

Electrostatic Bond Dipole Moments from Dimethyl Ether, Methanol, Methane and Water

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Bond dipole moments are derived for the O—H, C—H, and C—O bonds from *ab initio* calculated and experimentally determined electrostatic multipoles of dimethyl ether, methanol, methane and water, using an electrostatic model with point dipoles placed at the midpoints of the bonds between atoms and directed along the bonds. Multipole moments up to and including $L = 6$ moments for each of the molecules are used. It has been found that the model leads only to a fair description of the molecular potential. Owing to the large correlation between the carbon-oxygen bond moments and the oxygen-lone pair moments the latter could be omitted from the model without affecting the quality of the fits.

From a molecular-mechanics calculation, with the present electrostatic parameters, on the C_i and D_{3d} conformation of a crown ether molecule (18-crown-6), there followed a lower energy for the C_i conformation which is in agreement with experiment.

The electrostatic potential around a molecule can be calculated directly from the molecular wavefunction. It can be approximated by the potential of a distribution of point charges, situated at certain sites in the molecule, by application of Coulomb's law. Both charges and their sites are parameters in a procedure which fits the point-charge potential to the potential calculated from the wavefunction. For electrically neutral molecules, instead of site charges, *i.e.* electrostatic monopoles, electrostatic dipoles may be used, which automatically constrain the total electric charge of the molecule to zero.

In this paper we derive dipole moment parameters for the bonds between unlike atoms in dimethyl ether, methanol, methane and water optimized to describe the molecular potential in the volume outside a sphere enclosing the molecule and having the molecular van der Waals radius as its radius. The electrostatic model has been taken from the molecular-mechanics program MM2.¹ No attempt has been made to develop a more elaborate model. In the MM2 model point dipoles are placed at the midpoints of the bonds concerned and are directed along the bonds. The method to derive the parameters, *i.e.* the numerical values of the bond dipole parameters, uses the properties of the multipole expansion for the molecular potential based on tesseral harmonic functions. The method was applied earlier by Bauer and Huiszoon² to azabenzene molecules and will be summarized in the next paragraph. Both experimentally determined dipole moments and calculated moments of higher order have been used in the database.

To examine the predictive power of the bond dipole moments obtained, they are applied to eight related molecules not included in the fit. The bond dipole parameters are also applied in a molecular mechanics calculation, with the program MM2, on a crown ether molecule (18-crown-6).

The Method

In principle the parameters are obtained by minimizing the following least-squares objective function:

$$\chi = \sum_i (V_i - \tilde{V}_i)^2 \quad (1)$$

where V_i is the *ab initio* potential and \tilde{V}_i is the potential calculated from the model parameters. The index i refers to a point in configuration space. Both potentials in (1) are expanded as follows:^{3†}

$$V(R, \theta_i, \phi_i) = \sum_{LK} \left(\frac{4\pi}{2L+1} \right)^{1/2} M_K^L T_K^L(\theta_i, \phi_i) R^{-L-1} \quad (2)$$

where M_K^L is the expectation value of the K th component of the L th multipole moment:

$$M_K^L = \left(\frac{4\pi}{2L+1} \right)^{1/2} \langle 0 | \sum_i Z_i r_i^L T_K^L(\theta_i, \phi_i) | 0 \rangle \quad (3a)$$

and \tilde{M}_K^L is the K th component of the L th multipole moment calculated directly from the model parameters

$$\tilde{M}_K^L = \left(\frac{4\pi}{2L+1} \right)^{1/2} \sum_i Z_i r_i^L T_K^L(\theta_i, \phi_i). \quad (3b)$$

The summation in eqn (3a) is over all particles (electrons and nuclei) i of charges Z_i at positions $r_i = (r_i, \theta_i, \phi_i)$; the summation in eqn (3b) refers to a summation over the model parameters, in the present case these parameters are, oppositely charged point charges placed at a separation of 0.1 bohr \ddagger at the midpoints of the bonds to mimic the point bond dipoles. T_K^L is a normalized tesseral harmonic function.⁴ For $L=1$, $K=0, 1, -1$, the M_K^L are the z, x, y components of the molecular dipole moment, respectively. For $L=2$, $K=0, 1, -1, 2, -2$ one is dealing with the components of the quadrupole moment which are $(3z^2 - r^2)/2$, $3^{1/2}xz$, $3^{1/2}yz$, $3^{1/2}(x^2 - y^2)/2$, and $3^{1/2}xy$, respectively.

The next step is to replace the summation in eqn (1) over points in configuration space by an integration. Substitution of eqn (2) into eqn (1) gives the following least-squares objective function:

$$\chi = \int_R \int_{\theta, \phi} \left\{ \sum_{LK} \left(\frac{4\pi}{2L+1} \right)^{1/2} T_K^L(\theta, \phi) R^{-L-1} (M_K^L - \tilde{M}_K^L) \right\}^2 R^2 \sin \theta \, d\theta \, d\phi \, dR. \quad (4)$$

Carrying out the integration over the volume outside a sphere with radius R , and using the orthonormality of the tesseral harmonic functions, T_K^L , leads to the volume least-squares objective function:

$$\chi_V = \sum_{LK} \frac{1}{(2L+1)(2L-1)} R^{-2L+1} (M_K^L - \tilde{M}_K^L)^2. \quad (5)$$

Applying an integration over the surface of a sphere with radius R , one only has to integrate over angular space, which leads to the surface least-squares objective function:

$$\chi_S = \sum_{LK} \frac{1}{2L+1} R^{-2L-2} (M_K^L - \tilde{M}_K^L)^2. \quad (6)$$

[†] Formulae are given in the atomic system of units. Results of the calculations are given in S.I. units. Dipole moments are given in Debye: 1D = 3.335 64 × 10⁻³⁰ C m.

[‡] 1 bohr = 4πϵħ²/m_ee² = 5.292 × 10⁻¹¹ m.

When the fit has to be done for more than a single molecule the arithmetic sum of least-squares functions for the relevant molecules is taken as the least squares objective function. The functions, χ_V and χ_S , differ in the weighting functions, $W_V^{(L)}(R)$ and $W_S^{(L)}(R)$, which are $(2L+1)^{-1}(2L-1)^{-1}R^{-2L+1}$ and $(2L+1)^{-1}R^{-2L-2}$, respectively. Due to the extra factor, $2L-1$, in the denominator of the weighting factors in the expression for χ_V , the higher moments play a less important role in fits based on χ_V than in those based on χ_S for the same value of R . As we are mainly interested in parameters which describe the potential at or close to the molecular van der Waals surface, the use of the function χ_S is preferred over the use of the function χ_V . For future reference some formulae are given below.

The residual factor, R_a , is defined by:

$$R_a = \left(\frac{\sum_i \overline{(V_i - \tilde{V}_i)^2}}{\sum_i \overline{V_i^2}} \right)^{1/2} = \left(\frac{\sum_i \sum_{LK} W_L(M_K^L - \tilde{M}_K^L)^2}{\sum_i \sum_{LK} W_L(M_K^L)^2} \right)^{1/2} \quad (7)$$

where W_L is the weighting function of the particular fit. The summation over i now refers to the different molecular species included. The contribution of the L th multipole moment to the mean square potential at the surface of a sphere with radius R follows from (2) as:

$$\overline{V_L^2} = \sum_K \frac{1}{2L+1} (M_K^L)^2 R^{-2L-2} \quad (8)$$

and the relative contribution to the mean square potential of the L th moment is given by:

$$\left(\overline{V_L^2} \right)_{\text{rel}} = \frac{\sum_K (2L+1)^{-1} (M_K^L)^2 R^{-2L}}{\sum_{LK} (2L+1)^{-1} (M_K^L)^2 R^{-2L}} \quad (9)$$

An interesting feature of the method outlined above is that it allows the use of calculated as well as experimentally determined multipole moment components M_K^L . Considering for instance a dipolar molecule, we can use its experimental dipole moment together with calculated higher moments; the latter are not usually known from experiment. Generally, a potential represented in this way will be closer to the true potential than a potential represented by calculated moments only.

Model and Results

The model used for the description of the molecular electrostatic potential was that of Allinger and Chung⁵ and is currently applied in the MM2 force field.¹ In this force field no moments are assigned to C—H bonds. As this would lead to zero electrostatic potential for methane, which is one of the molecules included in the present study, the C—H bond dipole is a non-zero parameter in our calculations. As in ref. (1), lone pairs were positioned at 0.5 Å from the oxygen nuclei with an Lp—O—Lp angle of 140°.

Electrostatic Dipole Moments

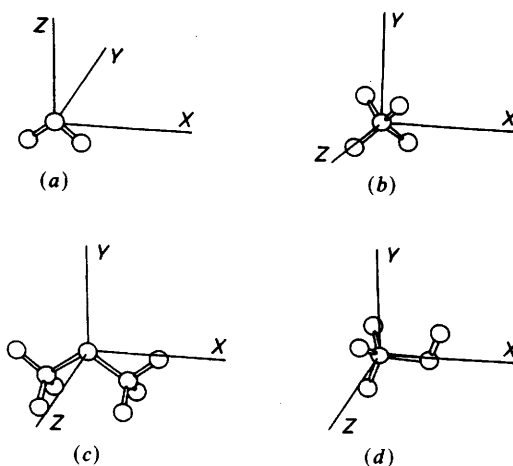


Fig. 1. Choice of coordinate axes.

Molecular electrostatic multipole moments up to and including $L=6$ components, have been calculated for each molecule from LCAO-SCF wavefunctions using an AO basis set of DZ quality,⁶ augmented with double d-polarization functions at the non-hydrogen, and p-polarization functions at the hydrogen atoms. The wavefunctions were calculated with the program HONDO 76 by Dupuis, Rys and King,⁷ and the multipole moments with the program MULTIPROP by Mulder and Berns.⁸ Details and results of the calculations, including the optimization of the exponents used for the polarization functions have been given by Huiszoon.⁹ Fig. 1 defines the choice of axes used.² As a result of molecular point-group symmetry many multipole moment components are identically zero. The numbers of the remaining non-zero components are: 15 (dimethyl ether and water), 27 (methanol) and 5 (methane) and thus the database consists of 62 numbers.

As the fits are based on the multipole expansion of the potential (2), instead of on the potential calculated directly from the wavefunction, it has been checked whether the expansion based on the *ab initio* calculated multipole moments represents the potential at the molecular van der Waals sphere. Results are given in table 1 for the points where the different cartesian axes cut the relevant molecular van der Waals spheres. The radii of the molecular van der Waals spheres have been estimated from the atomic radii given by Kitaigorodsky.¹⁰

As the relative contributions of the highest, $L=6$ multipole moments, to the mean-square potential at the surface of the van der Waals spheres are as small as *ca.* 1%, the deviations displayed in table 1 are mainly due to the penetration effect. Important penetration effects are found at the points situated on the x axis and the negative y axis for dimethyl ether; these are points where the methyl groups are approached rather closely. For methane also a large effect due to penetration is found. In the other points the multipolar potential yields a good representation of the molecular potential. The presence of penetration is inherent to the use of the multipole expansion of the potential and is a drawback of the present method in comparison with methods using the potential calculated directly from the wavefunction. As will be discussed below, the results of the fits for electrostatic models with only a few parameters are hardly influenced by the penetration effect. Four electrostatic models have been used, differing from each other by the number of bond dipole parameters. The first model, model I, has as parameters the O—H, O—Lp, C—H and the C—O bond dipoles. Results obtained with this four-parameter model are shown in table 2. First we note that the relative contributions

Table 1. Potentials at the points of intersection of the coordinate axes with the molecular van der Waals spheres

coordinates/Å			multipole moment potential/V	exact potential/V
x	y	z		
dimethyl ether				
3.2	0	0	0.415	0.660
0	3.2	0	-0.471	-0.487
0	-3.2	0	0.145	0.248
0	0	3.2	-0.171	-0.161
methanol				
3.1	0	0	-0.582	-0.521
-3.1	0	0	0.175	0.182
0	3.1	0	0.395	0.381
0	-3.1	0	-0.064	-0.069
0	0	3.1	-0.007	0.009
methane				
2.2	0	0	-0.146	-0.095
water				
2.1	0	0	0.768	0.781
0	2.1	0	-0.684	-0.670
0	0	2.1	-1.27	-1.27
0	0	-2.1	1.01	1.04

to the mean-square potential, as calculated with eqn (9), of the second non-zero moments are not negligible. For methanol, although the relative contribution of the dipole moment is large (45%) the quadrupole moment with a relative contribution of 31% also turns out to contribute significantly. The residual factors are satisfactory for the dipolar molecules but not for methane. A fit on methane separately yielded a residual factor of 36%, which is hardly better than the present one. It shows that the present electrostatic model is probably not a very favourable one for methane. The bond dipole moments obtained are listed in table 2(b), column I.

From table 2(c) it is seen that the O—H and the O—Lp dipole moment parameters are nearly fully correlated. This suggests the use of simply one single parameter instead of these two. We have chosen the O—H dipole as the parameter to be optimized and have constrained the O—Lp dipole to zero. The residual factors obtained for this three-parameter model, model II, are listed in table 3 together with the residual factors obtained for model I. The three-parameter model is found to be virtually as good as the four-parameter model. The bond dipole moments are given in table 2(b), as model II parameters. As methane, due to the absence of moments lower than the octupole moment, contributes little in the fits, which is reflected in the irregular behaviour of the residual factor as a function of R (see table 3), we have chosen for the C—H bond dipole parameter the value which fits the molecular octupole moment of methane. This will not worsen the fits seriously as for the three-parameter model a correlation as large as -0.86 was found between the C—H and C—O bond parameter.

The bond dipole parameters for this model are given in table 2(b) as model III parameters. The residual factors are in table 3. It may be clear that the agreement for the dipolar molecules, obtained with this two-parameter model, is not worse than that obtained with the four- and three-parameter models, and that it is considerably better for methane.

Table 2. Results of minimizing χ_S for four molecules at their van der Waals surfaces

(a) Residual factors, R_a , and relative contributions of the lowest non-zero moment of a particular molecule to the mean-square potential at the surface of the molecular van der Waals sphere

molecule	$(\overline{V}_1^2)_{\text{rel}}$	R_a
dimethyl ether	0.80	0.26
methanol	0.45	0.22
methane	0.73	0.38
water	0.75	0.20
all molecules	0.75	0.21

(b) Bond dipoles^a

model ^b	I	II	III	IV
—OH+	1.63 (0.22)	1.74 (0.05)	1.74 (0.05)	1.66 (0.06)
+OLp—	0.20 (0.38)	—	—	—
—CH+	0.96 (0.18)	0.97 (0.18)	1.05 (0.02)	1.07 (0.01)
+CO—	0.43 (0.30)	0.54 (0.21)	0.46 (0.11)	0.27 (0.12)

(c) Correlations between bond dipole parameters for model I

	OH	OLp	CH	CO
OH	1	-0.97	0.072	0.70
OLp		1	-0.078	-0.71
CH			1	-0.55
CO				1

^a Estimated standard deviations are given in parentheses, and Debye units are used. ^b Model I: four parameters; model II: as model I but no OLp moment; model III: two free parameters (the CH bond parameter has been taken from a fit on the octupole moment of methane separately). Model IV is similar to model III, the difference being that now experimental dipole moments have been used in the database, and that the CH parameter has been derived from the experimental octupole moment.

Fig. 2 displays the values of the parameters as functions of the radius R , both for the four-parameter model and for the two-parameter model. In the case of the four-parameter model, the parameters strongly depend on R , whereas in the two-parameter model this dependency has disappeared completely. The results given in fig. 2 and table 3, show that the two parameter model has to be preferred over the four-parameter model as it is simpler, the parameters do not depend on R , and the quality of the fits are virtually as good as those obtained with the four-parameter model. Since the parameters of the two-parameter model are virtually independent of R there will be no great influence due to the penetration effect. Fig. 3 and 4 give potential curves along the x , y and z directions for dimethyl ether and methanol, respectively, for both the *ab initio* potential, calculated directly from the molecular wavefunction, and for the potential calculated from the two-parameter model. In some regions the two potential curves are even indistinguishable, in other regions, e.g. at the positive x axis for methanol, a deviation of 40% occurs at $x = 5 \text{ \AA}$. The average deviations are given by the residual factors listed in table 3, model III.

In order to enhance the usefulness of the parameters the experimental dipole moments of dimethyl ether, methanol and water and the experimental octupole moment of methane have been used instead of the corresponding *ab initio* moments. The experi-

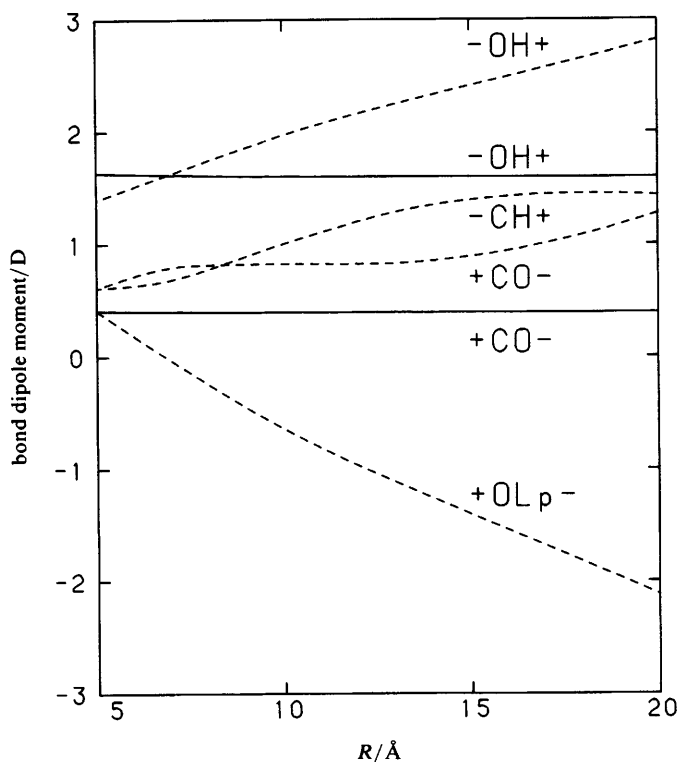


Fig. 2. Bond dipole moment parameters as function of the distance to the molecular centres. (---) Four-parameter model (model I); (—) two-parameter model (model III).

mental values of the dipole moments are given in table 4. The experimental octupole moment for methane was determined by Isnard *et al.*¹¹ as $(7.67 \pm 0.13) \times 10^{-50} \text{ C m}^3$. For the other multipole moments the *ab initio* calculated values were kept in the database. The molecular structural data of water are from ref. (12), those of the other molecules are from ref. (13). As before, the O—Lp moment was constrained to zero and the C—H moment was obtained from a fit to the octupole moment of methane. The O—H and the C—O bond dipole parameters were obtained from a fit of the potential at the relevant molecular van der Waals spheres and are listed in table 2(b) as model IV parameters.

With the dipole moment bond parameters the dipole moments of eight related molecules, not included in the fits, have been calculated. The results are shown in table 4. In column *a* of table 4 the moments calculated with model IV are listed. There is a rough agreement with the experimental moments; on the other hand, as higher molecular moments contribute to the bond dipoles some deviations have to be expected. The data in column *b* are obtained from a fit with large *R* and thus not influenced by the presence of higher molecular moments. The result is indeed a better agreement with the experimental dipole moments. Column *c* lists the moments calculated with the bond dipole moments which form a part of the MM2 force field. These parameters produce good agreement for both the ethers and the alcohols; the agreement for the oxides is less good, however. In all cases there is hardly any agreement for the pure hydrocarbon molecules isobutane and propane. As the calculated value for the molecular dipole moment of isobutane is too large and that of propane too small, the moments cannot be fitted with one single value of the C—H dipole moment.

Table 3. Residual factors (%) for three models used, for different values of R^a

$R/\text{\AA}$	dimethyl ether			methanol			methane			water			all molecules		
	I	II	III	I	II	III	I	II	III	I	II	III	I	II	III
van der Waals	26	26	26	22	22	22	38	37	36	20	20	20	21	21	21
5	15	14	14	15	15	16	45	43	16	8.6	9.0	8.9	13	13	13
10	8.7	9.4	9.4	10	10	10	9.6	13	8.2	5.1	4.7	4.8	8.2	8.3	8.3
12.5	7.7	8.6	8.8	9.3	9.4	9.4	19	53	6.6	4.3	3.7	4.0	7.2	7.4	7.5
15	7.0	8.0	8.5	8.7	8.8	8.8	33	86	5.5	3.8	3.0	3.5	6.5	6.8	7.0
17.5	6.5	7.6	8.3	7.9	8.2	8.4	38	110	4.7	3.4	2.6	3.2	6.0	6.3	6.7
20	6.1	7.2	8.2	7.4	7.8	8.1	37	128	4.2	3.2	2.3	2.9	5.6	6.0	6.5

^a The first column under the name of each compound refers to the four-parameter model (I), the second column to the three-parameter model (II), and the third column to the two-parameter model (III).

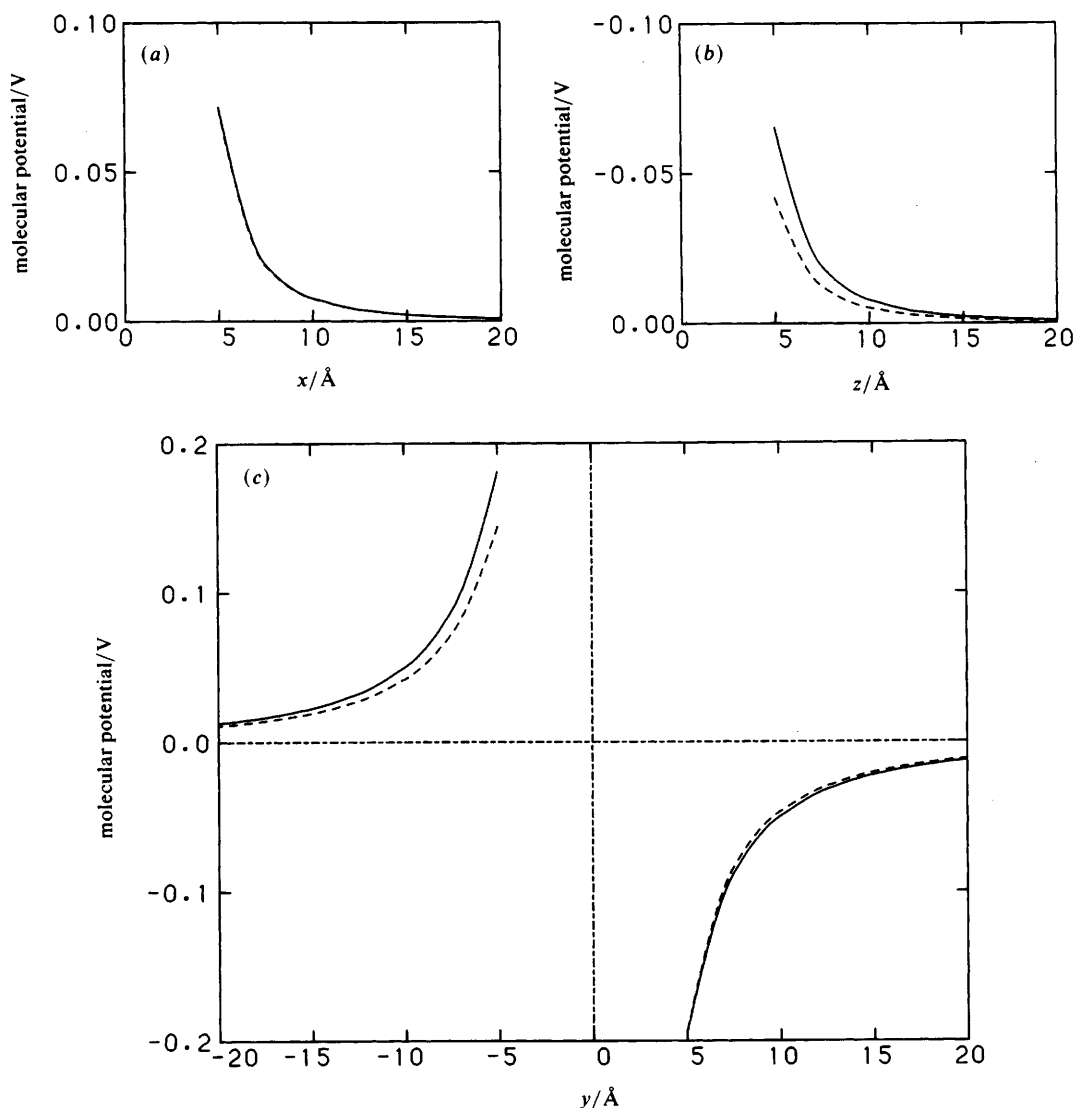


Fig. 3. Dimethyl ether. Molecular potential along the coordinate axes. (a) x , (b) z , (c) y . (—) potential calculated with parameters of model III; (---) potential calculated directly from the SCF wavefunction.

An Application to a Crown Ether (18-Crown-6)

We have applied the parameters of model IV, table 2(b), in a molecular-mechanics calculation with the MM2 program to the case of the 18-crown-6 ether molecule. We paid attention to two of the conformations in which the molecule occurs: the C_i and the D_{3d} conformations.¹⁹ The C_i conformation is adopted by the uncomplexed 18-crown-6 ether in the crystalline state. The molecule is almost planar and has a 'diamond-like' conformation with eight symmetry-related hydrogen atoms pointing towards the cavity. The D_{3d} conformation is found for complexes of 18-crown-6 ether with cations, e.g. K^+ . The molecule is now of a circular shape. The six oxygen atoms are alternately *ca.* 0.20 Å

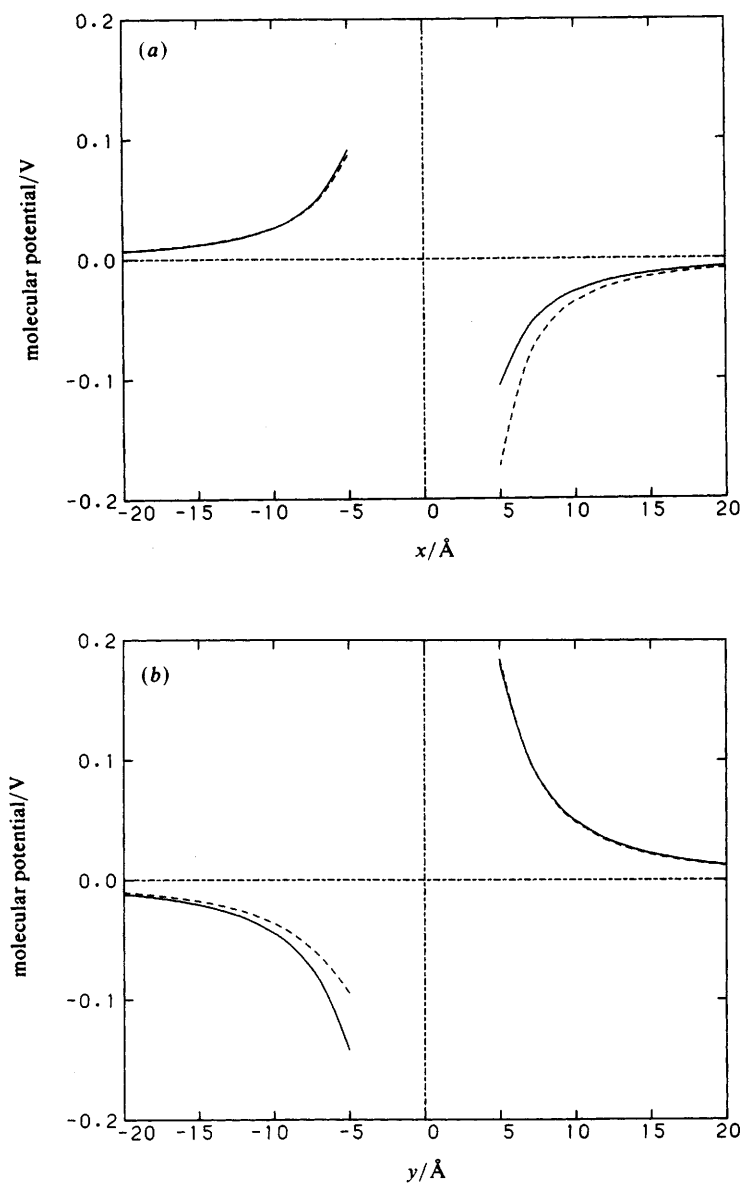


Fig. 4. Methanol. The curves are as in fig. 3.

above and below their mean plane and form a nearly planar hexagon of side *ca.* 2.80 Å. The hydrogen atoms point away from this cavity. The MM2 force field predicts an energy of the D_{3d} conformation which is lower by 10.6 kJ mol⁻¹ than the energy of the C_i conformation. One would expect, however, to find a lower energy for the C_i conformation, as this is the conformation of the uncomplexed molecule in the crystal. The present electrostatic parameters allow the oxygen atoms, due to the absence of O—Lp bond moments, to approach each other more closely. Also the hydrogen atoms which point into the cavity of the molecule, when it is in its C_i conformation, may lead

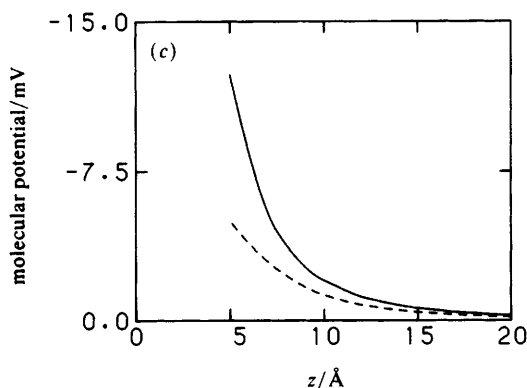


Fig. 4. (continued)

Table 4. Calculated and experimentally determined dipole moments

compound	dipole moments/D				ref.
	a	b	c	experiment	
diethyl ether	1.44	1.34	1.10	1.17	14(a)
methylethyl ether	1.47	1.37	1.11	1.22	14(b)
ethanol	1.80	1.66	1.65	1.73	14(c)
s-trioxane	2.56	2.39	0.82	2.08 ± 0.01	14(d)
ethylene oxide	1.31	1.16	0.76	1.88 ± 0.01	14(e)
trimethylene oxide	1.58	1.46	0.61	1.93 ± 0.01	14(f)
isobutane	0.314	0.314	—	0.132 ± 0.001	14(g)
propane	0.0327	0.0327	—	0.083 ± 0.001	15
dimethyl ether	1.49	1.39	1.11	1.31 ± 0.01	16
methanol	1.62	1.52	1.62	1.69	17
water	2.04	1.87	1.98	1.8479 ± 0.0006	18

^a Calculated with the parameters of model IV of table 2*b*: CH bond moment from octupole moment of methane, OH and CO bond moments from a fit at the surfaces of the molecular van der Waals spheres of dimethyl ether, methanol and water. ^b As *a* but the fits are done for large *R*, which eliminates the influence of multipole moments other than the dipole moments. ^c Calculated with the parameters of the MM2 force field.

to a lowering of the electrostatic energy due to the interactions of the C—H bond dipoles. It was found indeed that replacement of the MM2 dipole moment parameters by those of model IV, table 2(*b*), gave an energy for the *C_i* conformation which is lower by 9.9 J mol⁻¹ than that of the *D_{3d}* conformation. This example suggests that it may be worthwhile studying the possibilities of the present electrostatic model, having C—H bond dipole moments but no O—Lp moments, more extensively.

Conclusion

The present study on bond moments shows that in general the model used will give a fair description of the molecular electrostatic potential. This follows for the molecules included in the fit from the entries of table 3. For the other ether molecules and the

oxides, it follows from a comparison of the entries of table 4, columns *a* and *b*, with the experimentally determined dipole moments.

The situation is worse for the hydrocarbon molecules. The rather high residual factor of 36% for methane has already been mentioned in the preceding paragraph. From table 4 it is seen that the calculated dipole moment for isobutane is a factor of two larger than the corresponding experimental moment, whereas for propane the calculated moment is a factor two smaller than the experimental moment. This means that scaling the C—H bond dipole will not lead to a better agreement. Another electrostatic model will be required. In his study on Coulombic interactions in crystalline hydrocarbons Williams²⁰ applies a constant charge separation parameter $\Delta e = 0.414e$ for saturated hydrocarbons. This charge separation leads to a dipole moment for a C—H bond of 1.02 D, which is rather close to the value of 1.07 D reported in this work, table 2(*b*), models III and IV. In Williams's model the bond moment for a methylene C—H bond is 0.681 D, and similarly the moment of a C—H bond belonging to a methyl group is 0.511 D, all with positive charges at H and negative charges at C. According to this model the calculated dipole moments for isobutane and propane are 0.361 and 0.189 D, respectively. Both values are too large; it indicates nevertheless that a non-constant value of the C—H bond dipole may improve the fit.

It is clear that the description of the electrostatics of a C—H bond by one single dipole moment parameter that also should be transferable between different molecules containing C—H bonds is probably too serious a simplification. An even stronger conclusion, based on their *ab initio* study of the electron density in methane, has been drawn by Turner *et al.*,²¹ who state that 'the concept of the C—H bond moment in a molecule such as methane is elusive, illusive, and ill-defined'.

Several authors find an opposite polarity of the C—H bond moment having its negative side directed towards the proton. Among these are Wiberg and Wendoloski,²² who found, from an integration of 6-31G** wavefunctions for methane, ethene and ethane, a C—H moment with the negative side pointing to the proton, for the C—H bond moment in acetylene the opposite direction is found.

It is argued that their assignment of the directions of the C—H bond moments agrees with experimental data on stretching modes of the molecules that have been investigated. Their point of view is supported by Reed and Weinhold²³ who point out that a 'natural population analysis' and Mulliken charges leads to the assignment $-\text{CH}^+$, but that from a direct evaluation of the expectation value of the C—H bond moment of methane unambiguously the polarity $+\text{CH}-$ is found.

Bader *et al.*,²⁴ also from a 6-31G** study, confirm that for normal alkanes, ranging from methane up to and including hexane, the hydrogens form the negative end of the group dipole. These results concerning the $+\text{CH}-$ polarity have been recently questioned by Lazzarotti *et al.*,²⁵ who, on the basis of Thomas-Reiche-Kuhn populations find a bond moment of magnitude of 0.339 D having $-\text{CH}^+$ polarity.

Recently the importance of assigning a non-zero value to $\text{C}_{\text{sp}^2}-\text{H}$ bond moment has been shown by Allinger and Lii.²⁶ The moment will be included by a complete new force field (MM3) which has not yet been fully published. One may conclude that potential derived parameters lead to a CH dipole with its negative end directed towards the carbon atom. Parameters derived from some form of population analysis may yield opposite orientations of the C—H bond moment.

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