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Geometry optimization of acetonitrile monomer and dimers using CNDO/force method

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Abstract. The geometry optimization of monomeric acetonitrile and its dimers is carried out using CNDO/force method. The results are compared with the experimental and already reported theoretical parameters.

Keywords. Geometry optimization; CNDO/force; acetonitrile monomer and dimers.

1. Introduction

As of now, the structure of acetonitrile is still ambiguous. Dielectric polarization studies (Buckingham and Raab 1961) predict a dipole moment of 2·67 D for the gaseous dimer at 80° and suggest an anti-parallel alignment of the two molecules. Viscosity data (Saum 1966) suggest that in liquid acetonitrile, association does not exceed dimer level. The appreciable polar interaction is also evident from the large negative heat and entropy of dimerisation derived from second virial coefficient measurements (Lambert *et al* 1949; Prausnitz and Carter 1960). Molecular association in liquid acetonitrile is evidenced by spectroscopic studies. Matrix isolated infrared spectra on acetonitrile (Freedman and Nixon 1972) propose various structures for the acetonitrile dimer and favour an anti-parallel alignment of the CN groups based on IR assignments. Raman spectral studies (Givan and Loewenschuss 1983) of matrix isolated acetonitrile suggest the formation of a dimer involving interaction between the methylic hydrogens and the nitrile nitrogen, in addition to the centro-symmetric dimer. Molecular orbital studies have been reported for various associated species. Linear, anti-parallel and displaced anti-parallel structures were studied by CNDO/2 calculations (Paoloni and Hauzer 1975; Paoloni and Dagnino 1975; Gramstad and Tjessem 1977). *Ab initio* studies have been reported for head-to-tail and anti-parallel dimer structures (Dagnino *et al* 1976). In a series of papers from our group (Kanakavel *et al* 1976; Annamalai and Surjit Singh 1982a, b, c 1983a, b; Annamalai *et al* 1978, 1984; Jothi *et al* 1982; Brakaspathy *et al* 1985; Brakaspathy and Surjit Singh 1985), we have employed the CNDO/force method to evaluate geometrical parameters and force fields of various complex polyatomic molecules. We thought it of interest to use this method for geometry optimization of the dimeric species of acetonitrile.

Dedicated to Professor Sadhan Basu on the occasion of his 65th birth anniversary.

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2. Computational details

CNDO/force calculations are performed using a modified form (Kanakavel *et al* 1976) of the computer program CNINDO of Pople and Beveridge (1970). The optimization is carried out using the 'steepest descent method' proposed by Pulay and Torok (1973). In this method, the forces acting on each atom are computed for the experimental geometry of the molecule by analytically differentiating the total energy calculated using CNDO wave functions with respect to nuclear coordinates. The forces are then allowed to relax towards equilibrium by a small distance say 0·01 Å. The forces are computed again for the new geometry. This process is repeated till the norm of the forces reaches the preset value. During iterations, both the energy and the norm of the forces keep decreasing and when the norm of the forces is less than 0·001, it is found that further iterations do not alter the geometry of the molecule. This geometry is taken as the optimized geometry. All the calculations are done on an IBM 370/155 computer.

3. Results and discussion

The optimized geometry of the acetonitrile monomer is given in table 1. The geometrical parameters obtained in this method agree well with the experimental (Matsumura *et al* 1962) and *ab initio* values (Lien *et al* 1983; Edgecombe and Boyd 1983). The total energy of −27·89975 a.u. for acetonitrile monomer calculated using the CNDO/force method is better than the reported CNDO/2 value of −26·0869 a.u. (Gramstad and Tjessem 1977). There is a slight increase in C–C and C≡N bond lengths when compared to experimental values. However, the total energy calculated using this method is found to be higher than the STO-3G *ab initio* value (−130·27154 a.u.). Such discrepancies in energies calculated by *ab initio* and semiempirical methods have been already reported in literature (Pople and Beveridge 1970).

Four different structures are considered for the acetonitrile dimer viz, displaced anti-parallel, anti-parallel, hydrogen bonded and head-to-tail (figure 1). The geometry optimization is carried out in two stages. In the first stage, the intermolecular distance is optimized whereas in the second stage iterations are carried out on the whole species. For the displaced anti-parallel dimer, the displacement of the two molecules (l) was also optimized before optimizing the complete geometry. The variations of energy with

Table 1. Optimized geometry[a] of acetonitrile monomer.

Description	CNDO/ force	Experimental[b]	STO-3G[c]	3-21G[d]
R_{C-C}	1·4213	1·4583	1·486	1·457
$R_{C\equiv N}$	1·1920	1·1571	1·154	1·139
R_{C-H}	1·1187	1·1036	1·088	1·083
∠HCC	110·85	109·45	109·9	110·1
Total energy	−27·89975	—	−130·27154	−131·19060

[a] bond lengths in Å, bond angles in degrees and energies in atomic units; [b] Matsumura *et al* 1962; [c] Lien *et al* 1983; [d] Edgecombe and Boyd 1983.

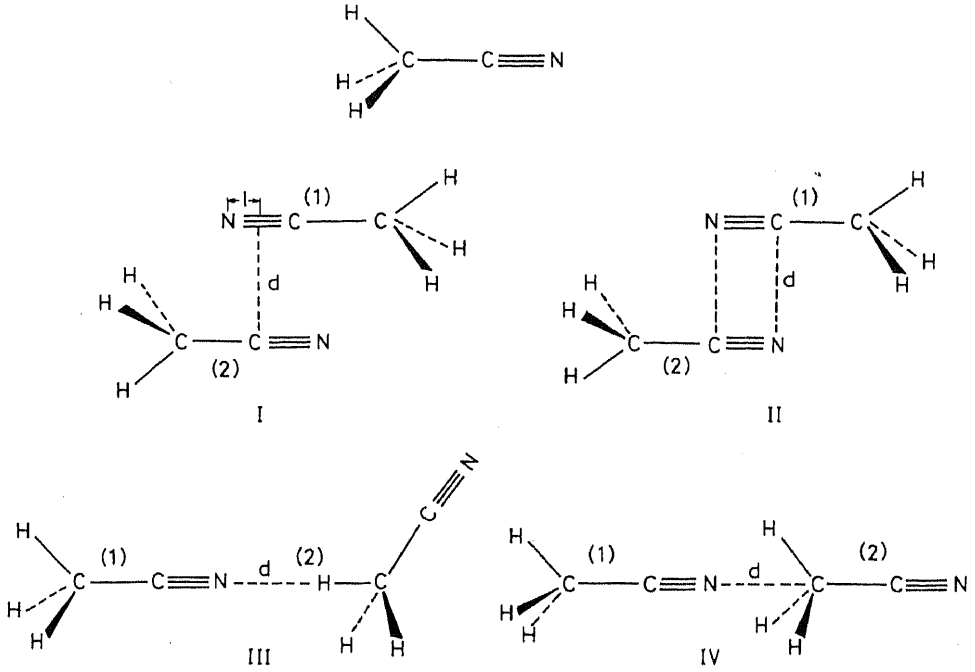

Figure 1. Structure of acetonitrile monomer and various dimers; displaced anti-parallel dimer (**I**), anti-parallel dimer (**II**), hydrogen bonded dimer (**III**) and head-to-tail dimer (**IV**).

intermolecular distance (d) and displacement (l) for the dimers considered are given in figure 2. The optimized geometries of the four dimers are given in table 2.

It is noticed from table 2 that the displaced anti-parallel dimer has the lowest energy (−55·83672 a.u.). The intermolecular and the displaced distances are 2·2034 Å and 0·8021 Å respectively. The energy of the displaced dimer is better than the reported CNDO/2 value of −55·7926 a.u. (Gramstad and Tjessem 1977). The reported intermolecular and displaced distances are 2·0 Å and 0·8 Å respectively. The interaction through the π–bond of the nitrile group increase the C≡N bond length. This may be noticed by the increase in the CN bond length from 1·1920 Å for the monomer to 1·2041 Å for the dimer. The C–C and C–H bond lengths also get affected as shown in table 2. The anti-parallel dimer has the next best energy with the value of −55·80864 a.u. Since the interaction is through C–N dipoles, both the nitrile groups of the dimer are affected to the same extent. This is evident from the symmetrical increase in CN bond lengths from 1·1920 Å to 1·1953 Å. The intermolecular distance for this dimer is calculated to be 2·1991 Å. The C–C and C–H bond lengths are also affected accordingly. The hydrogen-bonded dimer has an energy of −55·80512 a.u; the bonded CN bond length changes from 1·1920 to 1·1921 Å while the nitrile group of the other part of dimer decreases to 1·1911 Å. The bonded C–H bond length increases from 1·1187 Å to 1·1292 Å whereas the other C–H and C–C bond lengths show little changes. The intermolecular distance (N . . . H) is found to be 1·7914 Å. The head-to-tail model has the highest energy (−55·80293 a.u.) among the four models. The intermolecular distance is calculated to be 2·2940 Å whereas the *ab initio* (Dagino *et al* 1976) value is

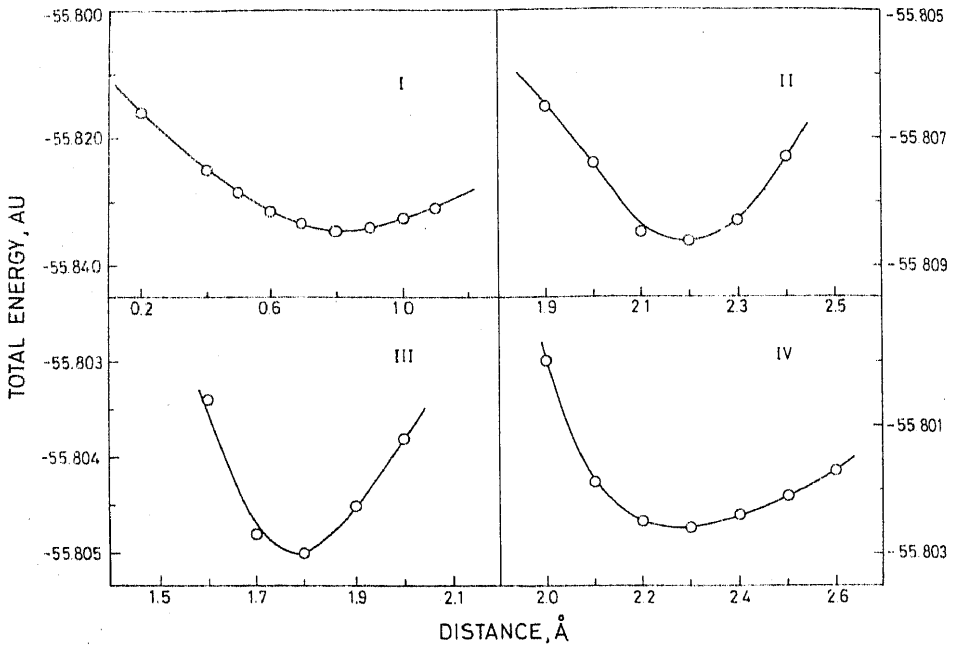

Figure 2. Variation of energy with displacement (l) for displaced anti-parallel structure (I) with $d = 2{\cdot}2$ Å and with intermolecular distance (d) for anti-parallel (**II**), hydrogen-bonded (**III**) and head-to-tail (**IV**) structures respectively.

Table 2. Optimized geometries[a] of acetonitrile dimer.

Description	Displaced anti-parallel	Anti-parallel	Hydrogen bonded	Head-to-tail
*R*C–C (1)	1·4301	1·4228	1·4211	1·4217
*R*C–C (2)	1·4301	1·4228	1·4209	1·4257
*R*C≡N (1)	1·2041	1·1953	1·1921	1·1930
*R*C≡N (2)	1·2090	1·1953	1·1911	1·1914
*R*C–H_1 (1)	1·1204	1·1206	1·1181	1·1187
*R*C–H_2 (1)	1·1204	1·1190	1·1186	1·1187
*R*C–H_3 (1)	1·1204	1·1190	1·1186	1·1187
*R*C–H_1 (2)	1·1204	1·1205	1·1292	1·1193
*R*C–H_2 (2)	1·1204	1·1190	1·1186	1·1192
*R*C–H_3 (2)	1·1204	1·1190	1·1186	1·1192
*R*N . . . x (d)	2·2034	2·1991	1·7914	2·2940
*R*C . . . π (1)	0·8021			
Total energy	−55·83672	−55·80864	−55·80512	−55·80293
Bonding energy	−5·19062	−5·16253	−5·15902	−5·15682
$-\Delta H_S$	23·35	5·74	3·53	2·15

[a]stabilization energies in kcal mol^{-1} other units as in table 1. Bond angles were also calculated but are not included here for the sake of brevity. The data can be obtained from the authors on request.

[b] (1) and (2) in parentheses denote molecules 1 and 2, respectively as shown in figure 1.

3·28 Å. It is generally observed that the intermolecular distance calculated by *ab initio* is higher than that calculated by semiempirical methods in associated species (Murthy *et al* 1970). The bonded CN bond length increases to 1·1930 Å while the other nitrile bond decreases slightly to 1·1914 Å. The C–C and C–H bond lengths experience slight increases. In all these models, it is noticed that interaction through the CN bond invariably weakens the bond. These results justify the decrease in $\nu C{\equiv}N$ from the gas to the liquid states (2267·0 to 2252·5 cm^{-1}) (Thomas and Orville-Thomas 1969).

The stabilization energy ($-\Delta H_S$) at the energy minimum for all the four models is calculated using the CNDO/force method. The displaced anti-parallel model has the highest stabilization energy of 23·35 kcals.$mole^{-1}$. This stabilization energy is better than the value calculated from the reported energies of monomer and dimer acetonitrile using CNDO/2 method (13·55 kcal mol^{-1}) (Gramstad and Tjessem 1977). The anti-parallel dimer has the next higher stabilization energy (5·74 kcal mol^{-1}) which is higher than the CNDO/2 value (4·49 kcal mol^{-1}) (Paoloni and Dagnino 1975) as well as the *ab initio* value (1·6802 kcal mol^{-1}). (Dagnino *et al* 1976). The stabilization energy of the hydrogen bonded dimer is calculated to be 3·53 kcal mol^{-1}. The head-to-tail dimer has the least stabilization energy (2·15 kcal mol^{-1}). The reported CNDO/2 and ab initio values for the head-to-tail dimer are 2·39 kcal mol^{-1}. (Paoloni and Dagnino 1975) and 1·2094 kcal mol^{-1} (Dagnino *et al* 1976) respectively.

It may be noticed from the above discussion that the stabilization energies of the dimers as well as the binding energies of various species calculated by the CNDO/force method are not comparable to the *ab initio* values. However, comparative studies of these energies can well be utilised to predict the most stable conformers. Further, the CNDO/force values are found to be better than the CNDO/2 values reported earlier. The geometrical parameters obtained are comparable with the previous results.

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