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Static Dipole Polarizabilities of Organic Molecules. Ab Initio Calculations and a Predictive Model

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Abstract: Large basis set ab initio electronic structure calculations have been carried out to find dipole polarizabilities of over 30 organic molecules containing up to four non-hydrogen atoms. For these molecules, we show that polarizabilities can be divided into transferable atomic contributions. From this demonstration of near-additivity of atomic contributions to the molecular polarizability tensor, a simple predictive scheme emerges. Tests of this scheme on molecules larger than in the original set show that individual tensor elements are predicted to within an average error of around 10% and isotropic polarizabilities have an average error of 3%. As predictions for experimental measurement, we report model values of dipole and quadrupole polarizabilities for certain series of molecules. The near-additivity of atomic contributions we find also has important implications for modeling polarization arising from intermolecular interaction.

Introduction

Dipole polarizabilities of organic molecules are important response properties. Dielectric constants, optical rotatory dispersion, other optical properties, and Raman scattering are manifestations of the capability of a substance to be polarized by an electric field (see, for example, refs 1 and 2). In addition, polarization is one of the contributors to non-bonding intermolecular interaction. Our own studies have shown an important role of polarization response on properties in intermolecular weak interaction,[3,4] and we have argued that the primary electronic structure change that occurs in weakly interacting, closed-shell species is that attributable to charge polarization. Many properties can be predicted by accounting for charge polarization. So, the capability to accurately predict or model polarizabilities may be of immediate utility in the evaluation of certain macroscopic properties and in the analysis of weak interaction. And, the capability to predict how the polarizability relates to the molecular structure is testable spectroscopically in a number of ways. This type of capability is developed here for static dipole polarizabilities of small and medium-sized organic molecules.

Over a half of a century ago, polarizabilities were already being viewed in terms of additive contributions associated with individual bonds.[5] Taking bonds as cylindrically symmetric, bond polarizabilities could have two independent tensor components, one along the bond and one for the two directions perpendicular to the bond. Tensor components for C−H, N−H, C−C, C=C, C≡C, and several other types of bonds were obtained by least-squares fitting of measured dipole polarizabilities.[5] The concept of bond polarizabilities has persisted with recent texts[6] presenting the scheme as a simple way to estimate polarizabilities. Hirschfelder, Curtis, and Bird[7] included a formal analysis to support the idea that contributions to the total polarizability could very well be additive, excluding "molecules in which there is resonance between two or more bond structures." And of course, if bonds are contributing units, then the combination of bonds into functional groups makes it appropriate to assign polarizabilities to small groups, and isotropic values of this sort may be found.[8] The idea of assigning additive polarizabilities to atoms rather than bonds is also quite old, going back to least to the work of Tessman et al.[9] on alkali halide crystals.

It is well-recognized that a point-multipole, classical analysis of polarization does not imply additivity. That is, if a classical charge distribution were represented as a distribution of a finite number of ideal dipole-polarizable points (e.g., bond or atomic dipole polarizabilities, α), the net dipole polarizability of the distribution will be greater than the sum of the α's from the points. This is because a dipole induced at one point by an external field will augment the field experienced at a neighboring point. Hence, the overall polarization is greater because of interaction between the polarizable centers. In turn, the net polarizability has an intrinsic dependence on the placement of the centers (geometry of the distribution) because the mutual interaction depends on distance between centers. Over 20 years ago, Applequist used a classical analysis to develop a powerful theory of optical rotation in terms of atomic polarizabilities and using the geometrical dependence of molecular response that is then a consequence of mutual interaction.[10] Modeling molecular polarizabilities via mutually interacting polarizable centers can be regarded as an approximation opposite to that of an additive model. The former dictates a response which will often be greater than the response of a true molecular charge cloud, whereas the latter precludes transmission of a local electrical influence along a molecular skeleton. Consequently, the choice of the type of model depends both on the particular application and on the practical success of a given scheme.

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In 1987, Liu and Dykstra[11] reported ab initio calculations of multipole polarizabilities and hyperpolarizabilities of a number of AH_n and ABH_n molecules (A, B = Li, C, N, O, F). An observation that was made in that report was that the isotropic dipole polarizability, $\bar{\alpha}$, of ABH_n (n = 0–6) molecules could be rather well predicted from the isotropic polarizabilities of the hydride of A and the hydride of B with a correction for multiple A–B bonding. This was a very simple additive model built on atomic polarizabilities rather than bond polarizabilities, The following formula was given to express it.

$$\bar{\alpha}(ABH_n) \approx \bar{\alpha}(AH_k) + \bar{\alpha}(BH_m) - 6.0(N_{AB} - 1) \qquad (1)$$

AH_k and BH_m are CH_4, H_2O, NH_3, and HF. ABH_n refers to HCCH, HCN, CO, and so on. N_{AB} is the AB bond order, and the value of 6.0 is in atomic units (au). This formula was applied to seven ABH_n molecules and the range in error relative to the corresponding calculated value was from −16% to +16%, with an average magnitude of error of 8%. The conclusion was that to a good extent, the isotropic polarizabilities of ABH_n molecules, and perhaps larger molecules, were the sums of dipole polarizabilities of the constituent heavy atoms with a correction for multiple bonding. (Interestingly, multiple bonding diminishes the polarizability.) We believe there is a stronger form for this relationship, one that leads to a more accurate and useful predictor scheme, We develop that scheme in this report through an extensive series of ab initio calculations of organic molecule dipole polarizabilities. The result is a model which seems quite accurate in predicting the static, purely electronic dipole polarizabilities of closed shell organic molecules, and we present predictions for certain types of molecules. The model also offers a valuable scheme for a distributed representation of polarization energetics, something that may be crucial to improved models of weak interaction.

Calculations

Ab initio calculations of the dipole polarizability tensor of a number of H, C, N, O, F molecules were carried out using the derivative Hartree–Fock (DHF) approach[12] which yields analytical derivative values to any order of self-consistent field (SCF) electronic energies. Electron correlation is neglected, but since that quite often falls in the range of a 5–15% correction (see, for examples, refs 13–19), additivity of atomic contributions should hold as well with a set of correlated polarizabilities as it should with SCF level values. In effect, we are using the SCF values to explore the modeling of organic molecule polarizabilities while recognizing that improvements in model parameters may be possible later as correlated calculations become available.

Mostly, the basis sets were the ELP (electrical properties) sets given by Liu and Dykstra.[11] These have diffuse s and p type functions added to a Dunning–Huzinaga[20] triple ζ (TZ) core-valence set, plus three sets of d-polarization functions on atoms other than hydrogen. For hydrogen, there are two p-polarization functions. The total number of functions in the largest of these calculations was 208.

Table 1. Assumed Geometrical Parameters for Calculation of Polarizabilities[a]

		Bond Lengths (Å)			
H−C	1.087	C═C(═)	1.308	C−N	1.368
H−N	1.020	C≡C	1.206	C═N	1.209
H−O	0.960	C−O	1.343	C≡N	1.153
C−C	1.459	C═O	1.208	N═O	1.212
C═C	1.339	N═N	1.251	C−F	1.350
		Bond Angles (deg)[b]			
H−C−C	110.2	H−N═N	110.0	X−N═O	108.6
H−C═C	121.3	H−C−X	109.5	X−C−N	119.0
F−C−C	111.0	H−N−X	106.7	X−N−C	119.0
F−C═C	123.5	H−O−X	104.5	X−N═C	128.0
C−C═C	120.3	X−C═O	124.5		

[a] Ab initio and model calculations were done at molecular geometries dictated by these values. [b] X is any other non−hydrogen atom.

Table 2. Calculated Dipole Polarizability Tensor Elements (in au) with Four Bases[a]

molecule	tensor element	ELP-basis	A-basis	B-basis	C-basis
HCC−CHO	*xx*	54.730	54.586	54.539	54.366
	xy	4.558	4.616	4.615	4.672
	yy	32.035	31.942	31.910	31.779
	zz	25.292	25.051	25.002	25.069
$HCC-CHCH_2$	*xx*	71.229	71.166	71.109	70.696
	xy	−10.913	−10.904	−10.899	−10.945
	yy	45.820	45.723	45.684	45.451
	zz	33.765	33.570	33.477	33.617
$CH_2CHCHCH_2$	*xx*	85.840	85.723	85.685	85.332
	xy	−10.224	−10.174	−10.165	−10.307
	yy	46.526	46.353	46.337	45.788
	zz	37.041	36.744	36.570	36.681

[a] Only unique, non-zero values are listed. See text for definition of the basis sets.

We selected a set of small molecules containing up to four C, N, O, or F atoms. To eliminate variances in properties arising from differences in geometries of certain bond types, all the geometries of the small molecules were fixed to approximate equilibrium structures according to parameter values in Table 1. That is, we assumed a particular standard set of bond lengths and bond angles rather than actual values. Our intent was to minimize differences in polarizabilities that might be associated with a variation in a bond length or bond angle.

A few selected calculations were carried out with basis sets that were smaller and less flexible than the ELP bases. Basis A was the ELP basis but with the extra, diffuse s function eliminated from the basis of each non-hydrogen center and with two sets of d-functions (exponents of 0.8 and 0.1) instead of three. Basis B was this set but with the two augmenting sets of diffuse p functions on each non-hydrogen center replaced by one set (exponents: C 0.0217, N 0.0287, O 0.0357, and F 0.0427). Basis C was the same as Basis B except that the diffuse s function on hydrogen was deleted and the two sets of p functions (exponents of 0.9 and 0.1) were replaced by one set (exponent of 0.3). These smaller sets were used in order to extend the molecular size of the species studied. Results with these sets were benchmarked against ELP basis results for several molecules. As shown in Table 2, the flexibility of the large ELP sets is of relatively small importance for intermediate and larger molecules, with differences of only a few percent resulting from using the smallest basis. The polarization of the molecule becomes increasingly a polarization in the valence regions along the nuclear backbone as molecule size increases. This leads to less stringent basis set requirements than does the

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Table 3. Calculated Dipole Polarizability Tensor Elements (in au)[a]

molecule	polarizibility element	DHF (ab initio)	model	% error
NC−CN	*xx*	51.98	51.10	−1.7
	yy = *zz*	21.77	21.69	−0.4
CH_3CN	*xx*	37.70	38.19	1.3
	yy = *zz*	23.36	23.49	0.5
HNCO	*xx*	33.73	35.48	5.2
	yy	16.24	17.53	8.0
	zz	15.89	16.20	2.0
NH_2CO	*xx*	31.18	31.18	0.0
	yy	27.89	26.92	−3.4
	zz	18.95	19.91	5.1
CH_2NH	*xx*	28.34	29.24	3.2
	yy	20.47	20.38	−0.4
	zz	16.06	16.14	0.5
cis-N_2H_2	*xx*	24.33	23.01	−5.5
	yy	16.56	15.96	−3.7
	zz	13.49	13.29	−1.5
CH_2CHCN	*xx*	52.65	50.06	−4.9
	yy	44.02	46.61	5.9
	zz	28.51	29.85	4.7
CH_2O	*xx*	21.33	19.93	−6.6
	yy	15.78	13.87	−12.1
	zz	12.22	10.96	−10.3
CH_2CO	*xx*	42.24	41.71	−1.3
	yy	21.06	21.96	4.3
	zz	21.34	19.06	−10.7
CH_2CCO	*xx*	78.38	80.80	3.1
	yy	28.20	28.51	1.1
	zz	25.71	25.61	−0.4
HCOOH	*xx*	23.23	23.23	0.0
	yy	21.78	21.84	0.3
	zz	14.88	14.82	−0.4
CO_2	*xx*	25.58	26.17	2.3
	yy = *zz*	12.39	11.02	−11.0
OC_3O	*xx*	89.15	87.04	−2.4
	yy = *zz*	25.09	25.66	2.3
C_2H_2	*xx*	32.29	34.50	6.9
	yy = *zz*	19.23	18.07	−6.0
C_4H_2	*xx*	81.49	78.74	−3.4
	yy = *zz*	30.74	31.13	1.3
C_2H_4	*xx*	36.87	35.47	−3.8
	yy	24.75	24.80	0.2
	zz	22.76	19.00	−16.5
C_4H_4	*xx*	113.79	113.64	−0.1
	yy	36.46	37.90	4.0
	zz	34.22	32.10	−6.2
C_2H_6	*xx*	27.90	25.29	−9.3
	yy = *zz*	25.76	25.29	−1.8
HCC−$CHCH_2$	*xx*	71.23	66.89	−6.1
	yy	45.82	48.32	5.5
	zz	33.77	34.57	2.4
HCC−CHO	*xx*	54.73	55.18	0.8
	yy	32.03	33.55	4.7
	zz	25.29	26.53	4.9
CH_3−CHO	*xx*	30.13	28.46	−5.6
	yy	29.99	30.63	2.1
	zz	22.43	23.61	5.3
CH_3−CCH	*xx*	49.27	52.02	5.6
	yy = *zz*	28.52	28.21	−1.1
cis-CH_2CHCHO	*xx*	50.14	50.43	0.6
	yy	42.65	43.63	2.3
	zz	27.70	29.97	8.2
trans-$C_2H_2O_2$	*xx*	33.17	31.62	−4.7
	yy	35.05	35.96	2.6
	zz	19.73	21.93	11.1
FHCO	*xx*	20.86	20.12	−3.5
	yy	15.56	13.81	−11.2
	zz	12.23	11.43	−6.5
FCC−CCH	*xx*	81.07	83.29	2.7
	yy = *zz*	30.25	29.09	−3.8
cis-FHC−CHF	*xx*	35.16	35.93	2.2
	yy	24.68	24.64	−0.1
	zz	20.34	19.94	−2.0
$F_2C{=}CH_2$	*xx*	35.45	35.93	1.4
	yy	25.00	24.64	−1.4
	zz	20.48	19.94	−2.6
CH_3−CH_2F	*xx*	25.02	25.66	2.6
	yy	24.29	25.08	3.2
	zz	26.07	25.76	−1.2
CH_2F−CH_2F	*xx*	25.75	26.03	1.1
	yy	26.17	24.86	−5.0
	zz	24.30	26.23	7.9

[a] Symmetry equivalence of two elements is indicated by "*yy* = *zz*".

evaluation of polarization of very small molecules which involves electron density shifts in fringe regions. On the basis of the results in Table 2, it is meaningful to compare model predictions to calculated values for large molecules where the ELP bases were not used; however, this may introduce intrinsic differences from the model of a few percent because the model has been developed from only large basis set results.

Additivity of atomic contributions to the molecular polarizability tensors was analyzed by a least-squares fit of the individual tensor elements. The fitting coefficients were the *xx*, *yy*, and *zz* elements of the polarizability tensors of the constituent atoms. Different atomic tensors were allowed for carbon and nitrogen in different bonding environments (hybridization). Certain symmetry constraints were imposed. For instance, the two components perpendicular to the triple bond of an sp type carbon were constrained to be the same. Using 90 diagonal tensor elements for the 30 small molecules, 25 parameters were obtained by least-squares adjustment.

Results and Discussion

Table 3 gives the ab initio calculated values for the diagonal components of the dipole polarizability tensors along with corresponding values obtained from the least-squares fit (i.e., with the model of additive atomic contributions). The polarizability values provide useful information on a collection of representative organic species, given that there are few instances of such wide scan evaluation of properties, particularly with extensive basis sets. However, the most important result is that individual tensor elements of this collection of molecules can be fairly accurately (usually to 10%) formed by addition of contributions from atoms. Table 4 presents the parameters from the least-squares fitting analysis done for the set of 30 molecules with polarizabilities in Table 3. Also in Table 4 are corresponding values that may be used for aromatic carbon centers, these having been obtained solely to match the calculated polarizability of benzene.[21] The Table 4 values are the three principal elements of the polarizability tensors of the different types of atoms, and it is quite appropriate to interpret them as characterizing a local atomic response to an applied field. For instance, we can see that an allenic carbon (=C=) is more polarizable than carbons in other bonding environments, that oxygen is generally less polarizable than carbon, and that fluorine is the least polarizable of C, N, O, and F.

We have tested the model on several molecules similar to those in the fitting set (Table 3) and to several larger molecules. These results are shown in Table 5. The error of the model in reproducing the DHF values is larger than for the set of molecules used to generate the parameters, but still small enough

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Table 4. Model Atomic Polarizabilities (in au)

atom type	tensor element	model parameter value	isotropic α
C (sp^3)	*xx* = *yy* = *zz*	12.6473	12.647
C (aromatic)[a]	*xx* = *yy*	12.8233	10.847
	zz	6.8933	
C (sp^2)	*xx*	17.7348	13.212
	yy	12.4018	
	zz	9.5010	
(O)=C (sp^2)	*xx*	21.7860	12.657
	yy = *zz*	8.0922	
=C=	*xx*	39.0865	17.395
	yy = *zz*	6.5497	
C (sp)	*xx*	22.1181	11.725
	yy = *zz*	6.5279	
(H)C (sp)	*xx*	17.2514	11.774
	yy = *zz*	9.0360	
N (sp^3)	*xx*	15.3680	11.085
	yy = *zz*	8.9430	
N (sp^2)	*xx*	11.5029	8.708
	yy	7.9783	
	zz	6.6439	
N (sp)	*xx*	25.5477	15.746
	yy = *zz*	10.8444	
O=	*xx*	2.1904	1.706
	yy = *zz*	1.4638	
−O−	*xx*	7.4233	5.047
	yy = *zz*	3.8583	
F	*xx*	−0.3205	0.206
	yy = *zz*	0.4686	

[a] The values for aromatic carbons were not fitting parameters, but instead are those reported previously[21] from a single calculation on benzene.

Table 5. Calculated Molecular Dipolar Polarizability Tensor Elements (au) Not Used To Find Model Parameters

molecule	polarizability element	DHF (ab initio)	model	% error
I.Up to Two Non-Hydrogen Atoms				
CH$_4$	*xx* = *yy* = *zz*	15.87	12.65	−25.5
H$_2$O	*xx*	8.34	7.42	−11.0
	yy	9.13	3.86	−57.7
	zz	7.85	3.86	−50.8
NH$_3$	*xx*	13.30	15.37	15.6
	yy = *zz*	12.85	8.94	−30.4
HCN	*xx*	22.67	42.80	47.0
	yy = *zz*	13.79	19.88	30.6
trans-HN=NH	*xx*	24.28	23.01	−5.5
	yy	17.08	15.96	−7.0
	zz	13.30	13.29	−0.1
NH$_2$−CH$_3$	*xx*	26.60	28.02	5.1
	yy	22.96	21.59	−6.4
	zz	22.80	21.59	−5.6
II.Three Non-Hydrogen Atoms				
NH$_2$CCH	*xx*	48.05	54.74	12.2
	yy	25.84	24.51	−5.4
	zz	25.42	24.51	−3.7
H$_2$CCCH$_2$	*xx*	65.17	74.56	12.6
	yy = *zz*	29.36	28.45	−3.1
HN=CHOH	*xx*	35.12	34.45	−2.0
	yy	23.46	26.45	11.3
	zz	18.55	20.00	7.3
FCCH	*xx*	33.10	39.05	15.2
	yy = *zz*	18.68	16.03	−16.5
HCCOH	*xx*	38.89	46.79	16.9
	yy	22.16	19.42	−14.1
	zz	21.31	19.42	−9.7
III.Four Non-Hydrogen Atoms				
C$_4$H$_6$	*xx*	85.84	70.94	−21.0
	yy	46.53	49.61	6.2
	zz	37.04	38.00	2.5
cis-CHO−CHO	*xx*	33.20	31.62	−5.0
	yy	33.59	35.96	6.6
	zz	19.69	21.93	10.2
trans-CH$_2$CHCHO	*xx*	60.18	55.36	−8.7
	yy	37.10	38.70	4.1
	zz	27.91	29.97	6.9
trans CHF=CHF	*xx*	35.09	35.93	2.3
	yy	24.44	24.64	0.8
	zz	19.93	19.94	0.03
IV.More Than Four Non-Hydrogen Atoms				
CH$_3$CFCF$_2$	*xx*	41.67	40.48	−3.0
	yy	43.15	45.53	5.2
	zz	28.94	33.06	12.4
H(CC)$_3$H	*xx*	147.93	122.98	−20.3
	yy = *zz*	41.89	44.18	5.2
HCC−CO−CHO	*xx*	73.23	74.77	2.1
	yy	44.41	47.74	7.0
	zz	31.61	37.49	15.7
H(CC)$_2$CHCO	*xx*	131.50	110.59	−18.9
	yy	60.11	65.30	8.0
	zz	43.19	47.68	9.4

to indicate that the model is a good predictor. The notable exceptions are molecules with only one or two non-hydrogen atoms, such as water and methane. For these, the errors can be sizable; however, these species have certain qualitative differences from larger species, the bonds being mostly to hydrogens rather than to other heavy centers. (We could, of course, include these in the model by adding parameters specific to these environments, but all that would accomplish is a specific set of parameters for a "water" oxygen, a specific set for a "methane" carbon, and so on.) It is interesting that for methane, water, and ammonia, the model tends to underestimate, not overestimate, the mean polarizabilities, and we will return to this point later. Success in modeling the polarizabilities of other than these small molecules is an important concern. For molecules with more than two non-hydrogen atoms, the mean of the absolute value of the percentage errors for the tensor elements in Table 5 is 8.4%.

The assumption of atomic additivity with the use of the values of Table 4 leads to mean or isotropic polarizabilities [i.e., $\bar{\alpha} = (\alpha_{xx} + \alpha_{yy} + \alpha_{zz})/3$] shown in Table 6 that are in very good agreement with the corresponding ab initio values. That this agreement is better than that for individual tensor elements indicates that the atomic additivity model has greater errors in the orientational features of the polarization response than in its size. This might partly arise from the use of point-dipole polarizabilities for each atom, and to the extent it does, it is intrinsic to the model.

Since the isotropic polarizabilities are particularly well represented by a sum of isotropic atomic polarizabilities, we may view these predictions as coming from a condensed model, one with only 12 parameters, the isotropic α's in Table 4. The results in Table 6 show that the isotropic polarizabilities of 45 molecules are reproduced with these 12 parameters to an average error of 2.9%.

An interesting result obtained by Beck and Gay[22] from ab initio calculations of the polarizabilities of unbranched alkanes is that for larger alkanes, there is an additive contribution of 12.29 au to the isotropic polarizability each time another CH$_2$ group is added to the chain. In our model, the contribution to the isotropic polarizability from increasing the chain length by one carbon would be a very similar value of 12.647 au (Table 4). Application of our model to polyyne chains, on the other hand, may require a more complete analysis of conjugation effects. Notice that the longitudinal polarizability (α_{xx}) parameter in Table 4 for =C= is nearly twice that of −C≡. Such a sizable difference may preclude using a single atom type for carbons in long, multiply-bonded chains.

We have used a chosen set of standard bond lengths and bond angles in the development of the model. More meaningful values of molecular properties will result if adjustments can be

Table 6. Error in the Additive Atomic Model for Isotropic Polarizabilities

molecule	DHF (ab initio)	model	% error
cis-N_2H_2	18.13	17.42	−3.9
trans-N_2H_2	18.22	17.42	−4.4
CH_2NH	21.62	21.92	1.4
NH_2-CH_3	33.10	34.58	4.5
CH_3CN	28.14	28.39	0.9
HNCO	21.95	23.07	5.1
HN=CHOH	25.71	26.97	4.9
NH_2CO	26.00	26.00	0.0
NH_2CCH	33.10	34.58	4.5
NC−CN	31.84	31.49	−1.1
CH_2CHCN	41.73	42.17	1.1
trans-CH_2CHCHO	41.73	41.34	−0.9
cis-CH_2CHCHO	40.16	41.34	2.9
CH_2O	16.44	14.92	−9.3
CH_2CO	28.21	27.58	−2.3
CH_2CCO	44.10	44.97	2.0
HCOOH	19.97	19.97	0.0
HCCOH	27.45	28.55	4.0
CO_2	16.78	16.07	−4.3
OC_3O	46.44	46.12	−0.7
C_2H_2	23.59	23.55	−0.2
C_4H_2	47.66	47.00	−1.4
C_6H_2	77.23	70.45	−8.8
C_2H_4	28.13	26.43	−6.0
C_3H_4	41.30	43.82	6.1
C_4H_4	61.49	61.22	−0.4
C_2H_6	26.47	25.29	−4.4
C_4H_6	56.47	52.85	−6.4
$HCC-CHCH_2$	50.27	49.92	−0.7
HCC−CHO	37.35	38.42	2.9
CH_3-CHO	27.52	27.57	0.2
CH_3-CCH	35.44	36.15	2.0
trans-$C_2H_2O_2$	29.32	29.84	1.8
cis-$C_2H_2O_2$	28.83	29.84	3.5
FHCO	16.22	15.12	−6.7
FCCH	23.49	23.70	0.9
FCC−CCH	47.19	47.15	−0.1
cis-FHC−CHF	26.73	26.84	0.4
trans-FHC−CHF	26.49	26.84	1.3
$F_2C=CH_2$	26.98	26.84	−0.5
CH_3-CH_2F	25.13	25.50	1.5
CH_2F-CH_2F	25.41	25.71	1.2
CH_3CFCF_2	37.92	39.69	4.7
HCC−CO−CHO	49.75	53.34	7.2
$H(CC)_2CHCO$	78.27	74.52	−4.8
	mean absolute error percentage		2.9

made to account for geometry differences between these standard geometries and equilibrium or else on-average geometries. The polarizabilities of molecules tend to vary rather slowly and simply with variations in geometrical parameters, and so, we foresee an extension of the model whereby geometrical variations are modeled by simple correction functions of the geometrical coordinates. The transferability of such functions seems likely on the basis of the transferability seen here, but that remains to be demonstrated.

In addition to providing a useful scheme for predicting molecular dipole polarizabilities, the model we have presented could provide a more global characterization of the energetic response to electrical perturbation. In this, the idea of distributing dipole polarizabilities is already in use. For instance, isotropic atomic polarizabilities have been used in force fields for interacting waters by Kollman and co-workers[23−25] and by Warshel and co-workers.[26,27] A means for finding distributed dipole polarizabilities directly from ab initio calculations has been devised by Stone.[28] As stated earlier, assigning polarizabilities to bonds rather than atoms is the alternate means of devising a predictive scheme,[5] one that could be used in force field generation. We initially attempted to use our data with this objective, but we feel it is significant that we found the number of bond types, and hence the number of different fitting parameters, needed to be greater than if the polarizability contributions were assigned to atoms.

A most direct test of additive contributions to molecular polarizabilities is simply evaluation for an individual molecule once a measurement of α has been made. Another type of test has come from measurement of depolarization ratios. For instance, Haverkort et al.[29] did not find perfect agreement for a series of *n*-alkanes and fluoroalkanes from additive bond contribution models. The measured depolarization ratio of a dilute gas sample is related to the isotropic and anisotropic dipole polarizabilities. Manipulation of the expression for the depolarization ratio,[29] ϱ, yields an expression for a quantity Δ, the mean-square ratio of the diagonal elements of α to the average α, in terms of the depolarization ratio, ϱ:

$$\Delta \equiv \frac{1}{3}\left(\frac{\alpha_{xx}^2}{\alpha^2} + \frac{\alpha_{yy}^2}{\alpha^2} + \frac{\alpha_{zz}^2}{\alpha^2}\right) = \frac{3 - 6\varrho}{3 - 4\varrho} \qquad (2)$$

The largest value of ϱ given for the species studied by Haverkort et al.[29] corresponds to $\Delta = 0.9959$. So, for a model to predict the depolarization ratios of the series correctly, the relative accuracy in individual α elements would have to be 0.2% and better, although the absolute accuracy could be much worse. The model given here is too coarse for that type of relative accuracy, and in fact, it would provide no differentiation in ϱ among the series of hydrocarbons.

Spatial distribution of atomic dipole polarizabilities in the representation of a charge distribution means there is automatically a polarization response to field gradients, a response characterized by the molecular *quadrupole* polarizability, and to higher order nonlinearities in the field. Our model allows for the atomic polarizabilities to be anisotropic, and that may offer suitable flexibility for the model representation to give a correct response to an applied field gradient. We have examined that by evaluating the quadrupole polarizability from ab initio calculation on several of the molecules studied and from the model. In Table 7, these values are presented. The evaluation has been done relative to their mass centers and is given in traceless form.[30] The agreement is not at the level we obtain for the dipole polarizabilities. Of course, for a single atom, the dipole polarizability does not contribute to the atom's quadrupole polarizability at all. So, it is only as molecule size increases that the polarization of atoms experiencing different field strengths (via applied field gradient) gives rise to the main part of an induced quadrupole moment. Thus, as suggested by results in Table 7, the model prediction of the quadrupole polarizabilities improves with molecular size. The errors remain larger than for dipole polarizabilities, but are still small enough to indicate the model's usefulness in characterizing the total polarization response of organic molecules of this size. Consequently, optimally chosen atomic dipole polarizabilities should

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Table 7. Model and ab Initio Values of Molecular Quadrupole Polarizabilities

molecule	element[a]	DHF (ab initio)	model	% error
CH_2CO	*xx,xx*	522	477	−9
	xx,yy	−242	−238	−2
	yy,yy	202	119	−41
	zz,zz	240	119	−50
CH_2CCO	*xx,xx*	1359	1482	9
	xx,yy	−655	−741	13
	yy,yy	416	370	−11
	zz,zz	463	370	−20
$HCC-CH_3$	*xx,xx*	862	772	−10
	xx,yy and *xx,zz*	−431	−386	−10
	yy,yy and *zz,zz*	338	193	−43
HCC−CHO	*xx,xx*	1265	1214	−4
	xx,yy	−682	−627	−8
	yy,yy	513	351	−32
	zz,zz	413	311	−25
cis-FHC−CHF	*xx,xx*	409	283	−31
	xx,yy	−262	−201	−23
	yy,yy	347	211	−39
	zz,zz	232	92	−60
$H(CC)_2H$	*xx,xx*	1934	2183	13
	xx,yy and *xx,zz*	−967	−1091	13
	yy,yy and *zz,zz*	569	546	−4

[a] Unique, diagonal traceless elements of the quadrupole polarizability tensor.

serve as a means for calculating the polarization energy due to applying not only a uniform electrical field but also a field gradient.

The idea that a molecule's response to an external electrical potential (fields, field gradients, and so on) can be mostly partitioned into additive responses of constituent heavy atoms underlies the model presented here. In one respect, this is not unlikely since the primary sites for localization of molecular charge are the non-hydrogen nuclei, and the charge distributions in these regions should dictate the overall response. In another respect, however, this approximation has limited applicability. In particular, an additive model fails to "transmit" polarization along a molecular skeleton. If a point dipole were placed at one end of a long molecule, the polarization occurring at the other end of the molecule in an additive model would be only that from a through-space interaction with the external point dipole. The true polarization would include that arising from mutual polarization along the charge distribution, a through-bond effect. Applequist's non-additive approach[10,31,32] incorporates this as a strictly classical, mutual polarization of point-polarizable atoms. Were we to use this non-additive approach, the assigned α's in Table 4 would be mostly smaller. α-values for carbon centers would be reduced to as small as half of the values given in order to reproduce the net polarizabilities of the molecules. The non-additive picture is valuable because it automatically leads to a dependence on molecular geometry parameters, and Applequist has shown that this dependence yields meaningful values for a number of optical and spectroscopic properties.[10,31,32] To do this with an additive model requires introducing an explicit dependence on geometry, and this still remains to be accomplished.

The ab initio data we have obtained offer some insight to representing the polarization response. First, hydrogen contributions are so small that they can be taken to be zero, and so, no values for hydrogen α's are to be found in Table 4. Second, the model already underestimates the isotropic polarizabilities for methane, water, and ammonia. A non-additive model would reduce these values even more, at least with the hydrogen's not contributing. The difficulty of a non-additive model is the inherent approximation in how an electrical influence is transmitted. Classical mutual polarization may be an appropriate picture for separate, distinct charge distributions, and we have argued that in studies on weak intermolecular interaction, but within the continuous charge distribution of a single molecule, this picture corresponds to a more severe approximation.

Our results provide an evaluation of the extent to which additivity is a workable premise for modeling overall polarization response of a molecule. Our judgement of the results is a positive one, especially if the ultimate application is to obtain intermolecular electrical interaction energies. For such energies, the contributions associated with polarizabilities are typically around 10%, the remainder being permanent moment interactions. Thus, the error sizes in an additive model of molecular polarizability will translate into 1−2% errors in energetics, and that is on the order of other error sources in contemporary force fields for intermolecular interaction. Furthermore, the additivity assumption as opposed to non-additivity greatly reduces computational cost for molecular simulations when using a force field which includes polarization energetics.

Appendix: Using the Model

To use the model for the calculation of an H, C, N, O, or F molecule other than those listed here, one begins by identifying each atom type according to those in Table 4. The x-axis is always defined to be along the major bond, and where there is a difference between y-axis and z-axis components, the y-axis is in the plane of connected atoms. For example, in formaldehyde, the x-axis is along the carbon−oxygen bond and the y-axis is in the plane of the molecule. If the molecule is colinear, then the molecular tensor elements are simply the sums of the corresponding tensor elements from Table 4. However, if a major bond is oriented at a non-zero angle with respect to the x-axis, then the atomic tensor must be rotated (transformed) before elements are summed. The general rotation scheme is,

$$\alpha^{\text{transformed}} = \mathbf{C}\alpha\mathbf{C}^{\mathrm{T}} \tag{3}$$

$$\mathbf{C} = \begin{bmatrix} \cos\phi\cos\theta & -\sin\phi & -\cos\phi\sin\theta \\ \sin\phi\cos\theta & \cos\phi & -\sin\phi\sin\theta \\ \sin\theta & 0 & \cos\theta \end{bmatrix} \tag{4}$$

where α is the diagonal polarizability tensor of the atom as given in Table 4, and θ and ϕ are the usual spherical polar angles describing the orientation of the bond vector in the coordinate system of the molecule. When all atoms' tensors have been rotated appropriately, corresponding tensor elements from the atoms are summed to obtain the molecular dipole polarizability tensor. Or, the rotated tensors, distributed at their atomic centers, may be used to obtain the molecular response to an external electrical potential.

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