

A New Empirical Method to Calculate Average Molecular Polarizabilities

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Abstract: A new empirical method is presented for the calculation of average molecular polarizabilities. It is based on the square of a sum of atomic hybrid components (ahc), namely, $\alpha(\text{ahc}) = (4/N)[\sum_A \tau_A]^2 (\text{\AA}^3)$, where the summation proceeds over all atoms $A = 1, 2, 3, \dots$, and N is the total number of electrons in the molecule. Only one parameter τ_A is required for an atom in a particular hybrid configuration. Calculated average molecular polarizabilities of approximately 240 molecules containing H, C, N, O, S, F, Cl, Br, and I yield results that are competitive with the method of summation of atomic and bond polarizabilities, and they are in excellent agreement with experimental results. In addition, the atomic polarizability $\alpha_A = (4/N_A)\tau_A^2$ calculated for each hybrid state provides an estimate of atomic size with $\rho_A = 1.05\sqrt{3}\sqrt{\alpha_0\alpha_A} \text{\AA}$, which compares well to the van der Waals radius of each atom.

Introduction

A new empirical approach to the calculation of the average molecular polarizability as a square of a sum of atomic hybrid components is presented. It requires fewer parameters than other methods and has the functional form

$$\alpha(\text{ahc}) = \frac{4}{N} \left[\sum_A \tau_A \right]^2 (\text{\AA}^3) \quad (1)$$

where N is the number of electrons in the molecule, and ahc refers to the atomic hybrid components τ_A of α for each atom in a particular hybrid configuration. The summation proceeds over all atoms A in the molecule. In the present formulation τ_A does not depend on atoms which are bonded to A , but it does depend on the type of bonding through the hybridization of atomic orbitals on A .

It is well known that the molecular polarizability cannot be written simply as a sum of atomic polarizabilities.^{2a} Each atom must be assigned a polarizability depending on the atoms to which they are bonded. Eisenlohr^{2b} and, more recently, Vogel³ have set up an extensive system of atomic refractions which have been supplemented by Batsanov,⁴ in which, for example, nitrogen in primary, secondary, and tertiary amines is assigned different values. Silberstein^{2a} pointed out "that the ever growing hierarchy of rules indicating how to treat the exceptions to the law of additivity, although helpful to the chemist, is the clearest confession of non-additivity."

To circumvent this problem, the concept of bond polarizability was introduced. Steiger⁵ and Smyth⁶ obtained bond polarizabilities directly from the atomic refractions.⁷ In contrast, Denbigh⁸ developed a system in which a unique bond polarizability is obtained directly for each kind of chemical bond from molar refractions,⁷ R ; for example, $R(\text{C-H})$ is $\frac{1}{4}R(\text{CH}_4)$, and for the alkanes

$$(n-1)R(\text{C-C}) + (2n+2)R(\text{C-H}) = R(\text{C}_n\text{H}_{2n+2})$$

from which $R(\text{C-C})$ follows. This method reproduces experimental values of refractivities within 1% for most cases considered by Denbigh.⁸

The empirical formula, eq 1, is presented as an additional method for the calculation of average molecular polarizabilities. It is easy to apply. Fewer parameters are needed in this approach than in other methods because only hybrid components are considered and not the specific atoms to which a given atom is bonded. And the results of the present approach are comparable to that of other methods.

For each atom, A , one value of τ_A is used for each type of hybridization; specifically, that for N(te²tetete) reproduces

the polarizabilities of primary, secondary, and tertiary amines to 1% of the experimental results, and this is only one example of many which illustrates the success of this approach. Thus, the number of and type of bonds as well as lone pairs are automatically incorporated into a parameter τ_A by the hybrid state of each atom. In the present method values of τ_A are determined systematically. For example, from the average polarizability of H₂, one obtains $(\alpha_{\text{H}}/8)^{1/2} = \tau_{\text{H}} = 0.314 \text{\AA}^{3/2}$, and then from α_{CH_4} , $\tau_{\text{C}} = \sqrt{10/4\alpha_{\text{CH}_4}} - 4\tau_{\text{H}} = 1.294 \text{\AA}^{3/2}$ for carbon in the tetrahedral hybrid configuration, C(tetete). Then ethylene ($\tau_{\text{C}} = 1.436 \text{\AA}^{3/2}$) and benzene ($\tau_{\text{C}} = 1.421 \text{\AA}^{3/2}$) yield an average of $\tau_{\text{C}} = 1.428 \text{\AA}^{3/2}$ for the hybrid state C(trtrtr π). Finally acetylene yields $\tau_{\text{C}} = 1.393 \text{\AA}^{3/2}$ for C(didi $\pi\pi$). Then NH₃, HCN, pyridine, and pyrrole yield values for nitrogen in the te²tetete, di²di $\pi\pi$, tr²trtr π , and trtrtr π^2 hybrid states. Lone pairs are denoted on nitrogen in HCN: by di² in di²di $\pi\pi$, etc. The notation and corresponding chemical groups are given in Table I along with the optimum values of τ for H, C, N, O, S, P, and the halogens, obtained by a systematic analysis of common organic compounds. Average polarizabilities calculated for more than 240 molecules, of which approximately 160 are reported in this paper, agree in most cases to 1% of the experimental values. In addition to the standard and accepted hybrid configurations of atoms, two types of carbon atoms in the trtrtr π state are considered: a branched π system as in graphite and a partially branched system as in benzene or ethylene.

The purpose of this paper is fourfold: (1) to present a new empirical approach for the calculation of average molecular polarizabilities; (2) to demonstrate that the concept of atomic hybrid states can be used in the formulation of a set of parameters, τ_A , to calculate molecular polarizabilities; (3) to obtain a set of atomic polarizabilities, α_A , for atoms in different hybrid states; (4) to demonstrate a correlation between α_A and atomic size ρ_A .

Rationalization of the Empirical Approach

The functional form of the empirical formula proposed in this investigation can be rationalized, but not proven, with the variational-perturbation approach proposed by Hylleraas⁹ and Hasse¹⁰ and approximated by Hirschfelder, Curtiss, and Bird¹¹ for the calculation of the x component of molecular polarizability:

$$\alpha_{xx} = \frac{4N}{a_0} [(\overline{x_1 - \bar{x}})^2 - (N-1)(\overline{x_1 - \bar{x}})(\overline{x_2 - \bar{x}})]^2 \quad (2)$$

where N is the number of electrons, \bar{x} is the average position

of an electron in the x direction, $\overline{(x_1 - \bar{x})^2}$ is the mean square deviation of an electron from its average position, and $\overline{(x_1 - \bar{x})(x_2 - \bar{x})}$ is the average correlation between two electrons in the x direction. The average value of the operator q

$$\bar{q} = \int \Psi^* q \Psi d\tau \quad (3)$$

is calculated with the zeroth-order wave function Ψ obtained from perturbation theory. If the term in brackets in eq 2 is rewritten to include a summation over all electrons $i, j = 1, 2, 3, \dots, N$, then

$$\alpha_{xx} = \frac{4}{Na_0} \left[\sum_{i,j} \overline{(x_i - \bar{x}_i)(x_j - \bar{x}_j)} \right]^2 \quad (4)$$

$$= \frac{4}{Na_0} [L_{xx}]^2 \quad (5)$$

The term in brackets in eqs 4 and 5 reduces to

$$L_{xx} = \sum_{i,j} \overline{x_i x_j} - \left(\sum_i \overline{x_i} \right)^2 \quad (6)$$

For closed-shell systems the zeroth-order wave function may be approximated by an antisymmetrized product of molecular orbitals, ψ_μ , $\mu = 1, 2, 3, \dots$, and spin functions η and $\bar{\eta}$ with z components equal to $\pm 1/2$:

$$\psi = (N!)^{-1/2} \mathcal{A} \{ \psi_1(1)\eta(1)\psi_1(2)\bar{\eta}(2) \dots \} \quad (7)$$

Substituting eq 7 into eq 6 yields

$$L_{xx} = -2 \sum_{\mu} \sum_{\nu} \int \psi_{\mu}^* x \psi_{\nu} d\tau \int \psi_{\nu}^* x \psi_{\mu} d\tau + 2 \sum_{\mu} \int \psi_{\mu}^* x^2 \psi_{\mu} d\tau \quad (8)$$

where μ and ν refer to the occupied molecular orbitals. The molecular orbitals are expanded as a linear combination of atomic orbitals χ_{At} :

$$\psi_{\mu} = \sum_A \sum_t c_{At\mu} \chi_{At} \quad (9)$$

where t may refer to s , p_x , p_y , and p_z atomic orbitals or to hybrid atomic orbitals on atoms $A = 1, 2, 3, \dots$. Substituting eq 9 into eq 8 and using the zero differential overlap approximation yields

$$L_{xx} = \sum_A \sqrt{a_0} \tau_{Axx} \quad (10)$$

where

$$\begin{aligned} \sqrt{a_0} \tau_{Axx} = & -2 \sum_{B,t,u,v} \sum_{\mu,\nu} c_{At\mu}^* c_{Au\nu} c_{Bv\nu}^* c_{Bw\mu} \\ & \times \int \chi_{At}^* x \chi_{Au} d\tau \int \chi_{Bv}^* x \chi_{Bw} d\tau + 2 \sum_{t,u} \sum_{\mu} c_{At\mu}^* c_{Au\mu} \\ & \times \int \chi_{At}^* x^2 \chi_{Au} d\tau \quad (11) \end{aligned}$$

provides the link between the proposed empirical formula, eq 1, and a molecular orbital model. Atomic orbitals t, u, v , and w are centered on atoms A and B in At, Au, Bv , and Bw .

It is convenient to assume that ψ_{μ} , $\mu = 1, 2, 3, \dots$, are the localized molecular orbitals studied extensively by England et al.^{12,13} Their orbitals, confined to the region of a chemical bond, are written as a sum of hybrid atomic or π orbitals. For acyclic hydrocarbons¹² two-center localized molecular orbitals are found, whereas for condensed hydrocarbons¹³ two- to four-center localized molecular orbitals connected through a set of adjacent atoms are obtained.

Now, the contributions to τ_{Axx} consist of two types of terms: the first in eq 11 connects atomic orbitals on a pair of atoms A and B , and the second involves only atomic orbitals on each

Table I. Atomic Components τ_A for Atoms in Various Hybrid Configurations Used in the Calculation of the Average Molecular Polarizability with Equation 1, and the Correlation to Atomic Size, ρ_A , Given by Equation 22

atom A	hybridiza- tion ^a of A	τ_A , Å ^{3/2}	group	ρ_A , Å
H	σ	0.314	—H	1.23
C	tetetete	1.294		1.59
C	trtrtr π	1.428		1.68
C		1.800		1.88
C	didi $\pi\pi$	1.393	—C≡	1.65
N	te ² tetetete	1.435		1.62
N	tr ² trtr π	1.262		1.52
N	trtrtr π^2	1.220		1.49
N	di ² di $\pi\pi$	1.304	≡N:	1.54
O	te ² te ² tete	1.290		1.48
O	tr ² tr ² tr π	1.216	≡O:	1.44
O	tr ² trtr π^2	1.099		1.37
F	σ	1.046	—F	1.30
Cl	σ	3.130	—Cl	1.91
Br	σ	5.577	—Br	2.13
I	σ	8.820	—I	2.42
P	te ² tetetete	3.000		1.93
S	te ² te ² tete	3.496		2.05
S	tr ² trtr π^2	2.982		1.89
S	tr ² tr ² tr π	3.967	≡S:	2.19

^a Lone pairs on each atom are indicated for each hybrid configuration by te^2 in te^2te^2tete for O in H_2O , etc.

atom A . The first term may be viewed as a bond contribution because the coefficients $c_{At\mu}^* c_{Bw\mu}$ and $c_{Au\nu} c_{Bv\nu}^*$, connected through common localized molecular orbitals ψ_{μ} and ψ_{ν} , are largest if A and B are adjacent atoms. If these bond contributions, which arise for each hybrid atomic orbital in ψ_{μ} on atom A connecting adjacent atoms, are partitioned between the two atoms A and B , then one has a rationale for the assignment of a unique value of τ_{Axx} for each hybrid atomic state. If eq 11 is written as

$$\begin{aligned} \sqrt{a_0} \tau_{Axx} = & -1/2 \sum_{B,t,u,v} \sum_{\mu,\nu} p_{AtBw} p_{AuBv}^* \int \chi_{At}^* x \chi_{Au} d\tau \\ & \times \int \chi_{Bv}^* x \chi_{Bw} d\tau + \sum_t q_{At} \int \chi_{At}^* x^2 \chi_{At} d\tau \quad (12) \end{aligned}$$

where

$$p_{AtBw} = 2 \sum_{\mu} c_{At\mu}^* c_{Bw\mu} \quad (13)$$

is the bond order for doubly occupied orbitals and $q_{At} = p_{AtAt}$, which arises because symmetry requires that $t = u$ in the second term of eq 11, is the electronic charge, then the bond and atomic terms are more obvious. Bond orders are small unless A and B are adjacent atoms.

This approximation ought to work well for covalently bonded systems in which the electron pairs are nearly equally shared by two atoms. For very polar systems, some modification of τ_{Axx} will be required. However, in this investigation, eq 1 reproduces experimental values of average molecular polarizabilities of organic compounds quite well.

Table II. Comparison of the Empirical Atomic Size ρ_A , Equation 22, and the Experimental van der Waals Radii

atom		$\rho_A(\text{ahc})^a$	$\rho_A(\text{Pauling})^b$	$\rho_A(\text{Bondi})^c$
H	σ	1.23	1.2	1.20
C	trtrtr π	1.68	1.70	1.70
	didi $\pi\pi$	1.65		
N	te ² tetete	1.62	1.5	1.55
	tr ² trtr π	1.52		
	trtrtr π^2	1.49		
	di ² di $\pi\pi$	1.54		
O	te ² te ² tete	1.48	1.40	1.52
	tr ² tr ² tr π	1.44		
	tr ² trtr π^2	1.37		
S	te ² te ² tete	2.05	1.85	1.80
	tr ² trtr π^2	1.89		
	tr ² tr ² tr π	2.19		
P	te ² tetete	1.93	1.9	1.80
F	σ	1.30	1.35	1.47
Cl	σ	1.91	1.80	1.75
Br	σ	2.13	1.95	1.85
I	σ	2.41	2.15	1.98

^a Calculated with eq 22. ^b Pauling's compilation, ref 15, of experimental values. ^c Bondi's compilation¹⁶ of experimental values in which $\rho_H = 1.00$ for hydrogen attached to an aromatic ring.

To complete the rationalization of eq 1, the components of polarizability α_{xx} , obtained with eq 2, and similarly α_{yy} and α_{zz} , are assumed to be calculated with the xyz coordinate system oriented along the principal axes of the polarization ellipsoid. If the contribution of τ_A along each principal axis is assumed to be given by

$$\tau_{Akk} = \sqrt{3} \cos \gamma_{kk} \tau_A \quad (k = x, y, \text{ or } z) \quad (14)$$

where

$$\sum_k \cos^2 \gamma_{kk} = 1 \quad (15)$$

then the average molecular polarizability

$$\alpha = \frac{1}{3} \sum_k \alpha_{kk} \quad (16)$$

is obtained from

$$\alpha_{kk} = \frac{4}{N} \left[\sum_A \tau_{Akk} \right]^2 \quad (17)$$

by combining eq 5 with eq 10 and 14 for $k = x$, and similarly for $k = y$ and z . The components τ_{Akk} are projections of $\sqrt{3}\tau_A$ onto the principal axes $k = x, y$, and z , or from the components of the polarizability

$$\sqrt{\alpha_{kk}} = \cos \gamma_{kk} \sqrt{3\alpha} \quad (18)$$

is the projection of 3α onto the principal axes.

In the case of condensed hydrocarbons,¹³ the localized molecular orbitals are delocalized over more than two atoms. The contribution to each atomic hybrid component is still obtained by partitioning the effect of terms involving A and B over each atom. The assumption is made that there are two values of τ_A for the trtrtr π hybrid states of carbon: $\tau_c = 1.428$ for one with a C-H bond and $\tau_c = 1.800$ for one in a branched configuration as in graphite. This is the only exception made in the formulation of the average molecular polarizability with parameters τ_A for atoms, A , in their conventional states of hybridization, and it is required to achieve agreement between $\alpha(\text{ahc})$ and $\alpha(\text{exp})$.

An alternate approach to that proposed in this investigation, in which τ_A represents atomic hybrid contributions, would be a summation over bond contributions with a formula like eq 1. In eq 11 or 12, terms involving atomic orbitals on atoms

would be partitioned onto pairs of atoms connected by a bond or several atoms encompassed by the localized molecular orbital in the case of condensed hydrocarbons, and τ would be accordingly redefined. The terms connecting pairs of atoms, A and B , are already cast into a form which could be viewed as bond contributions. This approach was not explored. It would require a set of parameters τ_{AB} for every pair of atoms with each particular bonding type, and consequently there would be a greater number of parameters than required in the present empirical approach.

The van der Waals radii can be correlated to the atomic polarizability

$$\alpha_A = \frac{4}{N_A} (\tau_A)^2 \quad (19)$$

calculated with eq 1 for each atomic hybrid contribution τ_A . Combining eq 19 with the Slater-Kirkwood approximation¹⁴

$$\alpha_A = \frac{4}{a_0} \left[\frac{r_A^2}{3} \right]^2 \quad (20)$$

yields

$$\sqrt{r_A^2} = \frac{\sqrt{3}}{2} \sqrt[4]{a_0 \alpha_A} \quad (21)$$

Experimental van der Waals radii agree well with the function obtained by adjusting eq 21 by 2.10, namely

$$\rho_A = 1.05 \sqrt{3} \sqrt[4]{a_0 \alpha_A} \quad (22)$$

and a comparison between them is made in Table II. ρ_A values for atoms in each hybrid configuration are presented in Table I, but it should be noted that a comparison to experimental van der Waals radii is meaningless for hybrid states such as tetetete in carbon.

Average Molecular Polarizabilities

In Tables III-XI the empirical average molecular polarizabilities $\alpha(\text{ahc})$ calculated with eq 1 with atomic hybrid components τ_A are compared to the experimental (exp) values of $\alpha(\text{exp})$. The percent error

$$\epsilon(\text{ahc}) = 100\{\alpha(\text{ahc}) - \alpha(\text{exp})\}/\alpha(\text{exp}) \quad (23)$$

is reported. Similarly $\epsilon(\text{bp})$ is reported to compare $\epsilon(\text{bp})$ obtained by the bond polarizability (bp) method with experimental results, and where appropriate $\epsilon(\text{ap})$ and $\alpha(\text{ap})$ are used in a discussion of the method of summation of atomic polarizabilities (ap). $\alpha(\text{exp})$ is taken from the reference indicated in each table, and, if $\alpha(\text{bp})$ is given, then $\epsilon(\text{bp})$ is calculated. Otherwise, to obtain $\alpha(\text{bp})$, the bond polarizabilities proposed by Denbigh⁸ or those obtained by Vogel and co-workers¹⁷ and summarized by Batsanov⁴ are used. These $\epsilon(\text{bp})$ are presented respectively in parentheses or brackets.

Alkanes, Halogenated Alkanes, Alkenes, and Alkynes and Halogenated Derivatives of Benzene. Polarizabilities of the alkanes are the easiest to reproduce. The present method of obtaining τ_c for the tetetete hybridization of carbon, given as an example in the Introduction, yields polarizabilities which compare to 1% of the experimental values as shown in Table III. Values calculated by Denbigh⁸ (not reported) by the method of addition of bond polarizabilities also reproduce the experimental results to approximately 1%. The value τ_{Br} was obtained initially from HBr and then adjusted to improve the agreement between the empirical (ahc) and the experimental polarizabilities studied in this investigation. In Table III the polarizabilities of $C_nH_{2n+1}Br$ calculated by the ahc method agree to approximately 1% of the experimental results, whereas results calculated by the addition of bond polarizabilities by Sanyal et al.,¹⁹ and listed in Table III, yield errors up to 21.8%

Table III. Empirical (ahc) and Experimental (exp) Average Molecular Polarizabilities of *n*-Alkanes and *n*-Brominated Alkanes Containing Atoms in the Hybrid States H(σ), C(tetete), and Br(σ), and the Percent Error ϵ in the ahc and Bond Polarizability (bp) Methods^a

<i>n</i>	C_nH_{2n+2}		$C_nH_{2n+1}Br$			
	$\alpha(\text{ahc}), \text{\AA}^3$	$\epsilon(\text{ahc}), \%$	$\alpha(\text{ahc}), \text{\AA}^3$	$\alpha(\text{exp}), \text{\AA}^3$	$\epsilon(\text{ahc}), \%$	$\epsilon(\text{bp}), \%$
1	2.60	0.0	5.55	5.53	0.4	-2.7
2	4.44	-0.6	7.29	7.28	0.1	1.0
3	6.29	0.0	9.06	9.07	-0.1	2.6
4	8.14	0.2	10.85	10.86	-0.1	4.1
5	9.98	0.3	12.65	12.65	0.0	5.1
6	11.83	0.4	14.46	14.44	0.1	9.9
7	13.68	0.5	16.27	16.23	0.3	6.5
8	15.52	0.5	18.09	18.02	0.4	7.1
9	17.37	0.1	19.92	19.81	0.5	7.5
10	19.22	0.6	21.74	21.60	0.7	21.8
11	21.06	0.1	23.57			
12	22.91	0.7	25.41	25.18	0.9	8.5
16			32.75	32.34	1.3	9.2
18			36.43	35.92	1.4	9.5

^a $\alpha(\text{ahc})$ is calculated with eq 1. The percent error $\epsilon(\text{ahc})$ or $\epsilon(\text{bp})$ is defined by eq 23. ^b A comparison is made to experimental data taken from ref 8 and 18. ^c $\alpha(\text{exp})$ and $\alpha(\text{bp})$ are taken from ref 19 to evaluate $\epsilon(\text{bp})$. $\epsilon(\text{bp}) < 4\%$ if bond polarizabilities from ref 8 are used to calculate $\alpha(\text{bp})$.

Table IV. Empirical (ahc) and Experimental (exp) Average Molecular Polarizabilities of Hydrocarbons and Chlorinated Hydrocarbons Containing Atoms in the Hybrid States, C(trtrtr π), C(didid π), and Cl(σ), and the Percent Error ϵ in the ahc and Bond Polarizability (bp) Methods^a

molecule	$\alpha(\text{ahc}), \text{\AA}^3$	$\alpha(\text{exp}), \text{\AA}^3$	$\epsilon(\text{ahc}), \%$	$\epsilon(\text{bp}), \%$	ref
ethylene	4.23	4.26	-0.8	(2.4)	18
2-pentene	9.76	9.84	-0.9	-0.1	8
1,4-pentadiene	11.38	11.49	-1.0	-0.1	8
1-hexene	11.60	11.65	-0.4	+0.2	8
1-heptene	13.45	13.51	-0.5	-0.0	8
acetylene	3.33	3.33	0.0	(16.4)	18
1-heptyne	12.57	12.87	-2.4	-1.4	8
methyl chloride	4.43	4.56	-2.9	(0.8)	18
methylene chloride	6.38	6.48	-1.6	(0.6)	18
chloroform	8.34	8.23	1.4	(2.5)	18
carbon tetrachloride	10.32	10.47	-1.5	-1.1	8
ethyl chloride	6.25	6.40	-2.4	(0.5)	18

^a Refer to footnote a, Table III. $\alpha(\text{exp})$ is taken from the indicated reference and $\epsilon(\text{bp})$ is evaluated with $\alpha(\text{bp})$ if given in the indicated reference. Otherwise values (in parentheses) are calculated with bond polarizabilities proposed by Denbigh.⁸

Table V. Empirical (ahc) and Experimental (exp) Average Molecular Polarizabilities of Halogenated Derivatives of Benzene, and the Percent Error ϵ in the ahc and Bond Polarizability Methods^a

molecule	$\alpha(\text{ahc}), \text{\AA}^3$	$\alpha(\text{exp}), \text{\AA}^3$	$\epsilon(\text{ahc}), \%$	$\epsilon(\text{bp}), \%$	ref
chlorobenzene	12.14	12.25	-0.9	(1.5)	18
bromobenzene	13.00	13.62	-4.6	(0.6)	18
<i>p</i> -dichlorobenzene	13.98	14.20	-1.5	(1.1)	18
fluorobenzene	10.01	9.86	1.5	[4.8]	20
1,2-difluorobenzene	9.79	9.80	-0.1	[4.9]	20
1,3,5-trifluorobenzene	9.70	9.74	-0.5	[5.1]	20
1,2,4,5-tetrafluorobenzene	9.68	9.69	-0.1	[5.1]	20
pentafluorobenzene	9.72	9.63	0.9	[5.2]	20
hexafluorobenzene	9.79	9.58	2.2	[5.3]	20

^a Refer to footnote a, Table III. $\alpha(\text{exp})$ is taken from the indicated reference. Values of $\epsilon(\text{bp})$ in parentheses are calculated with bond polarizabilities proposed by Denbigh⁸ and values in brackets are obtained with Vogel's¹⁷ system summarized by Batsanov.⁴

for $n = 10$. Their results are calculated theoretically and not with the empirical values of bond polarizabilities proposed by Denbigh,⁸ which would yield $\alpha(\text{bp})$ within 4% of experimental values.

Results for the alkenes, alkynes, and chlorinated alkanes obtained with the ahc method and presented in Table IV agree to approximately 1% of the experimental values. They are comparable to those obtained by the method of summation of bond polarizabilities. Because only one value of τ_A is assigned to each atom *A* in a given hybrid state, isomers all have the

same polarizabilities, and consequently, the results for 1-pentene and 2-pentene, etc., will be identical. In this paper, only one isomer of a compound will be reported in any comparison to experimental results.

Finally, results for several halogenated derivatives of benzene are presented in Table V. For the fluorinated derivatives of benzene $\epsilon(\text{bp}) \sim 5\%$ regardless of the number of fluorine atoms. Thus, the bond polarizability for the C-F bond cannot be adjusted to resolve this problem. For benzene, the value $\alpha(\text{bp}) = 10.51 \text{ \AA}^3$ differs from $\alpha(\text{exp}) = 10.40 \text{ \AA}^3$ by only

Table VI. Empirical (ahc) and Experimental (exp) Average Molecular Polarizabilities of Primary, Secondary, and Tertiary Amines and Other Compounds Containing Nitrogen in the Hybrid States: $N(\text{te}^2\text{tetete})$, $N(\text{trtrtr}\pi^2)$, $N(\text{tr}^2\text{trtr}\pi)$, and $N(\text{di}^2\text{di}\pi\pi)^a$

molecule	$\alpha(\text{ahc}), \text{\AA}^3$	$\alpha(\text{exp}), \text{\AA}^3$	$\epsilon(\text{ahc}), \%$	$\epsilon(\text{bp}), \%$	ref
$N(\text{te}^2\text{tetete})$					
isopropylamine	7.80	7.77	0.4	-0.5	8
diethylamine	9.65	9.61	0.4	0.2	8
di- <i>n</i> -propylamine	13.34	13.29	0.4	0.1	8
triethylamine	13.34	13.38	-0.3	-0.1	8
tri- <i>n</i> -propylamine	18.88	18.87	0.0	0.0	8
hydrazine	3.78	3.46	9.4		4
<i>N,N</i> -dimethylhydrazine	7.47	7.21	3.7		4
$N(\text{trtrtr}\pi^2)$					
aniline	11.49	11.58	-0.8	-2.6	4
<i>N</i> -methylaniline	13.34	13.50	-1.1	(2.2)	4
<i>N</i> -ethylaniline	15.19	15.32	-0.9	(2.0)	4
<i>N,N</i> -dimethylaniline	15.19	15.40	-1.4	(1.9)	4
<i>N,N</i> -diethylaniline	18.88	19.01	-0.7	(1.9)	4
pyrrole	8.03	7.94	1.2	[1.9]	21
<i>p</i> -nitrotoluene	13.97	14.10	-0.9	3.6	19
nitrobenzene	12.14	12.92	-6.0	[4.6]	18
<i>p</i> -toluidine	13.34	13.47	-0.9	-3.3	19
$N(\text{tr}^2\text{trtr}\pi)$					
pyridine	9.47	9.18	3.2	6.5	19
		9.47	0.0		18
quinoline	15.65	15.70	-0.3		21
phenazine	20.92	23.43	-10.7	-0.3	19
$N(\text{di}^2\text{di}\pi\pi)$					
<i>p</i> -cyanotoluene	14.05	13.90	1.1	-1.1	19
hydrogen cyanide	2.59	2.59	0.0	[0.1]	18
Mixed Types of Bonding					
3-aminobutyronitrile	9.63	9.17	5.0		4
3-dimethylaminobutyronitrile	13.32	12.87	3.5		4
pyrazole	7.15	7.23	-1.1		4
1-methylpyrazole	8.99	8.99	0.0		4
1,5-dimethylpyrazole	10.83	10.72	1.1		4
1-ethyl-5-methylpyrazole	12.67	12.50	1.4		4

^a Refer to footnote *a*, Table V. Values of $\epsilon(\text{bp})$ not enclosed in parentheses or brackets are calculated with $\alpha(\text{bp})$ given in the indicated reference.

1.2%, which suggests that the parameters for C-H and C-C(aromatic) are calibrated properly. Halogenated derivatives of aniline, toluene, naphthalene, and anthracene are given in subsequent tables, in which molecules with a variety of atoms in various hybrid configurations are listed.

Compounds Containing Nitrogen or Oxygen. The first critical test for this empirical approach lies in the calculation of molecular polarizabilities of primary, secondary, and tertiary amines. It is well known^{2a,8} that different atomic polarizabilities are required for nitrogen in each of these cases if the method of summation of atomic polarizabilities is used.^{2b,3,4} However, only one value of τ_N for $N(\text{te}^2\text{tetete})$ is required with eq 1 in the present empirical approach. It should be noted that in the method of bond polarizabilities⁸ only one value each for N-C and N-H is needed. Results of $\alpha(\text{ahc})$ for primary, secondary, and tertiary alkylamines and aniline and of their derivatives, reported in Table VI, agree to within 1% of the experimental values.

Polarizabilities for compounds containing nitrogen are grouped according to their hybrid states. Agreement with experimental results to 1% occurs in most cases and, in addition, the ahc method is competitive with the bond polarizability approach. Three notable exceptions are hydrazine, 3-aminobutyronitrile, and phenazine, the last of which is discussed in the section on condensed ring systems. Hydrazine, for which $\alpha(\text{ahc})$ is calculated with the $N(\text{te}^2\text{tetete})$ hybrid configuration, may be better described by a configuration intermediate

between this one and $N(\text{trtrtr}\pi^2)$ for which $\alpha(\text{ahc}) = 3.04$ with $\epsilon(\text{ahc}) = -12.1\%$. The steric hindrance of the two methyl groups in *N,N*-dimethylhydrazine may force the nitrogen to assume a te^2tetete hybrid configuration, which accounts for the agreement within 3.7%.

In Table VII average molecular polarizabilities of compounds containing oxygen in various hybrid states are reported. Both $\alpha(\text{ahc})$ and $\alpha(\text{bc})$ agree with $\alpha(\text{exp})$ in each case to approximately the same accuracy for alcohols, ethers, ketones, aldehydes, acids, esters, and furan. In water $\epsilon(\text{bp}) = -7.8\%$ is much larger than $\epsilon(\text{ahc}) = 1.4\%$. In both the ahc and bond polarizability methods, the mixed hybrids of $O(\text{te}^2\text{te}^2\text{tete})$ and $O(\text{tr}^2\text{tr}^2\text{tr}\pi)$ in the carboxylic acid and ester groups also show greater error than in compounds containing only one of these hybrid states of oxygen.

Potpourri of Compounds. Molecular polarizabilities of compounds containing halogens, nitrogen, oxygen, and derivatives of benzene are reported in Table VIII. The errors resulting from the use of eq 1 are on the average slightly smaller than those obtained by Sanyal et al.,¹⁹ who use the method of addition of bond polarizabilities. These studies demonstrate that the choice of atomic hybrid components τ_A can be combined in molecules with several different atoms in various hybrid configurations to reproduce $\alpha(\text{exp})$ well.

Compounds Containing Sulfur and Phosphorus. Parameters reported in Table I for compounds containing sulfur were deduced from average experimental molecular polarizabilities

Table VII. Empirical (ahc) and Experimental (exp) Average Molecular Polarizabilities of Compounds Containing Oxygen in the Hybrid States: O(te^2te^2tete), O($tr^2tr^2tr\pi$), and O($tr^2trtr\pi^2$)^a

molecule	$\alpha(ahc), \text{\AA}^3$	$\alpha(exp), \text{\AA}^3$	$\epsilon(ahc), \%$	$\epsilon(bp), \%$	ref
O(te^2te^2tete)					
water	1.47	1.45	1.4	(-7.8)	4
methanol	3.28	3.26	0.4	1.0	8
ethanol	5.11	5.07	0.8	1.2	8
1-propanol	6.95	6.77	2.6	(2.9)	4
glycol	5.85	5.71	2.5	0.6	8
dimethyl ether	5.11	5.16	-1.0	(1.2)	18
diethyl ether	8.79	8.73	0.7	(1.8)	18
<i>n</i> -propyl methyl ether	8.79	8.86	-0.8	0.3	8
<i>n</i> -propyl ethyl ether	10.63	10.68	-0.5	0.4	8
di- <i>n</i> -propyl ether	12.48	12.55	-0.6	0.1	8
O($tr^2tr^2tr\pi$)					
acetone	6.33	6.40	-1.1	-0.8	8
methyl ethyl ketone	8.17	8.19	-0.3	-0.1	8
diethyl ketone	10.01	9.93	0.8	(0.9)	18
methyl propyl ketone	10.01	9.93	0.8	(0.9)	18
diisopropyl ketone	13.70	13.53	1.2	(1.2)	18
<i>n</i> -propionaldehyde	6.33	6.35	-0.3	-0.1	8
<i>n</i> -butyraldehyde	8.17	8.18	-0.2	0.0	8
O($tr^2trtr\pi^2$)					
furane	7.23	7.23	0.0		21
Mixed Hybrid Types					
formic acid	3.47	3.32	4.5	(-0.8)	4
acetic acid	5.26	5.15	2.1	-0.4	8
propionic acid	7.07	6.96	1.5	0.0	8
methyl propionate	8.89	8.79	1.1	1.1	8
methyl acetate	7.07	6.81	3.8	(3.6)	4
butyric acid	8.89	8.58	3.6	(2.6)	4
methyl butyrate	10.72	10.41	3.0	(3.0)	4

^a Refer to footnote a, Table V. Values of $\epsilon(bp)$ not enclosed in parentheses are calculated with $\alpha(bp)$ obtained from the indicated reference.

of H_2S , C_2H_5SH , and $(C_2H_5)_2S$ for the te^2te^2tete hybrid state, of thiophene for the $tr^2trtr\pi^2$ hybrid state, and of CS_2 for the $tr^2tr^2tr\pi$ hybrid states. For phosphorus τ_P was determined by an analysis of PH_3 and PF_3 ; however, the value reported in Table I is obtained from a reasonable choice of ρ , and with eq 22.

Condensed Ring Systems and Compounds of Biological Interest. In condensed ring systems, listed in Tables X and XI, a discrepancy between the empirical results with eq 1 and the experimental values exists if $\tau_C = 1.428$ is used for C($trtrtr\pi$). The difficulty was traced to the two kinds of carbon atoms present in the π -electronic system. In ethylene and benzene the π system is directed only along two bonds, whereas in the 9 and 10 positions of naphthalene it is directed along all three bonds.

An adjustment, $\tau_C = 1.800$, for carbon atoms in a π system branched in three directions is sufficient to greatly improve agreement with experimental values as is seen by the corresponding results listed as $\bar{\alpha}(ahc)$ and $\bar{\epsilon}(ahc)$. Calculations of $\alpha(bp)$ yield errors $\epsilon(bp)$ which are of the same order as $\bar{\epsilon}(ahc)$. However, trends in the polarizabilities show in most cases that $\bar{\alpha}(ahc) > \alpha(exp)$ and $\alpha(bp) < \alpha(exp)$, and it suggests that a systematic error may be present in each method. In Table XII values of α are presented for cytosine, adenine, thymine, and acridine, a well-known intercalating and mutagenic agent, to test the applicability of the present empirical approach to the calculation of molecular polarizabilities of biological molecules.

Determination of Structural Formulas. The unique values of τ_A for each atomic hybrid configuration suggests that structural formulas of organic compounds can be determined

Table VIII. Empirical (ahc) and Experimental (exp) Average Molecular Polarizabilities of Compounds Containing Atoms in Various States of Hybridization, and the Error ϵ in the ahc and Bond Polarizability Methods^a

molecule	$\alpha(ahc), \text{\AA}^3$	$\alpha(exp), \text{\AA}^3$	$\epsilon(ahc), \%$	$\epsilon(bp), \%$
formamide	3.85	3.88	-0.8	-6.1
acetamide	5.66	5.39	5.0	-3.9
benzamide	13.38	12.75	4.9	0.8
<i>p</i> -fluoroaniline	11.16	11.51	-3.1	-1.6
<i>p</i> -chloroaniline	13.28	13.50	-1.6	0.4
<i>p</i> -bromoaniline	14.17	14.55	-2.6	2.3
<i>p</i> -nitroaniline	13.30	13.90	-4.3	-7.3
dichloroaniline	15.14	15.18	-0.3	-1.9
toluene	12.25	11.83	3.5	-0.4
<i>p</i> -fluorotoluene	11.85	11.70	1.2	-4.0
<i>p</i> -chlorotoluene	13.98	13.70	2.1	1.5
<i>p</i> -bromotoluene	14.81	14.80	0.1	0.9
<i>p</i> -iodotoluene	17.10	17.10	0.0	-6.6
<i>p</i> -cyanotoluene	14.05	13.90	1.1	-1.1
<i>p</i> -nitrotoluene	13.97	14.10	-0.9	3.6
<i>p</i> -xylene	14.10	13.70	2.9	2.3
mesitylene	15.94	15.38	3.7	-3.9
durane	17.79	17.40	2.2	-8.0
hexamethylbenzene	21.48	20.81	3.2	-11.2

^a Refer to footnote a, Table III. ^b $\alpha(exp)$ and $\alpha(bp)$ taken from ref 19 are used also in the calculation of $\epsilon(bp)$.

by the calculation of molecular polarizabilities. An example of the analysis of menthone, for which $\alpha = 18.35 \text{\AA}^3$, is given by Ioffe.²⁴ Its empirical formula is $C_{10}H_{18}O$. In Table XIII

Table IX. Empirical (ahc) and Experimental (exp) Average Molecular Polarizabilities of Compounds Containing Sulfur^a

molecule	hybrid state	$\alpha(\text{ahc})$	$\alpha(\text{exp})$	$\epsilon(\text{ahc})$	$\epsilon(\text{bp})$	ref
H ₂ S	te ² te ² tete	3.78	3.78	0.0	[0.7]	18
C ₂ H ₅ SH	te ² te ² tete	7.47	7.38	1.2	[2.5]	4
(C ₂ H ₅) ₂ S	te ² te ² tete	11.16	11.00	1.5	[3.0]	4
thiophene	tr ² trtr π^2	9.00	9.00	0.0		21
CS ₂	tr ² tr ² tr π	9.16	8.74	4.8	[8.0]	18

^a Refer to footnote a, Table V.**Table X.** Empirical (ahc) and Experimental Average Molecular Polarizabilities and Percent Error of Condensed Hydrocarbons^a

molecule	$\alpha(\text{ahc})^b$	$\alpha(\text{exp})$	$\epsilon(\text{ahc})^b$	$\bar{\alpha}(\text{ahc})^c$	$\bar{\epsilon}(\text{ahc})^c$	$\epsilon(\text{bp})$
benzene	10.40	10.39	0.2			(1.2)
naphthalene	16.59	17.48	-5.1	18.09	3.5	(0.0)
anthracene	22.77	25.93	-12.2	25.79	-0.5	(-6.1)
phenanthrene	22.77	24.70	-7.8	25.79	4.4	(-1.5)
naphthacene	28.95	32.27	-10.3	33.51	3.8	(-3.4)
1,2-benzanthracene	28.95	32.86	-11.9	33.51	1.9	(-5.1)
chrysene	28.95	33.06	-12.4	33.51	1.3	(-5.7)
1,2:5,6-dibenzanthracene	35.14	41.31	-14.9	41.22	-0.2	(-7.9)
acenaphthene	19.53	20.61	-5.3	21.01	1.9	(-1.5)
fluoranthene	25.49	28.35	-10.1	28.49	0.5	(-6.8)
pyrene	25.49	29.34	-13.1	30.05	2.4	(-5.8)
dodecahydrotriphenylene	30.32	29.89	1.4			(0.5)
fluorene	21.15	21.69	-2.5	21.15	-2.5	(-2.4)
2,3-benzofluorene	27.33	30.21	-9.5	28.81	-4.6	(-6.9)
difluorenyl	41.55	42.82	-3.0	44.51	4.0	(-4.2)
anthraquinone	23.03	24.46	-5.8	25.86	5.7	(4.9)
brazan	25.49	29.89	-14.7	30.05	0.5	(-9.6)
quinoline	15.65	16.57	-5.5	17.11	3.3	[-1.1]
acridine	21.84	25.49	-14.3	24.80	-2.7	[-9.5]
coronene	37.10	42.50	-12.7	46.32	9.0	(-3.3)
β -truxene	42.64	45.55	-6.4	47.10	3.4	(-6.7)
dixanthylene	41.85	45.27	-7.6	49.16	8.6	(-1.7)
diperinaphthylenethiophene	39.13	43.25	-9.5	48.11	11.2	[5.2]

^a Experimental data is taken from ref 22. Refer to footnote a, Table V. ^b Calculated with $\tau_c = 1.428$ for C(trtrtr π). ^c Calculated with $\tau_c = 1.800$ for the carbon atoms in a branched π hybrid such as at the 9 and 10 positions of naphthalene.**Table XI.** Empirical (ahc) and Experimental Average Molecular Polarizabilities of Condensed Ring Compounds with Atoms in Various Hybrid States with Two Parameters τ_c for C(trtrtr π). Percent Error ϵ in the Present Work and in the Bond Polarizability Approach^a

molecule	$\alpha(\text{ahc})^b$	$\alpha(\text{exp})^c$	$\epsilon(\text{ahc})^b$	$\bar{\alpha}(\text{ahc})^d$	$\bar{\epsilon}(\text{ahc})^d$	$\epsilon(\text{bp})^e$
9-chloroanthracene	24.48	27.35	-10.5	27.37	0.1	0.1
9-bromoanthracene	25.20	28.32	-11.0	27.91	-1.5	1.4
9-cyanoanthracene	24.57	28.32	-13.3	27.52	-2.8	5.6
phenazine	20.92	23.42	-10.7	23.82	1.7	-0.3
octafluoronaphthalene	15.54	17.64	-11.9	16.58	-6.0	

^a Refer to footnote a, Table III. ^b Calculated with $\tau_c = 1.428$. ^c References 19 and 20. ^d Calculated with $\tau_c = 1.800$ for branched π hybrids of carbon. ^e Data taken from ref 19 for the bond polarizability method.

ten classes of compounds with this formula are listed along with the calculated values of molecular polarizabilities. A comparison of this experimentally determined value with those calculated with eq 1, $\alpha(\text{ahc})$, with those calculated by a summation of atomic polarizabilities, $\alpha(\text{ap})$, and with those calculated by the summation of bond polarizabilities, $\alpha(\text{bp})$, suggests that menthone can be a cyclic ketone or aldehyde or a bicyclic alcohol or ether. Menthone is 2-isopropyl-5-methylcyclohexanone, a cyclic ketone. The close agreement between these three methods shows once again that the method proposed in this investigation is competitive with other approaches, and this example shows that structural differences can be predicted by empirical calculations of polarizabilities.

Discussion and Conclusion

The empirical approach proposed with eq 1 resulted from an attempt to obtain molecular polarizabilities from atomic

components, τ_A , and from atomic components the polarizabilities for atoms in various hybrid states. The atomic polarizabilities, eq 19, and correlation to van der Waals radii, eq 22, provide the data for the calculation of interactions between molecules and DNA^{25,26} in a semiempirical approach in which a $6 - n$ potential interaction

$$U_{ij} = \frac{A_{ij}}{\rho_{ij}^6} \left\{ -g_{ij}^6 + \frac{6}{n} g_{ij}^n \right\}$$

is used, where $g_{ij} = r_{ij}/(\rho_i + \rho_j)$ is the reduced distance, r_{ij} is the interatomic distance, and $\rho_i + \rho_j = \rho_{ij}$ is the sum of van der Waals radii of atoms i and j . The minimum of U_{ij} occurs when $g_{ij} = 1$. The coefficient

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

Table XII. Empirical (ahc) and Experimental Average Molecular Polarizabilities of Compounds of Biological Interest^a

molecule	$\alpha(\text{ahc})$	$\alpha(\text{exp})$	$\epsilon(\text{ahc})$	ref
cytosine	10.27 ^b	10.33	-0.6	23
adenine	12.75 ^b	13.11	-2.8	23
thymine	11.48 ^b	11.23	2.2	23
phenazine	{ 23.82 ^c 20.92 ^b	23.43	{ 1.7 -10.7	19
acridine	{ 24.80 ^c 21.84 ^b	25.49	{ -2.7 -14.3	22

^a Refer to footnote a, Table III. ^b Calculated with $\tau_c = 1.428$ for the branched π hybrid state of C(trtrtr π). ^c Calculated with $\tau_c = 1.800$ for the branched π hybrid state of C(trtrtr π).

Table XIII. Empirical Molecular Polarizabilities of Classes of Compounds with the Empirical Formula C₁₀H₁₈O^a

class	$\alpha(\text{ahc})$	$\alpha(\text{ap})$	$\alpha(\text{bp})$
acetylenic alcohols	18.75	18.99	19.17
acetylenic ethers	18.75	19.04	19.26
diethylenic alcohols	19.39	19.41	19.44
diethylenic ethers	19.39	19.46	19.53
cyclic alcohols with a double bond	18.89	18.72	18.78
cyclic ethers with a double bond	18.89	18.77	18.87
ethylenic ketones or aldehydes	19.00	19.00	19.01
cyclic ketones or aldehydes	18.50	18.31	18.35
bicyclic alcohols	18.39	18.04	18.12
bicyclic ethers	18.39	18.09	18.21

^a $\alpha(\text{ahc})$ is obtained with eq 1. $\alpha(\text{ap})$ is taken from ref 4. $\alpha(\text{bp})$ is calculated from bond polarizabilities proposed by Denbigh.⁸

contains atomic polarizabilities, α_i and α_j , and ionization potentials, I_i and I_j .²⁷

The empirical approach proposed in this investigation appears to have several advantages over other methods: (1) fewer parameters are required; (2) τ_A does not depend on atoms to which A is bonded, but rather bonding is contained implicitly in the choice of atomic hybrid components τ_A ; (3) only one component τ_A is needed for each atomic hybrid configuration. For a system containing M atoms, the method of addition of bond polarizabilities requires $M(M + 1)/2$ parameters in contrast to the ahc method which requires for each atom one τ_A for each hybrid configuration or less than $4M$ parameters.

One problem with the present method is that the components

of polarizability cannot be obtained directly from τ_A , but rather the components of the ellipsoid of polarizability must be determined geometrically, so that α_{xx} , α_{yy} , and α_{zz} can be calculated from α . In addition, the extension to compounds with very polar bonds and with groups which can form hydrogen bonds will require that each τ_A be dependent on the atoms to which A is bonded. The charge density or electronegativity of each atom may be required to yield a modification of this method. Nonetheless, the results of $\alpha(\text{ahc})$ compare with experimental data as well as those of other methods, and eq 1 appears to be more convenient to use.

Acknowledgments. The authors are grateful for the grant by Rensselaer Polytechnic Institute for computer time, and to the National Institutes of Health, Grant CA-1967A, for partial support of this work.

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