isolated molecule. Also, at each H atom (Fig. 2*c*) the region of electron depletion is not centered at the nucleus, but rather is extended towards the O atom with which it is H-bonded.* These features are consistent with theoretical calculations which indicate that H bonding is primarily an electrostatic interaction (Morokuma, 1977).

It is concluded that when used to reveal the effects of chemical binding, the simple pseudoatom model is about equally efficient when applied either to the experimental $|F_o^x|$ or to the theoretical $|F_o^t|$ structure amplitudes.

The pseudoatom model has recently been applied in crystallographic charge density studies of other molecules containing the ureide group. These include parabanic acid at room temperature (Craven & McMullan, 1979) and 123 K (He, Swaminathan, Craven & McMullan, 1984), barbital at 198 K (Craven, Fox & Weber, 1982), and alloxan at 123 K (Swaminathan, Craven & McMullan, 1984*b*). The detailed comparison and discussion of these results is deferred.

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* Symmetry-related H(2) atoms in the same molecule are both H-bonded to the same O atom which lies along the **c** direction on the twofold axis.

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Nonbonded Potentials for Azahydrocarbons: the Importance of the Coulombic Interaction

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Abstract

A transferable nonbonded N···N potential of the (exp − 6 − 1) type was obtained by fitting the crystal structure of α-nitrogen (N_2) and nine crystal structures of azahydrocarbon molecules which do not exhibit hydrogen bonding: ethanedinitrile (C_2N_2), ethylenetetracarbonitrile (C_6N_4), *cis*-1,2,3-cyclopropanetricarbonitrile ($C_6H_3N_3$), 1,1,2,2-cyclopropanetetracarbonitrile ($C_7H_2N_4$), triethylenediamine ($C_6H_{12}N_2$), hexamethylenetetramine ($C_6H_{12}N_4$), pyrimidine ($C_4H_4N_2$), pyrazine ($C_4H_4N_2$), and β-

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1,3,5-triazine ($C_3H_3N_3$). For initial refinement of the N···N nonbonded potential, nonbonded parameters for carbon and hydrogen were assumed as derived from hydrocarbon crystal structures. Net atomic charges were obtained by fitting the calculated *ab initio* molecular electrostatic potential surrounding the molecules (PD site charges). For aromatic N atoms additional lone-pair-electron PD site charges were included. To verify further the transferability between different molecules of the nonbonded parameters for H, C, and N interactions the nitrogen data-base structures were combined with a data base of 17 hydrocarbon crystal structures to derive the full set of H, C, and N nonbonded potential parameters from all 27 crystal structures simultaneously. The resulting nonbonded potentials were tested by using them to calculate predicted crystal structures for the 27 molecules in the data base. Comparisons of the results obtained were made to nonbonded potentials previously published in the literature. Additional crystal structure predictions were made for 2,2′-bipyridine ($C_{10}H_8N_2$), α-phenazine ($C_{12}H_8N_2$), and 1,2,4,5-tetrazine ($C_2N_4H_2$), which were not in the data base. Coulombic effects were generally found to be small only in saturated hydrocarbon crystal structures. Aromatic hydrocarbon crystals were found to have Coulombic energies as large as a 21% fraction of the total lattice energy. For most of the azahydrocarbon crystals considered Coulombic effects were found to be very important, ranging up to a maximum contribution of 59% of the total lattice energy in the case of 1,1,2,2-cyclopropanetetracarbonitrile. The tertiary amines triethylenediamine and hexamethylenetetramine were found to have relatively smaller Coulombic lattice energies of 13 and 15%, respectively.

Introduction

The importance of nonbonded and hydrogen-bonded forces for establishing the structure of proteins and their interaction with substrates is well established (Brant, 1972; Schulz & Schirmer, 1979). These forces are important in determining how the peptide chain folds to yield the active conformation of the protein, and also in determining the structural geometry and energy of complexation of the protein with substrate molecules. A successful model for nonbonded interactions would allow us to understand better and help to predict the geometry and energy of protein folding and protein-substrate complexation. As a step toward such a model, we seek accurate nonbonded potential-energy functions by deriving them from the crystal structures of small molecules.

If the nonbonded potential-energy functions are successful in modeling intermolecular interactions in crystals of smaller molecules, they should be transferable to the task of modeling larger molecules such as proteins and their interaction with substrates. This transferability property is very important and is considered further below. In this paper we report the derivation and testing of nonbonded N···N potential parameters, and we examine their compatibility with hydrocarbon H···H and C···C nonbonded potential parameters.

The atom–atom nonbonded potential-energy model, which was pioneered by Kitaigorodsky (1973), has proven to be a practical approximation. In this model each atom in the molecule is assigned interaction parameters a_j, b_j, c_j, and q_j such that the pairwise nonbonded potential energy is given by

$$E_{jk} = b_j b_k \exp\left[-(c_j + c_k) r_{jk}\right] - a_j a_k r_{jk}^{-6} + q_j q_k r_{jk}^{-1},$$

where r_{jk} is a nonbonded interatomic distance between atoms j and k in different molecules or between distant parts of the same molecule. This is referred to as an (exp−6−1) function. Alternatively, this function can be written as

$$E_{jk} = B_{jk} \exp(-C_{jk} r_{jk}) - A_{jk} r_{jk}^{-6} + q_j q_k r_{jk}^{-1},$$

where $B_{jk} = b_j b_k$, $C_{jk} = c_j + c_k$, and $A_{jk} = a_j a_k$. The physical significance of the terms is (1) a short-range strong repulsive energy due to overlapping electron clouds of filled shells; (2) a weak longer-range attractive dispersion energy; and (3) a very long-range Coulombic energy, which can be either repulsive or attractive, between site electrical charges.

The relative importance of these three energy types for nonpolar molecules goes in the same order; for ions and polar molecules the Coulombic energy becomes stronger. Term (1) may even be further approximated by the hard-sphere van der Waals radii (Pauling, 1960) or by a simple quadratic repulsion function (Williams, 1969). In practice, when repulsion-only models are used, the interesting volume of configuration space is at short intermolecular distances, consideration of which amounts to introduction of an implicit intermolecular attraction.

Addition of the dispersion term (2) explicitly includes a quantitative estimate of the intermolecular attraction which is present even for molecules with no site charges. The inclusion of an attractive term makes possible the calculation of the energy configurational surface of molecular clusters (Williams, 1980) and crystals (Williams, 1972*b*), for which the minimum-energy configuration can be compared to observed structures and energies. The attractive term also operates between distant parts of the same molecule, and its use improves the accuracy of intramolecular conformational calculations (Busing, 1982).

For hydrocarbons the Coulombic energy term (3) is small but not negligible (Williams, 1974). For organic molecules containing nitrogen or oxygen the Coulombic energy can be quite important. The force effect of the Coulombic energy term is relatively smaller than the energy effect because its functional form causes the energy to vary less with distance than the other energy types. The use of a dielectric constant for the Coulombic energy term is inappropriate when detailed summation is made over all charge sites and no polarization effects are included. To avoid error the Coulombic energy must be summed very carefully in a crystal because of its extremely long range and the poor convergence properties of the lattice sum.

The most prolific source of experimental data for calibration of nonbonded potential-energy functions is the very large number of crystal structures determined experimentally by diffraction methods (Kennard, 1970–82). The use of intermolecular data from crystal structures has a distinct advantage over the use of intramolecular data for the calibration of nonbonded potential parameters. Namely, the possibility of unwanted parameter correlation with intramolecular bond stretching, bond bending, or torsion-angle changes is eliminated. This elimination of correlation is important because the cited intramolecular effects are generally larger in magnitude and can predominate over the nonbonded effects.

Quantum-mechanical calculations have now progressed to the point where *ab initio* self-consistent-field methods can predict the structure and energy of very small molecular clusters such as molecular hydrogen dimer. These exhaustive calculations can also be used as 'observed' data and the intermolecular energy fitted by model functions (Starr & Williams, 1977). This source of information is particularly useful for establishing values for the nonbonded repulsion exponents. Also, intramolecular quantum-mechanical calculations are very useful for establishing values for the site charges in molecules. This is indeed a fortunate situation, since both the nonbonded repulsion exponents and the site charges are in general difficult to extract from crystal structure data.

Simplicity of the nonbonded model is important for at least two reasons. The first is to allow practical calculations in a reasonable length of time on large molecules such as proteins. The second reason is to make use of the intuitive physical meaning of a characteristic atom–atom potential for a given type of atom which implies that the potential is an atomic property and is transferable with the atom into different molecular environments.

A further important simplification is already implied by the form of the above equation: heteroatomic interactions are given by the geometric-mean combining law. Assumption of the geometric-mean combining law greatly reduces the number of independent nonbonded parameters. It also permits straightforward application of convergence acceleration techniques to obtain the crystal-lattice energy sum (see below).

Table 1. *Nonbonded* N···N *potential parameters for nitrogen in organic molecules*

The units are kJ mol^{-1} and Å.

Potential	A	B	C	D	n	r_e	$-E_e$
I	2615	0	0	2 472 744	12	3·52	0·691
II	1084	175 728	3·78	0	0	3·59	0·282
III	5146	0	0	9 501 684	12	3·93	0·697
IV	8452	0	0	363 590	9	4·01	0·677
V	1519	0	0	3 064 948	12	3·99	0·188
VI	1678	0	0	1 568 749	12	3·51	0·449
VII	3180	440 994	3·60	0	0	3·85	0·555
VIII	1204	66 735	3·4341	0	0	3·64	0·269
IX	1378	254 530	3·78	0	0	3·62	0·324

References: (I) Ferro & Hermans (1972). (II) Mirskaya & Nauchitel (1972). (III) Hagler, Huler & Lifson (1974), with $n = 12$. (IV) Same as (III), but with $n = 9$. (V) Momany, Carruthers, McGuire & Scheraga (1974), for amide nitrogen. (VI) Same as (V), but for primary and secondary amine nitrogen, and heterocyclic aromatic nitrogen. (VII) Govers (1975), set (*b*). (VIII) Allinger & Yuh (1980). (IX) This work.

Timofeeva, Chernikova & Zorkii (1980) have recently reviewed the literature for available sets of nonbonded potential functions. Some of these potentials use a two-parameter repulsive function of the type

$$Dr_{jk}^{-n}$$

instead of a two-parameter exponential function. Table 1 lists values of N···N nonbonded potential parameters that have been recently proposed for general use with nitrogen-containing organic molecules. Because different repulsive-energy functions are used it is useful to compare the equilibrium distance, r_e, and the nonbonded energy at the equilibrium distance, E_e. Note that the equilibrium nonbonded distance should not be confused with the commonly quoted van der Waals distance, since the latter is always expected to be considerably smaller. The last two rows of Table 1 show the equilibrium distance and energy for the potentials. The equilibrium distance varies from 3·51 to 4·01 Å and the well depth varies from −0·188 to −0·697 kJ mol^{-1} for the various potentials shown.

Since nonbonded potential parameters are generally highly correlated, the computational results using matched sets of parameters may be better than would be expected from looking at the individual potentials. For instance, the C···C potential in a matched set could change in a compensating way when combined with an apparently incorrect N···N potential to yield a good lattice-constant prediction for an azahydrocarbon crystal. However, such an unbalanced parameter set would not be expected to have good transferability over a wide range of compounds, as compared to a more balanced set.

Subdividing nitrogen nonbonded interactions into several types increases the number of adjustable empirical parameters; a better data fit is normally expected when this is done. The use of a single type of nonbonded potential for an element keeps the number of adjustable empirical parameters at a minimum. It also eliminates the need for making decisions as to which is the proper subtype to use in a given complicated molecular-bonding situation.

Detailed studies of the N···N nonbonded potential for crystalline molecular nitrogen alone (Kjems & Dolling, 1975) gave values ranging from 3·593 to 3·806 Å for the equilibrium distance and from −0·246 to −0·364 kJ mol^{-1} for the well depth. We seek here a N···N potential which is generally applicable to nitrogen-containing organic molecules, and therefore we are willing to allow some change from the potential which is optimum for what we regard as the atypical case of molecular nitrogen. It is interesting that the above ranges for the equilibrium distance and well depth are so large for such a simple case as molecular nitrogen. Nevertheless, we believe that a reasonable N···N potential which is to be transferable among nitrogen-containing organic molecules should have an equilibrium distance and energy approximately in the range that will also fit molecular nitrogen. Of the potentials shown in Table 1, only potentials (II) and (IX) satisfy this requirement. All of the other potentials have either or both of the equilibrium distance or energy outside of a reasonable range for molecular nitrogen. Further discussion of the individual potentials in the table is postponed until later.

Strategies and concepts for derivation of nonbonded potentials

In accordance with the concept of the atom–atom model we seek average nonbonded potentials for atoms of a given type, applicable to all bonding situations. It is intended that these potentials will be suitable for describing intermolecular interactions between both small and large molecules, and for intramolecular interactions between sufficiently separated parts of a molecule. Usually 'type' will signify the type of element. Only averaged nonbonded parameters can be obtained since the nonbonded characteristics of an atom will change slightly as a result of the atom being involved in different types of bonding. The decision whether to define element subtypes will depend on the amount of variation of the nonbonded characteristics of the element in different bonding situations and on the desired accuracy. Kitaigorodsky (1978) has emphasized the desirability of using the same nonbonded potential for each element regardless of its bonding environment in the molecule.

In practice we have set up as our desired accuracy targets for prediction of crystal structures the following 'threshold' values (Hsu & Williams, 1980): 1% for the lattice constants, 1° in the cell angles, 2° in the molecular rotation in the cell, and 0·1 Å in the molecular translation in the cell. The idea of threshold accuracy is that nonbonded potentials which give predictions better than the threshold are deemed to be fully satisfactory. The numerical threshold values given above are difficult to achieve in practice, even for simple hydrocarbon crystals. The threshold-value estimates are also used to calculate the weight matrix for nonbonded potential parameter derivation (see below).

The repulsion parameters b_j and c_j are highly correlated. Thus it is difficult in practice to derive independent values for both of these parameters. Usually it is best to make a reasonable estimate for c_j and vary only b_j. Starr (1976) has made theoretical estimates for values of c_j based on the method of Kita, Noda & Inouye (1976) of evaluating electron-cloud overlap. Starr's values for C, N, O, F, and Ne atoms are 1·62, 1·85, 2·18, 2·40, and 2·63 Å^{-1}. The regular trend indicates that the exponents are approximately linear with atomic number in going from carbon to neon.

As mentioned above, accurate quantum-mechanical calculations are available for molecular hydrogen dimer. Fitting these data (Williams, 1965) yielded an exponent of 1·87 Å^{-1} for hydrogen, based on the quantum-mechanical calculations of Mason & Hirschfelder (1957). More recently, Starr & Williams (1977) have fitted the quantum-mechanical calculations of Tapia, Bessis & Bratoz (1971) to give an exponent of 1·83; we consider this value not significantly different from the earlier one. The earlier calculation indicated a bond foreshortening of 0·07–0·10 Å; this reflected a shift of electron density into the bonding region which was consistent with the spherical electron-density-fit calculation of Stewart, Davidson & Simpson (1965). The more recent treatment of molecular hydrogen dimer (Starr & Williams, 1977) indicated a bond foreshortening of 0·16 Å.

Bacon (1975) has surveyed differences in X–H bond lengths as experimentally determined by X-ray or neutron diffraction. The observed X-ray bond lengths are always shorter than the neutron diffraction values because the X-rays are diffracted by the electron cloud, while the neutrons are diffracted by nuclei. The cited survey shows apparent X–H bond foreshortenings of 0·12 to 0·24 Å. The drawing of definitive conclusions about bond foreshortening from these data is difficult because of the presence of thermal motion and the normally large errors in determining hydrogen positions by X-ray diffraction.

Neglect of net atomic charges can cause errors in structure prediction well above threshold values, especially for polar molecules. Williams & Weller (1983) showed that, in the case of heterocyclic aromatic N atoms, lone-pair electron-site charges must be included in order to approach threshold accuracy. Our inclusion of lone-pair electron-site charges in these molecules is an example of extension of the nonbonded model (making it more complicated, of course) in order to approach the desired threshold accuracy level.

In this work we have found it satisfactory to define only one set of nonbonded potential parameters A, B, and C for each element. The values of q, however, are expected to vary for a given element. As discussed below, it is necessary to estimate q for each individual atom in a given molecule depending on its bonding situation.

Thermal motion of the molecules in the crystal generally can cause structural shifts (*e.g.* thermal expansion) of about the threshold values quoted. Thus it would be necessary to treat these thermal effects if better than threshold accuracy is desired; this would make the model more complicated. To avoid such complications, we did not include any explicit treatment of thermal effects in our model. The effects of normal thermal motion are implicitly included in the derived values of the nonbonded potential parameters and thus structural predictions with them also refer to crystals with normal thermal motion. Our choice of threshold-accuracy limits recognizes the minimum relative error caused by neglect of thermal effects as well as other approximations in the model.

Williams (1972*a*) and Busing (1983) have suggested methods for modification of the nonbonded potentials to account for thermal vibrations; the most important change resulting from thermal modification is an effective increase in the repulsive part of the potential with temperature. We note that there must be other factors which are at least as important as thermal effects in reducing the accuracy of crystal-structure prediction. For instance, there is no indication of unusually large thermal effects in crystalline 1,2,4,5-tetrazine as compared to benzene, yet the accuracy of prediction of the benzene structure is much better.

Since nonbonded properties are considered to be atomic properties it is further necessary to delineate how they are combined to yield the nonbonded potential, which is a property of atomic pairs. Usually this problem is posed in terms of the choice of combining law for the pair potential constants $A_{X\cdots X}$ and $A_{Y\cdots Y}$ to yield $A_{X\cdots Y}$. It is noted that the question of which combining law to use does not arise for the case of electron-site charges; Coulomb's law requires the use of the geometric mean for hetero-interactions. The *geometric mean combining* law also has been found suitable (Williams, 1967) for the repulsion and dispersion energies.

Net atomic charges (site charges) cannot be considered a purely atomic property, because the site charge varies over a wide range depending on what other atoms the given atom is bonded to. Thus we do not expect a hydrogen in an –OH group to have the same charge as in a –CH group. Atomic electronegativities give only a rough guide to atomic site charges. For anything beyond the simplest molecules, it is not possible to derive site charges from observed molecular dipole or multipole moments. There are also too many site charges to allow their derivation in general from crystal structure data. Some authors [for example, in potential (VII) above] avoid this problem by not using site charges at all. The neglect of site charges in molecules more polar than hydrocarbons can lead to prediction errors greatly in excess of threshold values. Also, a nonbonded potential based on the assumption of no site charges is expected to be less transferable, since the effects of site charges must be absorbed into the derived values of the potential constants A, B, and C. It is known that inclusion of net atomic charges increases accuracy of structural predictions even for crystals of relatively nonpolar hydrocarbons (Williams, 1974).

It is helpful to have a theoretical method for estimation of site charges. Advances in computational quantum mechanics have now made available high-quality *ab initio* self-consistent-field molecular-orbital wavefunctions for small- to medium-sized molecules. It is a relatively simple task to evaluate the electric potential at points in space around a molecule from its wavefunction. A site-charge model can be fitted to reproduce this surrounding electric potential. Cox & Williams (1981) have evaluated net atomic charges for a variety of small molecules using this method. These site charges are called potential-derived (PD) charges. PD charges reproduce the molecular electric potential more accurately than population-analysis charges (Cox & Williams, 1981; Williams & Weller, 1983).

An emerging topic of interest is the effect of lone-pair electrons on the surrounding molecular electrostatic potential. Williams & Weller (1983) found that explicit introduction of lone-pair electron sites in azabenzenes significantly improved the fit to the electrostatic potentials surrounding these molecules, and also improved prediction of these crystal structures by molecular packing analysis. According to the threshold concept, lone-pair site charges are only included in the nonbonded potential model when necessary to achieve satisfactory accuracy. Lone-pair site charges seem to be necessary for aromatic heterocyclic N atoms, but not for nonaromatic N atoms.

Hydrogen bonds resemble nonbonded interactions in that they often are present in competition with the latter and have the same characteristic of operating between molecules or between distant parts of the same molecule. Fortunately it is possible to select crystal structures which are not hydrogen bonded to define first the nonbonded potential before attempting to define the hydrogen-bonding potential. Treatment of nonbonding and hydrogen bonding together is not likely to lead to a good separation between the two. The availability of more accurate nonbonded potentials will allow better definition of the hydrogen-bonding potential by allowing more accurate subtraction of normal nonbonded interactions before consideration of the hydrogen bonding.

The hydrogen-bond potential energy may be introduced in competition with the nonbonded potential as a specific effect depending on the H···Y distance in X–H···Y, where X and Y are electronegative atoms such as N, O, or F. Potentials (I), (III), (IV), (V), and (VI) above give illustrations of such specific hydrogen-bonding potentials. In this work we have selected only crystal structures which do not show any significant hydrogen bonding. After normal nonbonded potentials are established, hydrogen-bonding potentials may be added in such a way as to give a good separation between nonbonded and hydrogen-bonded effects. Our primary emphasis is on the N···N nonbonded potential, but we also seek to establish good compatibility with H···H and C···C nonbonded potentials.

Description of calculations

The nitrogen nonbonded-potential data base of 10 crystal structures and the hydrocarbon data base of 17 crystal structures are listed in Table 2. There are 146 structural variables in this data base. For each crystal structure there is a maximum of six lattice constants, three molecular rotations, and three molecular translations for the structural variables. Table 2 lists the symmetry-allowed structural variables for all compounds in the data base. Often some of the structural variables are fixed by symmetry. As in previous work (Williams & Starr, 1977) X–H bond lengths were foreshortened by 0·07 Å.

The crystal-structure data were selected so as to give representation to a variety of types of molecular structures containing H, C, and N atoms, excluding hydrogen-bonded structures. Thus, the hydrocarbon crystal structures contain both aromatic and nonaromatic C atoms. The nitrogen-containing crystal structures have a large percentage of N atoms so as to well define the N···N potential. The crystal structures selected are of molecules containing nitrile groups, tertiary amines, and heterocyclic aromatic nitrogen. Molecules with N–H groups are generally hydrogen bonded and thus were excluded.

Values for the exponent parameters, C, were set as follows. For hydrogen, $C = 3{\cdot}74\ \text{Å}^{-1}$ from fitting quantum-mechanical calculations on molecular hydrogen dimer (Williams, 1965). For carbon, $C = 3{\cdot}60\ \text{Å}^{-1}$ from the crystal structure of graphite (Crowell, 1958). For neon, $C = 4{\cdot}36\ \text{Å}^{-1}$ from its crystal structure (Williams, 1972*a*). Exponents for nitrogen, oxygen, and fluorine were estimated by interpolation between carbon and neon: 3·78, 3·96, and 4·16 Å^{-1}, respectively. Only the exponents for hydrogen, carbon, and nitrogen are relevant to nonbonded interactions in azahydrocarbons. However, the cited value for oxygen was successfully utilized in a treatment of nonbonded interactions in oxohydrocarbons (Cox, Hsu & Williams, 1981).

Net atomic charges for the hydrocarbon molecules were defined as they were previously (Williams & Starr, 1977). New results are shown in Fig. 1 for the site charges of the azahydrocarbon molecules. For the aromatic nitrogen heterocyclics we used the scaled PD site charges of Williams & Weller (1983). These charges include lone-pair sites as well as atomic sites. For the remainder of the molecules, PD net atomic charges were obtained using the computer program of Marsh & Williams (1981) from MO wavefunctions formed from an STO-3G basis set. The charges shown in the figure have been scaled by a factor of 1·13 (Cox & Williams, 1981) to correct for the characteristic underestimate of charges when using this basis set. No lone-pair site charges were used for nonaromatic nitrogen.

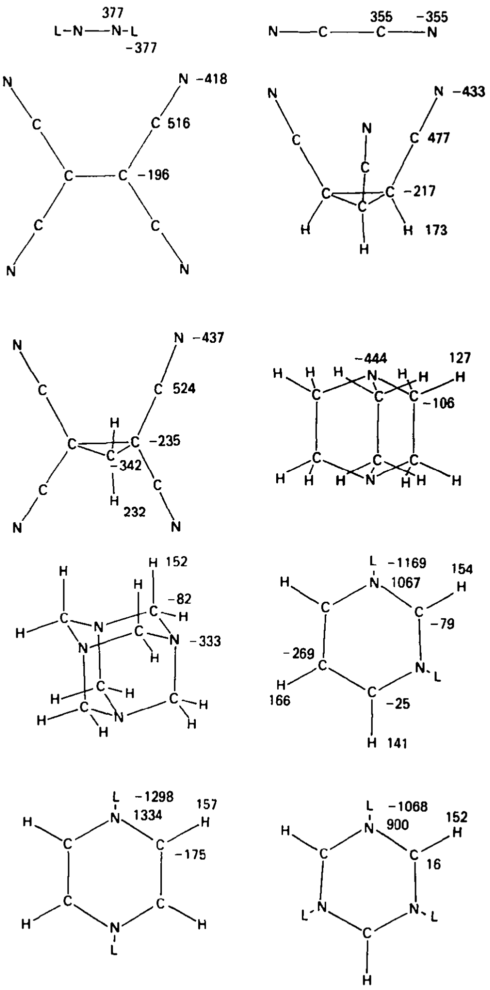

Fig. 1. The molecular structures and their scaled site charges (in electrons $\times 10^3$), determined by the potential-derived method, for the crystal structures in the azahydrocarbon data base. Lone-pair electron-site charges (L) located 0·25 Å out from the N atoms are given for molecular nitrogen and the nitrogen aromatic heterocyclic molecules.

Table 2. *References to the observed crystal structures and to the observed lattice energy (if available)*

The structural variables are those not fixed by the observed space-group symmetry.

Compound (reference)	Space group	Structural variables
1. *n*-Pentane Norman & Mathisen (1964) *Natl Bur. Stand. US* (1947). *Circ.* 461	$Pbcn$	a, b, c, θ_2, t_2
2. *n*-Hexane Norman & Mathisen (1961*a*) *Natl Bur. Stand. US* (1947). *Circ.* 461	$P\bar{1}$	$a, b, c, \alpha, \beta, \gamma, \theta_1, \theta_2, \theta_3$
3. *n*-Octane Norman & Mathisen (1961*b*) *Natl Bur. Stand. US* (1947). *Circ.* 461	$P\bar{1}$	$a, b, c, \alpha, \beta, \gamma, \theta_1, \theta_2, \theta_3$
4. Cubane Fleischer (1964)	$R\bar{3}$	a, c
5. Adamantane Donohue & Goodman (1967) Bratton, Szilard & Cupas (1967)	$P\bar{4}2_1c$	a, c, θ_3
6. Congressane Karle & Karle (1965)	$Pa3$	a
7. Bicyclopropyl Eraker & Rømming (1967)	$Cmca$	a, b, c, θ_1
8. 1-Biapocamphane Alden, Kraut & Taylor (1968)	$P\bar{1}$	$a, b, c, \theta_1, \theta_2, \theta_3$
9. 1-Biadamantane Alden, Kraut & Taylor (1968)	$P\bar{1}$	$a, b, c, \theta_1, \theta_2, \theta_3$
10. Benzene Bacon, Curry & Wilson (1964) *Natl Bur. Stand. US* (1947). *Circ.* 461	$Pbca$	$a, b, c, \theta_1, \theta_2, \theta_3$
11. Naphthalene Cruickshank (1957) Bradley & Cleasby (1953)	$P2_1/c$	$a, b, c, \beta, \theta_1, \theta_2, \theta_3$
12. Anthracene Mason (1964) Bradley & Cleasby (1953)	$P2_1/c$	$a, b, c, \beta, \theta_1, \theta_2, \theta_3$
13. Phenanthrene Trotter (1963) Bradley & Cleasby (1953)	$P2_1$	$a, b, c, \beta, \theta_1, \theta_2, \theta_3, t_1, t_3$
14. Chrysene Burns & Iball (1960) Hoyer & Peperle (1958)	$I2/c$	$a, b, c, \beta, \theta_1, \theta_2, \theta_3$
15. Triphenylene Ahmed & Trotter (1963) Hoyer & Peperle (1958)	$P2_12_12_1$	$a, b, c, \theta_1, \theta_2, \theta_3, t_1, t_2, t_3$
16. Perylene Camerman & Trotter (1964) Inokuchi, Shiba, Handa & Akamatsu (1952)	$P2_1/a$	$a, b, c, \beta, \theta_1, \theta_2, \theta_3, t_1, t_2, t_3$
17. Ovalene Donaldson & Robertson (1953) Inokuchi, Shiba, Handa & Akamatsu (1952)	$P2_1/a$	$a, b, c, \beta, \theta_1, \theta_2, \theta_3$
18. α-Nitrogen Kjems & Dolling (1975)	$Pa3$	a
19. Ethanedinitrile (cyanogen) Parkes & Hughes (1963) Hirshfeld & Mirsky (1979)	$Pbca$	a, b, c
20. Ethylenetetracarbonitrile Becker, Coppens & Ross (1973) Saggiamo (1957)	$Im3$	a
21. *cis*-1,2,3-Cyclopropanetricarbonitrile Hartman & Hirshfeld (1966) Boyd (1963)	$R3c$	a, c, θ_3
22. 1,1,2,2-Cyclopropanetetracarbonitrile Lemley, Skarstad & Hughes (1976)	$P2_12_12_1$	$a, b, c, \theta_1, \theta_2, \theta_3, t_1, t_2, t_3$
23. Triethylenediamine Nimmo & Lucas (1976)	$P6_3/m$	a, c, θ_3
24. Hexamethylenetetramine Stevens & Hope (1975) Mansson, Rapport & Westrum (1970)	$I\bar{4}3m$	a
25. Pyrimidine Furberg, Grogaard & Smedsrud (1979) Nabavian, Sabbah, Chestel & Laffite (1977)	$Pna2_1$	$a, b, c, \theta_1, \theta_2, \theta_3, t_1, t_2,$
26. Pyrazine Wheatley (1957) Reynolds (1973)	$Pmnn$	a, b, c, θ_1
27. β-1,3,5-Triazine Smith & Rae (1978)	$C2/c$	a, b, c, β, θ_3
28. 2,2'-Bipyridine Merritt & Schroeder (1956)	$P2_1/c$	$a, b, c, \beta, \theta_1, \theta_2, \theta_3$
29. α-Phenazine Hirshfeld & Schmidt (1957)	$P2_1/a$	$a, b, c, \beta, \theta_1, \theta_2, \theta_3$
30. 1,2,4,5-Tetrazine Bertinotti, Giacomello & Liquori (1956)	$P2_1/c$	$a, b, c, \beta, \theta_1, \theta_2, \theta_3$

Because of the size of the molecule, net atomic charges for hexamethylenetetramine were estimated from the results for triethylenediamine. For the special case of molecular nitrogen, lone-pair sites extending 0·25 Å from the N atoms were used. This choice of N atom to lone-pair distance is consistent with the placement of lone-pair sites used by Williams & Weller (1983) for nitrogen in azabenzenes. The magnitude of the site charges for molecular nitrogen was set by requiring them to reproduce the accurately known molecular quadrupole moment of 1·22 Buckinghams ($4{\cdot}07\times10^{-40}$ Cm^2) (Billingsley & Krauss, 1974). In the nitrogen crystal the quadrupole–quadrupole energy makes an important contribution to the lattice energy (Kjems & Dolling, 1975).

The energy scale of the nonbonded potential functions was set by requiring them to reproduce the accurately known observed crystal energies of molecular nitrogen, benzene, and *n*-hexane. Numerical values are given in Table 4; this table also gives reported observed crystal energies for the other structures, where available. We have chosen to fit accurately only the above-mentioned three values to scale our potentials; this procedure is believed to be better than scaling the potentials to a larger number of less accurately known crystal energies. The literature often shows widely scattered numerical values for crystal energies obtained by vapor-pressure methods; our selected values were obtained by direct calorimetry, a more accurate method.

The full-matrix method of potential-parameter derivation was used (Busing, 1970). This method was shown to be superior for the derivation of Cl···Cl nonbonded potential parameters from the crystal structures of chlorinated hydrocarbons (Hsu & Williams, 1980) and was about equally good as the diagonal-matrix method for hydrocarbons (Williams

& Starr, 1977). The diagonal-matrix method minimizes the function

$$R = \sum_{k=1}^{N} \sum_{i=1}^{M} w_{iik}F_{ik}^{2} + \sum_{k=1}^{N} w'_{k}(E^{o}_{k} - E^{c}_{k})^{2},$$

where $F_{ik} = -\partial E_k/\partial p_i$ designates a generalized force due to a change of the energy of the kth crystal structure with respect to the ith structural parameter. There are a total of N structures with M variables per structure. The energy weights w'_k are set sufficiently large so as to obtain the desired agreement between the observed and calculated energies. In this work we set w'_k to 1% of the observed crystal energy. The diagonal weights for the forces are given by

$$w_{ii} = \frac{\partial^2 E_k}{\partial p_i^2}[\sigma(p_i)]^{-2}$$

where the second derivative is the diagonal element of the structural Hessian matrix, **H**, and $\sigma(p_i)$ is the estimated threshold-allowed error in structural variable p_i.

The more general full-matrix method makes use of the off-diagonal elements of the Hessian:

$$R = \sum_{k=1}^{N} \sum_{i=1}^{M} \sum_{j=1}^{M} w_{ijk}F_{ik}F_{jk} + \sum_{k=1}^{N} w'_{k}(E^{o}_{k} - E^{c}_{k})^{2}.$$

The weight matrix is now $\mathbf{w}_k = [(\mathbf{H}_k)^t\mathbf{V}_k\mathbf{H}_k]^{-1}$, where $\mathbf{V}_k$ is a diagonal matrix with elements $V_{ii} = \sigma^2(p_i)$. If the Hessian is diagonal the two methods are identical. In practice, the off-diagonal elements of the Hessians for observed crystal structures are quite large, so that the full-weight method is preferred. Further details are given by Busing (1970) and Hsu & Williams (1980). The eigenvalues of the structural Hessian were always monitored during the calculations; a physically reasonable energy surface should have eigenvalues that are positive definite. Our eigenvalues were always positive definite, both during the nonbonded-parameter-derivation calculations and also during the lattice-energy minimization calculations. Williams & Weller (1983) showed that not using lone-pair electron site charges for azabenzene molecules often led to nonpositive-definite Hessians for the crystal structures of those molecules.

Care must be taken to sum accurately the nonbonded potentials over the crystal lattice, especially for the long-range Coulombic interactions. A mathematical technique, called the accelerated-convergence method, is routinely available which will dramatically increase both the accuracy and the speed of evaluation of crystal-lattice sums (Williams, 1971). We used a summation limit of 9 Å in the direct lattice with a convergence constant of 0·15 Å^{-1}. The reciprocal-lattice sum was found to be negligible in magnitude (less than 1%) and was omitted. For the structures containing N atoms the sums were always taken over entire molecules. For the hydrocarbons the site charges were sufficiently small that the 9 Å limit could be applied to all nonbonded distances. The lattice-sum evaluation error was estimated to be less than 1% for all structures. Values of $a_{\rm H}$, $b_{\rm H}$, $a_{\rm C}$, $b_{\rm C}$, $a_{\rm N}$, and $b_{\rm N}$ were derived from the data base; the ratio of observables to adjustable parameters is good, at 149 to 6.

Table 3. *The nonbonded potential parameters derived from observed crystal structures* 1–27 *with normalization to the crystal energies of n-hexane, benzene, and molecular nitrogen*

The hydrocarbon nonbonded parameters of Williams & Starr (1977), set II, are shown also. Note that parameters involving hydrogen interaction are based on X–H distances foreshortened by 0·07 Å.

Parameter	Williams & Starr	This work
$A_{\rm HH}$	136·0	136·4
$B_{\rm HH}$	11 677·	11 971·
$C_{\rm HH}$	3·74	3·74
$A_{\rm CC}$	2 414·0	2 439·8
$B_{\rm CC}$	367 250·	369 743·
$C_{\rm CC}$	3·60	3·60
$A_{\rm NN}$		1 378·4
$B_{\rm NN}$		254 529·
$C_{\rm NN}$		3·78

Results and discussion

The primary purpose of this study was to establish accurate nonbonded potential parameters which can predict to threshold accuracy the crystal structures of azahydrocarbon molecules that are not hydrogen bonded. A secondary goal was to determine the degree of transferability of hydrogen and carbon nonbonded potentials to these structures and *vice versa*.

Table 3 shows our derived values of nonbonded parameters for hydrogen, carbon, and nitrogen. The parameters of Williams & Starr (1977) derived from hydrocarbons only are included for comparison. Our derived parameter values for hydrogen and carbon from the full data base including nitrogen-containing molecules are nearly the same as those of Williams & Starr for hydrocarbons only. This suggests that their hydrocarbon nonbonded parameters have good transferability to azahydrocarbon molecules.

We tested the presently derived nonbonded parameters by using them to find the calculated lowest energy for each of the 27 crystal structures in the data base. Table 4 shows these results. The calculation conditions with regard to summation limits *etc.*, were the same as used for the derivation process. Starting from the observed structure, the crystal energy was minimized by the Newton–Raphson method using a local version of the computer program *PCK*6 (Williams, 1979). The calculation was terminated when all structural variable shifts were less than 0·0005 Å or 0·0005 rad or the energy decrease was less than 0·0002 kJ mol^{-1} per Newton–Raphson cycle.

Table 4. *Differences between the predicted (potential set* IX) *and observed structural parameters for each structure*

The second column gives the observed lattice energy (kJ mol^{-1}) (if available) and the third and fourth columns give the calculated lattice energy for the observed and predicted structures. The remaining columns list the predicted shifts in the cell edges (%), cell angles (°), molecular rotation (°), and molecular translation (Å).

Structure number	E_o	E_c	E_c	Δa	Δb	Δc	$\Delta\alpha$	$\Delta\beta$	$\Delta\gamma$	$\Delta\theta$	Δt
1	−41·5	−43·1	−43·6	2·1	−1·3	1·6	—	—	—	0·6	0·06
2	−52·6	−52·6	−53·4	1·1	−3·5	1·4	0·1	1·0	−1·6	3·8	—
3	−66·4	−69·0	−70·2	1·4	−4·0	0·5	0·1	0·3	−1·5	6·2	—
4		−62·1	−62·9	−1·2	(−1·2)	4·6	—	—	—	2·0	—
5	−62·3	−76·8	−77·0	0·0	(0·0)	1·3	—	—	—	0·0	—
6		−98·4	−98·5	−0·4	(−0·4)	(−0·4)	—	—	—	—	—
7		−61·7	−62·7	−1·1	0·7	−1·6	—	—	—	2·7	—
8		−122·3	−122·5	−1·4	−1·0	−0·5	—	—	—	0·6	—
9		−131·6	−131·9	−0·4	−0·8	−0·2	—	—	—	1·1	—
10	−52·3	−52·3	−52·5	0·4	−1·3	2·6	—	—	—	2·4	—
11	−72·4	−82·2	−83·0	−1·2	−1·8	−0·7	—	−1·2	—	2·3	—
12	−102·1	−112·7	−114·1	1·1	−0·9	0·6	—	−1·1	—	2·3	—
13	−86·6	−107·9	−109·6	−0·2	−1·8	−1·0	—	−2·8	—	2·4	0·04
14	−118·8	−141·7	−143·5	1·4	−2·5	−0·3	—	−1·0	—	1·3	—
15	−114·6	−130·9	−131·7	0·6	0·6	−0·9	—	—	—	0·5	0·10
16	−129·7	−147·2	−147·9	−0·7	1·3	−1·6	—	−3·9	—	4·0	0·07
17	−211·7	−220·4	−220·9	4·3	−4·3	−0·1	—	0·2	—	3·0	—
18	−8·3	−8·3	−8·6	−3·4	(−3·4)	(−3·4)	—	—	—	—	—
19	−36·2	−35·1	−35·2	−1·5	1·0	0·0	—	—	—	—	—
20	−86·1	−91·0	−91·0	−0·1	(−0·1)	(−0·1)	—	—	—	—	—
20[c]		−64·3	−67·4	−3·5	(−3·5)	(−3·5)	—	—	—	—	—
21		−92·2	−92·5	1·0	(1·0)	−0·7	—	—	—	1·1	—
22		−96·3	−97·7	0·1	0·4	1·9	—	—	—	2·7	0·11
23	−61·9	−67·1	−68·3	−1·2	(−1·2)	2·2	—	—	—	5·7	—
24	−74·9	−80·7	−81·4	−1·1	(−1·1)	(−1·1)	—	—	—	—	—
24[d]		−68·2	−74·9	−3·8	(−3·8)	(−3·8)	—	—	—	—	—
25	−48·8	−56·6	−57·3	0·0	2·7	−1·3	—	—	—	1·7	0·06
26	−60·7	−53·5	−54·2	1·7	−3·9	0·4	—	—	—	1·4	—
26[a]		−34·7	−40·0	7·3	−8·3	4·6	—	—	—	1·1	—
26[b]		−34·7	−40·0	6·9	−9·0	3·5	—	—	—	—	—
27		−55·3	−55·8	4·5	0·0	−1·7	—	3·1	—	7·3	—
28		−89·2	−90·9	−2·0	2·8	−1·6	—	2·4	—	4·1	—
28[a]		−64·0	−73·5	−6·2	5·3	1·1	—	6·3	—	8·2	—
28[b]		−64·0	−67·4	−5·6	2·2	0·1	—	−1·4	—	—	—
29		−103·2	−106·7	2·7	−1·1	0·2	—	−0·2	—	1·7	—
29[a]		−77·6	−85·8	−5·2	3·0	3·6	—	3·6	—	6·2	—
29[b]		−77·6	84·7	1·6	−7·3	5·9	—	−0·3	—	—	—
30		−61·1	−63·6	6·7	6·4	−7·9	—	7·8	—	18·4	—
30[c]		−47·2	−58·6	−28·4	35·3	−5·4	—	2·6	—	41·8	—

Notes: (*a*) Potential set (VI) with the net atomic charges reported by Momany, Carruthers, McGuire & Scheraga (1974). No accelerated convergence, a 10 Å truncation limit, and a C–H distance of 1·09 Å were used to reproduce the conditions of the original work; however, the energy was minimized with respect to all structural variables which were not fixed by symmetry. (*b*) As above, but without variation of the molecular angular orientation in the unit cell in order to reproduce the conditions of the original work. (*c*) Potential set (VII), no charges, no convergence acceleration, a 5·0 to 6·0 Å truncation limit, and a C–H distance 1·027 Å were used to reproduce the conditions of the original work. (*d*) Potential set (II) with compatible hydrocarbon potentials of Hirshfeld & Mirsky (1979), no charges, convergence acceleration, 9 Å truncation limit, and a C–H distance of 1·09 Å were used.

The predicted hydrocarbon structures may be compared with the results of Williams & Starr, potential set II. As could be expected from the similarity of the present potentials, the results are practically identical. The root-mean-square percentage error in the cell-edge lengths was 1·8%, slightly greater than the desired threshold. The r.m.s. error in the cell angles was 1·6°, in the molecular rotations 2·7°, and in the molecular translations 0·07 Å.

The new results for the ten azahydrocarbon structures are as follows, taken from Table 4. The r.m.s. error in the cell edges was 1·9%, in the cell angles 3·1°, in the molecular rotations 4·1°, and in the molecular translations 0·09 Å. The accuracy of prediction for azahydrocarbon crystal structures was not quite as good as the prediction of hydrocarbon crystal structures. Table 4 shows that threshold accuracy is difficult to achieve for both classes of compounds, with some shifts being as much as four times the desired threshold limits. Further improvement will likely only be obtained at the expense of defining more detailed empirical models. The improved accuracy of the present potentials reflects the use of the more accurate PD site charges, including lone-pair electron sites for aromatic nitrogen heterocyclic molecules.

As required by the calculation conditions, the crystal energies of benzene, *n*-hexane, and molecular nitrogen are fitted to close tolerance. The remainder of the crystal energies shown in Table 4 were not fitted. We think it possible that many of the other tabulated observed crystal energies contain significant errors characteristic of older values obtained from vapor-pressure measurements. The three crystal energies which were fitted were obtained by calorimetric methods. A more thorough comparison of crystal energies would require detailed consideration of the crystal heat capacity and zero-point energy and is beyond the scope of this paper. It would be helpful if a larger number of accurate experimental values were known for crystal energies.

Our calculations reaffirmed the importance of the Coulombic interaction in hydrocarbon crystals. Table 5 shows the repulsion, dispersion, and Coulombic-energy contributions for each crystal structure in the data base. The Coulombic energy was usually negative and it therefore favored crystal cohesion. However, for *n*-pentane, *n*-hexane, *n*-octane, and cubane the Coulombic energy was slightly positive and did not favor cohesion at the observed crystal structure. The ratio of the magnitude of the dispersion energy to the repulsion energy for the crystal structures considered ranged from 1·6 to 3·0. The lower ratios were encountered in crystals with a relatively large Coulombic attraction, such as 1,1,2,2-cyclopropanetetracarbonitrile. If the magnitude of the sum of the dispersion and Coulombic energies was divided by the repulsion energy the ratios became somewhat more uniform, ranging from 2·1 to 3·1.

The contribution to the crystal cohesion by the Coulombic energy was small (sometimes even opposing cohesion) for the saturated hydrocarbons, but it was often much larger for the aromatic hydrocarbons. The largest proportion of Coulombic energy in the hydrocarbons considered was found for benzene (21%), but naphthalene, anthracene, phenanthrene, and chrysene also showed large Coulombic energy fractions. The reason for the large fraction of Coulombic lattice energy in aromatic hydrocarbons is that these flat molecules can easily pack in such a way ('herringbone') that the positively charged hydrogens of one molecule can be close to the negatively charged carbons of another molecule. In contrast, the negatively charged carbons in saturated hydrocarbons are more buried in the molecule and cannot interact as well with positively charged hydrogens on adjacent molecules. Ovalene has a small Coulombic crystal energy because this large flat molecule is unusual in that it packs in a coplanar rather than a herringbone fashion.

The nitrile molecules have their strongly charged cyano groups exposed and accessible to intermolecular interaction. All of the nitriles studied showed a Coulombic lattice energy of more than 50%, with a maximum of 59% for 1,1,2,2-cyclopropanetetracarbonitrile. In the tertiary amines the nitrogen is less exposed and these molecules show a smaller Coulombic lattice-energy contribution. Triethylenediamine has a 13% Coulombic-energy component and hexamethylenetetramine has a 15% contribution.

In the aromatic nitrogen heterocycles the N atom with its highly charged lone-pair site is fairly exposed to intermolecular interaction, although not as much as the cyano groups in the nitriles. Note that there is effectively an atomic dipole on the N atom, since overall the N atom with its associated lone-pair electron site is nearly neutral. These distributed atomic dipoles (represented by the lone-pair electron-site charge and the nitrogen net charge) in these nitrogen aromatic heterocyclics are largely responsible for the 30% or more Coulombic lattice-energy contribution in the nitrogen heterocycles. For 1,2,4,5-tetrazine the N atoms and lone-pair sites are more numerous and are more exposed to adjacent molecules and the fraction of the Coulombic energy in the crystal rises to 50%.

Table 5. *Calculated contributions to the crystal-lattice energy* (kJ mol^{-1}) *at the observed structure* (*potential set* IX)

Crystal structure	Repulsion	Dispersion	Coulombic	% Coulombic
1	38·3	−81·4	0·1	−0
2	38·7	−91·6	0·2	−0
3	46·7	−116·3	0·6	−1
4	47·8	−86·5	2·1	−3
5	54·5	−130·0	−1·3	2
6	53·8	−148·8	−3·4	3
7	43·3	−104·2	−0·9	1
8	58·7	−177·7	−2·1	2
9	69·2	−197·7	−3·1	2
10	39·0	−80·5	−10·8	21
11	47·0	−116·2	−13·0	16
12	84·4	−177·0	−20·1	18
13	58·0	−147·9	−18·0	17
14	86·0	−202·2	−25·6	18
15	85·5	−205·2	−11·2	9
16	89·2	−225·5	−10·9	6
17	132·7	−349·8	−3·3	2
18	3·93	−11·43	−0·83	10
19	21·7	−38·5	−18·4	52
20	55·3	−96·4	−49·9	55
21	50·4	−91·4	−51·2	55
22	63·8	−103·7	−56·4	59
23	45·8	−104·3	−8·6	13
24	39·1	−107·9	−11·9	15
25	43·1	−79·1	−20·5	36
26	35·5	−71·8	−17·2	32
27	35·8	−73·4	−17·7	32
28	48·4	−124·8	−12·8	14
29	82·3	−170·8	−14·7	14
30	35·9	−66·5	−30·6	50

The present potentials were further tested by using them to predict three crystal structures not in the defining data base: 2,2′-bipyridine, α-phenazine, and 1,2,4,5-tetrazine. The results are discussed in the next section.

Comparisons with other work

We used the potentials shown in Table 1 (except for VIII, which was not intended for use in crystal structures) in a consistent manner to predict the energy and lattice constants for molecular nitrogen and ethanedinitrile. This uniformity of treatment was

Table 6. *Prediction of the crystal structure and crystal energy of molecular nitrogen and ethanedinitrile with nonbonded potentials* (I)–(VII) *and* (IX) *of Table* 1 *using standard calculation conditions of accelerated convergence, the geometric-mean combining law, and net atomic charges which reproduce the molecular quadrupole moment*

Potential	I	II	III	IV	V	VI	VII	IX
$E(N_2)$ (kJ mol^{-1}) (obsd. = −8·3)								
Initial	−15·7	−7·1	−17·3	−20·2	−5·0	−10·4	−14·1	−8·3
Final	−17·9	−7·7	−18·3	−20·7	−5·5	−12·0	−14·2	−8·7
Δa(%)	−6·5	−5·3	3·4	2·9	4·1	−6·9	1·3	−3·4
$E(C_2N_2)$ (kJ mol^{-1}) (obsd. = −36·2)								
Initial	−39·3	−33·1	−32·5	−40·3	−27·2	−36·7	−37·1	−35·1
Final	−39·6	−33·8	−48·8	−40·9	−27·7	−38·0	−39·0	−35·2
Δa(%)	−1·4	−4·0	7·0	2·2	1·5	−4·9	3·1	−1·5
Δb(%)	2·5	−1·4	5·0	−1·1	0·5	−2·2	1·4	1·0
Δc(%)	0·8	−1·9	8·3	3·6	3·0	−2·2	4·7	0·0

possible because only carbon and nitrogen potentials were needed and there was little doubt about the choice of the magnitudes of the site charges of these molecules since they are required to satisfy their known quadrupole moments. Also, the comparison of the predicted lattice constants is straightforward because the observed space-group symmetries do not allow molecular rotation or translation in either structure. The calculations were carried out under uniform conditions of accelerated convergence, geometric-mean combining law, and assumed site charges.

Table 6 shows that the present potential (IX) gave very good results for the crystal energy of molecular nitrogen, but the lattice constant was predicted 3·4% too small. Although potentials (III), (IV), and (VII) gave equal or better goodness of fit to the lattice constant, they gave poor results for the crystal energy. The remaining potentials gave worse results for the molecular nitrogen crystal structure.

The table shows that there was greater consistency of results for prediction of the crystal structure of ethanedinitrile when the various potential sets were used with their matching (and perhaps compensating) C···C potentials. Potential sets (I) and (IX) gave the best results. However, since potential set (I) did not transfer well to nitrogen, the calculations for both molecular nitrogen and ethanedinitrile overall gave support to the present potential (IX).

We now discuss and make comparisons of potentials (I) to (VII) on an individual basis.

Potential set (I) was derived from structures and energies of crystals of small molecules, as selected from several sources (Hermans, Ferro, McQueen & Wei, 1976). Net atomic charges obtained by the Del Re method were used with a unit dielectric constant, and hydrogen bonding was represented by a modified H···O potential. This N···N potential was part of a set specifically intended to meet the requirements of peptide and protein structures; it has recently been used to minimize the energy of the 54-residue protein rubredoxin (Ferro, McQueen, McCown & Hermans, 1980).

This potential was not transferable to molecular nitrogen because it has an unreasonably deep potential well (−0·691 kJ mol^{-1}) and yielded nearly twice the observed lattice energy and a lattice constant 6·5% too small (Table 6). However, it gave fairly good results for the lattice constants of ethanedinitrile. This behavior was explicable because of the use of a compensating matching C···C potential. Since no lone-pair electron effects are incorporated, this potential was not suitable for aromatic nitrogen heterocyclic molecules.

Potential set (II) was derived from the experimental lattice energy and crystal structure of nitrous oxide. This crystal structure is evidently disordered (Hamilton & Petrie, 1961) and therefore is not a good choice for derivation of the N···N potential assuming a theoretically ordered structure. Structural predictions were made with this parameter set for molecular nitrogen and hexamethylenetetramine (Mirskaya & Nauchitel, 1972). Our calculations with this parameter set essentially reproduced their results for nitrogen (Table 6); for hexamethylenetetramine we obtained a lattice energy of −74·9 kJ mol^{-1} and a predicted lattice constant 3·8% too small (Table 4, line 24*d*). Mirskaya & Nauchitel (1972) reported a lattice energy of −87·0 kJ mol^{-1} and a predicted lattice constant 2·6% too small under slightly different calculation conditions. Their observed lattice constants were extrapolated to absolute-zero temperature.

The work of Hirshfeld & Mirsky (1979) on ethanedinitrile used potential (II) for nitrogen. We repeated these calculations under identical conditions and obtained different results for the Coulombic lattice energy. Using the net atomic charges specified by Hirshfeld & Mirsky for their AC model, we obtained −15·1 kJ mol^{-1} for the Coulombic lattice energy (using convergence acceleration), instead of their reported value of −17·2. To check our calculations, we obtained −14·6 for the sum of the repulsion and dispersion energy, in good agreement with their reported value of −14·5. Thus, Hirshfeld & Mirsky's method of calculating the Coulombic lattice energy yielded a value that appears to be in error by about 2 kJ mol^{-1}.

An excellent technique for rapid and accurate evaluation of the Coulombic lattice sum was presented by Ewald (1921). Ewald's mathematical approach was given a more understandable physical interpretation by Bertaut (1952). Williams (1971, 1981) extended the method to include the dispersion energy and presented easy-to-use accelerated-convergence formulas for the Coulombic and dispersion-energy lattice sums. Because of the effectiveness of the accelerated-convergence method, we advocate its universal adoption in all work with crystal-lattice sums until something better appears. The use of accelerated convergence essentially eliminates summation convergence errors in the evaluation of crystal-lattice sums, and also greatly reduces the calculation time.

Potential sets (III) and (IV) were derived from the crystal structures, crystal energies, and dipole moments of several amide molecules. All of these structures are hydrogen bonded. The N–H···O hydrogen-bond potential was represented as the negative of a normal H···O nonbonded potential. Thus, the hydrogen bond was included by simply leaving out normal hydrogen net nonbonded repulsion. Net atomic charges with a unit dielectric constant were used for all of the molecules; the methyl, methylene, carbonyl and amino groups were assumed to be neutral fragments except in the case of formamide. The resulting potential was checked by calculation of the predicted crystal structures of the amide molecules. The two potential sets differ in the choice of the value of *n*. This potential set has recently been extended to include carboxylic acids (Lifson, Hagler & Dauber, 1979).

These potentials were not tested with any molecules in common with the present work. Like potential set (I), they gave a very large predicted lattice energy for molecular nitrogen. Potential (IV) gave better results for the ethanedinitrile crystal than potential (III). Since no provision was made for lone-pair electron-site charge effects for nitrogen, these potentials were not suitable for the crystal structures of the aromatic nitrogen heterocyclics.

Potentials (V) and (VI) were derived from a large data base of crystal structures including hydrocarbons, nitrogen heterocyclics, carboxylic acids, amides, and one primary amine. Some of the nitrogen-containing molecules were hydrogen bonded in the crystal (*e.g.* the amides) but some were not (*e.g.* pyrazine). The hydrogen-bond energy was represented by the (10–12) function

$$E_{\rm HB} = A' r_{{\rm H}\cdots X}^{-12} - B' r_{{\rm H}\cdots X}^{-10}.$$

Net atomic charges were calculated by population analysis of the CNDO/2 molecular orbital wavefunctions; the Coulombic energy was decreased by a factor of two by use of an effective dielectric constant. Two types of N atom potentials were distinguished: type (V) for primary or secondary amide nitrogen, and type (VI) for primary or secondary amine nitrogen and heterocyclic aromatic nitrogen. The resulting N···N potential was checked by calculation of the crystal structures of the nitrogen aromatic heterocyclics, amides, and methylamine.

Because of the large data base and the care taken in their derivation, these potentials deserve serious consideration. The calibration of potential set (V) for amide nitrogen was based on crystal structures which always contained hydrogen bonds, and thus there are no structures in common with the present work. However, potential (VI) for primary and secondary amine nitrogen was tested by the original authors with one molecule in common with the present work (pyrazine), and with two other azahydrocarbon molecules which are not hydrogen bonded (α-phenazine, 2,2′-bipyridine). Thus we can make detailed comparisons of potential set (VI) by performing calculations on these three crystal structures. Application of molecular-packing analysis to the latter two molecules will incidentally also test the transferability of the present potential set to compounds outside our defining data base. Note that potential set (VI) was calibrated to all three of these molecules, while the derivation of the present potential included only the first structure.

Table 4 shows the results of calculations using potential set (VI) for pyrazine (structure 26), 2,2′-bipyridine (structure 28), and α-phenazine (structure 29). We have attempted to reproduce exactly the specified calculation conditions of Momany, Carruthers, McGuire & Scheraga (1974) in the table (lines *b*). In their work the molecular position in the unit cell was held constant. We also made calculations with their potentials (lines *a*) in which the crystal energy was additionally minimized with respect to molecular position for comparison with the present work. Only changes in the molecular rotation angle are symmetry allowed in these structures.

The prediction of the pyrazine crystal structure with potential set (VI) was not good; this molecule contains heterocyclic aromatic nitrogen. Line 26*b* repeated the original calculation of Momany and coworkers, and agrees fairly well with their work. Line 26*a* allowed the additional variation of the molecular rotation angle in the unit cell, and may be compared with the present work in line 26. The present potential gave a larger crystal energy which was in better agreement with the value of −60·7 kJ mol^{-1} given by Reynolds (1973). In the present work the prediction of the lattice constants was better. The prediction of the molecular orientation was better than threshold with both potentials.

Lines 28 and 29 of Table 4 show comparisons of the results with the present potentials and potential set (VI) for the crystal structures of 2,2′-bipyridine and α-phenazine, respectively. Lines 28, 28*a*, and 28*b* compare results for the crystal structure of 2,2′-bipyridine. If allowed to vary the molecular orientation changed by 8·2°; this was accompanied by a worsening of the fit to the lattice constants (line 28*a*). The nonbonded potentials of the present work showed better overall agreement (line 28). Our lattice energy was larger in magnitude but there was no observed crystal energy available for comparison with the calculated values.

Lines 29, 29*a*, and 29*b* show similar calculations for the crystal structure of α-phenazine. If allowed to vary the molecular orientation changed by 6·2°

(line 29*a*). The present potentials nearly achieved threshold-prediction accuracy for this structure. Again, our calculated lattice energy was larger in magnitude but there was no observed crystal energy available for comparison.

Potential set (VII) was obtained from a set of crystal structures of nitriles and nitrogen aromatic heterocyclic molecules. The exclusion of hydrogen-bonded structures was a significant feature of this work. Although many of these molecules were known to be highly polar, no Coulombic effects were included. The resulting potential was checked only against the experimental crystal energies and not against the observed crystal structures.

The data base for potential (VII) has an azahydrocarbon molecule in common with the present work: ethylenetetracarbonitrile (structure 20). Table 4 (line 20*c*) shows that the lattice energy of ethylenetetracarbonitrile was predicted to be smaller in magnitude than the observed value given by Saggiamo (1957). The cubic lattice constant was predicted 3·5% too small. The present potential (line 20) showed improvement in agreement with both the observed energy and lattice constant.

The derivation of potential set (VII) included in its data base the crystal structure of 1,2,4,5-tetrazine. Table 4, line 30*c*, shows that this potential set failed badly for the prediction of the 1,2,4,5-tetrazine crystal structure. Potential (VII) neglected all Coulombic effects; as mentioned above, lone-pair electron-site charge effects were particularly important in this structure. The original derivation of potential (VII) was based only on fitting the crystal energy, and not the crystal-structure variables. All of the potentials (I) through (VII) were expected to give poor results for the prediction of the tetrazine crystal structure because of their neglect of lone-pair electron effects.

Potential set (VIII) was developed for use in the molecular-mechanics program *MM*2 (Allinger & Yuh, 1980). Although not intended for use in crystals, it was of interest to compare this potential to determine the similarity of intramolecular and intermolecular nonbonded effects. The transferability of r_e between intra- and intermolecular nonbonded effects seems very good. Set (VIII) shows an r_e of 3·64 Å compared with the value of 3·62 Å obtained in this work. The molecular-mechanics potential showed a shallower well depth. We note that, in general, molecular-mechanics potentials must cope with strained molecules which have very short nonbonded distances. Also, set (VIII) is based on different assumptions about electrostatic interactions. Both of these factors can lead to large energy terms which make the precise definition of the relatively shallow nonbonded well depth difficult in their presence.

Fig. 2 compares the non-Coulombic parts of the derived nitrogen potentials listed in Table 1. A significant spread exists between these potentials. Our derived potential (IX) is within the extreme limits of the ranges of the equilibrium distances and energies of all of the potentials. Since many different site-charge models (including no site charges at all) were used by other workers, it was difficult to draw any firm conclusions from comparison of the non-Coulombic parts of the potentials alone. Table 4 shows that the present N···N potential, when combined with the fully compatible hydrocarbon potentials shown in Table 3 and with PD site charges, generally gave the best results for the prediction of the azahydrocarbon crystal structures considered in this paper.

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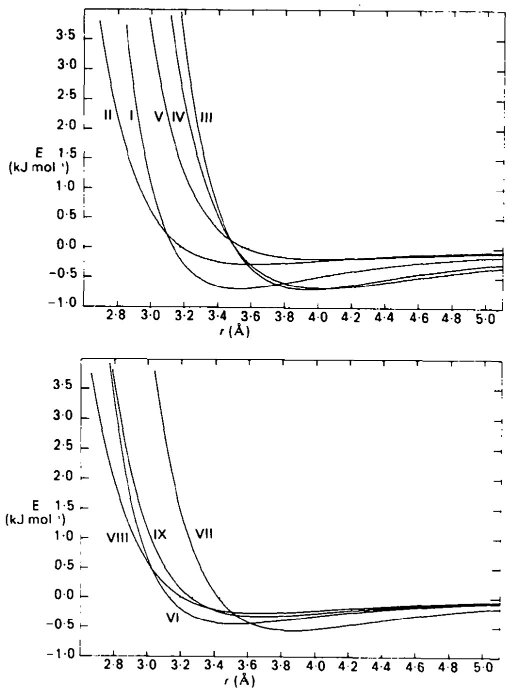

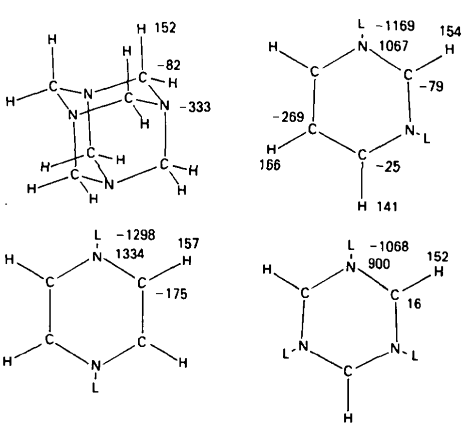

Fig. 2. The non-Coulombic parts of the N···N nonbonded potentials (I)–(IX). (The identification of the curves is the same as in Table 1.)

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