

The Intermolecular Dimer Potential for Ethanedinitrile

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Abstract:

The intermolecular potential of ethanedinitrile has been calculated using two independent estimates:

- (i) ab initio calculations for dimers on the 6-31G basis set level.
- (ii) atom-atom potential calculations.

While some consistent features emerge, there is qualitative disagreement in the majority of approach configurations. The atom-atom potential is over estimating the attractive part of the potential energy surface and underestimating the anisotropy of this surface in comparison with the ab initio method.

Introduction:

The difficulties associated with extending the Lennard-Jones representation to anisotropic molecules have been tackled in different ways. Electrostatic terms have been added to account for interaction between net charges. Kihara et al¹ and Buckingham et al² have introduced shape factors for the anisotropy of repulsive parts of the potential and the problem for molecular dynamics simulation is of course that the extra

terms contribute more in the condensed phase than in the dilute gas.

The electronic structure and potential functions for ethanedinitrile have been calculated using different MO methods³⁻⁶. Also different theoretical relations have been used⁷⁻⁹ to calculate the intermolecular potential for ethanedinitrile. The calculated intermolecular potential constants were compared^{7,8} with values determined from empirical expressions.

In this paper we report briefly on ab initio calculations on ethanedinitrile dimers using 6-31G basis set level. We aim to build up potential energy surfaces and to extract an analytical representation of the pair interaction potentials for direct use in molecular dynamics algorithms. Our MO calculations were compared with the atom-atom pair potentials.

Method of Calculation:

The ab initio calculations were carried out using the Gaussian 76 program of Pople and co-workers¹⁰ using the 6-31G basis set. The monomer geometry is kept at its experimental value¹¹ with the C-C distance taken to be 1.37 Å and the C-N distance has been set equal to 1.16 Å. The calculations were carried out on the Honeywell 6080/GDC 7600 system of Aberystwyth/UMRCC.

The atom-atom potential calculations have been carried out on a PDP 11/70 computer at Alexandria

University Computer Center with a Fortran IV program written by one of us (A.A.H.) which calculates first the atomic coordinates, and then the interaction energy at each intermolecular separation. The parameters used for the atom-atom potential calculations are as follows:

Atom interaction	σ (Å)	$\epsilon/k(^{\circ}\text{K})$
C ----- C	2.80	50.0
C ----- N	3.071	47.0
N ----- N	3.341	44.0

Results and Discussion:

The total energy of ethanedinitrile monomer calculated by the ab initio MO method was found to be -184.499141 a.u. at the 6-31G basis set level. The calculated atomic charges (C: +0.178819 and N: -0.178819) show that each carbon atom donates 0.178819 electrons to its neighbouring nitrogen atom and thus the calculated dipole moment is found to be zero.

The intermolecular potential depends on the mutual orientations of the molecules as well as the intermolecular distance. To reveal the characteristic features of this dependence nine typical mutual orientations^{1,12} of the two ethanedinitrile molecules have been considered. The calculated intermolecular potentials for these different dimer approaches are illustrated in Fig. 1.

In case of the [ZZ] approach, Fig. 1 (i), there is a disagreement between the ab initio calculated potential and the atom-atom potential. While the first is repulsive the

latter shows a shallow well of depth approximately 82°K at an intermolecular distance of 7.3 Å.

For the [ZX] approach, Fig. 1 (ii), there is a qualitative agreement between the ab initio and atom-atom potentials. Both methods predict that this dimer approach

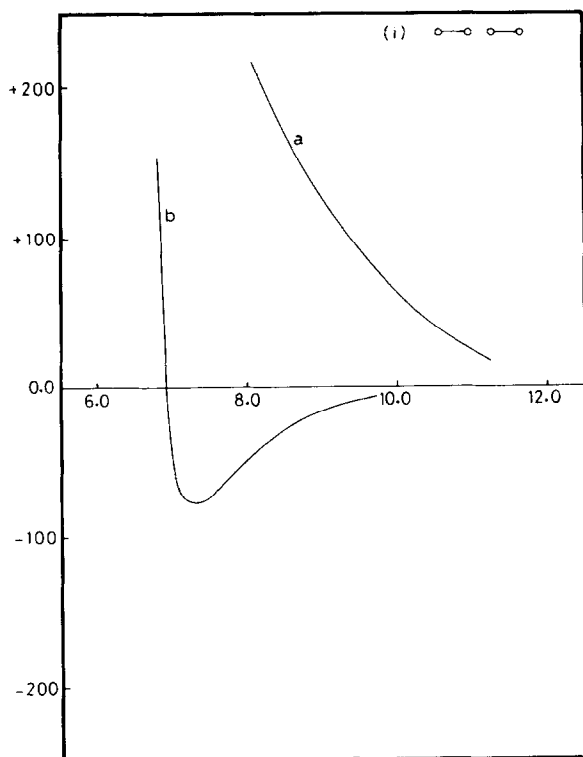
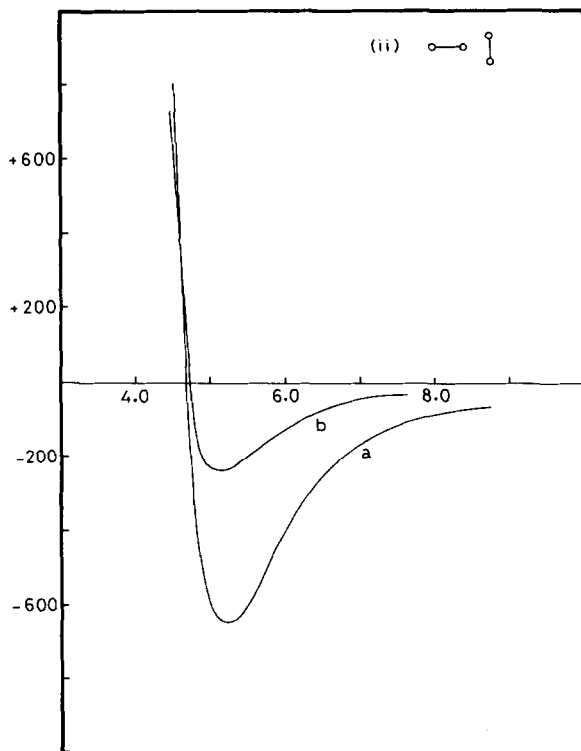


Fig.1- Intermolecular potentials for different ethanedinitrile dimers,
Ordinate: Kelvin; Abscissa: Å; a- 6-31 G ab initio calculations
 b- atom-atom potential calculations:

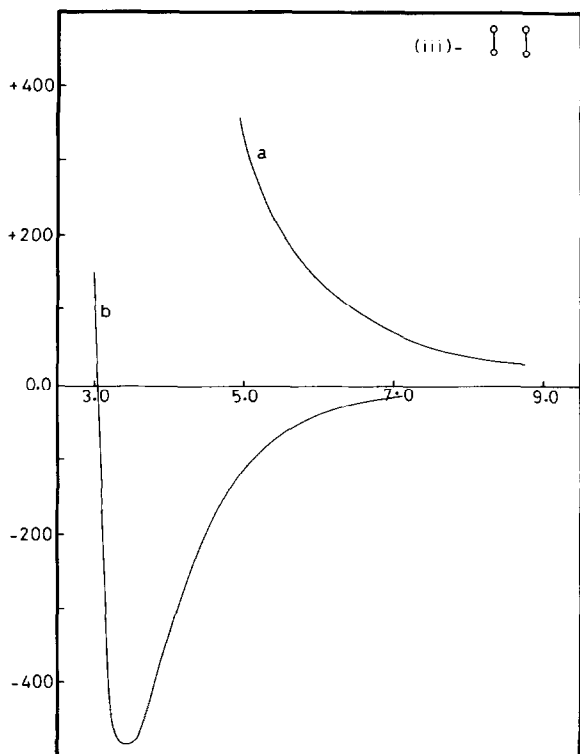
(i) (zz); (ii) (zx); (iii) (xx); (iv) (xy); (v) (zd);
 (vi) (xd); (vii) (dd); (viii) (d \bar{d}); (ix) (d \bar{d})

Where the z-axis is taken along the line connecting the two molecules and d stands for diagonal



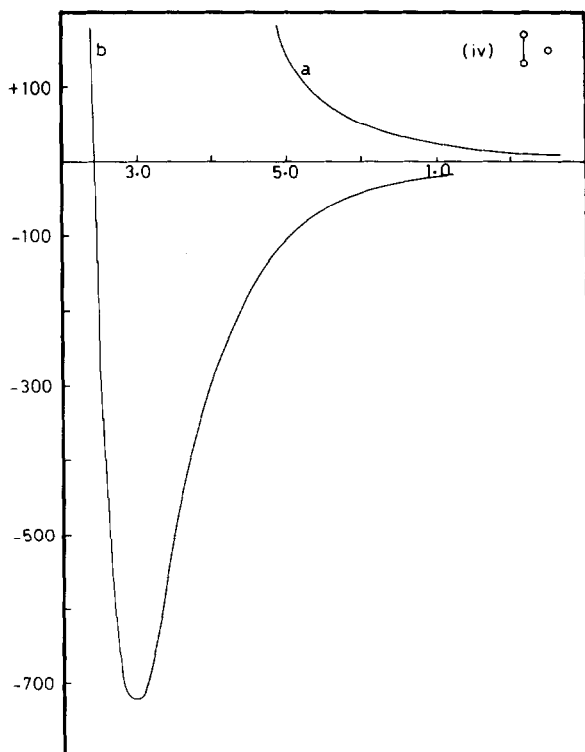
has a minimum energy configuration at an intermolecular distance of 5.15 \AA . The ab initio calculated potential well depth is considerably deeper (approximately 650°K) than the atom-atom potential one (approximately 240°K).

The potential of the [XX] approach Fig. 1 (iii), is calculated to be repulsive by the ab initio method but attractive using the atom-atom potential calculations. This dimer has a minimum energy configuration at an intermolecular distance of 3.4 \AA with a potential well of depth amounting to 480°K .



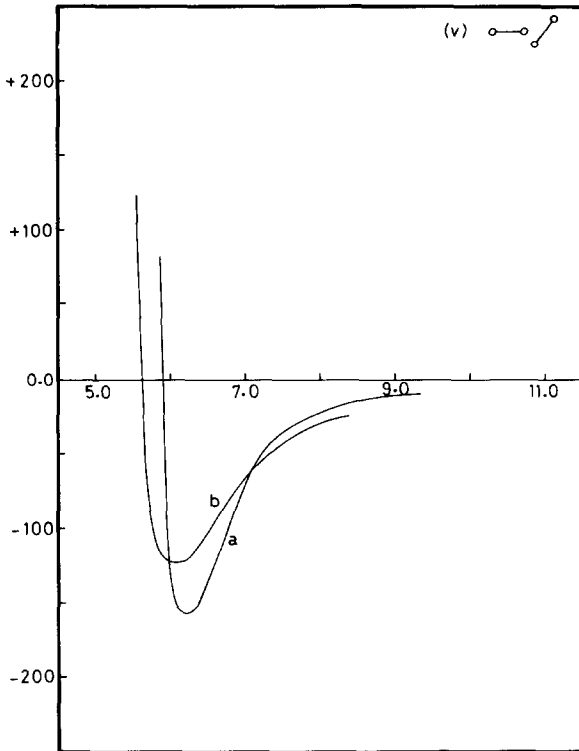
While the $[\text{XY}]$ approach is predicted to be repulsive by the *ab initio* method, the atom-atom potential calculations show that this approach is the most attractive one. The potential well has a depth of approximately 720°K at an intermolecular distance of 3.0 \AA , Fig. 1 (iv).

Similar to the $[\text{ZX}]$ approach, the *ab initio* calculated potential for the $[\text{Zd}]$ approach Fig. 1 (v), is attractive with a shallow well of depth approximately 170°K at an intermolecular separation of 6.2 \AA . The atom-atom potential is also attractive with a well depth of approximately 125°K at an intermolecular distance of 6.1 \AA .



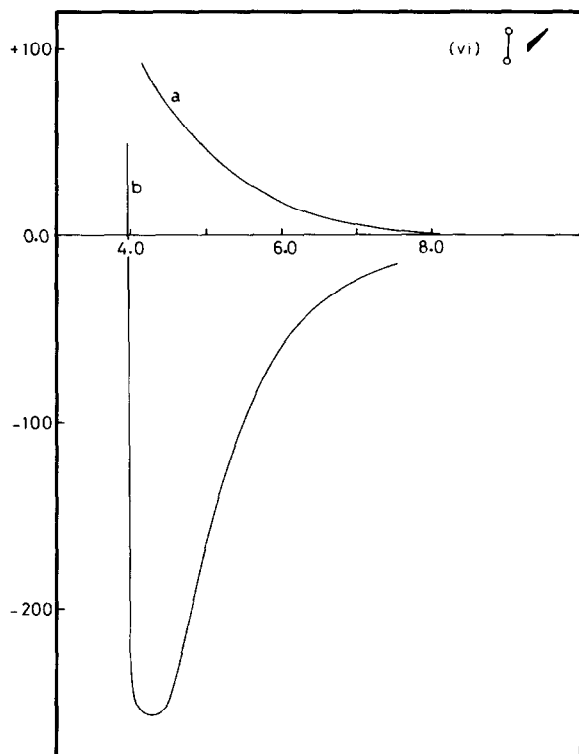
Again and similar to the case of [XY] approach the [Xd] approach Fig. 1 (vi), is repulsive using the ab initio calculations while attractive using the atom-atom potential calculations, but with much smaller intermolecular interaction energy. The potential well has a depth of only 275°K at an intermolecular separation of 4.3 Å.

For the [dd] approach, Fig. 1 (vii), there is a qualitative agreement between the ab initio and atom-atom calculated potentials. The ab initio potential has an attractive part with a minimum energy configuration at an intermolecular distance of 4.7 Å with an intermolecular



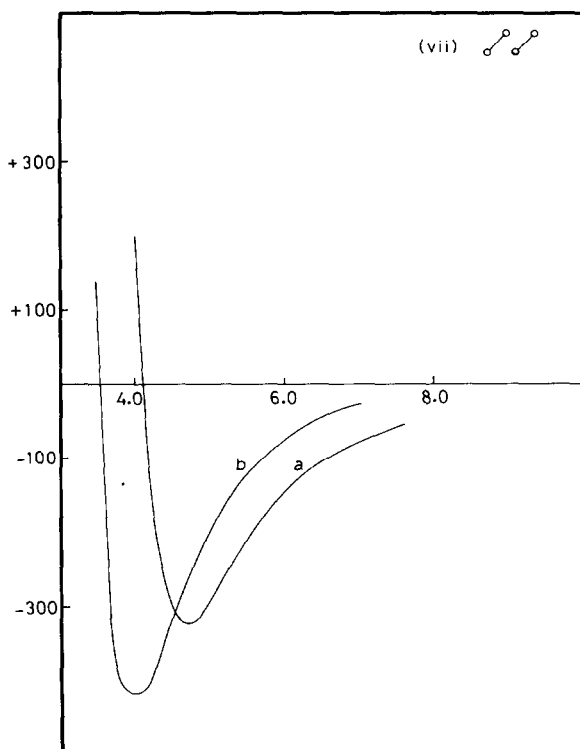
interaction energy amounting to 320°K . On the other hand the atom-atom potential well has a depth of 420°K at an intermolecular distance of 4.0°A .

The [dd'] approach Fig. 1 (viii), also shows an agreement between the ab initio and atom-atom calculated potentials. Both methods predict attractive potential wells of approximately the same depth, being 150°K using the ab initio method and 205°K using the atom-atom potential calculations. The minimum energy configuration has a shorter intermolecular separation using the atom-atom potential 4.8 \AA compared to that calculated by the ab initio method 5.2 \AA .

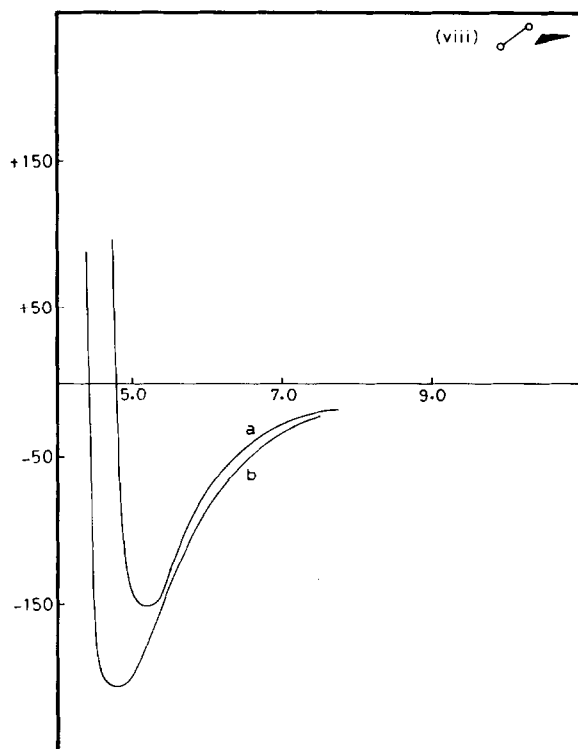


Finally the $[dd'']$ approach shows Fig. 1 (ix), a disagreement between the ab initio calculated potential and the atom-atom potential. While the former is repulsive the latter is attractive with a shallow well of depth approximately 110°K at an intermolecular separation of 5.8 \AA .

It is clear from the above results that some consistent features emerge but there is a disagreement in the majority of approach configurations. The atom-atom potential calculations predict that all the approaches considered here have attractive intermolecular dimer potentials with the $[XY]$ configuration being the most stable. On the other hand ab

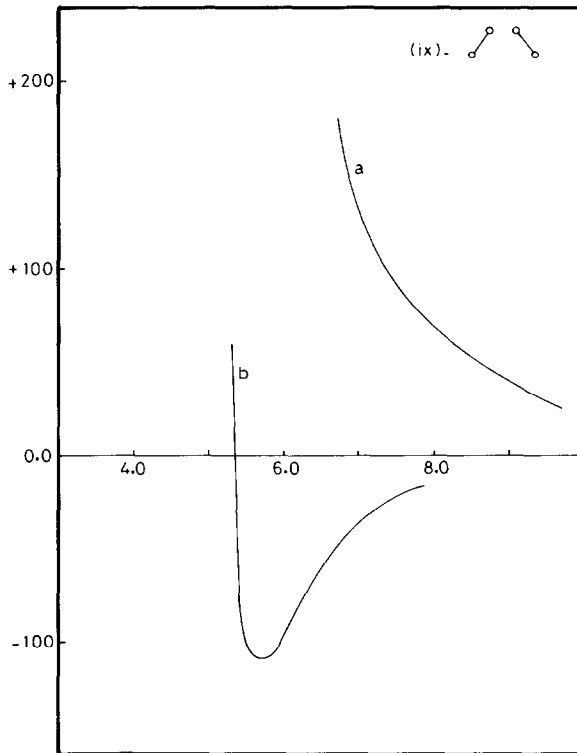


initio calculated potentials show that only the $[ZX]$, $[Zd]$, $[dd]$ and $[dd']$ configurations are attractive with the $[ZX]$ configuration being the most stable. We consider the minimum energy configuration as calculated by ab initio method. This disagreement may be attributed to an overestimation of the attractive part of the potential energy surface and an underestimation of the anisotropy of this surface by the atom-atom potential. The ab initio representation seems to be oversensitive to what we may term multipole-multipole repulsion specially at short intermolecular distances, in instances where the ab initio calculated potential is repulsive. Consideration



of polarizability via multipole-multipole interactions is important in accurately representing dimer interaction, and even more so in consequence when considering multimer clusters and non-pair additivity¹³. In general, the dependence of the potential depth on the molecular orientation is caused partly by the electrostatic multipole interactions between the molecules and it governs the structure of the molecular crystals¹.

In a previous paper¹⁴, a comparison of pair interaction potentials in methyl fluoride, an example



of polar liquids, has been done using ab initio method, atom-atom potential and the potential of Copeland and Cole¹⁵ which is based on gas viscosity, second pressure virial and second dielectric virial data. The ab initio and the experimental Copeland/Cole potentials were found to be more often in better agreement than with the atom-atom potential, but in some dimer configurations the Copeland/Cole potential failed to appreciate the strong repulsion between atoms at short intermolecular distances.

On the other hand and for non-dipolar linear molecules it has been found¹² that the atom-atom potential and the

Kihara/Koide potential¹ agree almost quantitatively in the majority of dimer configurations, so that the extra electrostatic features considered in the Kihara/Koide potential seem generally to have little effect on the atom-atom potential results.

The intermolecular forces are due to the interaction of the permanent, induced and correlated instantaneous charge distributions of the system. Thus a variational calculation of intermolecular potentials must account for the modification of the intermolecular interaction through exchange and overlap effects and it must correctly take into account closed shell repulsions at short distances¹⁶. The crucial problems in the variational calculations of intermolecular potentials are the coupling of inter- and intra-correlation effects as well as the variation of the intracorrelation energy with distance¹⁶.

In general ab initio molecular orbital calculations produce more realistic potentials and the disagreement with the atom-atom potential method imply that the latter is overestimating the attractive part of the potential energy surface and underestimating the anisotropy of it in comparison with the ab initio method. However, there are some discrepancies which obviously remain to be considered by some independent source such as how well spectral features can be reproduced using some representation of these potential surfaces in a molecular dynamic simulation. It is unlikely that variation of the parameters of the atom-atom potentials will remove

the discrepancies, but it is more likely that a parameterization of the ab initio surface will produce more realistic results from a molecular dynamics simulation of ethane-dinitrile.

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