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Calculation of the Molecular Polarizability Tensor

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Abstract: A semiempirical method is presented to compute the components of molecular polarizability with atomic polarizability components and the dipole tensor. Anisotropic atomic polarizabilities are oriented along the bonds and in the direction of all nonbonded atoms with a distance-dependent function. The average of the trace of each atomic polarizability matrix is the empirical result, α_A(ahp), for atom A calculated by K. J. Miller.[10] The dipole tensor is modified by omitting the terms connecting bonded atoms and damping the remaining ones to include the dipole approximation with increasing distance. The anisotropic atomic polarizabilites incorporate the nearest neighbor effects along the bonds and replace the dipole terms that overestimate contributions to the polarizability. The components of the molecular polarizability are scaled so that the average of the trace is equal to the empirical molecular polarizability, α(ahp). The results are invariant to rotations or translations of the coordinate system. A set of parameters is presented that yields a comparison between the scaled components of molecular polarizability and experimental results for approximately 120 molecules with a standard deviation of 3.5%. The method is simple to use and suitable for molecular mechanics calculations.

Introduction

Silberstein[1-3] proposed the theory of the atom dipole approximation. It was further developed by Rowell and Stein,[4] Mortensen,[5] DeVoe,[6] Applequist,[7] Birge,[8] and Thole.[9] If the atomic polarizability tensor for each atom i is given by α_i, a 3 × 3 matrix, then the induced dipole moment μ_i at each atom $i = 1, 2, 3, \ldots L$ is given by

$$\mu_i = \alpha_i[\mathbf{E}_i - \textstyle\sum_{j(\neq i)}\mathbf{T}_{ij}\mu_j] \qquad i, j = 1, 2, 3, \ldots, L \tag{1}$$

where μ_i and $\mathbf{E}_i$ (the applied electric field) are column vectors containing three elements, the x, y, and z components for atom i, and $\mathbf{T}_{ij}$ (3 × 3 matrices) are the dipole tensors connecting atoms i to j

$$T_{piqj} = -[\partial^2/\partial p_i \partial q_j][1/r_{ij}] \tag{2}$$

$$= [-1/r_{ij}^5][3p_i q_j - \delta_{pq} r_{ij}^2] \tag{2'}$$

where p, q = x, y, and z are the Cartesian components. The α_i and $\mathbf{T}_{ij}$ matrices will be modified in this paper in a theoretical development of a modified dipole approximation. The term in brackets of eq 1 is the total electric field. It is a sum of the applied plus the induced electric fields. Equation 1 may be inverted to yield

$$\alpha_i^{-1}\mu_i + \textstyle\sum_{j(\neq i)}\mathbf{T}_{ij}\mu_j = \mathbf{E}_i \tag{3}$$

or

$$\mathbf{A}\mu = \mathbf{E} \tag{4}$$

where A is the $3L \times 3L$ matrix representation of α_i^{-1} and $\mathbf{T}_{ij}$, and μ and $\mathbf{E}$ are the $3L \times 1$ column vectors of μ_i and $\mathbf{E}_i$ in eq 3, which can be expressed in the form

$$\mathbf{A}\mu = \begin{bmatrix} \alpha_1^{-1} & \mathbf{T}_{12} & \ldots & \mathbf{T}_{1L} \\ \mathbf{T}_{21} & \alpha_2^{-1} & \ldots & \mathbf{T}_{2L} \\ \cdot & \cdot & & \cdot \\ \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & & \cdot \\ \mathbf{T}_{L1} & \mathbf{T}_{L2} & \ldots & \alpha_L^{-1} \end{bmatrix} \begin{bmatrix} \mu_1 \\ \mu_2 \\ \cdot \\ \cdot \\ \cdot \\ \mu_L \end{bmatrix} \tag{5}$$

which is a matrix of 3 × 3 submatrices and 3 × 1 vectors for each atom i. The inverse $\mathbf{B} = \mathbf{A}^{-1}$ yields the induced dipole in the molecule from eq 4 as

$$\mu = \mathbf{BE} \tag{6}$$

which contains L equations for the induced dipole at each atom

$$\mu_i = \textstyle\sum_j \mathbf{B}_{ij}\mathbf{E}_j \qquad \mathrm{i} = 1, 2, 3, \ldots, L \tag{7}$$

If a constant external field is applied then $\mathbf{E}_1 = \mathbf{E}_2 = \ldots \mathbf{E}$. The total induced moment is a sum over μ_i, and the molecular polarizability tensor becomes a sum over all 3 × 3 matrices $\mathbf{B}_{ij}$ which, after diagonalization, yields α_{mol} with principal components, α_1(mol), α_2(mol) and α_3(mol), namely

$$\alpha_{\mathrm{mol}} = \mathbf{D}\{\textstyle\sum_{ij}\mathbf{B}_{ij}\}\mathbf{D}^{\mathrm{t}} \tag{8}$$

$$= \begin{bmatrix} \alpha_1(\mathrm{mol}) & \cdot & \cdot \\ \cdot & \alpha_2(\mathrm{mol}) & \cdot \\ \cdot & \cdot & \alpha_3(\mathrm{mol}) \end{bmatrix} \tag{8'}$$

The eigenvectors, $\mathbf{D}$, define the principal axes of molecular polarizability, where t is the transpose. The average molecular polarizability is the average of the trace, $\mathrm{Tr}(\alpha_{\mathrm{mol}})/3$ or

$$\alpha(\mathrm{mol}) = [\alpha_1(\mathrm{mol}) + \alpha_2(\mathrm{mol}) + \alpha_3(\mathrm{mol})]/3 \tag{9}$$

In the empirical methods to date, the set of atomic polarizabilities is adjusted until α(mol), α_1(mol), α_2(mol), and α_3(mol) approximate the experimental values. In the present approach, average atomic polarizabilities are taken as the empirical set α_A(ahp), atomic anisotropies are introduced and adjusted, the dipole approximation is modified and adjusted, and the molecular polarizability matrix is scaled uniformly so that $\mathrm{Tr}(\alpha_{\mathrm{mol}})/3 \rightarrow \alpha(\mathrm{ahp})$ and the normalized components approximate the experimental anisotropy.[10] Within the point dipole approximation eq 1 is exact. The extent to which the dipole approximation is applicable to molecular systems may be understood by introducing successive approximations. First the approximations will be presented, and then the importance of each will be discussed by reporting effects of each approximation.

The determination of atomic polarizabilities by Applequist et al.[7] that reproduced experimental molecular polarizabilities resulted from a set of abnormally small atomic polarizabilities when

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compared to α_A(ahp). Introduction of atomic anisotropic effects by DeVoe[6] and Birge[8] improved the results. The use of a potential interaction to define and orient α_i by Birge[8] and in greater detail by Thole[9] improved the atomic and molecular polarizabilities to yield 2–7% agreement between theory and experiment. The fact that the dipole approximation is a long-range one is an important aspect of the present method.

Isotropic Atomic Hybrid and Attenuated Dipole Tensor Approximations

In the present approach, three approximations were developed and used with eqs 3–9.

(1) The average atomic polarizability is constrained to the empirical values α_A(ahp) for atoms classified as atomic hybrids.[10] Anisotropy is introduced to reproduce experimental results on diatomic and then polyatomic molecules and also to replace the dipole terms between bonded atoms. The atomic polarizability is given by

$$\alpha_i(\mathrm{ahp}) = \alpha_i^{\circ}(\mathrm{ahp}) + \textstyle\sum_j l_{ij}^{-1} s_{ij} \exp(-g_{ij}) \mathbf{V}_{ij} \Delta\alpha_i(\mathrm{ahp}) \mathbf{V}_{ij}^{t} \qquad (10)$$

where α_i°(ahp) is the isotropic polarizability of atoms $i = 1, 2, ..., L$, t is the transpose, and

$$\Delta\alpha_i(\mathrm{ahp}) = \alpha_i(\mathrm{ahp})[3\mathbf{f}_i - \mathbf{I}] \qquad (11)$$

where

$$\mathbf{f} = \begin{bmatrix} f_{i\parallel} & 0 & 0 \\ 0 & f_{i\perp} & 0 \\ 0 & 0 & f_{i\perp} \end{bmatrix} \qquad (12)$$

is the scaled anisotropic correction ($f_{i\parallel} + 2f_{i\perp} = 1$) where $f_{i\parallel}$ is the fractional contribution of the atomic polarizability along a bond or direction i to j; $f_{i\perp}$ is the fractional component perpendicular to the direction of a bond or i to j; $l_{ij} = l_b$ is the number of atoms bonded to i, and $l_{ij} = l_n$, the total number of atoms − $l_b = L - l_b$, is 1 plus the number of atoms not bonded to atom i; $\mathbf{V}_{ij}$ is the unitary transformation, a 3 × 3 matrix, which transforms $\Delta\alpha_i$ from the local coordinate system i to j to the space-fixed system; $g_{ij} = 0$ if i is bonded to j and $g_{ij} = c[r_{ij} - d\rho_{ij}]/\rho_{ij}$ if i is not bonded to j, where $c = 2.54$ and $d = 0.25$ were found to be most effective; $\rho_{ij} = \rho_i + \rho_j$ is the sum of theoretical van der Waals radii of atoms i and j; and $s_{ij} = \rho_{ij}/r_{ij}$.

The weighting factors l_b and l_n deserve comment. The sum over atoms bonded to atom i includes exactly l_b atoms, whereas the sum over atoms not bonded to atom i is less than l_n. For example, in ethane, $l_n = 7$ for each of six hydrogen atoms, whereas $l_n = 4$ for each of two carbon atoms. In benzene, $l_n = 11$ for each of six hydrogen atoms and $l_n = 9$ for each of six carbons. These weight factors were found empirically.

The sum over all atoms bonded to atom i includes l_b terms, each weighted by l_b^{-1}. The average polarizability of atom i remains α_i(ahp), but the atomic polarizability matrix is redirected along a resultant of all bond directions. The sum over all atoms not bonded to atom i includes a different number of terms than l_n. These terms make no contribution to the average atomic polarizability because the trace of $\Delta\alpha_i$ and $\mathbf{V}_{ij}\Delta\alpha_i\mathbf{V}_{ij}^{t}$ vanishes so that the rotation of the anisotropic contribution $\Delta\alpha_i$ along the direction i to j continues to modify α_i but leaves its overall trace and average invariant. In summary

$$\mathrm{Tr}[\mathbf{V}_{ij}\Delta\alpha_i\mathbf{V}_{ij}^{t}] = \mathrm{Tr}[\Delta\alpha_i] = 0 \qquad (13)$$

$$\mathrm{Tr}(\alpha_i^{\circ})/3 = \alpha_i(\mathrm{ahp}) \qquad (14)$$

and

$$\mathrm{Tr}(\alpha_i)/3 = \alpha_i(\mathrm{ahp}) \qquad (15)$$

follows from eqs 10–12. These changes in α_i occur mainly along the bonded atoms because those along the nonbonded directions i to j are damped by $\exp(-g_{ij})$.

Table I. Atomic Hybrid Polarizabilities and Scaled Components[a]

atomic hybrid	α_A, Å^3	$f_1, f_\parallel$	$f_2, f_\perp$	$f_3, f_\perp$
H	0.387	0.3940	0.3030	0.3030
F	0.296	0.4600	0.2700	0.2700
Cl	2.315	0.4400	0.2800	0.2800
Br	3.013	0.4000	0.3000	0.3000
I	5.415	0.3600	0.3200	0.3200
CTE	1.061	0.4000	0.3000	0.3000
CTR	1.352	0.4150	0.2925	0.2925
CBR	1.896	0.3333	0.3333	0.3333
CDI	1.283	0.4500	0.2750	0.2750
NTE	0.964	0.4900	0.2550	0.2550
NTR2	1.030	0.4860	0.2570	0.2570
NPI2	1.090	0.5000	0.2500	0.2500
NDI	0.956	0.4500	0.2750	0.2750
OTE	0.637	0.5200	0.2400	0.2400
OTR4	0.569	0.4860	0.2570	0.2570
OPI2	0.274	0.4860	0.2570	0.2570
STE	3.000	0.4000	0.3000	0.3000
STR4	3.729	0.4860	0.2570	0.2570
SPI2	2.700	0.4000	0.3000	0.3000
PTE	1.538	0.4000	0.3000	0.3000

[a] Atomic hybrids are defined in Table 1 of ref 10. Scaled principal components of atomic polarizability are related by $f_\parallel = f_1$, $f_\perp = f_2 = f_3 = (1 - f_1)/2 = (1 - f_\parallel)/2$ in the present paper.

(2) The dipole tensor is adjusted by omitting terms when i is bonded to j, and the dipole interaction, eq 2, is damped to yield

$$T_{piqj} = [-1/r_{ij}^5][3p_iq_j - \delta_{pq}r_{ij}^2][1 - \exp[-s(r_{ij}/t\rho_{ij})^n]] \qquad (16)$$

when i is not bonded to j. The parameters $s = 1.0$, $t = 0.7$, and $n = 10$ were found to be most effective.

(3) After the molecular polarizability is computed with these approximations to α_i(ahp) and T_{piqj}, α_{mol} is scaled by the empirical molecular polarizability[10] to yield the empirical molecular hybrid polarizability matrix

$$\alpha(\mathrm{ahp}) = [\alpha(\mathrm{ahp})/\alpha(\mathrm{mol})]\alpha_{\mathrm{mol}} \qquad (17)$$

where the average unscaled molecular polarizability satisfies

$$\mathrm{Tr}(\alpha_{\mathrm{mol}})/3 = \alpha(\mathrm{mol}) \qquad (18)$$

and the molecular hybrid polarizability matrix satisfies

$$\mathrm{Tr}[\alpha(\mathrm{ahp})]/3 = \alpha(\mathrm{ahp}) \qquad (19)$$

The results are invariant to transformations of the entire molecule. The ahp, α(ahp), scaled principal components, f_1, f_2, f_3, unscaled molecular polarizabilities, α(mol), and orientation of the principal axes along with experimental results are presented in Table II. The rms deviation, between the empirical and experimental results is given by

$$\delta(f_M) = [\textstyle\sum_\mu [f_{M\mu}(\mathrm{ahp}) - f_{M\mu}(\mathrm{exp})]^2]^{1/2} \qquad (20)$$

with the scaled components $f_{M\mu}$, $\mu = 1, 2, 3$, for each molecule M. The principal components of molecular polarizability are given by

$$\alpha_{M\mu}(\mathrm{calc}) = \alpha(\mathrm{calc})f_{M\mu}(\mathrm{calc}) \quad \mu = 1, 2, 3 \qquad (21)$$

where calc is ahp or exp. In the present method, the scaled polarizability tensor is adjusted to fit the scaled experimental values, while in the previous paper[1] the average polarizability was parameterized to reproduce the average experimental values. They are combined to yield α(ahp). Each approximation, is designed to reproduce essential parts of the polarizability tensor: the principal components and the average molecular polarizability while retaining atomic polarizabilities from earlier parameterizations.

The standard deviation in the calculation of principal components for T molecules is the rms value

$$\sigma = [\textstyle\sum_{M(=1,\ T)} \delta(f_M)^2/(T-1)]^{1/2} \tag{22}$$

In Table II the molecules are grouped as follows: diatomic and triatomic molecules, alkanes and halogenated alkanes, alkenes, benzene and its derivatives, alkynes, alcohols, ethers, aldehydes and ketones, nitriles, NH_3 and amides, phosphates, DNA bases, rings containing O, N, S, and condensed ring hydrocarbons. The molecules were built by using standard bond lengths and bond angles. The torsional angles are for minimum-energy conformations unless specified. In several cases polarizabilities for alternate conformations are presented.

To test the effect variations in the geometry has on α(ahp), the calculations were repeated by scaling all coordinates uniformly by 1.04 on 1.08. The standard deviation changed by 0.0% and 0.1%, respectively, for the individual molecules. This weak dependence on geometry is attributed to approximations 1 and 3; the constraints that α_i(ahp) are used for atoms and the scaling of the molecular polarizability matrix to α(ahp).

The results of the present theoretical method are compared to the empirical approaches of Applequist et al.,[7] Birge,[8] and Thole[9] in Table III only for cases in which experimental values are available. For most molecules, the present method yields results that are as close to experimental values as the best of these three theoretical methods. It was noted by Miller[10] that the error in the average molecular polarizability is 0–4% for most molecules and in a few cases it may be as high as 8%. Birge[8] and Thole[9] estimated the experimental error in the polarizability at 3% and in the components, as high as 6%. Therefore, eqs 10, 16, and 17 yield a good estimate of molecular polarizabilities. The important adjustment in the dipole tensor entails omitting the effect of bonded atoms and attenuating the contributions from nonbonded atoms. Use of anisotropic rather than isotropic atomic polarizabilities yields only an additional 1% improvement in α_{mol}.

The principal axes are defined relative to symmetry planes and axes. For asymmetric molecules, the angles between the α_1, α_2, α_3 principal axes and the bonds X–Y are denoted by (α_1, XY) etc. The conformations selected were minimum-energy conformations unless specified. When there are small barriers to rotation, polarizabilities of several low-energy conformations rather then the average are reported to demonstrate the dependence on conformation. In general, the dependence of polarizability on the conformation is small for the molecules studied. Torsion angles about CTE–CTE bonds are t, g+, and g−, about H–CTE–CTR–OTR4 bonds are cis, and about H–NPI2–CTR–OTR4 bonds are trans. Methanol is cylindrically symmetrical with respect to rotation of the methyl (or OH) group and the components of polarizability in the H–CTE–OTE–H conformations of t, g+, and g− remain unchanged. The cis and trans CTE–CTE–OTE–H conformations of ethanol average to (f_1, f_2, f_3) = (0.2906, 0.3291, 0.3803) with an rms deviation of 0.6%. The case of di-*n*-propyl ether is presented in Table IV. In the extended form of the backbone

1 2 3 5 6 7
Me–C–C–O–C–C–Me
t t t t t t

the conformations are all trans. The van der Waals (6–14) potential energy, U, and the torsional energy, V_T, with a barrier of 3.0 kcal mol^{-1}, about the CTE–CTE bonds are reported for t, g+, and g− forms for rotations about selective bonds. If only these conformations with $V_T = 0$ are considered in the weight averaging, then the rms error tends toward 5%. The average orientation of the axes includes the mirror images, and consequently, w possibilities occur for each state listed.

In the present approach, several considerations influenced the development of the empirical formulas. Their importance may be understood now by noting the results, presented in Table V, for several representative molecules with four successive approximations to α_i and $\mathbf{T}_{ij}$ on seven representative molecules.

(1) If all $T_{piqj} = 0$ and α_i are isotropic, then the three diagonal components of $\mathbf{f}$ are equal and the rms error is 0.15.

(2) If all $T_{piqj} = 0$ and anisotropic α_i are used, then $\mathbf{f}$ yields an rms error of 0.080.

(3) If T_{piqj} is approximated by eq 16 and isotropic α_i are used, then the rms error is 0.065.

(4) If T_{piqj} and α_i are approximated by eqs 16 and 10, then $\mathbf{f}$ reproduces the experimental polarizability components to an rms value of 0.035.

T_{piqj} influences the computed unscaled molecular polarizabilities. Applequist et al.[7] and Birge[8] require smaller atomic polarizabilities, whereas Thole[9] obtains some larger values then the additivity models of Vogel[11] and the atomic hybrid method of Miller.[10] However, if α_{mol} is scaled by the empirical value α(ahp), which reproduces the experimental values accurately, a good approximation is obtained to the components of molecular polarizability, and advantage is taken of the calibration by the empirical ahc and ahp methods of ref 10. In approximation 1, T = 0 and isotropic atomic polarizabilities yield spherically symmetrical molecular polarizabilities. The principal axes are arbitrary. In the second approximation, T = 0 and anisotropic atomic polarizabilities yield improved results for the standard deviation, but the principal axes do not agree with the experimental results as well as with nonzero values of T_{piqj}. Approximation 3, T ≠ 0 and isotropic atomic polarizabilities also yield an improved standard deviation σ, but the principal axes do not consistently agree with experimental results. Approximation 4 combines the essential features, and the best results are obtained when T ≠ 0 and anisotropic atomic polarizabilities are used according to eqs 10, 16, and 17. Both are required to minimize the standard deviation and direct the principal axes in agreement with experimental results.

Discussion and Conclusion

The components of molecular polarizability are computed with approximations 10, 16, and 17. The optimum scaled components of atomic polarizability are reported in Table I along with the average atomic polarizability, α_A(ahp), from ref 10. The components add to 1, and the perpendicular components are set equal so that each contribution to α_i is cylindrically symmetrical about the direction i to j to simplify the transformation from the local coordinate system directed along i to j to the space-fixed system. They were initially chosen to reproduce the components of molecular polarizability in diatomic molecules and then adjusted to fit and optimize the entire set of data. The parameters s = 1.00, t = 0.700, and n = 10 are found to phase in the dipole approximation so that T_{piqj} approaches the classical dipole tensor, eq 2, as r_{ij} exceeds $t\rho_{ij} = 0.7\rho_{ij}$, which is approximately 1.5–2 bond lengths. The point dipole approximation is valid at large distances but must be modified at distances less than the sum ρ_{ij}. Thole[9] discussed this in terms of the atomic polarizabilities of atoms intersecting each other. In the present approximation, the effect of bonded atoms is included through anisotropic atomic polariz-

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Table II. Polarizabilities, Scaled Components, and Orientation of Principal Axes

molecule	α,[a] Å^3	f_1[b]	f_2[b]	f_3[b]	α(mol),[c] Å^3	% rms[d] $\sigma(f)$		ref[e]	orientation
H_2	0.77	0.3030	0.3030	0.3940	0.77	0.2	M		$\alpha_3 \parallel$ symmetry axis
	0.79	0.3038	0.3038	0.3924			E	LB	
N_2	1.91	0.2750	0.2750	0.4500	1.91	0.1	M		$\alpha_3 \parallel$ symmetry axis
	1.76	0.2746	0.2746	0.4508			E	LB	
O_2	1.14	0.2570	0.2570	0.4860	1.14	0.8	M		$\alpha_3 \parallel$ symmetry axis
	1.60	0.2536	0.2536	0.4926			E	LB	
Cl_2	4.63	0.2800	0.2800	0.4400	4.63	4.5	M		$\alpha_3 \parallel$ symmetry axis
	4.61	0.2617	0.2617	0.4772			E	LB	
HF	0.68	0.2889	0.2889	0.4223	0.68	2.7	M		$\alpha_3 \parallel$ symmetry axis
	0.80	0.3000	0.3000	0.4000			E	LB	
HCl	2.70	0.2833	0.2833	0.4334	2.70	4.6	M		$\alpha_3 \parallel$ symmetry axis
	2.63	0.3029	0.3029	0.3967			E	LB	
HBr	3.40	0.3003	0.3003	0.3993	3.40	1.2	M		$\alpha_3 \parallel$ symmetry axis
	3.61	0.3056	0.3056	0.3897			E	LB	
HI	5.80	0.3189	0.3189	0.3623	5.80	4.9	M		$\alpha_3 \parallel$ symmetry axis
	5.45	0.2991	0.2991	0.4024			E	LB	
CO	1.92	0.2820	0.2820	0.4360	1.92	1.0	M		$\alpha_3 \parallel$ symmetry axis
	1.95	0.2778	0.2778	0.4444			E	LB	
CO_2	2.42	0.2535	0.2535	0.4930	2.48	1.4	M		$\alpha_3 \parallel$ symmetry axis
	2.65	0.2478	0.2478	0.5044			E	LB	
SO_2	5.00	0.2456	0.3044	0.4500	5.06	2.4	M		$\alpha_1 \perp$ OSO plane, $\alpha_2 \parallel$ 2-fold axis
	3.90	0.2325	0.2983	0.4692			E	LB	
CS_2	8.74	0.2026	0.2026	0.5948	10.06	2.1	M		$\alpha_3 \parallel$ symmetry axis
	8.74	0.2113	0.2113	0.5774			E	LB	
H_2S	3.77	0.2959	0.3420	0.3621	3.79	1.3	M		$\alpha_1 \perp$ plane, $\alpha_2 \parallel$ 2-fold axis
	3.83	0.2994	0.3490	0.3516			E	LB	
N_2O	2.48	0.2466	0.2466	0.5068	2.60	4.1	M		$\alpha_3 \parallel$ symmetry axis
	3.00	0.2300	0.2300	0.5400			E	LB	
methane	2.61	0.3333	0.3333	0.3333	2.68	0.0	M		regular tetrahedron
	2.60	0.3333	0.3333	0.3333			E	LB	
ethane	4.44	0.3142	0.3142	0.3715	4.64	0.1	M		$\alpha_3 \parallel$ 3-fold axis
	4.48	0.3140	0.3140	0.3720			E	AP	
propane	6.28	0.2993	0.3197	0.3810	6.60	2.8	M		$\alpha_1 \perp$ CCC plane, $\alpha_2 \parallel$ 2-fold axis
	6.38	0.2999	0.2999	0.4002			E	AP	
neopentane	9.95	0.3333	0.3333	0.3333	10.48	0.0	M		regular tetrahedron
	10.20	0.3333	0.3333	0.3333			E	AP	
cyclopentane	9.18	0.2890	0.3533	0.3577	9.77	2.6	M		$\alpha_1 \perp$ average plane
	9.15	0.3060	0.3341	0.3599			E	AP	
cyclopentane	9.18	0.2890	0.3533	0.3577	9.77	2.6	M		$\alpha_1 \perp$ average plane
	9.15	0.3060	0.3341	0.3599			E	AP	
cyclohexane	11.01	0.2841	0.3580	0.3580	11.67	0.1	M		$\alpha_1 \perp$ 3-fold axis and $\parallel$ to axial CH bonds
	11.00	0.2842	0.3579	0.3579			E	AP	
CH_3F	2.52	0.3316	0.3316	0.3369	2.58	8.1	M		$\alpha_3 \parallel$ 3-fold axis
	2.62	0.2977	0.2977	0.4046			E	AP	
CHF_3	2.34	0.3298	0.3351	0.3351	2.39	1.3	M		$\alpha_1 \parallel$ 3-fold axis
	2.81	0.3191	0.3405	0.3405			E	AP	
CF_4	2.25	0.3333	0.3333	0.3333	2.26	0.0	M		regular tetrahedron
	2.92	0.3333	0.3333	0.3333			E	AP	
CH_3Cl	4.54	0.2848	0.2848	0.4305	4.76	1.7	M		$\alpha_3 \parallel$ 3-fold axis
	4.55	0.2916	0.2916	0.4161			E	AP	
CH_2Cl_2	6.47	0.2563	0.3124	0.4313	6.96	0.7	M		$\alpha_1 \perp$ ClCCl plane, $\alpha_2 \parallel$ 2-fold axis
	6.82	0.2620	0.3079	0.4306			E	AP	
$CHCl_3$	8.39	0.2542	0.3729	0.3729	9.25	1.1	M		$\alpha_1 \parallel$ 3-fold axis
	8.53	0.2634	0.3681	0.3681			E	AP	
CCl_4	10.32	0.3333	0.3333	0.3333	11.58	0.0	M		regular tetrahedron
	10.51	0.3333	0.3333	0.3333			E	AP	
C_2H_5Cl	6.37	0.2770	0.3086	0.4143	6.79	4.3	M		$\alpha_1 \perp$ CCCl plane, $(\alpha_2, \mathrm{CC}) = 39.6°$, $(\alpha_2, \mathrm{CCl}) = 69.9°$
	6.40	0.2609	0.3438	0.3953			E	LB	
CH_3Br	5.24	0.2940	0.2940	0.4121	5.44	0.2	M		$\alpha_3 \parallel$ 3-fold axis
	5.61	0.2947	0.2947	0.4106			E	AP	
CH_2Br_2	7.86	0.2754	0.2861	0.4385	8.30		M		$\alpha_1 \perp$ BrCBr plane, $\alpha_2 \parallel$ 2-fold axis
	8.68	0.0000	0.0000	0.0000			E	AP	
$CHBr_3$	10.49	0.2624	0.3688	0.3688	11.31	0.7	M		$\alpha_1 \parallel$ 3-fold axis
	11.84	0.2683	0.3660	0.3660			E	AP	
CH_3I	7.64	0.3046	0.3046	0.3907	7.86	0.7	M		$\alpha_3 \parallel$ 3-fold axis
	7.59	0.3017	0.3017	0.3961			E	AP	
CH_2I_2	12.67	0.2782	0.3050	0.4168	13.27		M		$\alpha_1 \perp$ ICI plane, $\alpha_2 \parallel$ 2-fold axis
	12.90	0.0000	0.0000	0.0000			E	AP	
CHI_3	17.69	0.2627	0.3686	0.3686	18.83	5.7	M		$\alpha_1 \parallel$ 3-fold axis
	18.04	0.3093	0.3453	0.3453			E	AP	
ethylene	4.25	0.2509	0.3509	0.3982	4.44	8.6	M		$\alpha_1 \perp$ plane, $\alpha_3 \parallel$ C=C axis
	4.26	0.2809	0.2809	0.4390			E	LB	
ethylene	4.25	0.2528	0.3516	0.3956	4.43		M		$\alpha_1 \perp$ plane, $\alpha_3 \parallel$ C=C axis
	4.26	0.0000	0.0000	0.0000			E	BR	
$CH_2{=}CCl_2$	8.11	0.2237	0.3643	0.4120	8.86	4.0	M		$\alpha_1 \perp$ plane, $\alpha_2 \parallel$ C=C axis
	7.83	0.2448	0.3742	0.3814			E	BR	

Table II (Continued)

molecule	α,[a] Å^3	f_1[b]	f_2[b]	f_3[b]	α(mol),[c] Å^3	% rms[d] $\sigma(f)$		ref[e]	orientation
cis-CHCl=CHCl	8.11	0.2250	0.3694	0.4056	8.78	5.0	M		$\alpha_1 \perp$ plane, $\alpha_2 \parallel$ 2-fold axis,
	7.78	0.2605	0.3342	0.4053			E	BR	$\alpha_3 \parallel$ C=C axis
trans-CHCl=CHCl	8.11	0.2260	0.2922	0.4818	8.84		M		$\alpha_1 \perp$ plane, (α_2, C=C) = 44°,
	7.78	0.0000	0.0000	0.0000			E		(α_2, CCl) = 134°, (α_3, Cl···Cl) = 0°
CHCl=CCl$_2$	10.04	0.2139	0.3519	0.4342	11.09	2.8	M		$\alpha_1 \perp$ pl, (α_2, C=C) = 39°, (α_2, geminal
	9.75	0.2366	0.3429	0.4209			E	BR	Cl···Cl) = 51°, (α_3, C=C) = 129°,
									(α_3, geminal Cl···Cl) = 39°
benzene	10.43	0.2012	0.3994	0.3994	11.70	0.5	M		$\alpha_1 \perp$ plane
	10.32	0.2051	0.3976	0.3976			E	LB	
benzene	10.43	0.2023	0.3989	0.3989	11.70	5.1	M		$\alpha_1 \perp$ plane
	9.90	0.2458	0.3771	0.3771			E	LS	
toluene	12.27	0.2052	0.3654	0.4294	13.94	0.8	M		$\alpha_1 \perp$ plane, $\alpha_3 \parallel$ CCH$_3$ axis
	12.26	0.2034	0.3714	0.4252			E	LB	
toluene	12.27	0.2060	0.3652	0.4288	13.94	6.3	M		$\alpha_1 \perp$ plane, $\alpha_3 \parallel$ CCH$_3$ axis
	11.83	0.2564	0.3494	0.3945			E	LR	
p-xylene	14.10	0.2069	0.3394	0.4537	16.25	3.8	M		$\alpha_1 \perp$ plane, $\alpha_3 \parallel$ CH$_3$C···C–CH$_3$ axis
	14.20	0.2066	0.3662	0.4272			E	LB	
m-xylene	14.10	0.2073	0.3657	0.4270	16.20	1.7	M		$\alpha_1 \perp$ plane, $\alpha_2 \parallel$ 2-fold axis
	14.18	0.2010	0.3799	0.4191			E	LB	
o-xylene	14.10	0.2063	0.3782	0.4156	16.08	1.4	M		$\alpha_1 \perp$ plane, $\alpha_3 \parallel$ 2-fold axis
	14.13	0.1958	0.3805	0.4237			E	LB	
C$_6$H$_5$Cl	12.36	0.1946	0.3587	0.4468	14.13	1.8	M		$\alpha_1 \perp$ plane, $\alpha_3 \parallel$ 2-fold axis
	12.25	0.2063	0.3603	0.4335			E	LB	
p-dichlorobenzene	14.29	0.1887	0.3273	0.4840	16.66	4.2	M		$\alpha_1 \perp$ plane, $\alpha_3 \parallel$ 2-fold axis
	14.20	0.2073	0.2930	0.4998			E	LB	
m-dichlorobenzene	14.29	0.1888	0.3633	0.4479	16.64	4.9	M		$\alpha_1 \perp$ plane, $\alpha_2 \parallel$ 2-fold axis
	14.24	0.2062	0.3858	0.4078			E	LB	
o-dichlorobenzene	14.29	0.1887	0.3799	0.4314	16.49	3.7	M		$\alpha_1 \perp$ plane, $\alpha_3 \parallel$ 2-fold axis
	14.17	0.2117	0.3510	0.4373			E	LB	
fluorobenzene	10.34	0.2023	0.3988	0.3989	11.62	4.9	M		$\alpha_1 \perp$ plane, $\alpha_3 \parallel$ 2-fold axis
	9.86	0.2414	0.3715	0.3867			E	AC	
1,2-difluorobenzene	10.25	0.2024	0.3987	0.3989	11.52	3.8	M		$\alpha_1 \perp$ plane, $\alpha_2 \parallel$ 2-fold axis
	9.80	0.2327	0.3772	0.3901			E	AC	
1,4-difluorobenzene	10.25	0.2025	0.3987	0.3989	11.52	4.0	M		$\alpha_1 \perp$ plane, $\alpha_3 \parallel$ F···F 2-fold axis
	9.80	0.2327	0.3731	0.3942			E	AC	
1,2,4,5-tetrafluoro-	10.07	0.2028	0.3985	0.3987	11.34	4.0	M		$\alpha_1 \perp$ plane, $\alpha_3 \parallel$ H···H 2-fold axis
benzene	9.69	0.2147	0.3660	0.4190			E	AC	
1,2,3,4-tetrafluoro-	10.07	0.2028	0.3985	0.3987	11.34	1.5	M		$\alpha_1 \perp$ plane, $\alpha_2 \parallel$ 2-fold axis
benzene	9.69	0.2147	0.3904	0.3946			E	AC	
pentafluorobenzene	9.98	0.2029	0.3985	0.3986	11.24	1.7	M		$\alpha_1 \perp$ plane, $\alpha_3 \parallel$ 2-fold axis
	9.63	0.2056	0.3853	0.4091			E	AC	
nitrobenzene	12.41	0.1844	0.3771	0.4384	14.38	4.3	M		$\alpha_1 \perp$ plane, $\alpha_3 \parallel$ 2-fold axis
	12.92	0.1999	0.3418	0.4582			E	LB	
acetylene	3.34	0.2501	0.2501	0.4999	3.50	1.6	M		$\alpha_3 \parallel$ symmetry axis
	3.33	0.2432	0.2432	0.5125			E	LB	
H$_2$O	1.41	0.2659	0.3294	0.4047	1.42		M		$\alpha_1 \perp$ plane, $\alpha_2 \parallel$ 2-fold axis
	1.45	0.0000	0.0000	0.0000			E	BA	
methanol	3.25	0.2939	0.3148	0.3913	3.38	3.5	M		$\alpha_1 \perp$ COH plane, (α_2, CO) = 62°,
	3.32	0.2661	0.3243	0.4106			E	AP	(α_2, OH) = 47°, (α_3, CO) = 28°,
									(α_3, OH) = 137°
ethanol	5.08	0.2905	0.3119	0.3976	5.37	2.5	M		$\alpha_1 \perp$ CCO pl, (α_2, CO) = 41°,
	5.08	0.2953	0.3268	0.3780			E	AP	(α_2, CC) = 69°, (α_3, CO) = 131°,
									(α_3, CC) = 21°, trans CCOH
ethanol	5.08	0.2907	0.3464	0.3629	5.32	2.5	M		$\alpha_1 \perp$ CCO pl, (α_2, CO) = 48°,
	5.08	0.2953	0.3268	0.3780			E	AP	(α_2, CC) = 62°, (α_3, CO) = 138°,
									(α_3, CC) = 28°, cis CCOH
ethanol	5.08	0.2906	0.3291	0.3803	5.35	0.6	M		average of cis and trans conformations
2-propanol	6.92	0.3081	0.3335	0.3585	7.26		M		$\alpha_3 \perp$ HCOH plane, (α_1, CO) = 90°,
	6.97	0.0000	0.0000	0.0000			E	AP	(α_2, CO) = 0°, C_s symmetry
2-propanol	6.92	0.2958	0.3337	0.3705	7.28		M		torsional angle (C, C, O, H) = 0°
	6.97	0.0000	0.0000	0.0000			E	AP	
cyclohexanol	11.65	0.2945	0.3465	0.3590	12.35		M		$\alpha_1 \perp$ average plane
	11.56	0.0000	0.0000	0.0000			E	AP	
cyclohexanol	11.65	0.2968	0.3469	0.3469	12.30		M		$\alpha_1 \perp$ average plane
	11.56	0.0000	0.0000	0.0000			E	AP	
ethylene oxide	4.31	0.3112	0.3181	0.3707	4.48		M		$\alpha_1 \parallel$ 2-fold axis, $\alpha_2 \perp$ COC plane,
	4.43	0.0000	0.0000	0.0000			E	AP	$\alpha_3 \parallel$ CC
dimethyl ether	5.08	0.2887	0.2965	0.4148	5.4	2.2	M		$\alpha_1 \perp$ COC plane, $\alpha_2 \parallel$ 2-fold axis
	5.24	0.2793	0.3142	0.4059			E	AP	
diethyl ether	8.75	0.2781	0.2962	0.4257	9.51	1.0	M		$\alpha_1 \perp$ CCOCC plane, $\alpha_2 \parallel$ 2-fold axis
	8.73	0.2700	0.3005	0.4299			E	LB	
di-*n*-propyl ether	12.42	0.2667	0.2851	0.4482	13.73	10.1	M		$\alpha_1 \perp$ average CCCOCCC plane,
	12.53	0.3113	0.3246	0.3645			E	LB	$\alpha_2 \parallel$ 2-fold axis, refer to Table IX
									and text
p-dioxane	8.61	0.2821	0.3251	0.3928	9.08	5.0	M		$\alpha_1 \perp$ plane, $\alpha_3 \parallel$ axial H's
	8.60	0.2713	0.3643	0.3643			E	AP	

Table II (Continued)

molecule	α,[a] Å^3	f_1[b]	f_2[b]	f_3[b]	α(mol),[c] Å^3	% rms[d] $\sigma(f)$		ref[e]	orientation
formaldehyde	2.70	0.2636	0.3416	0.3948	2.78	4.2	M		$\alpha_1 \perp$ plane, $\alpha_3 \parallel$ 2-fold axis
	2.45	0.2490	0.3755	0.3755			E	AP	
acetaldehyde	4.53	0.2782	0.3361	0.3857	4.76		M		$\alpha_1 \perp$ C(C=O)C plane, (α_2, CC) = 110°, (α_2, C=O) = 130°, (α_3, CC) = 20°, (α_3, C=O) = 140°
	4.590	0.000	0.0000	0.0000			E	AP	
acetone	6.37	0.2768	0.3425	0.3807	6.74	6.3	M		$\alpha_1 \perp$ C(C=O)C plane, $\alpha_2 \parallel$ C=O 2-fold axis
	6.39	0.2306	0.3845	0.3845			E	AP	
acetone	6.37	0.2768	0.3425	0.3807	6.74	3.8	M		$\alpha_1 \perp$ C(C=O)C plane, $\alpha_2 \parallel$ C=O 2-fold axis
	6.39	0.2546	0.3725	0.3735			E	AP	
methyl ethyl ketone	8.20	0.2712	0.3217	0.4071	8.79	3.8	M		$\alpha_1 \perp$ C(C=O)C plane, (α_2, C=O) = 14°, (α_3, C=O) = 104°, C_s symmetry
	8.13	0.2468	0.3506	0.4030			E	LB	
diethyl ketone	10.04	0.2662	0.3137	0.4202	10.88	3.5	M		$\alpha_1 \perp$ C(C=O)C plane, $\alpha_2 \parallel$ C=O
	9.93	0.2400	0.3360	0.4243			E	LB	
methyl propyl ketone	10.04	0.2660	0.3115	0.4225	10.87	3.6	M		$\alpha_1 \perp$ C(C=O)C plane, (α_2, C=O) = 3°, (α_3, C=O) = 87°, C_s symmetry
	9.93	0.2551	0.3404	0.4048			E	LB	
diisopropyl ketone	13.71	0.2938	0.3309	0.3753	14.62	3.1	M		$\alpha_2 \perp$ C(C=O)C plane, (α_1, C=O) = 161°, (α_2, C=O) = 109°, C_s symmetry
	13.53	0.2882	0.3117	0.3991			E	LB	
diisopropyl ketone	13.71	0.2832	0.3305	0.3863	14.71	2.3	M		$\alpha_2 \perp$ C(C=O)C plane, $\alpha_1 \parallel$ C=O axis, C_{2v} symmetry
	13.53	0.2882	0.3117	0.3991			E	LB	
HCN	2.63	0.2643	0.2643	0.4715	2.68	4.1	M		$\alpha_3 \parallel$ symmetry axis
	2.59	0.2471	0.2471	0.5045			E	LB	
$(CN)_2$	4.48	0.2261	0.2261	0.5477	4.94	3.9	M		$\alpha_3 \parallel$ symmetry axis
	5.01	0.2422	0.2422	0.5163			E	LB	
acetonitrile	4.46	0.2758	0.2758	0.4484	4.74	2.6	M		$\alpha_3 \parallel$ symmetry axis
	4.48	0.2865	0.2865	0.4271			E	AP	
$(CH_3)_3CCN$	9.97	0.3168	0.3168	0.3665	10.70	0.7	M		$\alpha_3 \parallel$ symmetry axis
	9.59	0.3139	0.3139	0.3723			E	AP	
CCl_3CN	10.25	0.3299	0.3299	0.3402	11.54	0.2	M		$\alpha_3 \parallel$ symmetry axis
	10.42	0.3292	0.3292	0.3420			E	AP	
NH_3	2.13	0.2761	0.3619	0.3619	2.16	6.1	M		$\alpha_1 \perp$ to 3-fold axis
	2.26	0.3215	0.3215	0.3569			E	LB	
$HCONH_2$	4.17	0.2317	0.3573	0.4110	4.40	2.4	M		$\alpha_1 \perp$ plane, (α_2, C=O) = 127°, (α_2, CN) = 113°, (α_3, C=O) = 37°, (α_3, CN) = 157°
	4.08	0.0000	0.5727	0.4281			E	AP	
$HCONHCH_3$	6.01	0.2456	0.3284	0.4260	6.45	6.2	M		$\alpha_1 \perp$ plane, (α_2, C=O) = 111°, (α_2, CN) = 129°, (α_3, C=O) = 21°, (α_3, CN) = 141°, CH_3 trans to C=O
	5.91	0.0000	0.6176	0.3818			E	AP	
$HCONHCH_3$	6.01	0.2465	0.3503	0.4032	6.41	3.0	M		$\alpha_1 \perp$ plane, (α_2, C=O) = 1°, (α_2, CN) = 119°, (α_3, C=O) = 89°, (α_3, CN) = 151°, CH_3 cis to C=O
	5.91	0.0000	0.6176	0.3818			E	AP	
$HCON(CH_3)_2$	7.84	0.2486	0.3648	0.3866	8.44	2.4	M		$\alpha_1 \perp$ plane, (α_2, C=O) = 92°, (α_2, CN) = 148°, (α_3, C=O) = 2°, (α_3, CN) = 122°
	7.81	0.0000	0.5962	0.4033			E	AP	
CH_3CONH_2	6.01	0.2485	0.3559	0.3956	6.41	0.2	M		$\alpha_1 \perp$ plane, (α_2, C=O) = 176°, (α_2, CN) = 56°, (α_3, C=O) = 94°, (α_3, CN) = 146°
	5.67	0.0000	0.6055	0.3939			E	AP	
$CH_3C(CH_2O)_3P$	12.24	0.3097	0.3097	0.3805	12.96	1.9	M		$\alpha_3 \parallel$ 3-fold axis
	13.32	0.3173	0.3173	0.3654			E	AL	
$CH_3C(CH_2O)_3PO$	12.87	0.2978	0.2980	0.4042	13.83	2.9	M		$\alpha_3 \parallel$ 3-fold axis
	12.84	0.3097	0.3097	0.3806			E	AL	
$CH_3C(CH_2O)_3PS$	15.24	0.2855	0.2859	0.4286	16.57	2.7	M		$\alpha_3 \parallel$ 3-fold axis
	15.74	0.2967	0.2967	0.4064			E	AL	
uracil	10.27	0.1888	0.3918	0.4194	11.81	5.7	M		$\alpha_1 \perp$ plane, (α_2, N3H3) = 5°, (α_3, N3H3) = 95°, (α_2, C4O4) = 52°, (α_3, C4O4) = 38°
	10.09	0.1943	0.3492	0.4569			E	BG	
guanine	15.68	0.1846	0.3570	0.4585	18.54	3.2	M		$\alpha_1 \perp$ plane, (α_2, C2N2) = 110°, (α_3, C2N2) = 20°, (α_2, C6O6) = 0°, (α_3, C6O6) = 90°
	13.60	0.1799	0.3819	0.4385			E	BO	
adenine	15.05	0.1911	0.3864	0.4225	17.40	0.8	M		$\alpha_1 \perp$ plane, (α_2, C6N6) = 29°, (α_3, C6N6) = 61°, (α_2, C8H8) = 66°, (α_3, C8H8) = 156°
	13.10	0.1863	0.3852	0.4282			E	BO	
cytosine	11.12	0.1868	0.3679	0.4452	12.87	3.3	M		$\alpha_1 \perp$ plane, (α_2, C2O2) = 87°, (α_3, C2O2) = 177°, (α_2, C4N4) = 34°, (α_3, C4N4) = 56°
	10.30	0.1919	0.3421	0.4654			E	BO	
thymine	12.11	0.1950	0.3625	0.4425	14.03	1.1	M		$\alpha_1 \perp$ plane, (α_2, C4O4) = 72°, (α_3, C4O4) = 18°, (α_2, C5Me) = 133°, (α_3, C5Me) = 43°
	11.23	0.2009	0.3535	0.4455			E	BO	
furan	7.23	0.2290	0.3634	0.4076	7.78	2.8	M		$\alpha_1 \perp$ plane, $\alpha_2 \parallel$ 2-fold axis
	7.23	0.2476	0.3426	0.4099			E	LL	
thiophene	9.66	0.2308	0.3675	0.4018	10.41	3.2	M		$\alpha_1 \perp$ plane, $\alpha_2 \parallel$ 2-fold axis
	9.00	0.2481	0.3756	0.3759			E	LL	
pyrrole	8.43	0.2138	0.3868	0.3995	9.28	3.7	M		$\alpha_1 \perp$ plane, $\alpha_3 \parallel$ 2-fold axis
	7.94	0.2431	0.3648	0.3917			E	LL	
pyridine	9.73	0.2029	0.3762	0.4209	10.84	0.6	M		$\alpha_1 \perp$ plane, $\alpha_2 \parallel$ 2-fold axis
	9.47	0.2034	0.3816	0.4182			E	LB	
pyridine	10.11	0.2003	0.3974	0.4023	11.36	4.1	M		$\alpha_1 \perp$ plane, $\alpha_2 \parallel$ 2-fold axis

Table II (Continued)

molecule	α,[a] Å^3	f_1[b]	f_2[b]	f_3[b]	α(mol),[c] Å^3	% rms[d] $\sigma(f)$	ref[e]		orientation
	9.20	0.2337	0.3779	0.3884			E	LL	
naphthalene	17.70	0.1822	0.3599	0.4579	20.93	5.6	M		$\alpha_1 \perp$ plane, $\alpha_3 \parallel$ (minor) 2-fold axis, $\alpha_3 \parallel$ (major) 2-fold axis
	16.57	0.2273	0.3339	0.4385			E	LR	
quinoline	17.00	0.1836	0.3481	0.4684	20.08	3.4	M		$\alpha_1 \perp$ pl, (α_2, N1···C4) = 2°, (α_3, N1···C4) = 88°, (α_2, N1···C8) = 88°, (α_3, N1···C8) = 178°
	15.68	0.2017	0.3571	0.4409			E	LL	
isoquinoline	17.00	0.1845	0.3652	0.4503	19.90	5.4	M		$\alpha_1 \perp$ pl, (α_2, N2···C3) = 9°, (α_3, N2···C3) = 81°, (α_2, N2···C7) = 81°, (α_3, N2···C7) = 171°
	15.62	0.1660	0.4085	0.4247			E	LL	
anthracene	24.97	0.1663	0.3264	0.5072	31.22	5.4	M		$\alpha_1 \perp$ plane, $\alpha_2 \parallel$ (minor) 2-fold axis, $\alpha_3 \parallel$ (major) 2-fold axis
	25.37	0.2037	0.3285	0.4677			E	LR	
pyrene	28.77	0.1603	0.3778	0.4619	36.04	5.5	M		$\alpha_1 \perp$ plane, $\alpha_2 \parallel$ (minor) 2-fold axis, $\alpha_3 \parallel$ (major) 2-fold axis
	28.22	0.2008	0.3402	0.4589			E	LR	
chrysene	32.24	0.1528	0.3211	0.5261	42.18	9.4	M		$\alpha_1 \perp$ pl, (α_2, C3···C2) = 22°, (α_3, C3···C2) = 68°, (α_2, C3···C9) = 68°, (α_3, C3···C9) = 158°
	32.15	0.2011	0.3406	0.4479			E	LR	
triphenylene	32.24	0.1533	0.4233	0.4233	41.46	1.5	M		$\alpha_1 \perp$ plane
	31.07	0.1652	0.4173	0.4173			E	LS	
coronene	43.62	0.1409	0.4295	0.4295	58.16	1.6	M		$\alpha_1 \perp$ plane
	44.77	0.1541	0.4229	0.4229			E	LS	

[a] α, line M, refers to α(ahp) = α(mhp);[10] α, line E, refers to the average experimental result. [b] f_1, f_2, and f_3, the scaled principal components of polarizability, sum to 1 within round off and experimental error. [c] α(mol), the average unscaled molecular polarizability, eq 9, is included to demonstrate the effect of scaling. [d] The rms deviation is defined by eq 20. [e] References: LB, ref 12; AP, ref 7; BR, ref 13; LS, ref 14; LR, ref 15; AC, ref 16; BA, ref 17; AL, ref 18; BG, ref 19; BO, ref 20; LL, ref 21.

abilities in place of components T_{ij} when atom i is bonded to j. In eq 10, $\Delta\alpha_i$ is rotated along the direction of ij, and if i is not bonded to j, its effect is attennated by a function of the distance between the atoms. The parameters $c = 2.54$ and $d = 0.25$ are found to refine the effect of the molecular environment on the anisotropic contributions to α_i and yield the present empirical formulation.

The point and modified dipole models[7-9] were based on finding a set of atomic polarizabilities that yielded principal components of molecular polarizability in agreement with experimental results. The dipole approximation is valid when the separation between dipoles is large compared to the induced dipole moments. Thole[9] analyzed this problem and noted that the polarizabilities, which are approximately the atomic volumes, could be used to design shape and size parameters in potential energy functions. He proposed several functional forms, which obey certain boundary conditions, and obtained good results.

In contrast, the present paper includes the effect of the dipole approximation with increasing distance, by omitting the terms with bonded atoms and assuming that these effects are replaced by atomic anisotropies. In the case of diatomic molecules, the anisotropies can be rationalized by using an atomic polarizability matrix that reproduces the molecular polarizability without the dipole tensor. These ideas are extended to the approximations for polyatomic molecules.

The neglect of nearest neighbor dipole terms on the polarizability tensor can be justified both qualitatively and quantitatively. Dipole expansions are valid for long-range interactions. Consequently, the adjustment of the atomic polarizabilities within the immediate molecular environment in the full dipole approximation[7-9] must compensate for overemphasis of these short-range interactions. The present empirical method replaces these neighbor terms with local bond polarizability components, with the result that the atomic hybrid polarizabilities need no further adjustment. The rationale is based on the fact that atoms undergo hybridization in the immediate bonding environment with virtually no influence from the nonbonded interactions. This strongly influences the polarizability parameters. For example, in an empirical analysis, the additivity of atomic hybrid components[10,11] supports the neglect of nonbonded effects in the present model of average molecular polarizability, as demonstrated by the transferability of parameters among many molecules without regard to the atomic environment.[10,11] The atom to which a given atom is bonded is not required, but only its state of hybridization. The same behavior appears valid for the components of molecular polarizability. The present data set yields results within experimental error. Consequently, small modifications in the atomic hybrid polarizabilities will not improve the empirical fit consistently for the entire data set, because they depend on the number of data points used and the manner in which the data set is partitioned. Revisions made every time new data were added did not yield an overall improvement. Until experimental data accurate to 1% are available, further refinements in the atomic components will not yield meaningful results.

A quantum mechanical and quantitative evaluation, support, and justification is found in recent calculations by Garmer and Stevens[22] on the transferability of molecular distributed polarizabilities. Their results on methane, ethane, propane, acetonitrile, methylamine, methanol, ethanol, and dimethyl ether support the present study. By using localized molecular orbital techniques, they partition the bond polarizabilities at the bond centroids for the purpose of developing a set of transferable bond polarizability tensors. They found that the bond centroids and the polarizability tensors for the C–H bonds are transferable with a standard deviation of 0.14, which is of the order of 3–4% for the average polarizability. This is equivalent to the errors in the experimental measurements. Although an exact derivation or extensive quantum mechanical calculations are not available for a partitioning into either bond or atomic contributions, it appears that the results to date support the importance of the influence of the local environment on the polarizability with long-range dipolar adjustments to obtain the proper molecular polarizability components. The present empirical method yields results that are within experimental errors and internally consistent. Another important feature is that it is sufficiently simple to code and it is an effective approximation for molecular modeling.

Effects of nonadditivity begin to appear in large polymeric systems. The increase in the longitudinal polarizabilities of conjugated polymers is the basis for their utilization in optical signal processing devices.[23] Theoretical longitudinal polarizabilities of polydiacetylene and polybutatriene have been calculated with the STO-3G and 4-31G basis sets by Kirtman and Hasan[23] and with the INDO method by Kirtman.[24] These calculations show that the increment by which the z component changes reaches a plateau in the INDO but not in the STO basis sets. The increment, $\Delta\alpha_{zz}/N$ for the change in PDA, C_6H_6 + NC_2H_2,

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Table III. Comparison of Molecular Polarizabilities among Several Methods

molecule	method[a]	α, Å^3	f_1	f_2	f_3	100δf,[b] %
H2	E	0.79	0.304	0.304	0.392	
	A	0.80	0.800	0.100	0.100	49.9
	B	0.80	0.304	0.304	0.392	0.0
	T	0.76	0.303	0.303	0.395	0.3
	M	0.77	0.304	0.304	0.392	0.2
N2	E	1.76	0.275	0.275	0.451	
	A	1.76	0.136	0.136	0.727	33.9
	B	1.76	0.275	0.275	0.451	0.0
	T	1.72	0.294	0.294	0.412	4.7
	M	1.91	0.275	0.275	0.450	0.1
O2	E	1.60	0.254	0.254	0.493	
	A	1.60	0.177	0.177	0.647	18.8
	B	1.60	0.255	0.255	0.490	0.4
	T	1.49	0.281	0.281	0.438	6.8
	M	1.14	0.252	0.252	0.490	0.8
CO	E	1.95	0.278	0.278	0.444	
	A	1.95	0.138	0.138	0.723	34.2
	B	1.95	0.277	0.277	0.445	0.2
	T	1.82	0.295	0.295	0.409	4.2
	M	1.92	0.282	0.282	0.444	1.0
ethane	E	4.48	0.314	0.314	0.372	
	A	4.46	0.267	0.267	0.466	11.6
	B	4.46	0.280	0.280	0.441	8.4
	T	4.46	0.316	0.316	0.368	0.5
	M	4.44	0.314	0.314	0.372	0.0
propane	E	6.38	0.300	0.300	0.400	
	A	6.58	0.257	0.289	0.453	6.8
	B	6.58	0.311	0.324	0.365	4.4
	T	6.29	0.302	0.317	0.381	2.6
	M	6.28	0.299	0.320	0.381	2.8
cyclopetane	E	9.15	0.306	0.334	0.360	
	A	9.05	0.264	0.367	0.369	5.5
	B	9.05	0.277	0.358	0.365	3.8
	T	9.12	0.306	0.334	0.360	2.1
	M	9.18	0.289	0.353	0.358	2.6
cyclohexane	E	11.00	0.284	0.358	0.358	
	A	10.95	0.254	0.373	0.373	3.7
	B	10.95	0.267	0.367	0.367	2.1
	T	10.95	0.288	0.288	0.356	5.0
	M	11.01	0.284	0.358	0.358	0.0
dimethyl ether	E	5.24	0.279	0.314	0.406	
	A	5.20	0.268	0.280	0.452	6.5
	B	5.20	0.268	0.347	0.385	8.4
	T	5.24	0.291	0.292	0.417	2.9
	M	5.08	0.289	0.297	0.415	2.2
p-dioxane	E	8.60	0.271	0.364	0.364	
	A	8.68	0.244	0.370	0.387	3.6
	B	8.68	0.248	0.362	0.389	3.4
	T	8.84	0.279	0.324	0.397	5.3
	M	8.61	0.282	0.325	0.393	5.0
methanol	E	3.32	0.266	0.324	0.410	
	A	3.04	0.291	0.302	0.407	3.4
	B	3.04	0.274	0.308	0.418	1.9
	T	3.34	0.295	0.310	0.395	3.6
	M	3.25	0.294	0.315	0.391	3.5
ethanol	E	5.08	0.295	0.327	0.378	
	A	5.11	0.256	0.280	0.463	10.4
	B	5.11	0.286	0.321	0.393	1.8
	T	5.26	0.289	0.306	0.405	3.5
	M	5.08	0.291	0.346	0.363	2.5
formaldehyde	E	2.45	0.249	0.376	0.376	
	A	2.31	0.135	0.316	0.549	21.6
	B	2.31	0.186	0.369	0.445	9.4
	T	2.54	0.244	0.354	0.402	3.4
	M	2.70	0.264	0.342	0.395	4.2
acetone	E	6.39	0.254	0.372	0.373	
	A	6.46	0.263	0.368	0.370	1.0
	B	6.46	0.264	0.365	0.371	1.2
	T	6.32	0.272	0.343	0.385	3.6
	M	6.37	0.277	0.343	0.381	3.8
acetonitrile	E	4.48	0.286	0.286	0.427	
	A	4.14	0.232	0.232	0.536	13.4
	B	4.14	0.263	0.263	0.474	5.7
	T	4.24	0.280	0.280	0.440	1.6
	M	4.46	0.276	0.276	0.474	2.6
$(CH_3)_3CCN$	E	9.59	0.314	0.314	0.372	
	A	9.84	0.319	0.321	0.360	1.6
	B	9.84	0.319	0.319	0.363	1.1
	T	9.83	0.319	0.319	0.362	1.3
	M	9.97	0.317	0.317	0.367	0.7
CCl_3CN	E	10.42	0.329	0.329	0.342	
	A	10.28	0.330	0.330	0.342	0.2
	M	10.24	0.330	0.330	0.340	0.3
CH_3F	E	2.62	0.298	0.298	0.405	
	A	2.47	0.337	0.337	0.326	9.6
	M	2.51	0.332	0.332	0.337	8.3
CHF_3	E	2.81	0.319	0.340	0.340	
	A	2.78	0.321	0.339	0.339	0.3
	M	2.32	0.330	0.335	0.335	1.3
CH_3Cl	E	4.55	0.292	0.292	0.416	
	A	4.54	0.267	0.267	0.467	1.7
	M	4.54	0.285	0.285	0.431	1.7
CH_2Cl_2	E	6.82	0.262	0.308	0.430	
	A	6.65	0.234	0.291	0.475	5.5
	M	6.47	0.256	0.312	0.431	0.7
$CHCl_3$	E	8.53	0.263	0.368	0.368	
	A	8.73	0.223	0.388	0.388	4.9
	M	8.39	0.254	0.373	0.373	1.1
CH_3Br	E	5.61	0.295	0.295	0.411	
	A	5.39	0.267	0.267	0.466	6.8
	M	5.24	0.294	0.294	0.412	0.2
$CHBr_3$	E	11.84	0.268	0.366	0.366	
	A	10.49	0.262	0.369	0.369	0.7
	M	11.89	0.225	0.387	0.387	5.3
CH_3I	E	7.59	0.302	0.302	0.396	
	A	7.29	0.269	0.269	0.463	8.2
	M	7.64	0.305	0.305	0.391	0.7
CH_3I	E	18.04	0.309	0.345	0.345	
	A	18.48	0.215	0.393	0.393	11.6
	M	17.69	0.263	0.369	0.369	5.7

[a] E, experimental results given by the indicated reference; A, theoretical results of Applequist et al.;[7] B, theoretical results of Birge;[8] T, theoretical results of Thole;[8] M, theoretical results of this paper. [b] δf is defined by eq 20.

Table IV. Polarizability Components of Minimum-Energy Conformations of di-*n*-Propyl Ether[a]

α_{mol}	f_1	f_2	f_3	α(ahp)	100δf, %	ref	U	conformation	*w*
12.42	0.2667	0.2850	0.4482	13.73	10.3	T	−6.4	ttOtt	1
12.53	0.3113	0.3246	0.3645			E			
12.42	0.2744	0.2995	0.4261	13.58	7.6	T	−6.5	ttOtg$^-$	4
12.53	0.3113	0.3246	0.3645			E			
12.42	0.2942	0.3064	0.3994	13.43	4.3	T	−6.7	g$^-$tOtg$^-$	2
12.53	0.3113	0.3246	0.3645			E			
12.42	0.2760	0.3271	0.3969	13.41	4.8	T	−6.8	g$^+$tOtg$^-$	2
12.53	0.3113	0.3246	0.3645			E			
12.4	0.2783	0.3055	0.4161	13.41	6.4	T	−6.6	average	

[a] Conformations about the etheral oxygen and along the Me–C–C–O–C–C–Me bond sequence are indicated. The average is calculated with the weighting factors *w*. δf is defined by eq 20.

Table V. Molecular Polarizability with Successive Approximations to α_A and T[a]

molecule	α(ahp), Å^3	f_1	f_2	f_3	α(mol), Å^3	$100\delta f$, %	approx
CS2	8.74	0.3333	0.3333	0.3333	8.74	29.9	1
	8.74	0.2498	0.2498	0.5004	8.74	9.4	2
	8.74	0.3045	0.3045	0.3910	8.88	22.8	3
	8.74	0.2070	0.2070	0.5860	9.99	1.1	4
	8.74	0.2113	0.2113	0.5774			exp
ethane	4.44	0.3333	0.3333	0.3333	4.44	9.2	1
	4.44	0.3244	0.3244	0.3512	4.44	7.0	2
	4.44	0.3108	0.3108	0.3784	4.55	3.7	3
	4.44	0.3148	0.3148	0.3704	4.64	4.6	4
	4.48	0.2961	0.2961	0.4085			exp
nitrobenzene	12.41	0.3333	0.3333	0.3333	12.41	18.3	1
	12.41	0.2703	0.3633	0.3664	12.41	11.8	2
	12.41	0.2275	0.3544	0.4181	13.45	5.0	3
	12.41	0.1854	0.3769	0.4377	14.36	4.3	4
	12.92	0.1999	0.3418	0.4582			exp
diethyl ether	8.75	0.3333	0.3333	0.3333	8.75	12.0	1
	8.75	0.3280	0.3281	0.3439	8.75	10.7	2
	8.75	0.2793	0.2996	0.4211	9.25	1.3	3
	8.75	0.2783	0.2962	0.4254	9.50	1.0	4
	8.73	0.2700	0.3005	0.4299			exp
guanine	14.59	0.3333	0.3333	0.3333	14.59	19.2	1
	15.68	0.2832	0.3545	0.3624	15.68	13.1	2
	14.59	0.2230	0.3436	0.4335	16.03	5.8	3
	14.59	0.1755	0.3582	0.4663	17.39	3.7	4
	13.60	0.1799	0.3819	0.4385			exp
$CH_3C(CH_2O)_3PO$	12.87	0.3333	0.3333	0.3333	12.87	23.2	1
	12.87	0.3097	0.3097	0.3806	12.87	3.6	2
	12.87	0.3076	0.3076	0.3846	13.54	0.5	3
	12.87	0.2969	0.2969	0.4062	13.98	3.1	4
	12.84	0.3097	0.3097	0.3806			exp
acetonitrile	4.46	0.3333	0.3333	0.3333	4.46	11.5	1
	4.46	0.3122	0.3122	0.3756	4.53	6.3	2
	4.46	0.2972	0.2972	0.4056	4.46	2.6	3
	4.46	0.2769	0.2769	0.4462	4.73	2.4	4
	4.48	0.2865	0.2865	0.4271			exp

[a] The four successive approximations are described in the text. α(ahp) is the average molecular or atomic hybrid polarizability. f_μ, μ = 1, 2, and 3 are the scaled principal components for each approximation. α(mol) is the nonscaled average molecular polarizability. δf is defined by eq 20.

Table VI. Atomic Polarizabilities for Various Methods[a]

atom	atomic hybrid	dipole models A, B	additive model V	ahp model M	modified dipole model T
H(alkane)	H	0.135	0.407	0.387	0.514
H(alcohol)	H	0.135	0.405	0.387	
H(aldehyde)	H	0.167		0.387	
H(amide)	H	0.161		0.387	
C(alkane)	CTE	0.878	1.027	1.061	1.405
C(carbonyl)	CTR	0.616	1.027	1.352	
C(nitrile)	CD1	0.36	0.928	1.283	
N(amide)	NPI2	0.530		1.090	1.105
N(nitrile)	ND1	0.52	1.236	0.956	
O(alcohol)	OTE	0.465	0.604	0.637	0.862
O(ether)	OTE	0.465	0.651	0.637	
O(carbonyl)	OTR4	0.434	0.841	0.569	
F		0.32	0.32	0.296	
Cl		1.91	2.32	2.315	
Br		2.88	3.465	3.013	
I		4.69	5.531	5.415	

[a] A, Applequist et al.;[7] B, Birge;[8] V, Vogel;[11] M, Miller;[10] T, Thole.[9]

increases by 21% for the INDO calculations and by 19% in sample calculations in the present unscaled modified dipole method. Similar results are obtained for polybutatriene. The interpretation within the present modified dipole model is that the components T_{piqj} contribute to the **A** matrix in eq 5 until the nearest, next nearest, etc. neighbor interactions become sufficiently damped so that the long-range contributions vanish. Then the **B** matrix in eqs 6 and 7 and finally the molecular polarizability matrix become saturated. The additivity and scaling methods used in the present semiempirical methods[10,11] apply to small molecules and should be used accordingly. Sufficient data on linear polymeric systems are not available to provide additional calibrations for nonlinear effects, especially on the components of polarizability.

Essential features of the present method are as follows: Atomic anisotropies are introduced to ensure that the average atomic polarizabilities remained fixed at the α_A(ahp) values[1] and the final molecular polarizability matrix is normalized and rescaled to yield α(ahp) and the principal components of molecular polarizability. The present approach unifies the additivity of atomic polarizabilities of the ahp method with a modified dipole tensor approximation.

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