Conclusion

Explicit expressions have been presented for calculating internuclear distances from NOE data. In addition, several conclusions can be drawn from the quantitative theory which are of value even when the enhancements can be used in only a qualitative manner. Some of these are as follows.

1. A zero NOE does *not necessarily* imply that the two spins are distant. It can be due to a cancellation of the direct and indirect ("three-spin") effects.

2. The relative values of the *enhancements of A*, $f_A(i), f_A(j), \ldots$, when the other spins $i, j, \ldots$ are saturated are a much better indication of the position of A with respect to those other spins than are the relative enhancements of the other spins when A is saturated.

3. If $f_A(m)$ and $f_A(x)$ are the *only* large enhancements of spin A, then

$$\frac{r_{ax}}{r_{am}} \approx \left(\frac{f_A(m)}{f_A(x)}\right)^{1/6}$$

This is, at least, a good way to get first approximations.

4. If the NOE between two spins is negative, another spin lies more or less between them. This conclusion is, however, only valid in the absence of chemical exchange effects.

5. Indirect effects through rapidly relaxing spins or groups of spins are small. Thus methyl groups or quadrupolar nuclei will not give large "three-spin" effects.

6. NOE enhancements are sensitive only to *relative* distances and the size of ρ^*. Large values of $f_i(j)$ and $f_j(i)$ imply only that i and j are closer to each other than to other spins. Large values of ρ^* will result in small NOE's but will not destroy the dependence of the NOE's on distance ratios.

Acknowledgment. We wish to thank Phillip A. Hart and Jeffrey P. Davis for many helpful and stimulating discussions and for initially bringing this problem to our attention.

An Atom Dipole Interaction Model for Molecular Polarizability. Application to Polyatomic Molecules and Determination of Atom Polarizabilities

Jon Applequist,* James R. Carl, and Kwok-Keung Fung

Contribution from the Department of Biochemistry and Biophysics, Iowa State University, Ames, Iowa 50010. *Received September 23, 1971*

Abstract: The Silberstein model for molecular polarizability is applied to polyatomic molecules. The atoms are regarded as isotropically polarizable points located at their nuclei, interacting *via* the fields of their induced dipoles. The theory is restated in a simple exact form suitable for numerical calculation of molecular polarizability tensors. The use of additive values for atom polarizabilities gives poor results, in some cases leading to artificial predictions of absorption bands. The theory is used to determine optimum polarizabilities of H, C, N, O, F, Cl, Br, and I in 41 different molecules including alkanes, alcohols, ethers, halomethanes, aldehydes, ketones, amides, and nitriles. The atom polarizabilities found are significantly smaller than the additive values in most cases. Using the new values, the agreement between calculated and experimental mean molecular polarizabilities is usually within 1–5%. Agreement for polarizability components is generally poorer but consistent with the view that molecular anisotropy originates to a large extent from atom dipole interactions.

It is often desirable to know the polarizabilities of various parts of a molecule, such as the atoms, bonds, or functional groups. This information enables one to predict total molecular polarizabilities and other interesting molecular properties, such as optical rotation[1] and London dispersion forces between parts of molecules.[2] A view which has prevailed for some time is that the polarizability of a molecule is simply the sum of the polarizabilities of its parts.[3] This is based on the finding that the molar refraction, which is proportional to the molecular polarizability, is an additive property; that is, the various atoms or functional groups in a molecule can be assigned refraction values whose sum for the whole molecule is the molar refraction, and the value for a given group or atom is fairly constant for a variety of molecules. Extensive tables of additive atom and group refractions are available.[3,4] The additivity hypothesis has been extended in the interpretation of anisotropy of polarizability;[5,6] thus polarizability tensors have been ascribed to various bonds and functional groups according to the hypothesis that componentwise addition of the group tensors gives the molecular polarizability tensor. Compilations of bond tensor data have been given by Denbigh[5] and LeFèvre and LeFèvre.[6]

However, the additivity hypothesis has been repeatedly criticized[2,7,8] on the grounds that it neglects the interactions among the groups in a molecule, such

(1) J. G. Kirkwood, *J. Chem. Phys.*, **5**, 479 (1937).
(2) K. S. Pitzer, *Advan. Chem. Phys.*, **2**, 59 (1959).
(3) J. R. Partington, "An Advanced Treatise on Physical Chemistry," Vol. 4, Longmans, Green and Co., London, 1953, p 42 ff.
(4) A. I. Vogel, *J. Chem. Soc.*, 1833 (1948).
(5) K. G. Denbigh, *Trans. Faraday Soc.*, **36**, 936 (1940).
(6) C. G. LeFèvre and R. J. W. LeFèvre, *Rev. Pure Appl. Chem.*, **5**, 261 (1955).
(7) H. A. Lorentz, "The Theory of Electrons," 2nd ed, Dover Publications, New York, N. Y., 1952 (first published 1915), p 150.
(8) L. Silberstein, *Phil. Mag.*, **33**, 92, 215, 521 (1917).

as those which occur by way of the electric fields of the induced dipole moments. The importance of these local field effects has remained nebulous because few calculations exist to show whether the effects are large or small, and accordingly the additive values for atom and group polarizabilities remain in current use for calculations of optical rotations and London dispersion forces. It was the failure of certain optical rotation calculations[9] that led us to examine the validity of additive values for the polarizabilities of atoms. In this paper we report the results of a study in which interactions between induced dipoles in the atoms are taken into account in calculating the molecular polarizabilities.

Theory

The theory of the atom dipole interaction model was first given by Silberstein[8] and has since appeared in various other contexts; for example, Rowell and Stein[10] and Mortensen[11] have used the same theory in studies of a bond dipole interaction model, and DeVoe[12] has developed a similar but more detailed theory for interactions of molecules in aggregates. We derive here equivalent results in the slightly different form used in our computations. The form is particularly suitable for extension to optical rotation calculations[9,12] and allows one to avoid the perturbation approximations used earlier.[1,9]

A molecule is regarded as a rigid arrangement of N units each of which has a polarizability concentrated at a point. In our calculations the atoms are taken as the units and their polarizabilities are placed at the nuclei. The same theory will, of course, apply to any other assignment of units in the molecule or to any array of point polarizable particles. If the polarizability tensor of unit i is α_i, then the induced dipole moment $\mathfrak{y}_i$ (a column vector) in unit i is

$$\mathfrak{y}_i = \alpha_i\left[\mathbf{E}_i - \sum_{\substack{j=1\\ j\neq i}}^{N}\mathbf{T}_{ij}\mathfrak{y}_j\right] \tag{1}$$

where $\mathbf{E}_i$ (a column vector) is the applied electric field at unit i and $\mathbf{T}_{ij}$ is the dipole field tensor whose matrix form is[13]

$$\mathbf{T}_{ij} = -\frac{3}{r^5}\begin{bmatrix} x^2 - {}^1/_3r^2 & xy & xz \\ xy & y^2 - {}^1/_3r^2 & yz \\ xz & yz & z^2 - {}^1/_3r^2 \end{bmatrix} \tag{2}$$

where r is the distance between units i and j and x, y, and z are the components of the vector from unit i to unit j in a Cartesian coordinate system fixed with respect to the molecule. The expression in brackets in eq 1 is seen to be the total electric field at unit i and consists of the applied field plus the fields of all of the other induced dipoles in the molecule. (We have omitted effects of permanent dipoles in the molecule since these do not affect the net moment induced by an external field.)

(9) J. Applequist, P. Rivers, and D. E. Applequist, *J. Amer. Chem. Soc.*, **91**, 5705 (1969).
(10) R. L. Rowell and R. S. Stein, *J. Chem. Phys.*, **47**, 2985 (1967).
(11) E. M. Mortensen, *ibid.*, **49**, 3732 (1968).
(12) H. DeVoe, *ibid.*, **43**, 3199 (1965).
(13) C. J. F. Böttcher, "Theory of Electric Polarization," Elsevier, Amsterdam, 1952, p 449.

Equation 1 may be rearranged to read

$$\alpha_i^{-1}\mathfrak{y}_i + \sum_{\substack{j=1\\ j\neq i}}^{N}\mathbf{T}_{ij}\mathfrak{y}_j = \mathbf{E}_i \tag{3}$$

Equation 3 is a system of N matrix equations equivalent to the single matrix equation

$$\begin{bmatrix} \alpha_1^{-1} & \mathbf{T}_{12}\cdots\mathbf{T}_{1N} \\ \mathbf{T}_{21} & \alpha_2^{-1}\cdots\mathbf{T}_{2N} \\ \cdot & \\ \cdot & \\ \cdot & \\ \mathbf{T}_{N1} & \cdots\alpha_N^{-1} \end{bmatrix}\begin{bmatrix} \mathfrak{y}_1 \\ \mathfrak{y}_2 \\ \cdot \\ \cdot \\ \cdot \\ \mathfrak{y}_N \end{bmatrix} = \begin{bmatrix} \mathbf{E}_1 \\ \mathbf{E}_2 \\ \cdot \\ \cdot \\ \cdot \\ \mathbf{E}_N \end{bmatrix} \tag{4}$$

or briefly

$$\tilde{\mathbf{A}}\tilde{\mathfrak{y}} = \tilde{\mathbf{E}} \tag{5}$$

where $\tilde{\mathbf{A}}$ is the $3N \times 3N$ matrix in eq 4 and $\tilde{\mathfrak{y}}$ and $\tilde{\mathbf{E}}$ are the corresponding $3N \times 1$ column vectors. Let $\tilde{\mathbf{B}} = \tilde{\mathbf{A}}^{-1}$. We write $\tilde{\mathbf{B}}$ also as a partitioned matrix with 3×3 elements $\mathbf{B}_{ij}$.

$$\tilde{\mathbf{B}} = \begin{bmatrix} \mathbf{B}_{11} & \mathbf{B}_{12}\cdots\mathbf{B}_{1N} \\ \mathbf{B}_{21} & \mathbf{B}_{22}\cdots\mathbf{B}_{2N} \\ \cdot & \\ \cdot & \\ \cdot & \\ \mathbf{B}_{N1} & \cdots\mathbf{B}_{NN} \end{bmatrix} \tag{6}$$

From eq 5 we have

$$\tilde{\mathfrak{y}} = \tilde{\mathbf{B}}\tilde{\mathbf{E}} \tag{7}$$

which is equivalent to the N matrix equations

$$\mathfrak{y}_i = \sum_{j=1}^{N}\mathbf{B}_{ij}\mathbf{E}_j \tag{8}$$

Let the molecule be in a uniform applied field, so that $\mathbf{E}_j = \mathbf{E}$ for all j. Then eq 8 becomes

$$\mathfrak{y}_i = \left[\sum_{j=1}^{N}\mathbf{B}_{ij}\right]\mathbf{E} \tag{9}$$

The coefficient of $\mathbf{E}$ in eq 9 is seen to be an effective (*i.e.*, additive) polarizability of unit i. The total moment induced in the molecule $\mathfrak{y}_{\text{mol}}$ is

$$\mathfrak{y}_{\text{mol}} = \sum_{i=1}^{N}\mathfrak{y}_i = \left[\sum_{i=1}^{N}\sum_{j=1}^{N}\mathbf{B}_{ij}\right]\mathbf{E} \tag{10}$$

from which it is seen that the molecular polarizability tensor α_{mol} is

$$\alpha_{\text{mol}} = \sum_{i=1}^{N}\sum_{j=1}^{N}\mathbf{B}_{ij} \tag{11}$$

which is exact for the model described. From energetic considerations it is known that α is a Hermitian matrix[14] and must therefore be symmetric if all elements are real. It can be readily verified that this symmetry condition holds for α_{mol} calculated by eq 11, starting with the observation that $\tilde{\mathbf{A}}$ and hence $\tilde{\mathbf{B}}$ are symmetric for real, symmetric α_i. This is true regardless of the symmetry of the molecule.

Equation 11 is suitable for numerical calculations of α_{mol}. In the case of a diatomic molecule AB whose atoms have isotropic polarizabilities α_A and α_B the

(14) M. Born, "Optik," Springer-Verlag, Berlin, 1933, p 308.

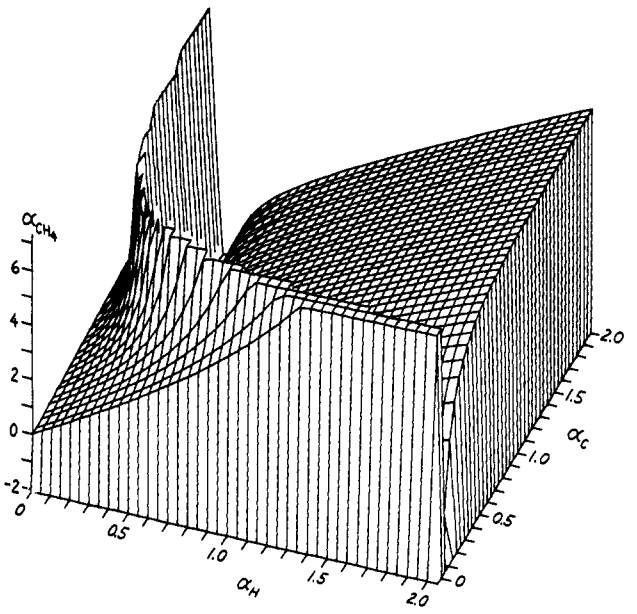


Figure 1. Polarizability of CH_4 as a function of polarizabilities of H and C. Units are Å^3. Drawn with a Calcomp plotter using subroutine THREED written by H. Jespersen, Iowa State University Computation Center. The vertical coordinate was truncated at +7 and −2 in order to achieve a reasonable scale.

results can be placed in a simple and more explicit form. The diagonal form of α_{mol} has two distinct components $\alpha_\parallel$ and $\alpha_\perp$, parallel and perpendicular, respectively, to the bond axis. Silberstein's equations[8,15] for this case are the following, which may also be derived from the above.

$$\alpha_\parallel = (\alpha_A + \alpha_B + 4\alpha_A\alpha_B/r^3)/(1 - 4\alpha_A\alpha_B/r^6) \quad (12)$$

$$\alpha_\perp = (\alpha_A + \alpha_B - 2\alpha_A\alpha_B/r^3)/(1 - \alpha_A\alpha_B/r^6) \quad (13)$$

These relations illustrate certain essential features of the atom dipole interaction model: (i) the molecule becomes anisotropic even though the atoms are isotropic; (ii) the predicted polarizability of a molecule parallel to its long axis is generally greater than that perpendicular to the long axis; (iii) deviations from additivity of polarizabilities become large as the atom polarizabilities approach r^3.

Calculations

Our original objective in this study was to determine whether the isotropic atom model was suitable for predicting anisotropies of polyatomic molecules. Early calculations had indicated that it works at least qualitatively for diatomic molecules.[15] We soon found, however, that the model fails badly when one uses additive values for atom polarizabilities assigned to the known positions of the nuclei. We therefore turned to a search for atom polarizability values which would satisfactorily predict molecular polarizabilities on the basis of the model. In this section we describe results which indicate the reasons for failure of the additive values and the manner in which more suitable values of the atom polarizabilities were established.

All calculations were carried out on an IBM 360/65 computer using double precision arithmetic. The main calculation involves specification of the matrix $\tilde{\mathbf{A}}$ and its inversion. The input data required are the coordinates of the nuclei, determined from available structural data, and the polarizabilities of the atoms. We have assumed isotropic atoms throughout this study, and in this case the α_i^{-1} appearing in eq 4 is just $\alpha_i^{-1}\mathbf{I}$ where $\mathbf{I}$ is the 3 × 3 identity matrix and α_i is the scalar polarizability. Matrix inversions were performed by means of subroutine DUMNV written by staff at the Iowa State University Computation Center. When necessary, calculated molecular polarizability tensors were diagonalized using the IBM library subroutine EIGEN, which calculates the three principal polarizability components α_1, α_2, and α_3 and the unit vectors specifying the corresponding principal axes of the molecule. The mean polarizability $\bar{\alpha}$ is obtained as $\bar{\alpha} = (\alpha_1 + \alpha_2 + \alpha_3)/3$.

As an example of the manner in which the molecular polarizability depends on the atom polarizabilities, we consider the isotropic molecule CH_4. Certain features of this dependence are illustrated by the surface in Figure 1. Additivity of atom polarizabilities would require that the surface be a plane. It is seen that this is approximately true in the vicinity of the origin, where interactions are small. However, the experimental polarizability of methane is 2.62 Å^3 (Table II), and this value is reached only in regions of the surface where the influence of interactions is quite marked. The most notable feature is a curve of discontinuity along which the polarizability approaches $\pm\infty$. This behavior is seen in the polarizability surfaces of several molecules that have been similarly explored. Its origin for diatomic molecules can be seen in eq 12 and 13, where the denominators vanish when $\alpha_A\alpha_B$ approaches $r^6/4$ or r^6, respectively. Thus α_A and α_B are inversely related along the curve of discontinuity for this case. Remarkably, we find from the computed data for CH_4 that the curve of discontinuity in the α_H–α_C plane follows the relation $\alpha_H\alpha_C = 0.193$ Å^6, which is of the form expected for diatomic molecules, though the numerical constant is not predictable from eq 12 or 13. (The general condition for infinite polarizability is $\det \tilde{\mathbf{A}} = 0$, as can be seen from eq 4 and 5; infinite polarizability means that $\tilde{\boldsymbol{\mu}}$ is nonvanishing when $\tilde{\mathbf{E}} = 0$, and this is possible only if $\det \tilde{\mathbf{A}} = 0$. Since $\det \tilde{\mathbf{A}}$ is a polynomial of degree $3N$ in the atom polarizabilities, the simple inverse relation between α_H and α_C for CH_4 implies that this polynomial contains the factor $\alpha_H\alpha_C - 0.193$.)

The significance of a polarizability of $\pm\infty$ is that the molecule is in a state of resonance and absorbs energy from the applied field. This occurs in spite of the fact that we have not introduced any absorption properties of the atoms. This behavior of the model can be understood from its close relation to the classical system of N coupled oscillators, which likewise shows resonance under conditions other than the resonance conditions of the isolated oscillators.[16] There is evidence that the absorption properties[17–19] of some types of systems can be predicted from the point dipole interaction approach used here, but it seems doubtful that this could

(15) H. A. Stuart, "Die Struktur des freien Moleküls," Springer-Verlag, Berlin, 1952, p 363 ff.

(16) See, for example, W. Kauzmann, "Quantum Chemistry," Academic Press, New York, N. Y., 1957, p 568 ff.
(17) G. D. Mahan, *J. Chem. Phys.*, **41**, 2930 (1964).
(18) W. Rhodes and M. Chase, *Rev. Mod. Phys.*, **39**, 348 (1967).
(19) M. R. Philpott, *J. Chem. Phys.*, **50**, 5117 (1969).

Table I. Polarizabilities of Atoms in Polyatomic Molecules at 5893 Å

Atom	Polarizability, Å³ — Interaction model	Additive model[a]
H (alkane)	0.135	0.407
H (alcohol)	0.135	0.405[b]
H (aldehyde)	0.167	
H (amide)	0.161	
C (alkane)	0.878	1.027
C (carbonyl)	0.616	1.027[b]
C (nitrile)	0.36[c]	0.928[b]
N (amide)	0.530	
N (nitrile)	0.52[c]	1.236
O (alcohol)	0.465	0.604
O (ether)	0.465	0.651
O (carbonyl)	0.434	0.841
F	0.32	0.32[d]
Cl	1.91	2.32
Br	2.88	3.465
I	4.69	5.531

[a] A. I. Vogel, *J. Chem. Soc.*, 1833 (1948); additional values collected in J. R. Partington, "An Advanced Treatise on Physical Chemistry," Vol. 4, Longmans, Green and Co., London, 1953, pp 48, 50. [b] Found by difference using tabulated refractions of functional group and of other atom. [c] Optimum values not well established; see text. [d] Tentative value.

be done reliably for molecules with our model; among other things,[18] the neglect of electron exchange between atoms is probably serious. In the immediate vicinity of the resonance condition the polarizability is bound to be in error because our model does not take into account damping effects, which would prevent the polarizability from going to infinity. Therefore, for the present we regard the resonance conditions wherever they appear simply as indications that the coupling between atoms has far exceeded the extent that can be treated by the model. (Indeed, it is an object of this study to learn whether coupling between atoms can be represented by the model at all.)

The resonance condition proves to be of major importance when one attempts to use additive atom polarizabilities in the interaction model. For CH_4, for example, the additive values $\alpha_H = 0.407$, $\alpha_C = 1.027$ (Table I) correspond to a point very near the discontinuity in Figure 1, with a molecular polarizability of -0.1 Å³. From this and similar results for other molecules we conclude that the additive values are invalid for calculating interactions between atoms by the point dipole model.

To pursue the significance of the resonance condition a bit further, we note that the directions of increasing α_H and α_C in Figure 1 are the directions of increasing frequency of the applied field, assuming the atoms show normal dispersion.[16] The resonance condition thus represents an upper limit on the frequency range in which we expect the theory to hold. Since we will consider molecules only in their normal dispersion range, we may therefore anticipate that the optimum values for the atom polarizabilities will fall on the side of the discontinuity closest to the origin in surfaces such as that in Figure 1.

Table I shows the optimum atom polarizabilities determined as described below. In general it is seen that these values fall significantly below the additive values, reflecting the fact that the interactions produce an overall enhancement of the molecular polarizability.

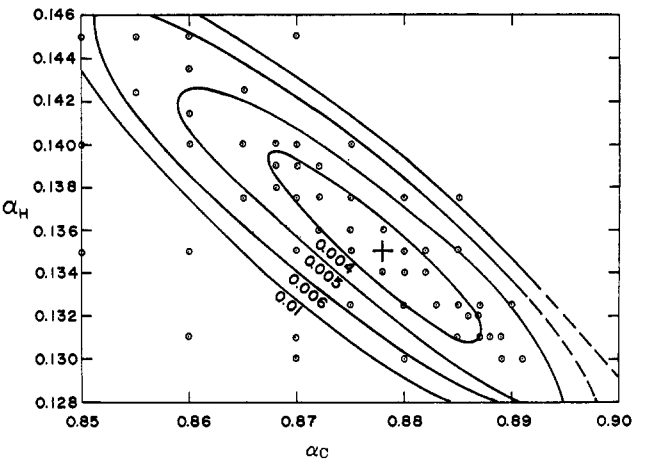


Figure 2. Contours showing the sum of squares of relative deviations of calculated mean polarizabilities of the six alkanes in Table II. Scale units are Å³. Circles indicate points at which calculations were made. Contours are based on rough interpolation between points. The cross indicates the optimum point at $\alpha_H = 0.135$, $\alpha_C = 0.878$, where the sum of squares of deviations is 0.00357.

The "interaction" values are probably accurate to two significant figures, judging from the sensitivity of the optimum to the choice of experimental data. Many values are given to three figures in order to be specific about the location of the optimum for the experimental data quoted here.

Our general procedure has been to select optimum atom polarizabilities as those which minimize the sum of the squares of relative (fractional) deviations of the calculated mean molecular polarizabilities from the experimental values for a selected set of molecules. In most cases we have not attempted to find an optimum fit to the polarizability components as well, because it appears that the model does not predict these as accurately as it does the mean, and because there is considerable variation in the uncertainties in experimental values for the components. Comparison between theory and experiment for the individual components of polarizability is therefore used primarily as an independent check on the validity of the model.

The experimental values of $\bar{\alpha}$ are based on the best documented sodium D line (5893 Å) refractive index data we could find, using the Lorentz–Lorenz relation

$$R = \left(\frac{n^2 - 1}{n^2 + 2}\right)\frac{M}{d} = \frac{4}{3}\pi N_0 \bar{\alpha} \qquad (14)$$

or

$$\bar{\alpha} = 0.3964R \ (R \text{ in cc}, \bar{\alpha} \text{ in Å}^3) \qquad (15)$$

where R is the molar refraction and n is the refractive index of the substance of molecular weight M and density d, and N_0 is Avogadro's number. Refractivity data on the gas state have been used wherever possible, since eq 14 is of less certain validity for liquids. Components of polarizability are available from Kerr effect and light scattering depolarization data. Values reported in the literature generally assume somewhat different mean polarizabilities from those adopted here; when this was the case we have corrected the components assuming the differences between components (the quantities determined directly by experiment) were the same as those given in the literature.

Table II. Polarizabilities (Å^3) of Alkanes, Ethers, and Alcohols at 5893 Å

Compound		$\bar{\alpha}$	α_1	α_2	α_3	Principal axes
Methane	Exptl[a]	2.62	2.62	2.62	2.62	
	Calcd[b]	2.58	2.58	2.58	2.58	
Ethane	Exptl[a,c]	4.48	5.49	3.98	3.98	$\alpha_1 \parallel$ threefold axis
	Exptl[a,d]	4.48	4.99	4.22	4.22	
	Calcd[b]	4.47	5.48	3.97	3.97	
Propane	Exptl[a,e,e]	6.38	5.74	7.66	5.74	$\alpha_1 \perp$ CCC plane
	Calcd[b]	6.58	5.08	8.94	5.71	$\alpha_2 \parallel$ twofold axis
Cyclopentane	Exptl[f,g]	9.15	9.88	9.17	8.40	$\alpha_1 \perp$ mirror plane[g]
	Calcd[h]	9.00	10.14	9.65	7.26	$\alpha_3 \perp$ ring "plane"
Neopentane	Exptl[i]	10.20	10.20	10.20	10.20	
	Calcd[b]	9.91	9.91	9.91	9.91	
Cyclohexane	Exptl[c,f]	11.00	9.38	11.81	11.81	$\alpha_1 \parallel$ threefold axis
	Calcd[b]	10.95	8.35	12.25	12.25	
Dimethyl ether	Exptl[j,k]	5.24	6.38	4.39	4.94	$\alpha_2 \perp$ COC plane
	Calcd[l]	5.22	6.98	4.51	4.18	$\alpha_3 \parallel$ twofold axis
p-Dioxane	Exptl[c,m,n]	8.60	9.40	9.40	7.00	$\alpha_1 \perp$ O–O axis
	Calcd[b,o]	8.68	10.06	9.63	6.35	$\alpha_3 \parallel$ axial C–H bonds
Methanol	Exptl[j,p]	3.32	4.09	2.65	3.23	$\angle(\alpha_1, \text{C–O}) = 22.3°$; $\angle(\alpha_1, \text{O–H}) = 50.4°$
	Calcd[q]	3.05	3.68	2.63	2.84	$\alpha_2 \perp$ COH plane
Ethanol	Exptl[r,s]	5.11	5.76	4.98	4.50	$\angle(\alpha_1, \text{C–O}) = 123.2°$; $\angle(\alpha_1, \text{C–C}) = 13.7°$
	Calcd[b,t]	5.11	6.64	4.56	4.12	$\alpha_3 \perp$ CCO plane
2-Propanol	Exptl[r]	6.97				$\alpha_1 \perp$ HCO plane
	Calcd[b,t]	7.02	8.85	6.68	5.54	$\angle(\alpha_2, \text{C–O}) = 27.3°$; $\angle(\alpha_2, \text{C–H}) = 82.2°$
Cyclohexanol	Exptl[f]	11.56				$\alpha_1 \perp$ C–O bond
	Calcd[b,t,u]	11.55	12.36	13.68	8.62	$\alpha_3 \parallel$ axial C–H bonds
Ethylene oxide	Exptl[j]	4.43				$\alpha_2 \parallel$ C–C bond
	Calcd[v]	6.52	3.20	12.23	4.13	$\alpha_3 \perp$ COC plane
Water	Exptl[w]	1.49				$\alpha_1 \perp$ HOH plane
	Calcd[z]	1.12	0.53	1.83	1.00	$\alpha_3 \parallel$ twofold axis

Symbols for type of data in references: S, molecular structure; D, light scattering depolarization; K, electrooptical Kerr effect; R, refractive index; g, gas state; l, pure liquid state; s, solution state. [a] H. E. Watson and K. L. Ramaswamy, *Proc. Roy. Soc., Ser. A*, **156,** 144 (1936), Rg. [b] Bond lengths (Å) C–H 1.095, C–C 1.54. All bond angles 109.471°. *Cf.* L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, Chapter 7. Staggered conformations about C–C bonds are assumed. Six-membered rings are in chair forms. [c] H. A. Stuart and S. v. Schieszl, *Ann. Phys.*, **2,** 321 (1948), Kg. [d] N. J. Bridge and A. D. Buckingham, *Proc. Roy. Soc., Ser. A*, **295,** 334 (1966), Dg. [e] Components recalculated assuming $\alpha_1 = \alpha_3$ and $\alpha_2 > \alpha_1$. [f] A. I. Vogel, *J. Chem. Soc.*, 1323 (1938), Rl. [g] R. J. W. LeFèvre and C. G. LeFèvre, *Chem. Ind. (London)*, 54 (1956), Ks; components were calculated from additive bond polarizabilities for an assumed nonplanar structure. [h] K. S. Pitzer and W. E. Donath, *J. Amer. Chem. Soc.*, **81,** 3213 (1959), S; we assume C_s symmetry with puckering parameter $q = 0.47$, bond lengths (Å) C–H 1.095, C–C 1.54. [i] S. W. Ferris, "Handbook of Hydrocarbons," Academic Press, New York, N. Y., 1955, p 21, Rl. [j] K. L. Ramaswamy, *Proc. Indian Acad. Sci., Sect. A*, **4,** 675 (1936), Rg. [k] H. A. Stuart, "Die Struktur des freien Moleküls," Springer-Verlag, Berlin, 1952, p 441, Dg, Kg. [l] U. Blukis, P. H. Kasai, and R. J. Myers, *J. Chem. Phys.*, **38,** 2753 (1963), S. [m] A. Weissberger, E. S. Proskauer, J. A. Riddick, and E. E. Toops, "Organic Solvents," Interscience, New York, N. Y., 1955, p 126, Rl. [n] Components recalculated from Kerr constant. [o] C–O bond length 1.41 Å by analogy with dimethyl ether, footnote *l*. [p] H. A. Stuart, *Z. Phys.*, **63,** 533 (1930), Kg. [q] J. D. Swalen, *J. Chem. Phys.*, **23,** 1739 (1955), S. [r] A. I. Vogel, *J. Chem. Soc.*, 1814 (1948), Rl. [s] C. G. LeFèvre, R. J. W. LeFèvre, B. P. Rao, and A. J. Williams, *ibid.*, 123 (1960), Ks. [t] Bond lengths (Å) C–O 1.428, O–H 0.967, by analogy with methanol, footnote *q*. Calculated polarizabilities are unweighted averages over three staggered OH positions. [u] Equatorial OH. [v] T. E. Turner and J. A. Howe, *J. Chem. Phys.*, **24,** 924 (1956), S. [w] P. Hölemann and H. Goldschmidt, *Z. Phys. Chem., Abt. B*, **24,** 199 (1934), Rg. [z] W. S. Benedict, N. Gailar, and E. K. Plyler, *J. Chem. Phys.*, **24,** 1139 (1956), S.

Tables II–IV show the comparison between theory and experiment for all of the polyatomic molecules studied thus far, using the optimum atom polarizabilities in Table I. Molecular structures assumed in the calculations are referred to in the footnotes to the tables. The principal optical axes listed are those found theoretically; these usually agree with assignments made in the experimental literature, though the experimental assignment is often uncertain, particularly where the principal axis does not coincide with a symmetry axis. The notation $\angle(\alpha_i, \text{A–B})$ denotes the angle between the ith principal axis and the bond A–B. C′ indicates the carbon in a carbonyl or nitrile group.

In the following we describe the optimization procedures for various sets of molecules.

Alkanes. The polarizabilities of C and H were adjusted simultaneously for an optimum fit to $\bar{\alpha}$ for the six alkanes in Table II. The preliminary search included numerous points in and beyond the regions of "resonance" for the various molecules. The only region in which a reasonable fit was obtained is that shown in Figure 2, where contours of the sum of squares of relative deviations of mean polarizability are shown. This plot establishes a minimum deviation at $\alpha_H = 0.135$, $\alpha_C = 0.878$ Å^3, as recorded in Table I. The contours around the minimum are elongated in a direction roughly paralleling the contours of the surface in Figure 1, as one might expect from the fact that the surfaces for all of the molecules are roughly similar in this region. The optimum lies on the low-interaction side of the resonance discontinuities for all of the molecules.

Alcohols and Ethers. The polarizability of O was adjusted to give a reasonable fit to $\bar{\alpha}$ for dimethyl ether, *p*-dioxane, and the four alcohols listed in Table II, assuming C and H (including hydroxyl H) have the values found for alkanes. Only methanol shows a serious discrepancy. Otherwise, the fit is very nearly optimal, and we have not tried to improve it by further adjustment of O and hydroxyl H polarizabilities. Calculations for ethylene oxide and water are also shown in Table II, using the same atom polarizabilities as for ethers and alcohols. The agreement with experiment is poor in both cases. This probably reflects the chem-

Table III. Polarizabilities (Å³) of Halomethanes at 5893 Å

Compd		$\bar{\alpha}$	α_1	α_2	α_3	Principal axes
CH_3F	Exptl[a,b]	2.62	3.18	2.34	2.34	$\alpha_1 \parallel$ threefold axis
	Calcd[c]	2.47	2.41	2.49	2.49	
CHF_3	Exptl[d,e]	2.81	2.69	2.87	2.87	$\alpha_1 \parallel$ threefold axis
	Exptl[d,f]	2.81	2.63	2.90	2.90	
	Calcd[g]	2.78	2.68	2.83	2.83	
CF_4	Exptl[h]	2.92	2.92	2.92	2.92	
	Calcd[i]	2.95	2.95	2.95	2.95	
CH_3Cl	Exptl[a,e]	4.55	5.68	3.98	3.98	$\alpha_1 \parallel$ threefold axis
	Exptl[a,j]	4.55	5.40	4.12	4.12	
	Exptl[a,f]	4.55	5.58	4.03	4.03	
	Calcd[k]	4.41	6.18	3.53	3.53	
CH_2Cl_2	Exptl[a,l]	6.82	5.36	8.81	6.30	$\alpha_1 \perp$ ClCCl plane
	Calcd[m]	6.65	4.67	9.47	5.80	$\alpha_3 \parallel$ twofold axis
$CHCl_3$	Exptl[a,f]	8.53	6.74	9.42	9.42	$\alpha_1 \parallel$ threefold axis
	Exptl[a,j]	8.53	6.98	9.31	9.31	
	Calcd[n]	8.73	5.85	10.17	10.17	
CCl_4	Exptl[a]	10.51	10.51	10.51	10.51	
	Calcd[o]	10.61	10.61	10.61	10.61	
CH_3Br	Exptl[a,j]	5.61	6.91	4.96	4.96	$\alpha_1 \parallel$ threefold axis
	Exptl[a,b]	5.61	6.66	5.09	5.09	
	Calcd[k]	5.39	7.54	4.32	4.32	
CH_2Br_2	Exptl[p,q]	8.68				$\alpha_1 \perp$ BrCBr plane
	Calcd[r]	8.87	5.91	13.23	7.45	$\alpha_3 \parallel$ twofold axis
$CHBr_3$	Exptl[p,s]	11.84	9.53	13.00	13.00	$\alpha_1 \parallel$ threefold axis
	Calcd[t]	11.89	8.04	13.82	13.82	
CH_3I	Exptl[a,b]	7.59	9.02	6.87	6.87	$\alpha_1 \perp$ threefold axis
	Calcd[k]	7.29	10.12	5.87	5.87	
CH_2I_2	Exptl[p,q]	12.90				$\alpha_1 \perp$ ICI plane
	Calcd[u]	12.95	8.89	19.57	10.40	$\alpha_3 \parallel$ twofold axis
CHI_3	Exptl[s]	18.04	16.74	18.69	18.69	$\alpha_1 \parallel$ threefold axis
	Calcd[u]	18.48	11.91	21.77	21.77	

Symbols used in footnotes are defined in Table II. [a] K. L. Ramaswamy, *Proc. Indian Acad. Sci., Sect. A*, **4**, 675 (1936), Rg. [b] C. G. LeFèvre and R. J. W. LeFèvre, *Rev. Pure Appl. Chem.*, **5**, 261 (1955), Ks. [c] F. A. Anderson, B. Bak, and S. Brodersen, *J. Chem. Phys.*, **24**, 989 (1956), S. [d] K. L. Ramaswamy, *Proc. Indian Acad. Sci., Sect. A*, **2**, 630 (1935), Rg. [e] R. J. W. LeFèvre and G. L. D. Ritchie, *J. Chem. Soc.*, 3520 (1965), Kg. [f] N. J. Bridge and A. D. Buckingham, *Proc. Roy. Soc., Ser. A*, **295**, 334 (1966), Dg. [g] S. N. Ghosh, R. Trambarulo, and W. Gordy, *J. Chem. Phys.*, **20**, 605 (1952), S. [h] H. E. Watson and K. L. Ramaswamy, *Proc. Roy. Soc., Ser. A*, **156**, 144 (1936), Rg. [i] C. G. Thornton, *Diss. Abstr.*, **14**, 604 (1954), S. [j] H. A. Stuart and H. Volkmann, *Ann. Phys.* **18**, 121 (1933), Kg. [k] C. C. Costain, *J. Chem. Phys.*, **29**, 864 (1958), S. [l] H. A. Stuart and S. v. Schieszl, *Ann. Phys.*, **2**, 321 (1948), Kg. Dg. [m] R. J. Myers and W. D. Gwinn, *J. Chem. Phys.*, **20**, 1420 (1952), S. [n] P. N. Wolfe, *ibid.*, **25**, 976 (1956), S. [o] L. S. Bartell, L. O. Brockway, and R. H. Schwendeman, *ibid.*, **23**, 1854 (1955), S. [p] A. I. Vogel, *J. Chem. Soc.*, 1833 (1948), Rl. [q] D. Izsak and R. J. W. LeFèvre, *J. Chem. Soc., B*, 102 (1966), Ks; polarizability components not determined. [r] E. L. Plyler and W. S. Benedict, *J. Res. Nat. Bur. Stand.*, **49**, 1 (1952), S. [s] R. J. W. LeFèvre and G. L. D. Ritchie, *J. Chem. Soc.*, 4933 (1963), Ks. [t] Q. Williams, J. T. Cox, and W. Gordy, *J. Chem. Phys.*, **20**, 1524 (1952), S. [u] O. Hassell and H. Viervoll, *Acta Chem. Scand.*, **1**, 149 (1947), S; supplemented by assumptions C–H dist = 1.095 Å, ∠HCH = 109.471°.

ical dissimilarity of these compounds to the ethers and alcohols and indicates that caution must be used in applying our atom polarizabilities to distantly related molecules.

Halomethanes. The polarizability of each halogen in the compounds listed in Table III was adjusted for an optimum fit to $\bar{\alpha}$ for the 3–4 molecules containing that halogen. The alkane values for H and C polarizabilities were assumed.

Aldehydes and Ketones. The carbonyl C and O polarizabilities were adjusted simultaneously for an optimum fit to $\bar{\alpha}$ for CH_3COCH_3 and $COCl_2$ and to α_1, α_2, and α_3 for CH_3COCH_3. A contour map qualitatively similar to Figure 2 helped to locate the optimum. The component data were included in this case because the optimum could not be well established with two values of $\bar{\alpha}$. The component data of Stuart (Table IV) were used in preference to those of LeFèvre (Table IV) because a good fit to the latter could not be found and because the former were based on gas phase measurements using both depolarization and Kerr constant data. Polarizabilities of H, Cl, and alkane C were assumed to be as determined above. The aldehyde H polarizability was then adjusted for an optimum fit to $\bar{\alpha}$ for CH_3CHO and HCHO.

Amides. The amide N and H polarizabilities were adjusted simultaneously to fit $\bar{\alpha}$ for the five amides in

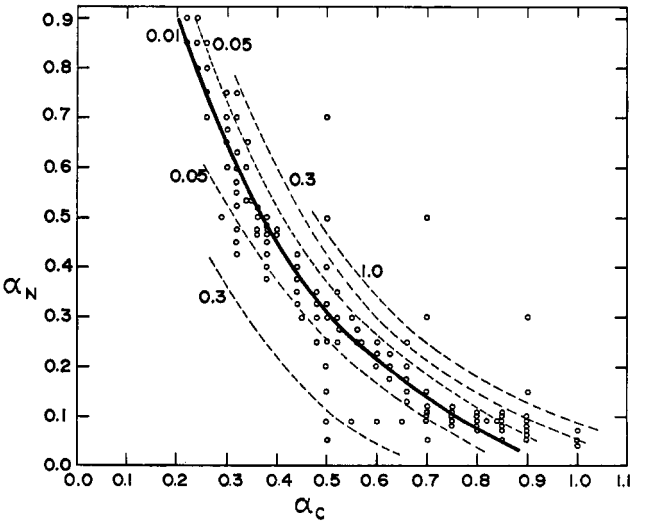


Figure 3. Contours showing the sum of squares of relative deviations of calculated mean polarizabilities of the seven nitriles in Table IV. See Figure 2. The solid line is the locus of points having an approximate minimum in the sum of squares of deviations.

Table IV. Polarizabilities (Å^3) of Aldehydes, Ketones, Amides, and Nitriles at 5893 Å

Compd		$\bar{\alpha}$	α_1	α_2	α_3	Principal axes
CH_3COCH_3	Exptl[a,b]	6.39	7.37	4.42	7.37	$\alpha_2 \perp$ CCC plane
	Exptl[a,c]	6.39	7.16	4.88	7.14	$\alpha_3 \parallel$ C–O bond
	Calcd[d]	6.44	7.17	5.02	7.13	
HCHO	Exptl[e,f]	2.45	2.76	1.83	2.76	$\alpha_2 \perp$ HCH plane
	Calcd[g]	2.46	2.84	0.93	3.59	$\alpha_3 \parallel$ C–O bond
CH_3CHO	Exptl[h]	4.59				$\angle(\alpha_2, C'–O) = 29.2°$; $\angle(\alpha_2, C–C) = 94.7°$
	Calcd[i]	4.56	6.63	3.96	3.09	$\alpha_3 \perp$ CCO plane
$COCl_2$	Exptl[j]	6.78				$\alpha_2 \perp$ ClCCl plane
	Calcd[k]	6.75	7.63	3.83	8.83	$\alpha_3 \parallel$ C–O bond
$HCONH_2$	Exptl[l]	4.08	5.24	$\alpha_2 + \alpha_3 =$	7.01	$\angle(\alpha_1, C'–N) = 147.8°$; $\angle(\alpha_1, C'–O) = 24.2°$
	Calcd[m]	4.07	6.87	4.04	1.32	$\alpha_3 \perp$ NCO plane
CH_3CONH_2	Exptl[l]	5.67	6.70	$\alpha_2 + \alpha_3 =$	10.30	$\angle(\alpha_1, C'–N) = 102.4°$; $\angle(\alpha_1, C'–O) = 22.6°$
	Calcd[n]	5.72	7.50	5.79	3.87	$\alpha_3 \perp$ NCO plane
$HCONHCH_3$	Exptl[l]	5.91	6.77	$\alpha_2 + \alpha_3 =$	10.95	$\angle(\alpha_1, C'–N) = 99.2°$; $\angle(\alpha_1, C'–O) = 24.4°$
	Calcd[o]	5.81	6.79	7.23	3.40	$\alpha_3 \perp$ NCO plane
$HCON(CH_3)_2$	Exptl[l]	7.81	9.45	$\alpha_2 + \alpha_3 =$	13.97	$\angle(\alpha_1, C'–N) = 128.7°$; $\angle(\alpha_1, C'–O) = 5.1°$
	Calcd[p]	7.83	10.18	7.97	5.34	$\alpha_3 \perp$ NCO plane
$CH_3CONHCH_3$	Exptl[q]	7.82				$\angle(\alpha_1, C'–N) = 140.5°$; $\angle(\alpha_1, C'–O) = 15.5°$
	Calcd[n]	7.91	7.71	10.57	5.43	$\alpha_3 \perp$ NCO plane
CH_3CN	Exptl[r,s]	4.48	5.74	3.85	3.85	$\alpha_1 \parallel$ CCN axis
	Calcd[t]	4.15	6.67	2.90	2.90	
CH_3CH_2CN	Exptl[u]	6.24				$\angle(\alpha_2, C–C') = 65.4°$; $\angle(\alpha_2, C–C) = 45.1°$
	Calcd[v]	6.25	8.99	5.48	4.27	$\alpha_3 \perp$ CCC plane
$(CH_3)_2CHCN$	Exptl[s]	8.05				$\angle(\alpha_1, C–C') = 11.5°$; $\angle(\alpha_1, C2–H) = 98.0°$
	Calcd[w]	8.22	9.83	9.07	5.75	$\alpha_2 \perp$ HCCN plane
$(CH_3)_3CCN$	Exptl[s]	9.59	10.71	9.03	9.03	$\alpha_1 \parallel$ CCN axis
	Calcd[w]	9.88	10.62	9.51	9.51	
$CH_2(CN)_2$	Exptl[s]	5.79				$\alpha_1 \perp$ CCC plane
	Calcd[x]	6.07	3.32	9.52	5.36	$\alpha_2 \perp$ HCH plane
CH_2ClCN	Exptl[s]	6.10				$\angle(\alpha_2, C–C') = 55.7°$; $\angle(\alpha_2, C–Cl) = 53.8°$
	Calcd[w]	6.22	9.81	5.68	3.90	$\alpha_3 \perp$ CCCl plane
CCl_3CN	Exptl[s]	10.42	10.70	10.29	10.29	$\alpha_1 \parallel$ CCN axis
	Calcd[y]	10.28	10.49	10.17	10.17	

Symbols used in footnotes are defined in Table II. [a] D. M. Cowan, G. H. Jeffery, and A. I. Vogel, *J. Chem. Soc.*, 171 (1940) Rl. [b] R. J. W. LeFèvre, *ibid.*, 4041 (1953), Ks. [c] H. A. Stuart, "Die Struktur des freien Moleküls," Springer-Verlag, Berlin, 1952, p 441, Dg, Kg. [d] J. D. Swalen and C. C. Costain, *J. Chem. Phys.*, **31,** 1562 (1959), S; assumed CH_3 conformations, C–H eclipsing C–O. [e] J. Timmermans, "The Physico-chemical Constants of Binary Systems in Concentrated Solutions," Interscience, New York, N. Y., 1960, p 20, Rs; molar refractions of HCHO and H_2O were assumed to be additive. [f] S. Parthasarathy, *Indian J. Phys.*, **7,** 139 (1932), Dg; components of polarizability calculated assuming $\alpha_1 = \alpha_3$ and $\alpha_1 > \alpha_2$ as suggested by theory to a rough approximation. [g] D. W. Davidson, B. P. Stoicheff, and H. J. Bernstein, *J. Chem. Phys.*, **22,** 289 (1954), S. [h] J. R. Partington, "An Advanced Treatise on Physial Chemistry," Vol. 4, Longmans, Green and Co., London, 1953, p 52, Rl. [i] R. W. Kilb, C. C. Lin, and E. B. Wilson, *J. Chem. Phys.*, **26,** 1695 (1957), S. [j] H. Lowery, *Proc. Roy. Soc., Ser. A*, **133,** 188 (1931), Rg. [k] G. W. Robinson, *J. Chem. Phys.*, **21,** 1741 (1953), S. [l] M. J. Aroney, R. J. W. LeFèvre, and A. N. Singh, *J. Chem. Soc.*, 3179 (1965), R, Ks. Experimental components were calculated assuming the dipole moment is parallel to the α_1 axis; the theoretical α_1 is taken as the component most nearly parallel to C'–O and is not necessarily comparable to the experimental value. [m] R. J. Kurland and E. B. Wilson, Jr., *J. Chem. Phys.*, **27,** 585 (1957), S. [n] M. Kimura and M. Aoki, *Bull. Chem. Soc. Jap.*, **26,** 429 (1953), S. [o] Assumed by analogy with other amides (footnotes *m*, *n*): bond lengths (Å) C–H 1.09, C'–H 1.094, C'–O 1.243, C'–N 1.343, C–N 1.44, N–H 0.995; bond angles (deg) C'NH 117, C'NC 117, HC'N 103.9, NC'O 123.58, NCH 109.5, HCH 109.5; N–H trans with respect to C'–O as in L. A. LaPlanche and M. T. Rogers, *J. Amer. Chem. Soc.*, **86,** 337 (1964); C–H assumed eclipsing N–C'. [p] Same bond lengths and angles as in footnote *o*, except $\angle$CNC' taken as 120°. Assumed CH_3 conformations: C_{cis}–H eclipsing N—C' and C_{trans}–H eclipsing N–C_{cis}, where cis and trans denote location with respect to O. [q] G. F. D'Alelio and E. E. Reid, *J. Amer. Chem. Soc.*, **59,** 109 (1937), Rl. [r] K. L. Ramaswamy, *Proc. Indian Acad. Sci., Sect. A*, **4,** 675 (1936), Rg. [s] R. J. W. LeFèvre, B. J. Orr, and G. L. D. Ritchie, *J. Chem. Soc.*, 2499 (1965), Ks. [t] C. C. Costain, *J. Chem. Phys.*, **29,** 864 (1958), S. [u] G. H. Jeffery and A. I. Vogel, *J. Chem. Soc.*, 674 (1948), Rl. [v] R. G. Lerner and B. P. Dailey, *J. Chem. Phys.*, **26,** 678 (1957), S. [w] Assumed by analogy with hydrocarbons and other nitriles (footnotes *t*, *v*): bond lengths (Å) C–H 1.095, C–C 1.54, C–C' 1.46, C'–N 1.157, C–Cl 1.77; bond angles 109.471°. [x] N. Muller and D. E. Pritchard, *J. Amer. Chem. Soc.*, **80,** 3483 (1958), S. [y] J. G. Baker, D. R. Jenkins, C. N. Kenney, and T. M. Sudgen, *Trans. Faraday Soc.*, **53,** 1397 (1957), S.

Table IV, taking the polarizabilities of other atoms determined as described above. In $HCONH_2$ and its derivatives the HCO atoms were considered identical with the corresponding atoms in aldehydes. A contour map qualitatively similar to Figure 2 helped to locate the optimum.

Nitriles. The nitrile C and N polarizabilities were adjusted simultaneously to fit $\bar{\alpha}$ for the seven nitriles in Table IV. The previous values for H, Cl, and alkane C polarizabilities were assumed. Instead of a unique fit to the mean polarizabilities, an almost continuous locus of "optimal" points in the α_C–α_N plane was found (Figure 3). This remarkable behavior suggests that the polarizability surfaces of the seven molecules are essentially parallel in the vicinity of the optimal locus. In an effort to obtain a better defined optimum we have made use of the additional experimental quantity $\alpha_1 - \alpha_2$, which is known for the molecules CH_3CN, $(CH_3)_3CCN$, and CCl_3CN. An optimum fit to the seven values of $\bar{\alpha}$ and three values of $\alpha_1 - \alpha_2$ was sought along the optimal locus in Figure 3, using the sum S of squares of relative deviations of the ten quantities as the criterion. S had a minimum of 1.17 at (α_C, α_N) = (0.36, 0.52), and hence these values are accepted tentatively as optimal. However, the variation in S along the optimal locus is too gradual to define the optimum well, as illustrated by the values S = 1.82 at the point (0.75, 0.11) and S = 3.57 at (0.22, 0.85).

This means that it is difficult to obtain physically meaningful parameters for the C and N atoms separately, but we find a broad range of values that seem almost equally valid for representing the CN group as a whole.

Diatomic Molecules. We wish to compare our results for polyatomic molecules with corresponding results for diatomic molecules. Early calculations[8,15] for such cases were not based on accurate internuclear distances, and we have therefore recalculated a number of cases in a form suitable for the present comparison. The results are given in Tables V and VI. For homonuclear diatomic molecules the only unknown for our model is the polarizability of each atom, α_A. We have determined the value of α_A which gives the correct experimental $\bar{\alpha}$ and then calculated $\alpha_\parallel$ and $\alpha_\perp$ by eq 12 and 13. For heteronuclear diatomic molecules eq 12 and 13 provide a unique solution for the polarizabilities of the two atoms, α_A and α_B, when $\alpha_\parallel$ and $\alpha_\perp$ are known; thus the experimental and calculated molecular polarizabilities are identical in Table VI. One does not, however, learn from this which atom is A and which is B.

Table V. Polarizabilities (Å^3) of Homonuclear Diatomic Molecules and Their Atoms for Yellow Light

Compd	r,[a] Å	α_A		Molecular polarizability $\bar{\alpha}$	$\alpha_\parallel$	$\alpha_\perp$
H_2	0.7413	0.168	Exptl[b]	0.79	0.93	0.72
			Calcd	0.80	1.92	0.24
N_2	1.0976	0.492	Exptl[b]	1.76	2.38	1.45
			Calcd	1.76	3.84	0.72
O_2	1.2074	0.562	Exptl[b]	1.60	2.35	1.21
			Calcd	1.60	3.11	0.85
Cl_2	1.988	1.934	Exptl[b]	4.61	6.60	3.62
			Calcd	4.61	7.62	3.10

[a] "Tables of Interatomic Distances and Configuration in Molecules and Ions," *Chem. Soc. Spec. Publ.*, **No. 11**, 1 (1958); see also *ibid.*, **No. 18**, 1 (1965). [b] A. Eucken and K. H. Hellwege, Ed., "Landolt-Börnstein Zahlenwerte und Funktionen," 6th ed, Vol. I, Part 3, Springer-Verlag, Berlin, 1951, p 510.

Table VI. Polarizabilities (Å^3) of Heteronuclear Diatomic Molecules and Their Atoms for Yellow Light

Compd	r,[a] Å	α_A	α_B	Molecular polarizability[b] $\bar{\alpha}$	$\alpha_\parallel$	$\alpha_\perp$
HCl	1.2745	2.39	0.059	2.63	3.13	2.39
HBr	1.408	3.31	0.071	3.61	4.22	3.31
HI	1.609	4.89	0.129	5.45	6.58	4.89
CO	1.1282	1.624	0.071	1.95	2.60	1.625

[a] Footnote *a*, Table V. [b] Footnote *b*, Table V.

Discussion

Of the 43 molecules in Tables II–IV the mean polarizabilities are given by the theory to within 1% of the experimental value in 20 cases. The discrepancy exceeds 5% in only five cases (CH_3OH, CH_2CH_2O, H_2O, CH_3F, and CH_3CN). The uncertainty in the theory is thus for the most part comparable to experimental uncertainty.

Discrepancies between theory and experiment for the principal components of polarizability are, however, often of the order of 10%. This probably reflects a real shortcoming in the model, since errors of 10% in the components may imply errors of the order of 100% in differences between components, which are the quantities determined experimentally to an accuracy presumably much better than this. We can claim only that the model predicts anisotropies in a semiquantitative way.

In most cases the errors in the theory are in such a direction as to exaggerate the anisotropy of the molecule. One might seek to remedy this by treating the atoms as anisotropic and adjusting their anisotropies to give better overall agreement with molecular anisotropies. Pitzer[2] has illustrated this for Cl_2, a case for which the anisotropy of the atoms could be determined unambiguously. In a closely related approach, Rowell and Stein[10] have attempted to fit the polarizability data for ethane by a model in which point polarizabilities and anisotropies were assigned to the bonds. Their results were discouraging for the prospects of determining anisotropies of bonds accurately, though some improvement might be gained by simultaneous treatment of several molecules. This approach would involve twice as many variables as the isotropic unit model and therefore has the disadvantage of a great increase in computer time for the optimization. Moreover, it is not certain that anisotropies of the units (atoms or bonds) determined in this way would be physically meaningful, since they represent only one type of parameter that could be adjusted to improve the overall fit. Alternatively, locations of the polarizable centers could be varied. One might, for example, improve the fit for homonuclear diatomic molecules by increasing the distance r (arbitrarily equated with the internuclear distance in the present model) while maintaining isotropic atoms.[15] The present model has the advantage of simplicity, and our calculations of molecular anisotropies show that the atom polarizabilities determined in this study have at least approximate validity. They are much superior to the additive values for calculating polarizability interactions between atoms.

The existence of substantial interatomic interactions raises the question as to why additivity relationships should hold at all, as various authors have noted.[2,7,8] To answer this we consider the effective (additive) polarizability of the carbon atom in methane and halomethanes, calculated using the coefficient of **E** in eq 9 and the same parameters used for the total molecular polarizabilities. The results are given in Table VII.

Table VII. Effective Mean Polarizability (Å^3) of Carbon Atom n Methane and Halomethanes

Compd	$\bar{\alpha}_C'$	Compd	$\bar{\alpha}_C'$
CH_4	1.99	CCl_4	2.07
CH_3F	1.69	CH_3Br	1.80
CHF_3	1.61	CH_2Br_2	1.91
CF_4	1.58	$CHBr_3$	1.97
CH_3Cl	1.85	CH_3I	1.74
CH_2Cl_2	2.02	CH_2I_2	1.83
$CHCl_3$	2.04	CHI_3	2.03

(The effective polarizability of an atom in this model is in general anisotropic, but we report only the mean $\bar{\alpha}_C'$ for illustration.) It is seen that the effective polarizability is remarkably insensitive to the atoms to which carbon is bound, even though this polarizability is con-

siderably different from the "true" value, 0.878 Å^3. Thus the existence of additivity relationships is not due to absence of interaction effects but rather to a relative constancy of these effects for a given atom. A disturbing finding is that the effective values in Table VII are twice as large as the additive value 1.027 Å^3 normally accepted for carbon (Table I). This seems to imply that the additive constants are not uniquely determined or are very sensitive to the set of polarizabilities chosen to determine them.

A key assumption in our determination of optimum polarizabilities is that the polarizability of carbon is constant for all compounds in which it is tetrahedrally bonded. The overall agreement between theory and experiment tends to support this assumption but does not rule out the possibility that a better optimum could be found, say, for the halomethanes, with a different value of α_C. Thus it is interesting to find support for our assumption in the fact that C in diamond has a polarizability of 0.837 Å^3, determined from its molar (or atomic) refraction.[8] This is within 5% of our optimum value for alkane C. The values should have comparable significance, because the Lorentz–Lorenz relation is based on an approximate treatment of the same local field effects in a macroscopic sample as we have considered here for a single molecule. Silberstein[8] had, in fact, suggested that the atomic refraction of diamond be taken as the true refraction of carbon in its compounds.

The calculations for diatomic molecules are suggestive of some general limitations of our model. Among the homonuclear molecules one notices in Table V an increasing exaggeration of the theoretical anisotropy on going up the table. The trend suggests that the model becomes less realistic as the fraction of valence shell electrons involved in the covalent bond increases. This might be expected, since the sharing of electrons between atoms is a form of interaction quite distinct from the point dipole interaction assumed here. The results for the hydrogen halides (Table VI) seem reasonable in ascribing a much smaller polarizability to one atom than the other, the smaller polarizability being assignable to H. Comparison of the hydrogen polarizabilities among these and the organic molecules even suggests a rough correlation with the electronegativity of the atom to which hydrogen is bonded. The case of CO seems anomalous, however, in similarly ascribing most of the polarizability to one atom. This may be an artifact resulting from the tendency of model to exaggerate the anisotropy; since the calculated anisotropy depends on the product $\alpha_A\alpha_B$ (eq 12 and 13), this can be reduced artificially by making one of the factors very small. For this reason the hydrogen halide results must also be interpreted with caution.

To summarize, the major conclusions of this study are (i) the atom polarizabilities determined here are suitable for calculating reasonably accurate molecular polarizabilities of polyatomic molecules, and probably have greater validity in general than additive values for calculating interactions among atoms in molecules, and (ii) the anisotropies of a wide variety of polyatomic molecules can be largely attributed to atom dipole interactions, in support of Silberstein's suggestion.[8]

Acknowledgments. This investigation was supported by a research grant from the National Institute of General Medical Sciences (GM-13684) and an undergraduate research participation grant from the National Science Foundation (GY-5990) supporting J. R. C.