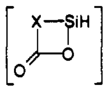
J. Am. Chem. Soc. 1993, 115, 2005-2014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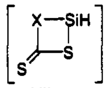
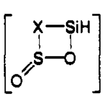

VII

that the X-containing scission product controls partitioning. This is particularly clear for the reaction of CO_2 with HSiS$^-$ and HSiNH$^-$. In both of these cases the Si-containing ring-scission product would be HSiO$^-$, but only X = NH gives any ring-scission product (see VI). Since the X = NH and O anions have similar reactivity, we might expect that intermediate VI with X = O would also undergo ring scission. It is likely that it does, but this decomposition is nothing more than a reversal of the formation of VI.

The partitioning of products from a particular four-membered ring intermediate cannot be assessed using thermochemistry since the requisite heats of formation are unknown. Nevertheless, in looking at the reactions we have studied, it seems reasonable that thermochemical factors are dominant. Thus, in almost every case ring extrusions dominate because HSiXO$^-$ or HSiXS$^-$ and CO, CS, or SO products are favored over the corresponding XCO, XCS, or XSO and HSiO$^-$ or HSiS$^-$. In the two examples in which ring scission occurs in greater the 10% relative yield, HNCO/HSiO$^-$ and HNSO/HSiO$^-$ (see VIII) form. Although we presume that these channels are thermochemically competitive with the ring extrusion ones, we cannot rule out dominant kinetic effects.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Conclusions

We have examined the detailed reactions of HSiS$^-$ and HSiNH$^-$ with a variety of neutral reagents. While their reaction chemistry is very similar and best explained using a model which was first developed for HSiO$^-$, their reactivities differ significantly. Thus, HSiNH$^-$ and HSiO$^-$ have similar reactivities and are much more reactive than HSiS$^-$. Computational studies of both HSiS$^-$ and HSiNH$^-$ have also been carried out.

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An Empirical Method To Calculate Average Molecular Polarizabilities from the Dependence of Effective Atomic Polarizabilities on Net Atomic Charge

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Abstract: An empirical method for the calculation of average molecular polarizability is introduced. In this method, the effective atomic polarizabilities are described as a function of net atomic charges which are obtained with the modified partial equalization of orbital electronegativity (M-PEOE) method. The effective atomic polarizability is derived with the aid of the Thomas-Fermi model of multiply-charged spherical ions. The calculated polarizabilities agree well with experimental data. Nonbonded potential parameters are also calculated as a function of net atomic charges from the effective atomic polarizabilities.

Introduction

It is useful to calculate the polarizabilities of parts of molecules, *fractional polarizabilities*, based on the *additivity hypothesis*. This hypothesis has been tested by several workers.[1-8] The parts of a molecule are usually the bonds[5-7] or the functional groups in the molecules.[4,8] According to the extensive studies mentioned above, the molecular polarizability can be written as a sum of atomic polarizabilities. However, the environment of the atoms in a molecule must be considered in the parametrization of the polarizability. The additivity hypothesis works well if hybrid atomic, group or bond parameters are used in the analysis instead of atomic polarizability. These fractionally-decomposed polarizabilities can be used for the calculation of molecular polarizabilities and other molecular properties such as molar refraction[3,4] that can be regarded as additive sums of their individual contributions. Applequist et al.[7c] introduced an interaction model instead of the additivity model. In their work, the suitability of an isotropic atom model for predicting anisotropy of polyatomic molecules was considered. The computed average polarizabilities agreed well with experimental data (with an error of between 1 and 5%), and the discrepancies between theory and experiment for the principal components of the polarizability were often of the order of 10%.

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The individual atomic polarizabilities can also be used for the computation of London dispersion forces in atom–atom pair interactions and of the polarization of each atom in the electric field produced by its environment. Since most of the empirical potential energy functions used for conformational studies of relatively large molecules, especially biological molecules, introduce the atom–atom pairwise approximation, it is very important to obtain physically realistic *fractional polarizabilities* within the limitations of the additivity approximation.

Miller and Savchik[9] proposed an empirical approach to calculate average molecular polarizabilities, α(ahc), based on the square of the sum of atomic hybrid components τ_A(ahc) and on the classification of the atoms in molecules through the features of atomic hybridization (ah). Additivity was shown to work well when the features of atomic hybridization are introduced in the parametrization.[9] The following empirical formula was proposed[9] on the basis of molecular orbital theory using the zero differential overlap approximation,

$$\alpha(\text{ahc}) = (4/N)\Big[\sum_A \tau_A(\text{ahc})\Big]^2 \tag{1}$$

where τ_A(ahc) is an atomic hybrid component of atom A in a given state of hybridization, and N is the total number of electrons in the molecule.

Kang and Jhon[10] used an additivity approximation to determine the atomic polarizabilities and obtained an optimum set of atomic hybrid polarizabilities, α_A(ahp), which reproduce experimental molecular polarizabilities within the additivity approximation, with approximately a 1–3% error, with the following formula:

$$\alpha(\text{ahp}) = \sum_A \alpha_A(\text{ahp}) \tag{2}$$

In order to obtain an additive linear function, Miller[11] introduced the average atomic polarizability, α^*(ahc), in a form similar to that of eq 1 as

$$\alpha_A^*(\text{ahc}) = (4/N_A)[\tau_A(\text{ahc})]^2 \tag{3}$$

where N_A is the number of electrons in atom A. Then, the corresponding ahc molecular polarizability, α^*(ahc), can be written as a sum of the average atomic polarizabilities, as in eq 2, within the additivity approximation.

$$\alpha^*(\text{ahc}) = \sum_A \alpha_A^*(\text{ahc}) \tag{4}$$

Thus, Miller's introduction of α^*(ahc) was intended as a description of molecular polarizability analogous to that of Kang and Jhon. Miller[11] reoptimized the parameters τ_A(ahc) and α_A(ahp) separately for the ahc and ahp methods, eqs 1 and 2, respectively. The average molecular polarizabilities of approximately 400 compounds were obtained with the optimized ahc parameters, τ_A(ahc), and also with the optimized ahp parameters, α_A(ahp). Equations 1 and 2 reproduce the experimental values with average errors of 2.2% and 2.8%, respectively.

In order to demonstrate the extent of transferability of parameters between the ahc and ahp methods, the corresponding parameters, τ_A^*(ahp) and α_A^*(ahp) were introduced, and calculated[11] from the following formulas:

$$\tau_A^*(\text{ahp}) = [N_A \alpha_A(\text{ahp})/4]^{1/2} \tag{5}$$

$$\alpha^*(\text{ahp}) = (4/N)\Big[\sum_A \tau_A^*(\text{ahp})\Big]^2 \tag{6}$$

The parameters τ_A(ahc) and α_A(ahp), and the corresponding parameters τ_A^*(ahp) and α_A^*(ahc), are listed in Table I of ref 11. To test for the transferability between the ahc and ahp methods, the corresponding polarizabilities, α^*(ahc) and α^*(ahp), were also calculated[11] using eqs 4 and 6, respectively. The differences, α(ahc) − α^*(ahc) and α(ahp) − α^*(ahp), respectively, are listed in Table II of ref 11. Interconversion between the ahc and bond or group polarizabilities was also tested and exhibited good interconvertability.[11]

It is well known that molecular polarizabilities cannot be written simply as a sum of atomic polarizabilities of neutral atoms. The reason for the nonadditivity might arise mainly from the formation of the bonds in a molecule, which could lead to (i) a redistribution of the electrons in the bonds and (ii) restriction of the motions of the electrons by the nuclei in the molecule. Since factor (i) increases the transition probability for the electron from occupied atomic orbitals to more polarizable unoccupied atomic orbitals, and factor (ii) works in the opposite direction because the attractive Coulombic interaction between nuclei and the electrons in bonding orbitals increases, the net effect will determine the changes in the magnitudes of molecular polarizabilities. In general, experimental molecular polarizabilities are smaller than those calculated from the sums of the polarizabilities of the neutral atoms from which the molecules are constituted. In order to minimize the error arising from nonadditivity in the description of molecular polarizability as the sum of atomic contributions, an effective atomic polarizability which depends on the chemical environment and on the influence of electron redistribution must be introduced to take account of both factors (i) and (ii).

The purpose of this work is to obtain effective atomic polarizabilities that take account of both of the factors mentioned above. In this work, the effective atomic polarizability will be described as a function of net atomic charge. The effective atomic polarizability will be used for the computation of London dispersion forces, especially for the atoms in those molecules, e.g., organic ions, whose polarizabilities are not available from experiment.

Empirical Formulation of Molecular Polarizability with the Thomas–Fermi Model

Shevelko and Vinogradov[12] derived the dipole polarizability of multiply-charged ions using the Thomas–Fermi model.[13] According to this model, the potential of the electric field $\phi(r)$ at any point r inside a neutral atom or ion satisfies the following Poisson equation:

$$\Delta\phi(r) = (4/3\pi)p^3(r) = \frac{8\sqrt{2}}{3\pi}\left[\phi(r) - \frac{Z-N}{r_0}\right]^{3/2} \tag{7}$$

where $p(r)$ is the Fermi momentum, and Z, N, and r_0 are the nuclear charge, the number of electrons, and the radius of the atom or ion, respectively. The approximate dipole polarizability derived from the above equation is given by eq 18 of ref 12, when $Z \gg N$, viz.,

$$\alpha \simeq \frac{1}{3}\int_0^{r_0} \frac{4\sqrt{2}}{\pi}\left(\frac{Z}{r} - r_0\right)^{1/2} r^4\,\mathrm{d}r = \frac{N^3}{Z^4}V \tag{8}$$

where V is a constant which has the dimensions of volume. According to this result, the polarizability of a neutral atom or ion is a function of the nuclear charge, the electron population, and the size of the sphere. The ionic charge is ($Z - N$).

In this paper, we modify this polarizability for atoms and ions in order to compute the effective polarizabilities of atoms under the assumption that the motions of the electrons in a molecule are strongly restricted by the nuclei in a molecule (the sum of *all* the nuclear charges, $\sum Z$, is greater than the number of electrons, N, in any given atom; therefore, eq 8, which holds for $Z \gg N$, can be used for molecules). In this modification, the atoms in a molecule are assumed to be perturbed by their environments, mainly through bonding. The perturbation could be the changes in electron population (dq), the changes in effective nuclear charge (dZ), and the changes in the sizes of the atoms in a molecule, as the isolated atoms are combined to form a molecule. These factors appear in eqs 9–11. We replace each quantity in eqs 9–11 by the effective quantity (designated by an asterisk superscript) which incorporates the perturbation as follows:

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$$Z_i \rightarrow Z_i^* = Z_i + dZ_i \tag{9}$$

$$N_i \rightarrow N_i^* = N_i - dq_i \tag{10}$$

$$V_i \rightarrow V_i^* \tag{11}$$

where dZ_i represents the changes in effective nuclear charge arising from the influence of the environment (mainly due to chemical bonding). It includes the screening by the other electrons and the restrictions by the other nuclei of the neighboring atoms. N_i and dq_i represent the number of electrons of the neutral atom i and the changes in net atomic charge of the ith atom, respectively. V_i is the volume of the neutral atom, and V_i^* is its effective volume and is a function of both Z and N:

$$V_i^* = V_i^*(Z_i^*,N_i^*) = V_i^*(Z_i + dZ_i, N_i - dq_i) \tag{12}$$

Expanding this equation about N_i, we obtain

$$V_i^*(Z_i^*,N_i - dq_i) = V_i^*(Z_i^*,N_i) - V_i^{*\prime}(Z_i^*,N_i)\cdot dq_i + (1/2)V_i^{*\prime\prime}(Z_i^*,N_i)\cdot dq_i^2 - ... \tag{13}$$

where $V_i^{*\prime}$ and $V_i^{*\prime\prime}$ are the first and second derivatives of V_i^* with respect to q_i, respectively. Let

$$V_i^*(Z_i^*,N_i) \equiv V_i^\dagger \tag{14}$$

$$V_i^{*\prime}(Z_i^*,N_i) \equiv V_i^{\dagger\prime} \tag{15}$$

i.e., $V_i^\dagger$ represents the average change in volume as the charge changes by 1 electronic charge unit, and eq 13 may be approximated by

$$V_i^*(Z_i^*,N_i - dq_i) = V_i^\dagger - V_i^{\dagger\prime}\cdot dq_i \tag{16}$$

Using eqs 8, 10, and 16, the effective dipole polarizability of the ith atom in a molecule can be expressed as follows

$$\alpha_i^* = \frac{N_i^{*3}}{Z_i^{*4}}\cdot V_i^* = \frac{1}{Z_i^{*4}}(N_i - dq_i)^3[V_i^\dagger - V_i^{\dagger\prime}\cdot dq_i] \tag{17}$$

$$\alpha_i^* \simeq \frac{1}{Z_i^{*4}}(N_i^3 - 3N_i^2\cdot dq_i)[V_i^\dagger - V_i^{\dagger\prime}\cdot dq_i) \tag{18}$$

$$\alpha_i^* \simeq \frac{V_i^\dagger\cdot N_i^3}{Z_i^{*4}} - \frac{1}{Z_i^{*4}}(V_i^{\dagger\prime}\cdot N_i^3 + 3V_i^\dagger\cdot N_i^2)dq_i + \frac{1}{Z_i^{*4}}3V_i^{\dagger\prime}\cdot N_i^2\cdot dq_i^2 \tag{19}$$

$V_i^\dagger$, $V_i^{\dagger\prime}$, and Z_i^*, become defined for atomic species i when the chemical environment around atom i is specified. Therefore, the subscript i must be replaced by two indices, i and j. The index j represents a specific chemical environment, usually the valence state of atom i. Equation 19 can be written as a function of dq_{ij}, with a term-by-term correspondence between eqs 19 and 20.

$$\alpha_{ij}^* = \alpha_{ij,0}^* - a_{ij}\cdot dq_{ij} + b_{ij}\cdot dq_{ij}^2 \tag{20}$$

The third term plays an important role over a wide range of dq, especially for light atoms. For the hydrogen atom, since $V_H^{\dagger\prime}$ is very large compared with $V_H^\dagger$, a rough estimate of the ratio a/b is $V^{\dagger\prime}\cdot N_i^3/3V^{\dagger\prime}\cdot N_i^2$ or 1/3, since $N_i = 1$. For small changes, dq, in q, the charge dependence of the effective atomic polarizability (CDEAP) for atoms heavier than hydrogen, α_{ij}^*, can be expressed as a linear function of dq_{ij}, i.e., by neglecting the dq_{ij}^2 term. Therefore, eq 20 can be approximated by

$$\alpha_{ij}^* = \alpha_{ij,0}^* - a_{ij}\cdot dq_{ij} \tag{21}$$

Determination of the Optimum Parameters for the Effective Atomic Polarizabilities

For a description of the effective atomic polarizability, both the net atomic charge, q_{ij}, and the two parameters $\alpha_{ij,0}^*$ and a_{ij} are needed. The net atomic charge, especially, must be a good representative of the electron population. There are many ways to calculate the effective net atomic charge around a specified atom. The most widely used method is the Mulliken population analysis. Empirically-determined point charges located on atomic centers, and even point charges not necessarily located on atomic centers, obtained by using the potential derived (PD) method,[14–16] are also used widely for calculating the electrostatic potential and field around a molecule. Since the PD charges are not transferable, even for atoms located in similar chemical environments,[17] the magnitudes of the PD charges are not suitable for representing the electron populations of the atoms in a molecule, although the PD charges are good representations for the electrostatic potentials or fields around a molecule if a reliable basis set is used. The Mulliken charges are not good representations for the electrostatic potentials or fields around a molecule; however, they represent the electron populations of the atoms in a molecule better than the point charge sets that are designed mainly for the calculation of electric properties such as electric moments, electrostatic potentials or fields, etc. Although there is no well-defined definition for the net atomic charge or the electron population of an atom in a molecule, i.e., no quantum mechanical operator exists, the electron populations obtained from the Mulliken population analysis are relatively reliable. However, Mulliken charges are laborious to calculate with a reliable basis set. Therefore, in the calculations in this paper, we will introduce the set of net atomic charges that are more easily calculated with the modified partial equalization of orbital electronegativity (M-PEOE) method.[17,18] The magnitudes of the M-PEOE point charges are similar to the Mulliken charges and are transferable. The details of the M-PEOE method are described in our previous papers.[17,18]

Table I. Optimized Parameters for Expressing the Effective Atomic Polarizability

atom and valence state	$\alpha_{ij,0}^*$, Å^3	α_{ij}, Å^3	α_i^f,[g] Å^3	$\bar{\alpha}_{i,j}^*$, Å^3	IP,[h] eV
C1 sp^2 (ethylene)	1.516	0.568	1.76	1.555	11.22
C2 sp^2 (aromatic)	1.450	0.763		1.499	11.22
C3 sp^2 (carbonyl)[a]	1.253	0.862		1.077	11.22
C4 sp^3	1.031	0.590		1.015	14.57
H1 sp^{3,}[b]	0.396	0.219	0.67	0.389	13.61
H2 sp^{2,}[c]	0.298	0.404		0.254	13.61
O1 sp^2	0.720	0.347	0.80	0.829	17.25
O2 sp^3	0.623	0.281		0.728	18.40
N1 sp^2 (aromatic)[d]	0.871	0.424	1.10	1.055	14.51
N2 sp^2 (aromatic)[e]	0.656	0.436		0.905	12.25
N3 sp^2 (amide)[f]	0.821	0.422		1.020	12.25
N4 sp^3	0.966	0.437		1.107	14.31
S1 sp^3 (–S–)	2.688	1.319	2.93	3.316	10.36
F1	0.226	0.144	0.56	0.248	17.42
Cl1	2.180	1.089	2.18	2.321	12.97
Br1	3.114	1.402	3.05	3.318	11.82
I1	5.166	2.573	4.70	5.443	10.45

[a] Carbon atom in carbonyl group, for examples, amides. [b] Hydrogen atom bonded to saturated system and in amides. [c] Hydrogen atom bonded to aromatic system. [d] Nitrogen atom in aromatic system having three bonds, e.g., pyrrole. [e] Nitrogen atom in aromatic system having two bonds, e.g., pyridine. [f] Nitrogen atom in amides. [g] Polarizabilities of the free atom, taken from ref 19. [h] Ionization potential of neutral atom, used for calculating London dispersion parameters and taken from refs 20–22.

As pointed out above, the atomic species, with subscript i, are classified with a subscript j to specify the valence state or chemical environment; the effective atomic polarizability α_{ij}^* pertains to the ith atom in the jth classification. The classifications[17,18] are summarized in Table I, with data obtained from refs 19–22. The optimum values of the parameters $a_{ij,0}^*$ and a_{ij}, for each classified

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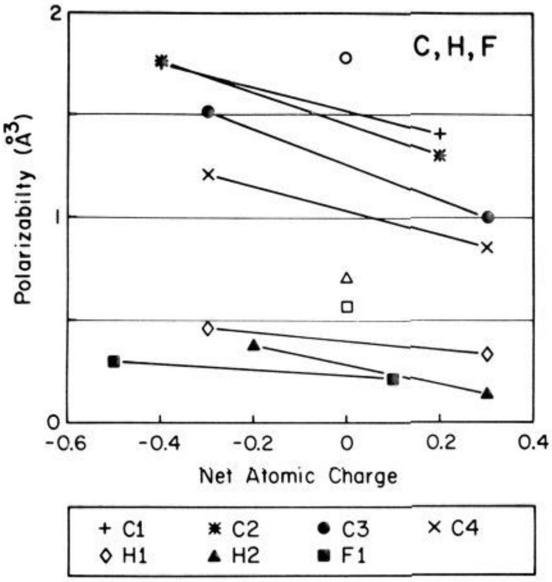

Figure 1. Relation between the atomic polarizability, α^*, and the net atomic charge dq of carbon, hydrogen, and fluorine: ○, α^f_C; Δ, α^f_H; □, α^f_F.

species, were obtained by the following optimization procedure, in which the difference between the calculated and the experimental average molecular polarizabilities, described by the following function F_{opt} (average percent error), was minimized.

$$F_{opt} = \frac{1}{N}\sum_{k}^{N}\frac{|\alpha^{obs}_{m,k} - \alpha^{calc}_{m,k}|}{\alpha^{obs}_{m,k}} \times 100 \qquad (22)$$

where $\alpha^{obs}_{m,k}$ and $\alpha^{calc}_{m,k}$ represent the observed and calculated molecular polarizabilities (m) of the kth molecule; the values of $\alpha^{calc}_{m,k}$ were obtained by summing the values of α^*_{ij} for each atom of the molecule, computed with eq 21. The optimum parameters for C, H, O, N, S, and halogen atoms were determined according to their classifications. For this purpose, 230 observed average molecular polarizabilities were used in eq 22 during the optimization procedures. The optimized parameters are listed in Table I.

To test for the influence of the parameter b_{ij}, appearing in eq 20, on the calculated average molecular polarizability, for a light atom for which its influence might be expected to be greatest, the quadratic expression for the effective atomic polarizability for the H atom was introduced. a_{H_1}, b_{H_1}, a_{H_2}, and b_{H_2} were optimized with the same 230 molecules, keeping all the other a's and b's of Table I fixed (where H_1 and H_2 are the two types of hydrogens listed in Table I). The value of F_{opt} decreased by only a small amount (<5%) because the a,b parameters were already near their optimum values. The computed ratios, a_{H_1}/b_{H_1} and a_{H_2}/b_{H_2}, were 0.46 and 0.34, respectively. These values are approximately the same as the estimated value, 1/3.

Results and Discussion

In Figures 1 to 3, the effective atomic polarizability of each species (computed with eq 21) is plotted as a function of the net atomic charge dq (in electronic charge units). All the α^*_{Cj}'s are smaller than the atomic polarizability of the free carbon atom, α^f_C, and depend very much on the classification, j (Figure 1). The contribution of each carbon atom in a conjugated molecule to the molecular polarizability is not influenced much by the number of double bonds. The α^*_C's for ethylene-type, α^*_{C1}, and for aromatic, α^*_{C2} carbons are very close over a large range of net atomic charge. The polarizability of an sp^3 carbon is lower than those of the other types of carbons.

The $\alpha^*_{H_j}$'s are much smaller than α^f_H for the free H atom, and the polarizability of an H atom bonded to an unsaturated system is smaller than that of an H atom bonded to a saturated system. Since the H atom has only a +1 nuclear charge, the polarization of the electron of the H atom is strongly influenced by the other nuclei in its environment. The α^*_O and α^*_N show a similar trend (Figure 2).

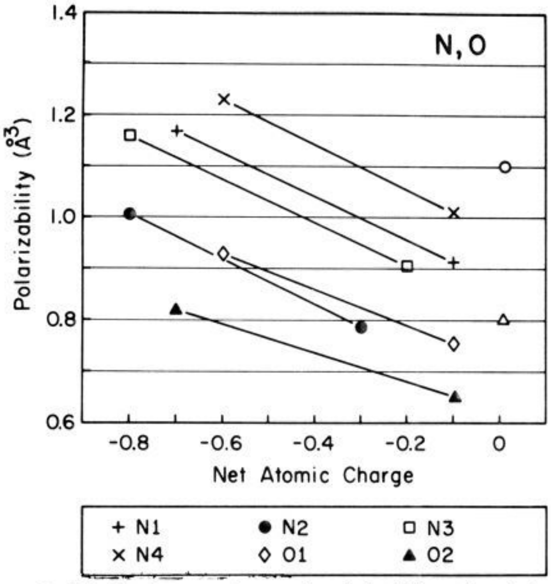

Figure 2. Relation between the atomic polarizability, α^*, and the net atomic charge dq of nitrogen and oxygen: ○, α^f_N; Δ, α^f_O.

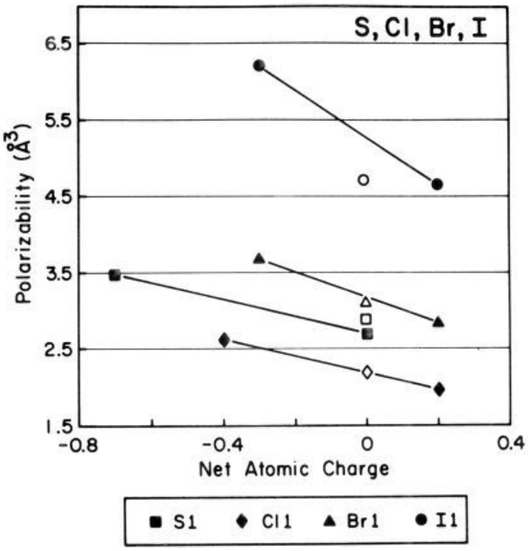

Figure 3. Relation between the atomic polarizability, α^*, and the net atomic charge dq of sulfur and the halogens: ○, α^f_I; Δ, α^f_{Br}; □, α^f_S; ◇, α^f_{Cl}.

For the sulfur atom, α^*_S increases considerably (Figure 3) as its electron population increases because the sulfur atom has empty diffuse orbitals. Therefore, the electrons from the other atoms bonded to the S atom move in and occupy these highly polarizable orbitals. α^*_F is less than half of α^f_F (Figure 1), and α^*_{Cl} and α^*_{Br} have almost the same magnitude as α^f_{Cl} and α^f_{Br}, respectively (Figure 3). The value of α^*_I is larger than that of α^f_I.

In Table I, the effective average atomic polarizabilities and α^f's are listed. The values of α^* were calculated as an average from the average net atomic charge, $\overline{dq}_{ij}$, for each particular species. The averaging was carried out over all the molecules used in this work.

$$\bar{\alpha}^*_{ij} = \alpha^*_{ij,0} + a_{ij}\cdot\overline{dq}_{ij} \qquad (23)$$

Comparison of $\bar{\alpha}^*_{ij}$, $\alpha^*_{ij,0}$ and α^f_i provides information about electron redistributions after formation of bonds from the neutral atoms. Most of the observed molecular polarizabilities, α_m, have smaller values than the sums of the atomic polarizabilities α^f of the *free* atoms except for molecules composed of large, strongly electro-

Table II. Calculated and Experimental Molecular Polarizabilities (in Å^3) of Saturated Aliphatic Hydrocarbons and Hydrogen Halides

compound	exptl	Miller[a] (ahc)	Kang–Jhon[b] (ahp)	this work (CDEAP)	refs for exptl values
H_2	0.79	0.78	0.77	0.79	23
methane CH_4	2.60	2.59	2.61	2.62	23
ethane C_2H_6	4.47	4.43	4.44	4.46	23
propane C_3H_8	6.29	6.27	6.28	6.29	23
butane C_4H_{10}	8.12	8.12	8.11	8.12	23
pentane C_5H_{12}	9.95	9.96	9.95	9.95	24
hexane C_6H_{14}	11.78	11.80	11.78	11.78	23
heptane C_7H_{16}	13.61	13.64	13.62	13.61	7a
octane C_8H_{18}	15.44	15.49	15.42	15.44	23
nonane C_9H_{20}	17.36	17.33	17.29	17.27	7a
decane $C_{10}H_{22}$	19.10	19.17	19.12	19.10	23
undecane $C_{11}H_{24}$	21.03	21.02	20.96	20.93	7a
dodecane $C_{12}H_{26}$	22.75	22.86	22.79	22.76	23
isobutane C_4H_{10}	8.14	8.12	8.11	8.12	23
neopentane	10.20	9.96	9.95	9.95	25
cyclopentane	9.09	9.22	9.18	9.15	7a
cyclohexane C_6H_{12}	10.99	11.06	11.01	10.98	7a
3-methylheptane C_8H_{18}	15.44	15.49	15.45	15.44	23
2,2,4-trimethylpentane	15.44	15.49	15.44	15.44	23
CH_3F	2.62	2.45	2.52	2.37	25
$C_5H_{11}F$	9.95	9.68	9.86	9.69	26
$C_6H_{13}F$	11.80	11.52	11.69	11.52	26
$C_7H_{15}F$	13.66	13.35	13.53	13.35	26
$C_8H_{17}F$	15.46	15.19	15.36	15.18	26
$C_9H_{19}F$	17.34	17.03	17.20	17.01	26
$C_{10}H_{21}F$	19.18	18.86	19.03	18.84	26
$C_{11}H_{23}F$	21.00	20.70	20.87	20.67	26
$C_{12}H_{25}F$	22.83	22.54	22.70	22.50	26
$C_{14}H_{29}F$	26.57	26.23	26.37	26.16	26
CH_3Br	5.61	5.53	5.23	5.52	27
C_2H_5Br	7.28	7.27	7.07	7.34	27
C_3H_7Br	9.07	9.03	8.90	9.17	27
C_4H_9Br	10.86	10.81	10.74	11.00	27
$C_5H_{11}Br$	12.65	12.61	12.57	12.83	27
$C_6H_{13}Br$	14.44	14.42	14.41	14.66	27
$C_7H_{15}Br$	16.23	16.23	16.24	16.49	27
$C_8H_{17}Br$	18.02	18.04	18.08	18.32	27
$C_9H_{19}Br$	19.81	19.86	19.91	20.15	27
$C_{10}H_{21}Br$	21.60	21.69	21.75	21.98	27
$C_{12}H_{25}Br$	25.18	25.34	25.42	25.65	27
$C_{16}H_{33}Br$	32.34	32.67	32.76	32.97	27
$C_{18}H_{37}Br$	35.92	36.34	36.43	36.63	27
CH_2Br_2	8.68	8.74	7.86	8.35	25
$CHBr_3$	11.84	11.97	10.49	11.15	25
CH_3I	7.59	7.56	7.64	7.72	25
CH_2I_2	12.90	12.81	12.66	12.72	25
CHI_3	18.04	18.07	17.69	17.70	25
CH_3Cl	4.56	4.48	4.54	4.53	23
CH_2Cl_2	6.48	6.48	6.46	6.39	23
$CHCl_3$	8.23	8.50	8.39	8.23	23
ethyl chloride	6.40	6.30	6.37	6.35	23
HF	0.80	0.79	0.68	0.61	23
HCl	2.63	2.69	2.70	2.66	23
HBr	3.61	3.84	3.40	3.61	23
HI	5.45	5.88	5.80	5.74	23
av percent error[c]		0.86	1.09	1.03	

[a] Data taken from ref 11. [b] Data taken from ref 11, because Miller reoptimized the ahp parameters. [c] The average percent error, F_{opt}, is defined in eq 22.

negative atoms and small, weakly electronegative atoms, e.g., HI. Miller[9,11] and Kang and Jhon[10] used separate parameters for branched and condensed carbons in conjugated systems, i.e., for sp^2 carbon. In our calculations, these two kinds of carbons are not classified separately. Since they have different net atomic charges, they contribute differently to the molecular polarizability.

The calculated polarizabilities of 230 molecules[7,23–37] are listed in Tables II–VIII, as follows: saturated aliphatic hydrocarbons (Table II), halogenated saturated aliphatic hydrocarbons and

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Table III. Calculated and Experimental Molecular Polarizabilities (in Å^3) of Alkenes, Halogenated Alkenes, and Aromatic Compounds

compounds	exptl	Miller[a] (ahc)	Kang–Jhon[b] (ahp)	this work (CDEAP)	ref for exptl values
ethylene	4.26	4.24	4.25	4.26	23
1-pentene	9.65	9.76	9.76	9.85	7a
2-pentene	9.84	9.76	9.76	9.94	7a
1-hexene	11.65	11.60	11.59	11.68	7a
1-heptene	13.51	13.44	13.43	13.51	7a
CH_2=CCl_2	7.83	8.04	8.11	8.09	28
trans-dichloroethylene	8.15	8.04	8.11	8.11	29
cis-dichloroethylene	8.03	8.04	8.11	8.11	29
CHCl=CCl_2	10.03	10.04	10.04	9.98	28
trans-chlorobromoethylene	9.28	9.05	8.81	9.06	29
cis-chlorobromoethylene	9.19	9.05	8.81	9.06	29
benzene	10.39	10.45	10.43	10.71	30
toluene	11.83	12.29	12.27	12.64	27
1,3,5-trimethylbenzene	16.14	15.98	15.94	16.48	7a
durene $C_{10}H_{14}$	17.40	17.82	17.77	18.41	27
hexamethylbenzene	20.81	21.50	21.44	22.14	27
fluorobenzene	9.86	10.13	10.34	10.53	31
chlorobenzene	12.25	12.25	12.36	12.59	23
bromobenzene	13.62	13.02	13.06	13.55	23
1,2-difluorobenzene	9.80	9.98	10.25	10.34	32
o-dichlorobenzene	14.17	14.15	14.29	14.46	23
m-dichlorobenzene	14.23	14.15	14.29	14.46	23
p-dichlorobenzene	14.20	14.15	14.29	14.47	23
1,4-difluorobenzene	9.80	9.98	10.25	10.34	31
1,3,5-trifluorobenzene	9.74	9.94	10.16	10.15	31
1,2,3,4-tetrafluorobenzene	9.69	9.97	10.07	9.96	31
1,2,4,5-tetrafluorobenzene	9.69	9.97	10.07	9.96	31
pentafluorobenzene	9.63	10.05	9.98	9.78	31
hexafluorobenzene	9.58	10.18	9.89	9.59	31
p-fluorotoluene	11.70	11.97	12.18	12.45	27
p-chlorotoluene	13.70	14.09	14.20	14.51	27
p-bromotoluene	14.80	14.83	14.89	15.47	27
p-iodotoluene	17.10	16.76	17.30	17.59	27
o-xylene	14.10	14.13	14.10	14.56	23
m-xylene	14.18	14.13	14.10	14.56	23
p-xylene	14.22	14.13	14.10	14.56	23
naphthalene	17.48	17.77	17.70	17.19	30
anthracene	25.93	25.10	24.97	23.66	30
phenanthrene	24.70	25.10	24.97	23.66	30
naphthacene (2,3-benzanthracene)	32.27	32.44	32.24	30.26	30
1,2-benzanthracene $C_{18}H_{12}$	32.86	32.44	32.24	30.14	30
chrysene $C_{18}H_{12}$	33.06	32.44	32.24	30.23	30
1,2:5,6-dibenzanthracene	41.31	39.77	39.51	36.61	30
acenaphthene $C_{12}H_{10}$	20.61	20.69	20.60	20.23	30
fluoranthracene	28.34	27.82	27.68	23.48	30
pyrene $C_{16}H_{10}$	28.22	28.96	28.77	26.74	30
fluorene $C_{13}H_{10}$	21.68	21.25	21.15	21.96	30
2,3-benzfluorene $C_{17}H_{12}$	30.21	28.55	28.42	28.44	30
triphenylene	31.07	32.44	32.24	30.19	33
coronene $C_{24}H_{12}$	42.50	44.02	43.62	38.84	30
α-methylnaphthalene	19.35	19.61	19.54	19.11	29
β-methylnaphthalene	19.52	19.61	19.54	19.26	29
α-ethylnaphthalene	21.19	21.45	21.37	21.13	29
β-ethylnaphthalene	21.36	21.45	21.37	21.13	29
α-chloronaphthalene	19.30	19.50	19.63	19.12	29
β-chloronaphthalene	19.58	19.50	19.63	19.06	29
α-bromonaphthalene	20.34	19.13	19.24	20.08	7a
α-iodonaphthalene	22.41	21.95	22.73	22.20	29
β-iodonaphthalene	22.95	21.95	22.73	22.14	29
octafluoronaphthalene	17.64	16.86	16.98	15.59	31
α-naphthalenecarboxaldehyde	19.75	20.11	20.17	19.12	29
β-naphthalenecarboxaldehyde	20.06	20.11	20.17	19.12	29
α-naphthylamine	19.50	18.83	19.18	18.65	29
β-naphthylamine	19.73	18.83	19.18	18.65	29
α-bromonaphthalene	20.34	20.09	20.33	20.08	7a
styrene	14.41	14.49	14.46	14.27	1
α-methylstyrene	16.05	16.33	16.29	16.38	1
α,β,β-trimethylstyrene	19.64	20.00	19.96	20.34	1
9-chloroanthracene	27.35	26.78	26.90	25.54	27
9-bromoanthracene	28.32	27.27	27.60	26.49	27
av percent error[c]		1.98	2.05	3.69	

[a] Data taken from ref 11. [b] Data taken from ref 11. [c] The average percent error, F_{opt}, is defined by eq 22.

hydrogen halides (Table II); alkenes and halogenated alkenes (Table III), aromatic compounds with and without halogen substitutions (Table III); aliphatic nitrogen-containing compounds and nitrogen-containing heterocyclic compounds (Table IV);

Table IV. Calculated and Experimental Molecular Polarizabilities (in Å^3) of Nitrogen-Containing Compounds

compound	exptl	Miller[a] (ahc)	Kang–Jhon[b] (ahp)	this work (CDEAP)	ref for exptl values
NH_3	2.26	2.14	2.13	2.26	23
n-propylamine	7.70	7.67	7.63	7.77	7a
isopropylamine	7.77	7.67	7.63	7.77	7a
diethylamine	9.61	9.51	9.46	9.56	7a
di-*n*-propylamine	13.29	13.19	13.13	13.22	7a
triethylamine	13.38	13.19	13.13	13.18	7a
tri-*n*-propylamine	18.87	18.72	18.64	18.67	7a
pyridine	9.18	9.51	9.72	9.68	27
quinoline	15.70	16.80	16.99	16.14	34
isoquinoline	16.43	16.80	16.99	16.38	29
1-methylquinoline	18.65	17.89	18.06	17.93	29
1-methylisoquinoline	18.28	17.89	18.06	18.08	29
quinoxaline	15.13	15.85	16.29	15.14	35
2,3-dimethylquinoxaline	18.70	19.53	19.96	19.38	35
phenazine $C_{12}H_8N_2$	23.43	23.14	23.56	21.54	27
hydrazine	3.46	3.55	3.48	3.71	29
phenylhydrazine	12.91	12.93	13.26	13.18	29
1,1-methylphenylhydrazine	14.81	14.78	15.10	15.08	29
1,1-ethylphenylhydrazine	16.62	16.62	16.93	16.90	29
pyrazole	7.23	7.17	7.72	7.10	29
N-methylpyrazole	8.99	9.01	9.56	8.99	29
1,5-dimethylpyrazole	10.72	10.84	11.39	10.91	29
1-ethyl-5-methylpyrazole	12.50	12.68	13.23	12.75	29
av percent error[c]		2.56	3.52	2.59	

[a] Data taken from ref 11. [b] Data taken from ref 11. [c] The average percent error, F_{opt}, is defined by eq 22.

alcohols, ethers, ketones, aldehydes, esters, halogenated carboxylic acids, and carboxylic acids (Table V); amides (Table VI); sulfur-containing compounds (Table VII); and biological compounds that were not included in the optimization of the parameters (Table VIII). The average percent error between observed and calculated values in each group lies mainly between 1 and 4%. Our calculations give worse results than those of Miller[11] for aromatic rings, especially for conjugated hydrocarbons. The difference arises mainly from the description of the net atomic charges in the M-PEOE method.[17,18] In the M-PEOE method, the point charge approximation is used, and the charges are determined by requiring that they produce good electric dipole moments; hence, it is difficult to represent the electron populations of atoms in conjugated molecules by localized point charges. Since the parameters of the M-PEOE method were determined[17,18] with a finite-size group of molecules, they may not always be applicable to obtain the point charges of other types of molecules. For example, the M-PEOE parameters of an sp^3 nitrogen (optimized with experimental dipole moments of amines) may not be applicable to calculate the point charges of the $-NH_2$ group in substituted anilines. For the oxygen-containing compounds in Table V, the CDEAP results are better than those of Miller[11] and Kang-Jhon.[10] The CDEAP method gives better results than those of these authors,[10,11] especially for carboxylic acids and amides (Tables V and VI) because the M-PEOE parameters were designed especially for the biomolecules that include the fragments of polypeptides. The parameters are especially well-designed for the carbonyl, –OH, and $-NH_2$ groups. The better the point charge set is, the more accurate is the description of the effective atomic polarizabilities that can be obtained. There are several valence states for both S and P atoms. In this work, the effective atomic polarizability is described only for the sp^2 sulfur atom with two bonds because the M-PEOE charges have not yet been calculated for molecules containing S or P atoms other than sp^2 sulfur.[38]

The CDEAP method works better than the other methods that (i) use the additivity approximation and (ii) maintain the effective atomic polarizabilities constant, even though the redistribution of the electrons in a molecule may be relatively large. The molecules in Table VIII were not included in the determination of parameters, and the CDEAP polarizabilities are better than those of Miller[11] and much better than those of Kang and Jhon.[10]

The atomic polarizabilities of some amino acid zwitterions were also calculated with the CDEAP method and with 6-31G** ab initio wave functions. The results are summarized in Table IX. The calculated ab initio molecular polarizabilities (obtained from a 6-31** basis SCF calculation) are about 35% lower than the CDEAP values. The dependence of the calculated molecular polarizability on the choice of basis set has been well summarized by Spackman.[39] The average ratio of the calculated CDEAP molecular polarizabilities and the SCF 6-31G** molecular polarizabilities is 1.34. As shown in Table IX, when the ab initio molecular polarizabilities are multiplied by 1.34, the average error between the two methods is only 2.9%. All the ab initio molecular polarizabilities were calculated with 6-31G**-optimized geometries.[40]

Application to London Forces. The polarizabilities of the atoms in charged molecules are essential for predicting the degree of polarization of each atom or functional group[13] of an ion in solution. They are also needed to calculate the stabilization energy due to polarization. The effective atomic polarizability is also essential for determining the London dispersion coefficient in an atom–atom pairwise interaction approximation. The following two formulas, proposed by London (eq 24)[41] and by Slater and Kirkwood (eq 25)[42], are usually used for calculating the nonbonded attraction coefficients[43] for an *i*, *j*, atom pair.

$$C_{ij} = \frac{3\alpha_i\alpha_j I_i I_j}{2(I_i + I_j)} \tag{24}$$

$$C_{ij} = \frac{3}{2}\left[\frac{eh}{me^{1/2}}\right]\frac{\alpha_i\alpha_j}{(\alpha_i/N_i)^{1/2} + (\alpha_j/N_j)^{1/2}} \tag{25}$$

where *I* is the ionization potential of the neutral atom, *N* is the number of effective electrons, and the other symbols have their

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Table V. Calculated and Experimental Molecular Polarizabilities (in Å^3) of Oxygen-Containing Compounds

compound	exptl	Miller[a] (ahc)	Kang–Jhon[b] (ahp)	this work (CDEAP)	ref for exptl values
water	1.45	1.41	1.41	1.45	29
methanol	3.26	3.20	3.25	3.25	7a
ethanol	5.07	5.02	5.08	5.08	7a
1-propanol	6.77	6.86	6.92	6.91	29
propan-2-ol	6.97	6.86	6.92	6.91	25
cyclohexanol	11.56	11.65	11.65	11.60	25
glycol $C_2H_6O_2$	5.71	5.71	5.72	5.70	7a
dimethyl ether	5.16	5.02	5.08	5.01	23
diethyl ether	8.73	8.70	8.75	8.66	23
n-propyl methyl ether	8.86	8.70	8.75	8.66	7a
n-propyl ethyl ether	10.68	10.53	10.59	10.49	7a
di-*n*-propyl ether	12.53	12.37	12.42	12.32	23
dioxane	8.60	8.63	8.61	8.40	23
acetone	6.40	6.33	6.36	6.33	7a
methyl ethyl ketone	8.19	8.16	8.20	8.15	23
diethyl ketone	9.93	10.00	0.04	9.98	23
methyl propyl ketone	9.93	10.00	0.04	9.98	23
diisopropyl ketone	13.53	13.68	13.70	13.63	23
formaldehyde	2.45	2.68	2.69	2.69	25
acetaldehyde	4.59	4.74	4.82	4.46	25
n-propionaldehyde	6.35	6.33	6.36	6.33	7a
n-butyl aldehyde	8.18	8.16	8.20	8.16	7a
anthraquinone	24.46	25.22	25.34	23.73	30
formic acid	3.32	3.41	3.33	3.32	29
acetic acid	5.15	5.19	5.17	5.13	7a
propionic acid	6.96	7.00	7.00	6.95	7a
butyric acid	8.58	8.81	8.84	8.78	29
methyl formate	5.05	5.19	5.17	5.06	29
ethyl formate	6.88	7.00	7.00	6.88	29
methyl acetate	6.81	7.00	7.00	6.86	29
ethyl acetate	8.62	8.81	8.84	8.69	29
methyl propionate	8.97	8.81	8.84	8.69	7a
ethyl propionate	10.41	10.64	10.67	10.51	29
methyl butyrate	10.41	10.64	10.67	10.52	29
ethyl butyrate	12.23	12.47	12.51	12.34	29
CH_2OHCH_2OH	5.61	5.71	5.72	5.70	29
$CH_2OHCH_2OCH_3$	7.44	7.52	7.55	7.46	29
$CH_2OHCH_2OC_2H_5$	9.28	9.34	9.39	9.28	29
CH_2ClCH_2OH	6.88	6.99	7.01	6.97	29
$CH_2ClCH_2OCH_3$	8.71	8.80	8.84	8.73	29
$CH_2ClCH_2OC_2H_5$	10.56	10.62	10.68	10.55	29
$CH_2ClCH_2CH_2COOH$	10.45	10.78	10.76	10.68	29
$CH_2ClCH_2CH_2COOCH_3$	12.27	12.59	12.60	12.41	29
$CH_2ClCH_2CH_2COOC_2H_5$	14.11	14.41	14.43	14.24	29
$CH_3CHClCH_2COOH$	10.54	10.78	10.76	10.67	29
$CH_3CHClCH_2COOCH_3$	12.31	12.59	12.60	12.40	29
$CH_3CHClCH_2COOC_2H_5$	14.13	14.41	14.43	14.23	29
$CH_3CH_2CHClCOOH$	10.61	10.78	10.76	10.66	29
$CH_3CH_2CHClCOOCH_3$	12.33	12.59	12.60	12.39	29
$CH_3CH_2CHClCOOC_2H_5$	14.16	14.41	14.43	14.22	29
$C_2H_5CHClCH_2OH$	10.70	10.62	10.68	10.63	29
$CH_3CHClCH_2CH_2OH$	10.38	10.62	10.68	10.63	29
$CH_3CHClCH_2OH$	8.89	8.80	8.84	8.80	29
$CH_2ClCH_2CH_2OH$	8.84	8.80	8.84	8.80	29
$CH_3CH_2CHClCOOH$	10.87	10.78	10.76	10.66	29
$CH_3CHClCH_2COOH$	10.80	10.78	10.76	10.67	29
$CH_2ClCH_2CH_2COOH$	10.69	10.78	10.76	10.68	29
$CH_3CH_2CH_2CHClCOOH$	12.69	12.59	12.60	12.49	29
$CH_3CH_2CHClCH_2COOH$	12.57	12.59	12.60	12.50	29
$CH_3CHClCH_2CH_2COOH$	12.53	12.59	12.60	12.50	29
av percent error[c]		1.57	1.55	1.09	

[a] Taken from ref 11. [b] Taken from ref 11. [c] The average percent error, F_{opt}, is defined by eq 22.

usual meanings. The C_{ii}'s for each species of Table I, calculated with eq 24, are plotted as a function of net atomic charge in Figures 4–7. In Table X, the values of the C_{ii}'s are listed for all the species of Table I, calculated with both formulas. The average value of the net atomic charge of each species is needed for these calculations. In this work, the net atomic charges obtained for the compounds used in this study were averaged separately for each atom type. The C_{ii}'s for the atoms in ionic functional groups, and the ionic groups in amino acid zwitterions, were also obtained. The dispersion coefficients depend strongly on the net atomic charges, as shown in the figures.

As shown in Table X, the magnitudes of the dispersion coefficients, C_{ii}, differ from method to method. Since the C's play an important role in the calculation of the interaction energy between groups in molecules, especially nonpolar ones, a large change in the magnitude of C means a large change in the conformation around the sites of molecules. Therefore, the large difference in C between methods makes it difficult to compare the results of conformational studies obtained with different sets of dispersion coefficients, $\{C_{ii}\}$. The atoms that usually participate in nonpolar group interactions are C_1, C_2, C_4, H_1, and H_2. The $C_{C_1C_1}$ (or $C_{C_2C_2}$) of Lifson et al.[44] are two and four times larger

Table VI. Calculated and Experimental Molecular Polarizabilities (in Å^3) of Amides

compound	exptl	Miller[a] (ahc)	Kang-Jhon[b] (ahp)	this work (CDEAP)	ref for exptl values
formamide	4.08	3.85	4.17	4.06	29
acetamide	5.39	5.66	6.01	5.86	27
N-methylformamide	5.89	5.66	6.01	5.83	29
N,*N*-dimethylformamide	7.69	7.48	7.84	7.57	29
N-ethylacetamide	9.45	9.31	9.68	9.45	29
N-methylacetamide	7.82	7.48	7.84	7.63	25
N,*N*-diethylacetamide	12.96	12.97	13.35	13.00	29
av percent error[c]		3.31	3.34	2.09	

[a] Taken from ref 11. [b] Taken from ref 11. [c] The average percent error, F_{opt}, is defined by eq 22.

Table VII. Calculated and Experimental Molecular Polarizabilities (in Å^3) of Sulfur-Containing Compounds

compound	exptl	Miller[a] (ahc)	Kang-Jhon[b] (ahp)	this work (CDEAP)	ref for exptl values
H_2S	3.83	3.78	3.77	3.76	23
C_2H_5SH	7.38	7.46	7.44	7.46	29
$(C_2H_5)_2S$	11.00	11.14	11.11	11.11	29
$(CH_3)_2S$	7.53	7.46	7.44	7.46	36
av percent error[c]		1.15	1.14	1.24	

[a] Taken from ref 11. [b] Taken from ref 11. [c] The average percent error, F_{opt}, is defined by eq 22.

Table VIII. Calculated and Experimental Molecular Polarizabilities (in Å^3) of Some Biological Compounds That Were Not Included in the Optimization of Parameters

compound[a]	exptl	Miller[b] (ahc)	Kang-Jhon[c] (ahp)	this work (CDEAP)	ref for exptl values
guanine	13.60	14.26	15.68	13.07	37
adenine	13.10	13.74	15.05	12.84	37
cytosine	10.30	10.29	11.12	10.31	37
thymine	11.23	11.50	12.11	11.23	37
av percent error[d]		3.06	11.49	1.50	

[a] These compounds are not included in the CDEAP parameter optimization but are included in both the ahc and ahp parameter optimizations. [b] Taken from ref 11. [c] Taken from ref 11. [d] The average percent error, F_{opt}, is defined by eq 22.

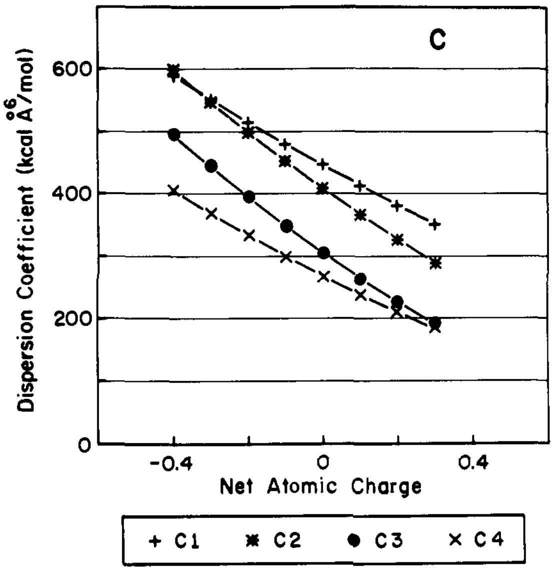

Figure 4. Relation between the dispersion coefficient of carbon and the net atomic charge dq.

Table IX. Calculated Molecular Polarizabilities (in Å^3) of Some Amino Acid Zwitterions by the CDEAP and ab Initio Methods

compound	this work	6-31G**[a]	scaled 6-31G**[b]	error[c] (scaled[d]), %
alanine	8.48	5.98	8.08	29.5 (4.7)
serine	8.64	6.41	8.65	25.8 (0.1)
histidine	14.91	11.09	14.98	25.6 (0.5)
hydroxyproline	11.42	8.98	12.14	21.4 (6.3)
valine	12.14	8.41	11.27	30.72 (7.16)
threonine	10.94	8.22	11.01	24.86 (0.69)
cysteine	11.18	9.27	12.42	17.09 (11.10)

[a] Calculated at the 6-31G** optimized geometries. [b] Scaled by a factor of 1.34; i.e., the ab initio polarizability was multiplied by 1.34, to obtain a fit between the ab initio and the CDEAP results. [c] Percent error defined as error = $(|\alpha_{\text{this work}} - \alpha_{6\text{-}31G^{**}})/\alpha_{\text{this work}} \times 100$. [d] Error calculated with the scaled 6-31G** polarizabilities.

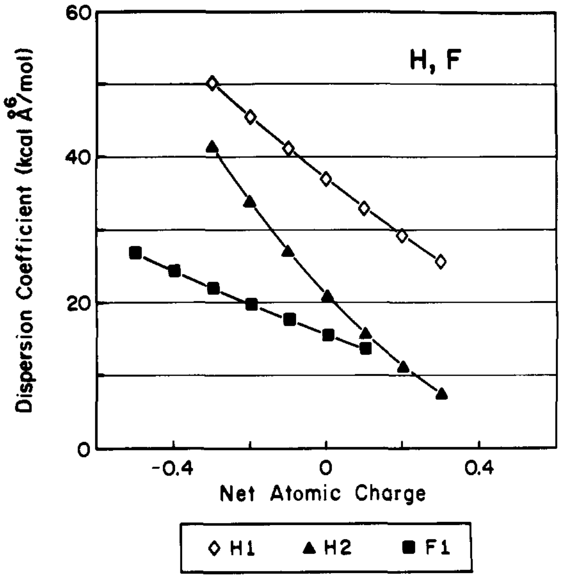

Figure 5. Relation between the dispersion coefficient of hydrogen and fluorine and the net atomic charge dq.

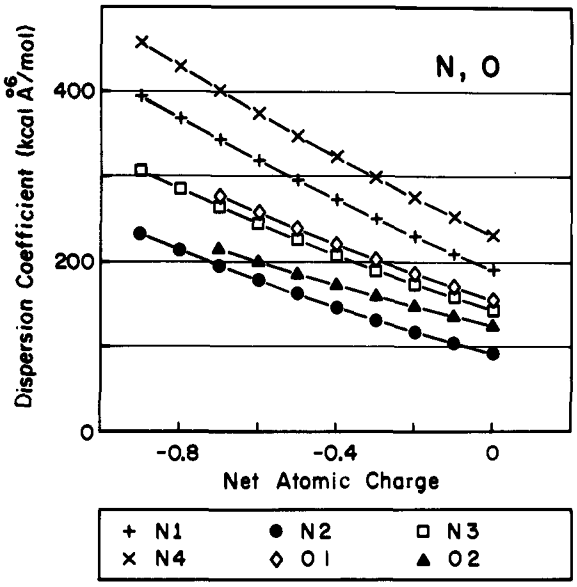

Figure 6. Relation between the dispersion coefficient of nitrogen and oxygen and the net atomic charge dq.

than those of this work (based on the Slater-Kirkwood formula) and ECEPP/2, respectively. The $C_{H_1H_1}$'s are comparable between the methods in Table X, and the $C_{H_2H_2}$'s vary considerably depending on the methods used. The choice of an appropriate value of C is very important for conformational studies because the

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(44) Lifson, S.; Hagler, A. T.; Dauber, P. *J. Am. Chem. Soc.* **1979**, *101*, 5111.

Table X. Comparison of Dispersion Coefficients, C_{ii} (kcal·Å^6/mol), Calculated with the Slater–Kirkwood and London Formulas, with Those of Other Authors

	this work		ECEPP/2[43]	Lifson et al.[44]	MM2[32]
type[a]	Slater–Kirkwood	London	Slater–Kirkwood	Slater–Kirkwood	Slater–Kirkwood
C1, C2[b]	774.14	448.37	370.5	1340.0	616.53
C3[c]	470.10	230.37	766.6	1340.0	616.53
C4[d]	427.43	203.10	370.5	532.0	544.10
C5[e]	223.01	110.78			
H1[f]	40.68	35.81	45.5	32.9	32.87
H2[g]	21.13	14.95	45.5	32.9	32.87
H3[h]	30.38	24.26	45.5	0.0	
O1[i]	363.73	238.13	369.0	502.0	429.61
O2[j]	279.63	206.54	217.2	502.0	429.61
O3[k]	450.12	170.06			
N1[l]	484.83	279.34			
N2[m]	385.20	173.54			
N3[n]	467.02	224.35	401.3	1230.0	588.08
N4[o]	523.95	305.51	401.3	1230.0	588.08
N5[p]	577.16	347.56			
S1[q]	3870.31	1762.26	2274.4		1647.82

[a] Atom types C5, H3, O3, and N5 were not included in the optimization. For C5, H3, O3, and N5, the $\alpha^{*}_{ij,0}$ and a_{ij} parameters of C3, H1, O1, and N4, respectively, are used. [b] Aromatic and conjugated alkene. [c] Carbonyl (–CONH$_2$). [d] Aliphatic. [e] Zwitterion (COO–). [f] Aliphatic. [g] Aromatic. [h] Hydroxyl (–OH). [i] Carbonyl. [j] Hydroxyl. [k] Zwitterion (COO–). [l] Pyrrole. [m] Pyridine. [n] Amide (–COONH$_2$). [o] Amine. [p] Zwitterion (–NH$_3^+$). [q] H$_2$S (CH$_3$)$_2$S.

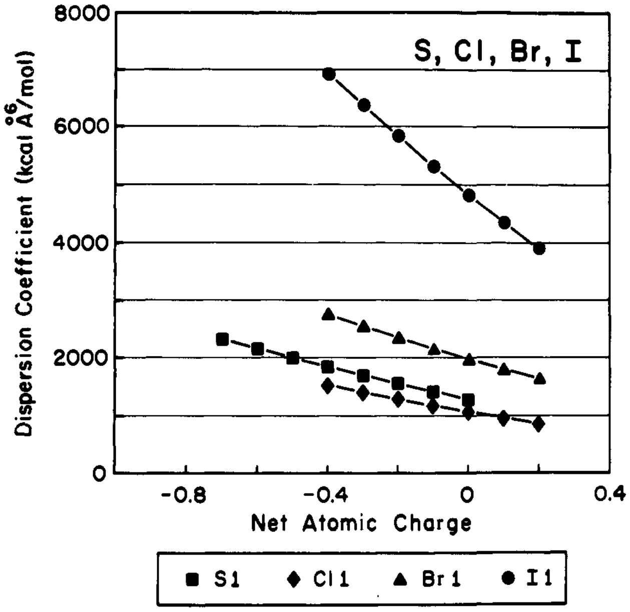

Figure 7. Relation between the dispersion coefficient of sulfur and halogens and the net atomic charge dq.

coefficient of the repulsion potential function is highly dependent on the magnitude of the attractive coefficient C. A direct comparison of the magnitudes of the values of C alone between methods does not have much meaning, because both C and the repulsive coefficient work cooperatively in nonbonded potential functions.

Conclusions

Averaged molecular polarizabilities are calculated as sums of effective atomic polarizabilities (α^{*}_{ij}) which are described as a function of net atomic charges. The α^{*}_{ij}'s are derived with the Thomas–Fermi model of multiply-charged spherical ions as a function of net atomic charge. The α^{*}_{ij}'s are assumed to be a linear function of the net atomic charges. The slope and intercept for each α^{*}_{ij} as a function of charge are obtained by optimization procedures in which calculated average molecular polarizabilities are matched to experimental values. The calculated molecular polarizabilities agree well with experimental data. The nonbonded potential parameters are calculated for several different atom types.

The advantage of the CDEAP method is the ability to calculate molecular polarizabilities that cannot be obtained by experiment. The polarization of each atom or functional group of a molecule can be calculated. Finally, nonbonded interaction energies, including those involving ionic groups, can be calculated accurately.

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