A Potential Function for Intermolecular Interaction in the Acetonitrile Dimer Constructed from ab Initio Data

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Following preliminary calculations that revealed the need to consider electron correlation and to avoid the basis set superposition error, MP2/6-311+G* calculations were carried out in order to determine the energy of intermolecular interaction for 336 configurations of dimeric acetonitrile, to which an analytic potential function was fitted. The minimum of the function (-20.8 kJ mol^{-1}) corresponds to an antiparallel geometry with C_{2h} symmetry where the C−H bonds in the symmetry plane are oriented toward the nitrogen atom of the other molecule. Rotating the methyl group 60° affords a transition state with an energy 1.7 kJ mol^{-1} above the minimum. Several minima for the trimer and tetramer were also characterized that revealed a tendency of the molecules to retain the antiparallel arrangement.

1. Introduction

Successful simulation of molecular behavior by molecular dynamics or Monte Carlo methods[1] requires the use of a potential function accurately describing molecular interactions. As a step toward an analytical description of interactions in solutions of salts and polar solutes in the polar solvent acetonitrile, in this paper we present a potential function that describes the energy of interaction between two acetonitrile molecules. X-ray and neutron diffraction studies[2−6] that have satisfactorily elucidated the intramolecular geometry of acetonitrile in the liquid state have also shown that, unlike water, liquid acetonitrile is relatively unstructured, the orientation of any given molecule being correlated only with those of its immediate neighbors.

Existing potential functions for acetonitrile are of either of two types: three-center functions that forsake explicit treatment of the hydrogen atoms[7,8] in order to expedite simulations and functions that explicitly include all six atoms.[9−11] Of the latter, at least one has been successfully applied to liquid-phase simulations.[9,12,13] However, all classical simulations of acetonitrile[7−9,12−15] carried out to investigate structural or dynamic issues in the liquid or gas phase have hitherto used potential functions obtained empirically or semiempirically on the basis of liquid-phase data or have employed[16] a method, as reverse MC, that avoids the use of a potential function by using experimental data. The proposed potential function presented here was fitted to the results of MP2/6-311+G* ab initio calculations for over 300 points on the potential surface of the acetonitrile dimer.

2. Methods

This work comprised four stages: (1) preliminary ab initio calculations intended to select an appropriate basis set and computational level; (2) calculation of the interaction energy for a large number of configurations of the acetonitrile dimer, spanning the potential surface as thoroughly as possible; (3) optimization of the parameters of a preset analytical function so as to fit the ab initio data; and (4) a series of tests (described under Results) intended to check that the function obtained would behave as expected.

2.1. Selection of Basis Set and Computational Level. Ab initio calculations of energies of intermolecular interaction must be especially accurate because the energies to be calculated are generally no greater than a few tens of kJ mol^{-1}. The straightforward "supermolecule" method[17−19] calculates the energy of interaction between a molecule A and a molecule B, ΔE_{AB}, simply as the difference between the energy of the dimer and that of the two isolated molecules,

$$\Delta E_{AB} = E_{AB}(AB) - E_A(A) - E_B(B) \qquad (1)$$

where the arguments in parentheses indicate the basis set being used. The basis set superposition error[19−21] (BSSE) is usually avoided by using the counterpoise[22] (CP) method, where the energies of both the dimer and the monomers are calculated by using the full basis set for the dimer, which lengthens computations:

$$\Delta E_{AB} = E_{AB}(AB) - E_A(AB) - E_B(AB) \qquad (2)$$

We selected the basis set and computational level to be employed from preliminary calculations at the SCF and MP2 levels, using eqs 1 and 2 with three different basis sets (6-311++G**, 6-311+G*, and 6-31G**). All ab initio calculations were performed by using the program package GAUSSIAN-94.[23]

2.1.1. Acetonitrile Monomer. Table 1 lists the geometries and miscellaneous parameter values calculated for the acetonitrile monomer, together with their experimental counterparts. Calculated geometries were obtained under the constraint of C_{3v} symmetry. Experimental geometries are based on the results of microwave spectroscopy[24] and X-ray and neutron diffraction studies of liquid acetonitrile;[2−6] the liquid-phase and gaseous-phase results are quite similar, except for a slightly lengthened C−N distance in the liquid phase.

At a given computational level, the size of the basis set hardly affected the calculated geometry, except for minor variations in bond lengths. Taking electron correlation into account significantly lengthened the C−N distance but had little effect on the other geometric parameters. In general, however, they approached the experimental results for liquid acetonitrile.

As expected, the dipole moment was overestimated by SCF calculations; the near coincidence of the experimental value[25]

TABLE 1: Properties of Acetonitrile Calculated ab Initio, and the Corresponding Experimental Values[a]

	6-311++G**		6-311+G*		6-31G**		
	HF	MP2	HF	MP2	HF	MP2	expt[b]
r_{C-N}	1.1296	1.1737	1.1295	1.1738	1.1348	1.1795	1.17 (1.157)
r_{C-C}	1.4652	1.4625	1.4655	1.4624	1.4668	1.4621	1.46 (1.458)
r_{C-H}	1.0916	1.0916	1.0813	1.0907	1.0817	1.0874	1.087 (1.102)
θ_{C-C-H}	109.6	109.9	109.8	110.0	109.8	110.0	109.8 (109.5)
μ	4.20	3.88	4.18	3.95	4.07	3.71	3.92[c]
$\alpha_{\|}$	36.96	36.71	34.92	36.71	32.11	32.60	40.90[d]
$\alpha_{\perp}$	19.82	20.25	19.30	20.73	17.17	17.33	25.17[d]
α	25.53	25.74	24.51	25.73	22.15	22.42	28.86

[a] Distances in angstroms and angles in degrees, dipole moment in debye, and polarizabilities in au. [b] Geometry for the liquid phase,[3] with values obtained by microwave spectroscopy[24] in parentheses. [c] From ref 25. [d] From anisotropy and mean polarizability[26] data.

with the HF/6-31G** value was probably accidental. All MP2 calculations provided smaller dipole moments, those obtained with 6-311++G** and 6-311+G* being within 1.1% of the experimental value. As expected, all calculated dipole–dipole polarizabilities were farther from the experimental value,[26] with errors greater than 10%; in this case, MP2 provided values only marginally better than those of SCF.

Overall, the data in Table 1 suggest that, although a highly accurate description of the acetonitrile monomer requires using a good basis set (possibly better than any used in this work), computation time may be saved by dispensing with the use of polarization functions and diffuse functions for hydrogen atoms since their inclusion seems to hardly affect the results.

2.1.2. Acetonitrile Dimer. At this preliminary stage of the study, the energy of intermolecular interaction of the acetonitrile dimer was calculated by using both eq 1 and eq 2 for dimer configurations of C_{2h} symmetry similar to the minimum-energy configuration reported by Böhm et al.:[9] the two molecules were antiparallel, with the central carbon atoms C and C′ related by a C−N−C′ angle of 80°. Calculations were carried out at several C−C′ distances, with intramolecular geometry corresponding to the configuration derived from experimental studies of liquid acetonitrile.[3]

All SCF calculations underestimated the energy of interaction, even when BSSE was not avoided (Table 2). The differences between the SCF and MP2 results show that electron correlation contributes about 20% of the energy of interaction in configurations near the minimum and even more when the two molecules are closer together. The MP2 values obtained by the counterpoise method were fairly close both to those obtained from the semiempirical potential[9] of Böhm et al. and, for C−C′ distances of 3.3−3.5 Å, to reported values[9−11,27] of the energy of

interaction at the minimum, which ranges from −21.8 to −23.0 kJ mol⁻¹. When BSSE was not avoided, the MP2 results considerably overestimated the energy of interaction. These results were considerably better with diffuse functions for heavy atoms than without them (no doubt as a result of a more accurate description of the space between the two molecules); however, as with the monomer, including diffuse and polarization functions for the hydrogen atoms had little effect.

In view of the above results, all further ab initio calculations were performed by the MP2 method, using 6-311+G* basis set.

2.2. Exploration of the Potential Surface. To save computation time, it is customary in exploring the potential surfaces of dimers to assume that the monomers retain the geometries they have in isolation.[1,26] In acetonitrile, this approximation ignores the existence of an IR band at 360 cm⁻¹ that suggests the possibility of C−C−N bending as the result of interaction between neighboring monomers.[28] Preliminary calculations were therefore carried out so as to determine whether this was an oversimplification; thus, the geometry of the dimer in its minimum-energy conformation was calculated by optimizing (a) all coordinates, (b) intermolecular coordinates (with intramolecular coordinates fixed at the values obtained for the isolated monomer using the same computational level and basis set), and (c) intramolecular coordinates (with intermolecular coordinates fixed at the values obtained in step b). In all three cases, once the minimum-energy geometry had been determined, the interaction energy was recalculated by using the counterpoise method to avoid BSSE.

The geometry calculated with complete optimization is a structure of C_{2h} symmetry where the axes of the monomers lie in the symmetry plane and the hydrogen atoms in this plane are oriented toward the nitrogen atom of the other molecule (Table 3). The monomers lose their C_{3v} symmetry through very slight C−C−N bending. The energy of interaction for this geometry is −21.02 kJ mol⁻¹ and thus similar to reported values.[9−11,27]

The geometry calculated with fixed intramolecular coordinates differs only slightly from the completely optimized geometry (Table 3); the main differences are the linearity of the molecular axes and the equivalence of the three hydrogen atoms in each molecule. When the intermolecular coordinates thus calculated were fixed and the intramolecular coordinates optimized, the parameter values obtained (Table 3) were, with one minor exception, intermediate between those obtained with complete optimization and by fixing the intramolecular geometry. The energies of interaction provided by all three procedures were within 0.5 kJ mol⁻¹ of one another.

TABLE 2: Interaction Energies (kJ mol⁻¹) Calculated ab Initio, with and (in Parentheses) without CP, for Acetonitrile Dimers with Antiparallel Molecules (with C_{2h} Symmetry and the H Atoms in the Symmetry Plane Pointing toward the N of the Other Molecule), for Several Distances between the Central Carbon Atoms[a]

R_{C-C} (Å)	6-311++G**		6-311+G*		6-31G**		Böhm et al.[b]
	HF	MP2	HF	MP2	HF	MP2	
2.9	13.58	−3.06	14.08	−1.94	13.45	0.02	
	(12.02)	(−12.47)	(12.42)	(−11.77)	(8.63)	(−12.17)	5.91
3.1	−5.57	−16.28	−5.18	−15.79	−5.26	−13.82	
	(−6.77)	(−23.54)	(−6.55)	(−23.36)	(−9.69)	(−23.55)	−17.26
3.3	−13.77	−20.60	−13.44	−20.43	−13.11	−18.46	
	(−14.76)	(−26.29)	(−14.62)	(−26.41)	(−17.23)	(−26.39)	−22.67
3.5	−16.44	−20.70	−16.17	−20.73	−15.59	−18.78	
	(−17.30)	(−25.25)	(−17.20)	(−25.53)	(−19.36)	(−25.27)	−20.32
3.7	−16.49	−19.05	−16.29	−19.20	−15.58	−17.33	
	(−17.25)	(−22.70)	(−17.18)	(−23.06)	(−18.92)	(−22.55)	−20.22
3.9	−15.43	−16.85	−15.28	−17.07	−14.52	−15.30	
	(−16.08)	(−19.79)	(−16.05)	(−20.16)	(−17.36)	(−19.38)	−17.77

[a] Intramolecular geometry was fixed in the configuration deduced from experimental studies of liquid acetonitrile.[3] [b] Reference 9.

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TABLE 3: Geometry of the Acetonitrile Dimer As Given by MP2/6-311+G* Calculations (a) with Complete Optimization, (b) with Intramolecular Geometry Fixed, and (c) Optimizing Intramolecular Geometry with Intermolecular Geometry Fixed in the Configuration Determined by Procedure b[a]

	a	b	c
R_{C-C}	3.3462	3.3302	3.3302
Θ_{N-C-C}	79.7	80.2	80.2
$\varphi_{N-C-C-N}$	180.0	180.0	180.0
r_{C-N}	1.1743	1.1738	1.1742
r_{C-C}	1.4610	1.4624	1.4608
θ_{C-C-N}	179.3	180.0	179.8
r_{C-H}	1.0909	1.0907	1.0909
θ_{C-C-H}	109.0,110.0	110.0	109.0, 110.0
$\Delta E(CP)$	−21.02	−20.63	−20.92

[a] The interaction energy of the minimum was in each case recalculated with CP.
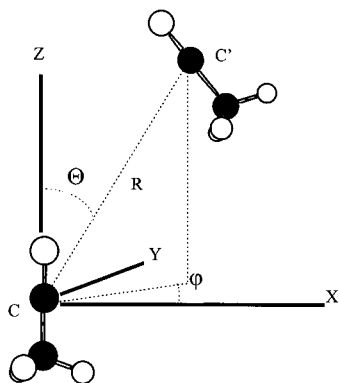
Figure 1. Definition of the coordinates R, Θ, and φ used in the definition of acetonitrile dimer configurations.

In view of these results, the potential surface of the dimer was explored by keeping the intramolecular geometry fixed at the values listed in Table 1 (MP2/6-311+G* calculations). The intermolecular coordinates used were the spherical coordinates for the central carbon atom of one molecule, C′, relative to that of the other (R, Θ, and φ as in Figure 1, where the xz plane contains one of the hydrogen atoms of the molecule at the origin) and the Euler angles describing the orientation of the former molecule. The energy of intermolecular interaction was calculated for configurations with C′ at up to seven different points on each of 17 rays from the origin: those defined by $\varphi = 0$, 30, or 60° and $\Theta = 30, 60, 90, 120,$ or 150°, in addition to the rays $\Theta = 0$ and 180° with $\varphi = 0$. For each point, at least two sets of Euler angles for the C′ molecule were randomly chosen from a finite set spanning the whole of orientation space discretely but uniformly. In addition, the energy of interaction was also calculated for a number of other configurations close to the minimum so as to ensure a good fit of the potential function in this region.[29] The overall number of configurations used was 357, of which those with energies of interaction exceeding 100 kJ mol^{-1} were discarded, leaving a final sample of 336 configurations. At each point, the interaction energy was corrected for BSSE by using the CP method.

2.3. Fitting the Potential Function. The analytical function fitted to the ab initio data obtained as described above contains the distances between atoms of different molecules as independent variables and assumes that the contributions of the various atom pairs, E_{ij}, are additive:[1,26]

$$\Delta E_{AB} = \sum_{i \in A} \sum_{j \in B} E_{ij} \tag{3}$$

where each E_{ij} is a function depending on r_{ij} (the distance

TABLE 4: Atomic Charges Calculated by Mulliken Analysis and by Optimizing Point Charges for Best Approximation of the Molecular Electrostatic Potential Calculated ab Initio Using the Basis Set 6-311+G*[a]

	Mulliken		fitted	
	HF	MP2	HF	MP2
C	0.372	0.349	0.481	0.475
N	−0.389	−0.310	−0.532	−0.494
CM[a]	−0.850	−0.933	−0.479	−0.552
H	0.289	0.298	0.177	0.190
μ (D)	3.88	3.09	4.18	3.95

[a] CM indicates the methyl group carbon.

between atom i of molecule A and atom j of molecule B). One of the analytical expressions usually employed for this purpose is of the *exponential* $+ R^{-6}$ type, where the exponential part is intended to represent the repulsive part of the potential and the R^{-6} term the dispersion contributions to the interaction energy, in addition to a term for Coulombic interaction between point charges. Thus, for each pair ij

$$E_{ij} = A_{ij} \exp(-B_{ij} r_{ij}) - C_{ij}/r_{ij}^{6} + D_{ij}/r_{ij} \tag{4}$$

Because of the significance of the electrostatic term for a polar molecule such as acetonitrile, it may be unwise to obtain D_{ij} from a global fit, so we adopted a different strategy to ensure acceptable values for these parameters. Before the expression defined by eqs 3 and 4 was fitted to the ab initio data, D_{ij} values were calculated as the products of point charges considered to be located on atoms i and j and to be unaffected by changes in the dimer configuration. Although the usual way of calculating the charge on an atom is by Mulliken analysis,[30] Mulliken charges generally do not allow accurate reproduction of electrostatic interactions; indeed, the dipole moment calculated from Mulliken charges, 3.09 D, differs by 0.8 D from the experimental value,[25] 3.92 D (Table 4). We therefore obtained our point charges as those affording the molecular electrostatic potential (MEP) that best fitted the MEP obtained from MP2/6-311+G* calculations for the minimum-energy configuration[31,32] under the constraint that the resulting dipole moment must equal the value provided by the MP2/6-311+G* calculations, 3.95 D (less than 0.04 D different from the experimental value).

Once D_{ij} was obtained, A_{ij}, B_{ij}, and C_{ij} were calculated by optimizing the expression defined by eqs 3 and 4. The optimization procedure was a Levenberg−Marquardt least-squares method,[33] appropriate constraints being imposed to ensure physical behavior of the resulting function. To facilitate fitting in the neighborhood of attractive configurations, data points were given weights

$$w = 1 + 100 \exp(-\Delta E/kT) \tag{5}$$

where k is the Boltzmann constant, T the temperature (taken to be 298 K), and ΔE the difference between the interaction energy for the configuration considered and that for the most attractive configuration in the sample, −20.6 kJ mol^{-1}.[34]

The final parameters used in the potential function are listed in Table 5. As can be seen from Figure 2, the overall quality of the fit was good, and only for repulsive configurations were the deviations significant (reflecting the effect of the weighting function).

3. Results

3.1. Contour Maps. To check whether the fitted potential function behaved reasonably well for configurations not included

TABLE 5: Parameters of the Analytic Function (Eqs 3 and 4) Fitted to the MP2(CP)/6-311+G* Data for 336 Configurations of the Acetonitrile Dimer[a]
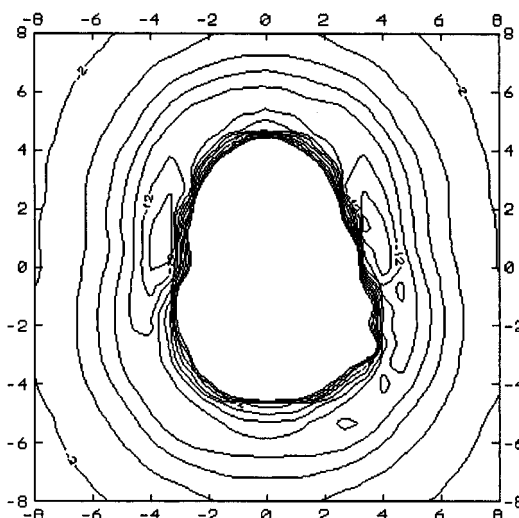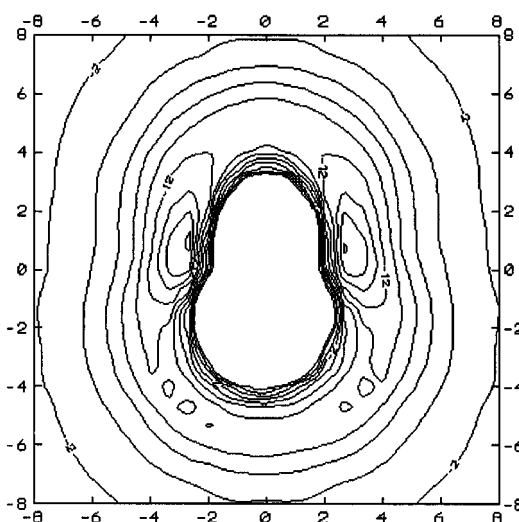
		A_{ij}	B_{ij}	C_{ij}	D_{ij}
C	C	0.189660e+03[b]	0.936 73	0.633536e+04	0.31365e+3
C	N	0.137310e+06	3.123 52	0.109067e+05	−0.32632e+3
C	CM	0.564358e+06	3.936 04	0.262901e+04	−0.36416e+3
C	H	0.115670e+04	2.323 24	−0.174261e+03	0.12561e+3
N	N	0.243127e+06	3.809 90	−0.130444e+04	0.33951e+3
N	CM	0.249670e+05	2.585 22	−0.188654e+04	0.37887e+3
N	H	0.622787e+05	3.651 97	0.218886e+04	−0.13068e+3
CM	CM	0.121153e+06	2.776 05	0.308785e+05	0.42279e+3
CM	H	0.183749e+09	9.888 21	−0.184078e+04	−0.14583e+3
H	H	0.108103e+05	4.397 95	0.308306e+02	0.50303e+2

[a] CM indicates the methyl group carbon. Units: A_{ij}, kJ mol^{-1}; B_{ij}, Å^{-1}; C_{ij}, kJ mol^{-1}Å;[6] D_{ij}, kJ mol^{-1}Å. [b] Read as 0.189660×10^3.
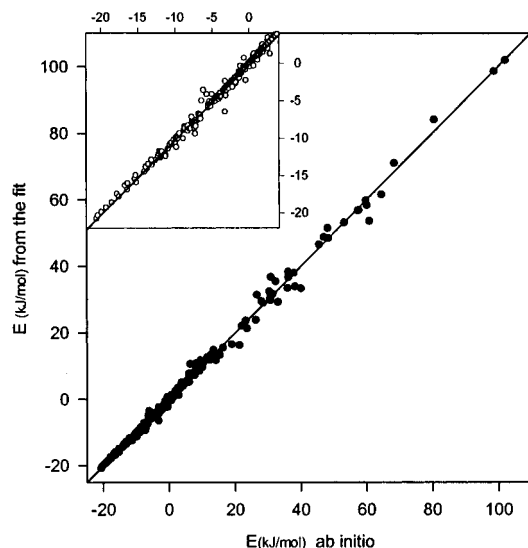
Figure 2. Correlation between the energies of acetonitrile dimer configurations calculated ab initio (*x* axis) and the corresponding values of the fitted potential function.

Figure 3. A contour map of the fitted potential in the plane $y = 0$.

Figure 4. A contour map of the fitted potential in the plane $y = 2.0$ Å.

Figure 5. A contour map of Böhm et al.'s[9] potential in the plane $y = 0$.

in the sample, isoenergetic contour maps were obtained by using the program MOLSIM[35] as follows: one of the molecules was positioned with its center of mass at the origin, its axis along the *z* axis (with the N atom in the positive region), and one of its hydrogen atoms in the *xz* plane. A contour map in any given plane was obtained by (a) calculating, for each point of a lattice in that plane, the minimum value of the fitted potential function when the second molecule was placed with its center of mass at the lattice point and allowed to rotate around this point and then (b) by interpolating between the lattice points. Figures 3 and 4 show the results for the planes $y = 0$ and 2 Å. The contours are satisfactorily smooth, with no irregularities. There is a strongly attractive region relatively close to the center of mass that corresponds to geometries similar to that of the minimum. The nitrogen atom and methyl group are also associated with moderately attractive regions, while the small additional potential well near the methyl group arises from interaction between the out-of-plane methyl hydrogens and the nitrogen atom of a molecule placed in this region. Very similar contour maps were obtained by using the semiempirical potential function of Böhm et al.[9] (Figures 5 and 6), except that the surface obtained from the potential of Böhm et al. was always more attractive.

3.2. Stationary Points. Figure 7 shows the geometries of the most important stationary points of the potential function, which were located and classified according to the number of negative eigenvalues of the Hessian, using the program ORI-
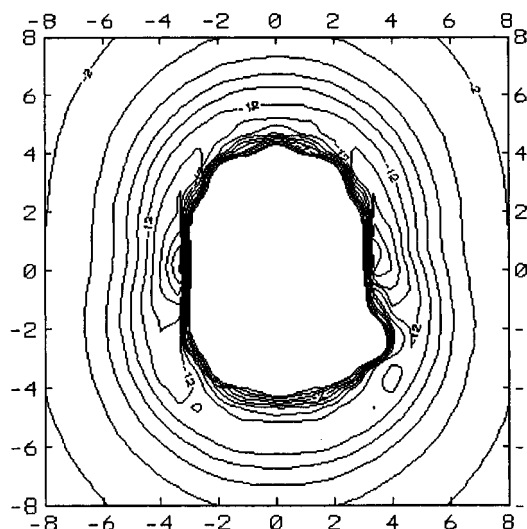
ENT.[36] The only minimum observed corresponds to a configuration where the two molecules are antiparallel and the hydrogen atoms in the plane defined by their axes pointing toward the nitrogen atom of the other molecule. This config-
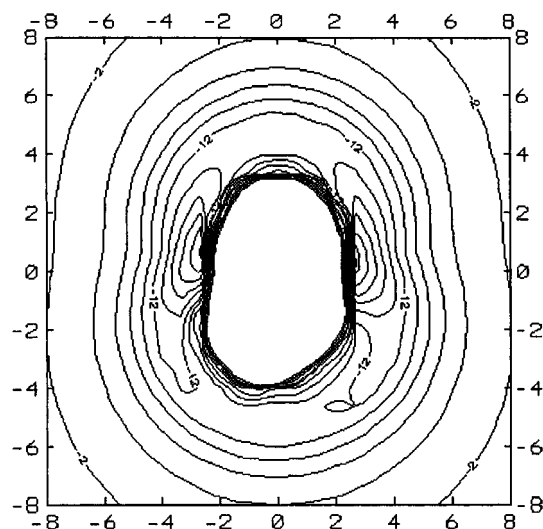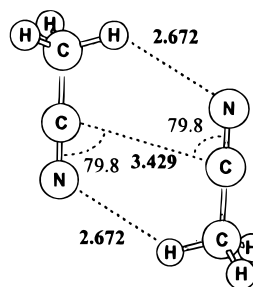
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Figure 6. A contour map of Böhm et al.'s[9] potential in the plane $y = 2.0$ Å.

C_{2h} **Minimum. (ΔE=-20.81 kJ·mol^{-1})**

Saddle point. (ΔE=-19.09 kJ·mol^{-1})

C_{2h} **Order 2. (ΔE=-17.38 kJ·mol^{-1})**

Head-to tail. Order 2. (ΔE=-9.14 kJ·mol^{-1})

Figure 7. Several stationary points of acetonitrile dimer. R is in angstroms and angles in degrees.

uration is quite similar to the minimum-energy geometry obtained from ab initio calculations at a fixed intramolecular geometry (Table 3); the difference (notably the lengthening of about 0.10 Å in the C−C′ distance) can probably be ascribed not so much to poor fit as to the ab initio geometries of Table 3 being obtained without using the full basis set for the dimer in monomer calculations in order to avoid BSSE. (Since BSSE results in overestimation of the interaction energy, it could have shortened the intermolecular distance.) The energy of interaction of the minimum of the potential function, −20.81 kJ mol^{-1}, is virtually the same as the ab initio value obtained with the CP method for any of the optimized geometries shown in Table 3. Lambert et al.[27] estimated the energy of interaction of the acetonitrile dimer to be −21.8 kJ mol^{-1}, and the semiempirical potential of Böhm et al.[9] provided a value of −23.1 kJ mol^{-1} for a structure very similar to the minimum-energy structure shown in Figure 7. The relative accuracies of these three slightly different values cannot be evaluated until a reliable value for the gas-phase interaction becomes available.
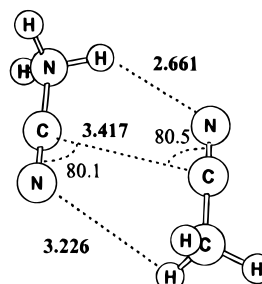
Rotating one of the methyl groups by 60° from the minimum-energy configuration leads to a transition state. Both its geometry and its energy relative to the minimum (about 1.7 kJ mol^{-1}) are similar to those for the transition state predicted by the semiempirical potential function of Böhm et al.[9] Rotating both methyl groups by 60° from the minimum-energy configuration gives rise to a second-order transition state with an interaction energy of 3.4 kJ mol^{-1} relative to the minimum (whereas this configuration corresponds to the minimum of one of the potentials of Popelier et al.,[11] for which our minimum-energy geometry is a second-order transition state).

Since the potential of Popelier et al.[11] predicts an energy minimum for a linear, head-to-tail configuration for which there appears to be a certain amount of experimental evidence,[37] we also sought stationary points of this kind; however, the only one we found was a second-order transition state with an energy of 11.7 kJ mol^{-1} relative to the minimum.
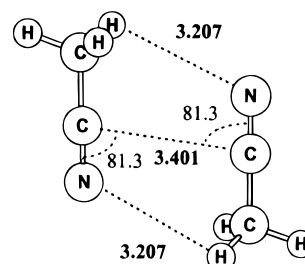
Table 6 lists the frequencies of the intermolecular vibration modes for the three stationary points of lower energy, as calculated by using the fitted potential function and HF and MP2 ab initio data. All these frequencies are below the lowest intramolecular frequency (viz. 360 cm^{-1} for the C−C−N bending mode).[28] The only intermolecular vibration frequencies to have been detected experimentally,[38] two bands at 124 and 105 cm^{-1}, are quite consistent with the highest frequencies
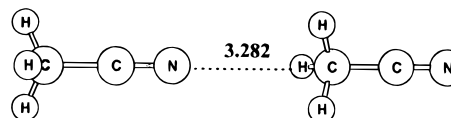
predicted by the MP2 calculations. Almost all the frequencies predicted by the fitted potential function for the minimum-energy structure are lower than the MP2 results and very similar to them but higher than the corresponding SCF values; the discrepancies are likely to be due to the potential-fitting process having slightly smoothed the neighborhood of the minimum somehow, although, again, it should be borne in mind that the MP2 geometry was obtained without any steps being taken to avoid BSSE and frequencies may be affected by curvature changes in the surface arising from the omission.[21] As regards the other structures, the number of imaginary frequencies predicted by the *ab initio* results confirms the orders of these stationary points; the differences, however, are greater.

3.3. Results for the Trimer and Tetramer. As a further application of the fitted potential function, we used it for a cursory investigation of the structure of the acetonitrile trimer.

TABLE 6: Frequencies (cm⁻¹) of the Intermolecular Vibrations of the Acetonitrile Dimer in Its Three Stationary Point Configurations of Lowest Interaction Energy, As Calculated ab Initio and Using the Potential Function Obtained in This Work[a]

	function	HF	MP2
mínimum	106, 94, 80, 78, 62, 32	80, 80, 69, 68, 62, 40	119, 107, 77, 77, 68, 35
saddle	90i, 102, 80, 78, 53, 33	44i, 90, 70, 68, 67, 42	24i, 116, 105, 79, 76, 37
order 2	90i, 89i, 82, 81, 45, 34	48i, 46i, 71, 68, 66, 44	75i, 72i, 70, 66, 65, 43

[a] The letter *i* denotes imaginary frequencies.

TABLE 7: Main Geometric Parameters of Four Acetonitrile Trimer Configurations of Locally Minimum Energy According to the Potential Function Obtained in This Work[a]

	$R(i,j)^a$	$\phi(i,j)^b$	ΔE
M1	4.79, 3.47, 3.37	56.7, 144.0, 133.9	−39.33
M2	6.48, 3.52, 3.52	2.0, 177.3, 177.3	−38.38
M3	3.55, 4.72, 5.01	170.1, 96.8, 86.5	−37.81
M4	4.82, 4.82, 4.82	120.0, 120.0, 120.0	−37.55

[a] Distances between centers of mass ((1,2), (1,3), (2,3)). [b] Angles between molecular axes ((1,2), (1,3), (2,3)).

The four structures of locally minimum energy found (there may well be others that we missed) are listed in Table 7 and illustrated in Figure 8. Most showed a tendency to maintain the antiparallel geometry of the dimer. The most stable was M1; however, all others had quite similar energies, and even the least attractive structure possessed an energy only 2 kJ mol⁻¹ higher than that for M1. We can compare our results for the trimer with those reported by Popelier and Stone.[11] These authors obtained three different minima for the acetonitrile trimer that roughly correspond to our three minima of larger interaction energy. The structures are quite similar, with only minor differences. The interaction energies for the minima are also similar; however, all the structures obtained from our potential are more attractive, the differences being smaller than 5 kJ mol⁻¹. Böhm's potential function provided a similar set of structures with virtually the same characteristics; however, the interaction energy was greater than that obtained from our potential, consistent with the behavior obtained for the dimer.

We also studied potential minima for the tetramer. In previous work,[11,39] two different minima were characterized. Al-Mubarak et al.[39] obtained two different structures by employing Böhm's potential[9] in such a way that the antiparallel alignment of the dipoles was favored. Also, Popelier and Stone[11] started from these two structures and found two different minima in which dipole alignment was not so obvious. These authors also characterized one of the minima of ref 39 as a saddle point.

The three minima with the highest interaction energy are shown in Figure 9. As can be seen, they also exhibit a strong tendency to mantain an antiparallel arrangement of the molecules that favors dipole interaction. The most attractive configuration corresponds to one of the structures obtained by Al-Mubarak et al.[39] using Böhm's potential function. We characterized another structure (M2) with an interaction energy only 2 kJ mol⁻¹ smaller than that for M1; this new structure also enables antiparallel alignment of the dipoles.

The other structure proposed by Al-Mubarak et al.,[39] where three molecules point in the same direction and the fourth one is reversed, is in fact a saddle point consistent with the results of Popelier and Stone.[11] As shown by these authors, there is a symmetric pathway from this saddle point to two equivalent minima (M3) of smaller interaction energy than M1 or M2, which reveals that the antiparallel alignment of the dipoles for this structure is partially lost.

The interaction energies for these structures are in general much larger than those reported by Popelier and Stone,[11] but somewhat smaller than those obtained from Böhm's potential.[39]
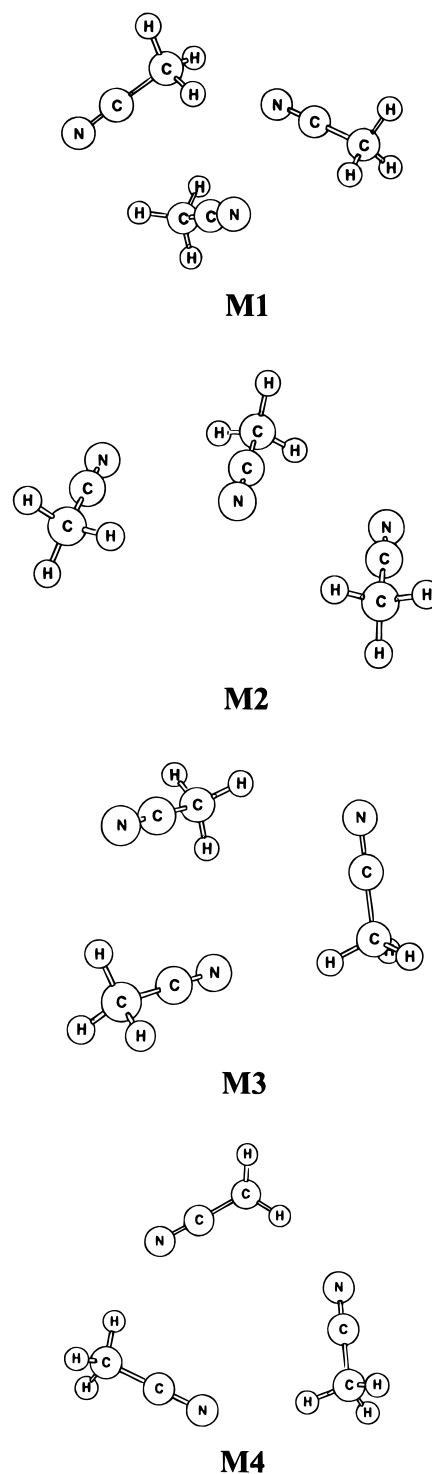
Figure 8. Four configurations of the acetonitrile trimer of locally minimum energy.

This is not suprinsing because one must take into account that Böhm's potential implicitly includes interactions among more than two molecules whereas our potential function is a true pair additive potential; this effect may be significant with larger aggregates, where nonadditive terms could be substantial.
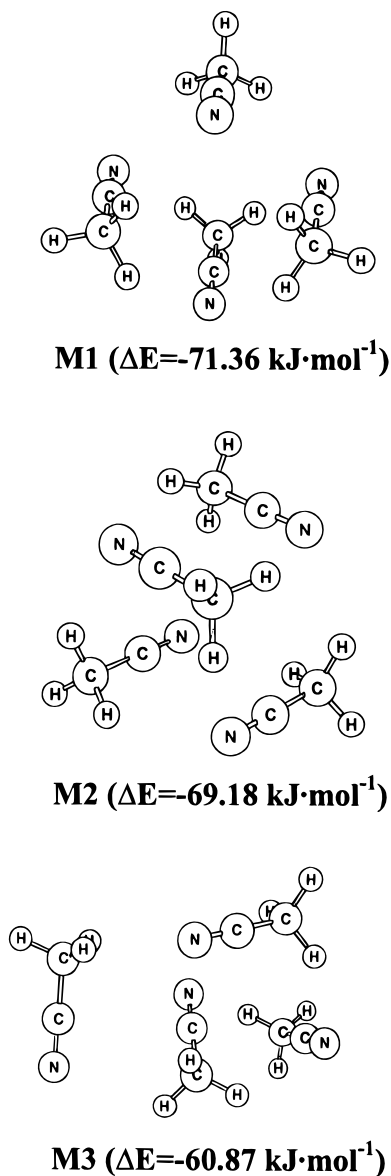
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M1 (ΔE=-71.36 kJ·mol⁻¹)

M2 (ΔE=-69.18 kJ·mol⁻¹)

M3 (ΔE=-60.87 kJ·mol⁻¹)

Figure 9. The most attractive minima of acetonitrile tetramer.

4. Conclusions

Based on MP2/6-311+G* calculations, the acetonitrile dimer possesses a C_{2h} symmetry with the two molecules antiparallel to each other and the hydrogen atoms in the symmetry plane pointing toward the nitrogen atom of the other molecule. MP2-(CP)/6-311+G* calculations provide an energy of interaction of −21.02 kJ mol⁻¹ for this structure.

Since the contribution of electron correlation to the total interaction energy is not negligible, a method including correlation effects must be used to explore the potential surface of the dimer. SCF calculations significantly underestimate the interaction energy. However, computation time can be saved during exploration of the surface by using a fixed intramolecular geometry since the dimer geometries and energies thus obtained differ very little from those obtained with complete optimization. (The minimum energies differ by less than 0.5 kJ mol⁻¹.)

An analytical potential function for the dimer was fitted to the ab initio energies of over 300 configurations, using a weighting scheme that favored low-energy configurations so as to ensure satisfactory fit in these regions. Isoenergetic contour maps constructed from the fitted potential were smooth and similar to maps constructed by using a reported semiempirical potential function.

The minimum of the fitted potential function, −20.81 kJ mol⁻¹, differs little from the ab initio minimum, and the corresponding geometries are also similar. As in previous studies of the acetonitrile dimer, rotating one of the methyl groups by 60° from the minimum-energy configuration leads to a first-order transition state, which with our potential has an energy 1.7 kJ mol⁻¹ higher than the minimum. Rotating both methyl groups by 60° gives rise to a second-order transition state with an energy 3.4 kJ mol⁻¹ above the minimum. (Like the minimum-energy configuration, this state possesses C_{2h} symmetry, but the C−H bonds in the symmetry plane point away from each other.) The intermolecular vibration frequencies calculated for the stationary point configurations using the fitted potential are reasonably close to the experimental and MP2 values, especially for the minimum-energy configuration; also, the number of ab initio calculated imaginary frequencies for the transition states confirms their order. In addition, the characterized structures for the trimer and tetramer show that the most favorable arrangements are those that permit the dipoles to adopt an antiparallel arrangement.

In summary, the fitted potential function satisfactorily represents the interaction between two acetonitrile molecules, at least in the gas phase, except for highly repulsive configurations. It remains to be seen whether it allows satisfactory simulation of liquid-phase behavior, either as it stands (i.e., assuming the additivity of pairwise interactions) or following refinement to take many-body effects such as induction into account.

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