecules. Pair-

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* This work forms part of a thesis by Govers (1974).

wise additivity and isotropy are assumed. The potential functions describing these energies are mostly of the Buckingham (B) or Lennard–Jones (LJ) type and they contain two or more parameters. These must be known before the potential functions can be used for calculation. The purpose of this work was the derivation of a set of CN, HN, and NN non-bonded atom–atom pair potential function parameters, which could be used in combination with some set of CC, CH, and HH parameters as derived by other investigators. The combined set of parameters will be used for the calculation of lattice energies of unitary and binary molecular crystals in which N is involved as cyano or azine groups.

Parameters of non-bonded atomic interactions, in which the N atom in combination with C and H atoms is involved, have been derived and used in the past. Values for these parameters are given in Table 1. De Santis, Giglio, Liquori & Ripamonti (1963, 1965) have used NN parameters which were ultimately derived from noble-gas atom interactions in the vapour phase. Simple analogy argument was used by them. From these parameters and those of HH and CC interaction they derived the mixed interactions CN and HN by special combination rules. Scott & Scheraga (1966) have derived attractive and repulsive parameters of the LJ type interactions CN, HN and NN from van der Waals radii, atomic polarizabilities, and an effective number of valence-shell electrons in a rather general way. Di Nola & Giglio (1970) have tested some NN parameters of rather different origin for structure prediction of α-N_2 crystals. The most successful of these parameters, combined with the CC potentials of Bartell (1960) in order to form the parameters of CN interaction, also proved to be the most successful to predict the structure of orthorhombic cyanogen. These sets of CN and NN parameters are included in Table 1. Mirskaya & Nauchitel (1972) have derived NN parameters from the lattice energy and crystal structure of N_2O at 0 K. OO parameters were taken from Kitaigorodskii, Mirskaya & Nauchitel (1970) and NO parameters were again found with the help of combination rules.

Jacobi & Schnepp (1973) have derived NN parameters from the experimental Raman spectrum of α-N_2.

The above derivations of parameters are either less systematic or based on limited or non-crystalline experimental information. Often no mention is made of the summation limits. In some cases the electrostatic energy and hydrogen-bonding energy are also calculated in the derivation. The parameters were mainly used for calculation of intra- or intermolecular structure, whereas we wanted to obtain parameters in order to calculate lattice energies and closely related properties of molecular crystals with mainly van der Waals forces between the molecules. Moreover, we wanted a consistent set of non-bonded potential parameters involving C, H and N atoms. As the relevant theories for binary molecular crystals are still less developed than those for unitary systems a simple theoretical model had to be used when deriving the parameters. The above considerations led us to the procedure used by Williams (1966, 1967) in his derivation of CC, CH and HH parameters. Our calculated CN, HN and NN parameters can be regarded as an extension of his set.

Method

The general form of the atomic interaction E_{kij} between atom i of a central molecule and atom j of a surrounding molecule k is considered to be (Liquori, Giglio & Mazzarella, 1968)

$$E_{kij} = -A_{tij}r_{kij}^{-6} + B_{tij}\exp{(-C_{tij}r_{kij})}r_{kij}^{-D_{tij}}. \quad (1)$$

In this expression the first term on the right-hand side represents the atomic attraction and the second term the atomic repulsion. The subscript tij represents the type of atoms that are involved. A_{tij}, B_{tij}, C_{tij} and D_{tij} are parameters. With $C_{tij}=0$ an LJ curve is formed, $D_{tij}=0$ results in a B potential. Another parameter sl_{tij} represents the summation limit of the interaction.

The distance r_{kij} is calculated from

$$r_{kij} = \mathbf{Ds}_k\mathbf{D}^{-1}(\tilde{\mathbf{R}}\mathbf{K}_{jo} + \mathbf{T}) + \mathbf{Dt}_k - (\tilde{\mathbf{R}}\mathbf{K}_{io} + \mathbf{T}). \quad (2)$$

In this expression $\mathbf{D}$ denotes the matrix which transforms atomic coordinates in unit-cell space to an orthogonal axial system fixed with respect to the unit cell. The elements of $\mathbf{D}$ are a function of the cell parameters $a,b,c,\alpha,\beta,\gamma$ (Williams, 1972). $\mathbf{R}$ denotes the symmetrical matrix which transforms coordinates from the latter orthogonal system to the system of the principal moments of inertia of the molecule, i.e. into the atomic vectors $\mathbf{K}_{io}$. This transformation further needs the vector $\mathbf{T}$ of the centre of gravity of the molecule in the above-mentioned orthogonal system. The elements of $\mathbf{R}$ are written as a function of the Eulerian angles φ,θ,ψ, which define the orientation of the molecule with respect to the unit-cell fixed orthogonal system (Wilson, Decius & Cross, 1955). The matrix $\mathbf{s}_k$ and the vector $\mathbf{t}_k$ form the symmetry operation which is needed to generate the coordinates of the atoms of the surrounding molecules from the asymmetric unit. The

Table 1. *Parameters of interatomic potentials involving nitrogen*

Units are kcal mole^{-1} and Å. No summation limits were given in the references cited. tij gives the kind of atoms which are involved. A_{tij}, B_{tij}, C_{tij} and D_{tij} are parameters (cf. under *Method*).

tij	A_{tij}	B_{tij}	C_{tij}	D_{tij}	Reference
CN	202·2	178500	2·304	6	De Santis *et al.* (1965)
CN	366	216000	0	12	Scott & Scheraga (1966)
CN	340	340000	0	12	Di Nola & Giglio (1970)
HN	497·6	19820	3·839	0	De Santis *et al.* (1965)
HN	125	27000	0	12	Scott & Scheraga (1966)
NN	125·1	105700	4·608	0	De Santis *et al.* (1965)
NN	0	7200	0	9·99	De Santis *et al.* (1965)
NN	363	161000	0	12	Scott & Scheraga (1966)
NN	354	387000	0	12	Di Nola & Giglio (1970)
NN	259	42000	3·78	0	Mirskaya *et al.* (1972)
NN	687·7	1073637	0	12	Jacobi & Schnepp (1973)

translational part t_k includes cell translations. R, φ, θ, ψ, K_{io} and T can be calculated from the atomic coordinates in unit-cell space and the atomic masses. D can be calculated from the cell parameters and s_k, t_k are given by the space group and by the summation limits sl_{tij}, which define the surrounding molecules to be included.

The heat of sublimation, ΔH^{subl}, is calculated from

$$\Delta H^{subl} = -\tfrac{1}{2} \times 1\cdot 25 N \sum_k^z \sum_i^n \sum_j^n E_{kij}(r_{kij}) . \tag{3}$$

In this expression N is the number of molecules in the lattice, z the number of molecules surrounding a central one and lying within the summation limits, and n the number of atoms per molecule. The factor $1\cdot 25$ is introduced because of the existence of summation limits of about 6 Å, which yield only 80% of the total lattice energy (Williams, 1966; Govers, 1974). It should consequently be used in the derivation as well as the application of the potential parameters. The derivatives of ΔH^{subl} to the structural parameters p (cell parameters, Eulerian angles, and coordinates of the centre of gravity) are equated to zero:

$$\delta \Delta H^{subl}/\delta p = 0 . \tag{4}$$

From (1), (3), (4) and with $D_{tij}, C_{tij}, sl_{tij}$ fixed, a set of linear equations is composed:

$$-A_1 \sum {}_{1s}U_a + B_1 \sum {}_{1s}U_r \ldots - A_q \sum {}_{qs}U_a$$
$$+ B_q \sum {}_{qs}U_r = \Delta H_s^{subl} \tag{5}$$
$$-A_1 \sum {}_{1s}\Delta_p U_a + B_1 \sum {}_{1s}\Delta_p U_r \ldots - A_q \sum {}_{1s}\Delta_p U_a$$
$$+ B_q \sum {}_{qs}\Delta_p U_r = 0 . \tag{6}$$

$A_1, B_1 \ldots A_q, B_q$ are the different parameters which have to be derived. $\sum_{1s}U_a$ is a summation of contributions of the type r_{kij}^{-6}, of interatomic attractions denoted by the index a. This summation only takes place over interactions with $tij = 1$. The index s denotes that these equations have been constructed for compound s of which the heat of sublimation and the crystal structure have been determined experimentally. The factors $\sum_{1s}\Delta_p U_a$ represent the same kind of summations, but now over contributions of the type $\delta r_{kij}^{-6}/\delta p$ in which p represents one of the structural parameters of compound s, whereas the other structural parameters are held constant at the experimental values on differentiation. In the repulsion contributions $\sum_{1s}U_r$ and $\sum_{1s}\Delta_p U_r$ an analogous summation takes place over $\exp(-r_{kij}C_1)r_{kij}^{-p_1}$ and $\delta[\exp(-r_{kij}C_1)r_{kij}^{-p_1}/\delta p]$, respectively. Analogous contributions are constructed for potentials of types other than 1. The equations of type (5) are based on (3), those of type (6) on (4). In these observational equations (obs. eqns.) the contributions of the CC, CH and HH interactions are already known – we used the parameters of Williams (1967) – and they are shifted to the right-hand side of (5) and (6). Furthermore, each of the obs. eqns. must be adequately weighted. After this has been done a

simple least-squares procedure is used to solve the over-determined linear equation system. The calculated standard deviations in the calculated parameters are regarded as a criterion for the success of the derivation in combination with the deviation of the calculated heats of sublimation from the experimental ones.

Experimental data

As follows from the above we need crystalline structural parameters and heats of sublimation, both experimentally determined, in order to derive atomic interaction parameters. When looking for this information not every compound containing C,H,N; C,N; or N is appropriate. First there must be a sufficient amount of N in the compound. If this is not the case the contribution of the N interactions to the heat of sublimation may be of the same order of magnitude as the experimental error in e.g. the heat of sublimation, and very inaccurate values may be found. We selected crystals containing more than 25% N atoms. Secondly, as a consequence of the theoretical assumptions of the method, hydrogen bonding, electrostatic mono- and multi-poles in the molecule, and intermolecular covalent bonds should be absent as far as possible. Compounds which are capable of forming hydrogen bonds between C and N atoms were chosen only if the distances between these atoms were larger than 3 Å. With respect to the electrostatic energy and intermolecular covalent bonding no explicit criterion was applied. Thirdly, the structure determination must be accurate and complete enough to minimize inaccuracy in the calculated heat of sublimation (Govers, 1974). C and N atomic coordinates and cell dimensions determined with standard deviations of less than about 0·03 Å and an R of less than about 10% were tolerated. Furthermore, for our purposes compounds containing cyano and azine groups were sought. In Table 2 the selected compounds, the above-mentioned selection criteria, the temperature, the space group, the number of molecules per unit-cell (Z), the number of cell parameters, the number of Eulerian angles, the number of coordinates of the centre of gravity (T_1, T_2, T_3), and the authors of the structure determinations are listed. The shortest distances in the crystals not containing H are within parentheses because hydrogen bonding is impossible in these cases. However, intermolecular donor–acceptor bonding is possible (Britton, 1974). All molecules are centrosymmetric except for pteridine. Although cyanogen and dicyanoacetylene are nearly linear – and consequently two orientational parameters would probably be sufficient to define the molecular orientation in the cell – three Eulerian angles have been used for practical reasons. The inaccuracies in the structures of cyanogen, dicyanoacetylene and pteridine may influence the derived parameters rather seriously. C–H bond lengths were put equal to 1·027 Å (Williams, 1966). Furthermore, we used the heat of sublimation of cyanogen (7·75 kcal mole^{-1} at 224 K) found by

Perry & Bardwell (1925) and the heat of sublimation of dicyanoacetylene (10·58 at 0 °C) found by Saggiomo (1957). From Table 2 it can be seen that we can use 45 obs. eqns. at a maximum.

Derivation of the parameters

Before the equational system (5), (6) was solved, Eulerian angles, coordinates of the centre of gravity, and atomic coordinates in the molecule-fixed axial system of the principal axes of inertia of the molecule were calculated. Neighbouring molecules were pre-selected in the following way. Firstly the distance of the centre of the surrounding molecule to the centre of the central molecule was calculated. If this distance was greater than the sum total of the greatest dimension of the molecule and the highest summation limit involved, then the surrounding molecule was said to have a zero interaction with the central one. Thereafter an exact calculation was performed of the contributing surrounding molecules and of the heats of sublimation.

In the parameter derivation, potentials of the B and LJ type were tried. Concerning the B-type potentials the C_{tij} parameters of the interactions containing N were taken equal to those of the interactions containing C by analogy. So $C_{CN} = C_{NN} = 3\cdot60$ Å^{-1} and $C_{HN} = 3\cdot67$ Å^{-1}, according to the C_{CC} and C_{CH} values of Williams (1966, 1967). Throughout the calculations the summation limits $sl_{CN} = sl_{NN} = 6$ Å and $sl_{HN} = 5\cdot5$ Å were used in combination with an 80% yield of heat of sublimation.

The calculations are collected in Tables 3 and 4. The parameter A_{HN} had to be regarded as known in order to obtain an acceptable value for B_{HN}. Several values for A_{HN} were tried. In calculation (a) the value $A_{HN} = 125$ of Scott & Scheraga (1966) was tried. Because the heats of sublimation calculated by means of the resulting parameters seemed to be correct in comparison with the experimental values of cyanogen and dicyano-

acetylene and seemed to be of the right order of magnitude in comparison with those of s-triazine (10·3) as found by Mason & Rae (1968), of benzene (10·7) as found by Milazzo (1956) and of naphthalene (17·3 kcal mole^{-1}) as found by Bradley & Cleasby (1953), in the calculations (b), (c) and (d) only slightly different values for A_{HN} were tried. In (b) and (d) the value $A_{HN} = 143$ was tried. This value was obtained by application of the geometric-mean combining rule to the values $A_{HH} = 27\cdot3$ of Williams (1967) and $A_{NN} = 762$ of calculation (a) of Table 3. Finally in calculation (c) a value $A_{HN} = 98$ was used. This value resulted from $A_{HH} = 27\cdot3$ of Williams (1967) and $A_{NN} = 354$ of Di Nola & Giglio (1970) by application of the geometric-mean combining rule. The weights of the obs. eqns. of type (5) of cyanogen and dicyanoacetylene were taken equal to 129 and 94·6 respectively (= 1000/ΔH^{subl}). All other weights were put equal to 1. This was done in accordance with the procedure of Williams (1966). The potential curves involved in calculations (b) and (d) and of the sets (e) and (f) are drawn in Fig. 1.

In Table 3 under (e) a set of parameters is given which equals the C, H parameters of Williams (1967). In this set the N atom is taken identical to the C atom. Set (f) of Table 3 is a miscellaneous set of Scott &

Table 3. *Derivation of* CN, HN *and* NN *parameters*

Units are kcal mole^{-1} and Å. A_{HN} has been varied externally and has not been derived. $\bar{\sigma}$% is the mean percentage standard deviation per derived parameter. The parameters of (e) and (f) are those of other investigators.

Nr	B/LJ	A_{HN}	A_{CN}	B_{CN}	B_{HN}	A_{NN}	B_{NN}	$\bar{\sigma}$%
(a)	B	125	374	11340	4401	762	105600	7·9
(b)	B	143	375	11480	4833	760	105400	7·9
(c)	LJ	98	372	103300	13980	733	1154000	9·0
(d)	LJ	143	376	109500	18230	717	1126000	8·9
(e)	B	125	568	83630	8766	568	83630	–
(f)	LJ	125	340	340000	27000	354	387000	–

Table 2. *Selected* C, (H) N *compounds for parameter derivation*

	Cyanogen C_2N_2	Dicyano-acetylene C_4N_2	Tetracyano-ethylene C_6N_4	s-Tetrazine $C_2H_2N_4$	Pteridine $C_6H_4N_4$	Pyridazino-[4,5-d]pyridazine $C_6H_4N_4$
% N atoms	50	33	40	50	29	29
Distance (Å)	(3·54)	(3·30)	(3·09)	3·27	3·33	3·349
St.dev. (Å)	0·03	0·01?	0·01	0·01	0·02–0·05	0·002
R (%)	8·65	13	8·3–9·12	6·1–7·7		6·2
Temperature	−95 °C	5 °C	Room	−20 °C	Room	Room
Space group	Pcab	P2₁/a	P2₁/n	P2₁/c	Pna2₁	P2₁/c
Z	4	2	2	2	4	2
Unit-cell parameters	3	4	4	4	3	4
φ, θ, ψ	3	3	3	3	3	3
T_1, T_2, T_3	0	0	0	0	3	0
	Parkes & Hughes (1963)	Hannan & Collin (1953)	Bekoe & Trueblood (1960)	Bertinotti, Giacomello & Liquori (1956)	Hamor & Robertson (1956)	Sabelli, Tangocci & Zanazzi (1969)

Table 4. *Heats of sublimation calculated with the help of the parameters of Table* 3 (kcal mole^{-1})

Nr	Cyano-gen	Dicyano-acetylene	Tetra-cyano-ethylene	s-Tetra-zine	Pteri-dine	Pyridazi-no[4,5-d]-pyridazine
(a)	7·5	10·6	13·6	11·3	15·9	21·6
(b)	7·5	10·6	13·6	11·6	16·2	22·1
(c)	7·4	10·6	13·8	11·0	15·8	21·8
(d)	7·4	10·6	13·8	11·7	16·7	23·4
(e)	2·73	7·1	5·9	7·3	11·6	14·6
(f)	4·6	7·6	9·7	8·7	12·7	17·2

Scheraga (1966) for the A_{HN} and B_{HN} parameters and of Di Nola & Giglio (1970) for the A_{CN}, B_{CN}, A_{NN} and B_{NN} parameters. As these investigators have not used explicit summation limits per type of atomic interaction, we used the same limits as in the foregoing calculations. In Table 4 the heats of sublimation calculated by means of these sets are given. These calculations were performed in order to test the need for our own derivation.

Discussion of the results and conclusions

In all our four calculations the mean percentage standard deviation in the derived parameters is about 8%, thus rather large. The values of the derived parameters are roughly equal for the same type of potential. An exception to this is the value found for B_{HN}, which is highly correlated to the value used for A_{HN}. The experimental heat of sublimation of cyanogen is reproduced by means of all derived sets of parameters within about 4%, that of dicyanoacetylene within 1%. The four sets predict about the same values for the heats of sublimation of the other four compounds. No essentially different results are obtained from interaction curves of type B or LJ. However, the appearance of the two types may be quite different [Fig. 1, curves (b) and (d)]. The geometric-mean combining rule (Williams, 1972) does not hold for the derived parameters A_{CN}, B_{CN} and B_{HN}. The calculations (b) and (d) are considered better because they are more obedient to this rule for the parameter A_{HN}. This criterion is, however, highly disputable.

A comparison of the values of the derived parameters to the corresponding values of Table 1 shows only rough agreement (*cf*. also Fig. 1). In particular the values for A_{NN} and B_{NN} differ greatly. An exception has to be made for the parameters A_{NN} and B_{NN} as derived by Jacobi & Schnepp (1973) which are rather similar to our LJ parameters. However, different sets of parameters are to be expected because we used a different method of derivation and other experimental basic information. Furthermore, because there are often high correlations between the individual parameters within one set, one should not ascribe too much significance to differences between individual parameters of different sets (Williams, 1966, 1974).

Our conclusion is that the parameters as given in Table 3, calculation (b), form a useful set of atomic
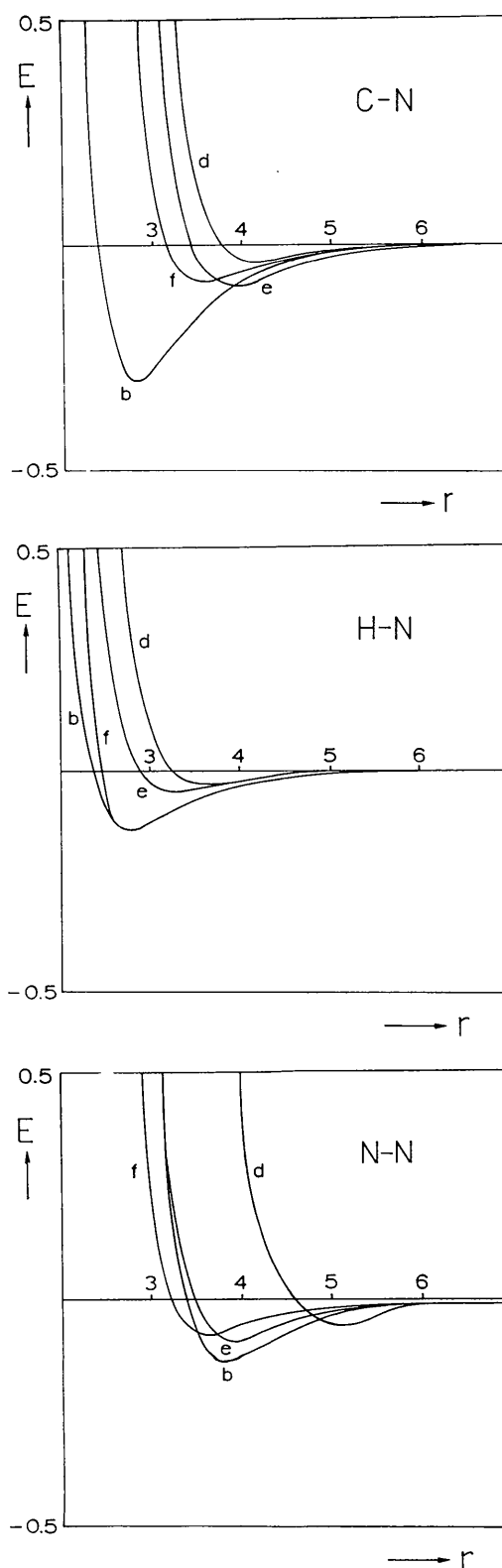

Fig. 1. Carbon–nitrogen (C–N), hydrogen–nitrogen (H–N) and nitrogen–nitrogen (N–N) interaction curves. The symbols b,d,e and f correspond to the symbols (b),(d),(e) and (f) of Table 3. Units are kcal mole^{-1} (for E) and Å (for r).

non-bonded interactions in which C, H and N atoms are involved in combination with the parameters of Williams (1967), which are also of the B type. Because of the theoretical model we used and because of the experimental basic data, the parameters will probably give the most reliable results for molecular crystals in which N is involved as cyano or azine groups.

A comparison of the results obtained by the three sets of potential parameters $(b),(e),(f)$ (Table 4) shows that it is necessary to use our set (b) in calculating the heat of sublimation. It is not sufficient to take the N equal to the C atom [set (e)] as had been expected before. Set (f) gives an improvement, but at the same time it is clearly not appropriate to predict the correct heats of sublimation of cyanogen (7·75) and of dicyanoacetylene (10·58 kcal mole^{-1}). Concerning the other compounds experimental information is lacking. Only a comparison with the heats of sublimation of the related compounds s-triazine (10·3), benzene (10·7), and naphthalene (17·3 kcal mole^{-1}) is possible. This comparison is also in favour of our derived set (b).

All three sets (b), (e) and (f) predict the same order of magnitude of the heats of sublimation. In particular, the difference between the heats of sublimation of the isomers pteridine and pyridazino[4,5-d]pyridazine is remarkable; a difference of 5·9 kcal mole^{-1} is found with set (b). The relatively high heat of sublimation of the latter compound might be in accordance with its high melting point (290°C) as opposed to 140°C for pteridine and 80°C for naphthalene, but more information about e.g. the heats of melting and vaporization is needed to confirm this suggestion.

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