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Transferability of topologically partitioned polarizabilities: the case of n-alkanes

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Distributed polarizabilities of a series of n-alkanes C_nH_{2n+2} (n = 2–7) in various conformations have been determined using Bader's topological theory of atoms in molecules. Using an appropriate localization scheme, a simple distributed model is constructed, where the methyl and methylene groups are characterized by their dipole polarizability tensors in local frames, and all charge flow polarizabilities between them are retained. A set of average polarizability parameters is proposed that takes into account the local environment of the methyl and methylene groups, and that not only reproduces the polarizability tensor for any member of the n-alkane series in an arbitrary conformation, but also is suitable for the calculation of induction energies.

1. Introduction

Additivity and transferability of group polarizabilities is well established experimentally. One of the most extensively studied cases is that of the alkanes, where it has been found that the addition of a methylene unit increases the average polarizability by about 11·98 au for the higher members of the series. More sophisticated additivity schemes, based on bond polarizability tensors whose longitudinal and transverse components may differ, have been compiled by Le Fèvre [1]. The theoretical basis for such additivity has been questioned on the grounds that the local field experienced by a given atom or bond is quite different from the external field, and strongly dependent on the actual molecular structure, because of induced moments on other parts of the molecule [2]. This role of the local field has been emphasized by Applequist's model, where a dipole–dipole interaction scheme is used to take the influence of the molecular environment into account [3]. Nevertheless, it seems that the 'in-molecule' effective polarizabilities are reasonably transferable, which can be explained by the relative constancy of the immediate environment of a given atom or bond in various molecular systems [4].

The rigorous theory of distributed polarizabilities [5] overcomes the limitations of earlier approximate models used to describe the interactions between subunits within the molecule. All intramolecular interactions are handled by quantum mechanics, and

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non-local group polarizabilities are determined by an appropriate partitioning of the total charge-density response function. This leads to a scheme in which the fields in a given region of the molecule induce moments not only in that region but in all the other regions also. Furthermore, differences in electrostatic potential between regions lead to charge flow. Thus we have

$$\Delta Q_t^a = -\alpha_{tu}^{ab} V_u^b, \tag{1}$$

where ΔQ_t^a is some moment (charge, dipole, quadrupole, etc.) in region a induced by fields V_u^b (the potential and its derivatives) at the origin of region b. For brevity we refer to the (arbitrary) origin of region a as 'site a'.

There are several possible partitioning schemes [6], but the most stable one, leading to physically plausible group contributions [7], is that based on Bader's theory of atoms in molecules (AIM) [8, 9]. The boundary surfaces between atomic regions or 'basins' Ω_A are the zero-flux surfaces $S_A(\mathbf{r})$ on which the charge density has zero gradient normal to the surface: $\nabla\rho(\mathbf{r})\cdot\mathbf{n}(\mathbf{r}) = \mathbf{0}\ \forall\, \mathbf{r} \in S_A(\mathbf{r})$. It has been shown that this particular partition of properties ensures a maximal transferability between different systems [8].

Bader and his coworkers have developed a group polarizability scheme using the theory of atoms in molecules [10], but their approach, which considers the effect of a uniform perturbing field on the molecule, is different from our topological partitioning of electric properties (TPEP) [11, 12], which is valid in arbitrary non-uniform external fields as well.

The distributed polarizability scheme summarized in equation (1) has the disadvantage of requiring a large number of polarizabilities α_{tu}^{ab} to describe the effect of an arbitrary external potential. The distributed polarizabilities as produced initially by the calculation are very difficult to assimilate or interpret. For each pair of sites a and b there is a 4×4 array of charge-flow and dipole polarizabilities; for a single configuration of heptane this gives 28×16 numbers. It is possible to transform to a scheme in which the moments induced on site b by fields at site a are expressed in terms of a multipole expansion about site a [17]. This yields a much simpler localized description at the expense of less satisfactory convergence characteristics. Le Sueur and Stone [17] found that the charge flow polarizabilities (the flow of charge in response to potential differences) could not be localized satisfactorily in this way, but relatively few numbers are needed to characterize these.

2. Method

Fully distributed group polarizabilities were calculated by the coupled perturbed Hartree–Fock (CPHF) method, as described in [7], using one-electron transition matrix elements corresponding to the functional groups. A functional group (here methyl or methylene) is the union of several atomic basins, defined according to Bader's theory of atoms in molecules. The group multipole moment operators $\hat{Q}_{lm}^a$ are defined by their matrix elements:

$$\langle i|\hat{Q}_{lm}^a|j\rangle = \int_{\Omega_a} \mathrm{d}\mathbf{r}\ \phi_i^*(\mathbf{r})\, R_{lm}(\mathbf{r}-\mathbf{a})\, \phi_j(\mathbf{r}), \tag{2}$$

where $R_{lm}(\mathbf{r}-\mathbf{a})$ is a regular spherical harmonic whose argument is the vector from a suitable origin $\mathbf{a}$ for the functional group, and the volume of integration extends over

the atomic basins comprising the group, limited by the appropriate zero-flux surface of the unperturbed molecule.

Total molecular polarizabilities can be calculated either by replacing the group transition integrals in expression (2) by molecular ones, or by reconstituting them from distributed polarizabilities via translation of the atomic components to the common molecular origin [5]. The two procedures are in principle equivalent but give slightly different numbers in practice, reflecting the error in the numerical integration scheme (usually 0·001 au).

Distributed polarizabilities were calculated for the series of molecules ethane, propane, *trans*-butane, *gauche*-butane, *tt*-pentane, *tg*-pentane, *gg*-pentane, *ttt*-hexane and *tttt*-heptane, at the SCF/6-31G* optimized geometries determined by the GAUSSIAN 92 program [13]. Polarizability calculations were performed using the basis set of Spackman [14], optimized for molecular polarizabilities, which consists of (8s4p1d)/[4s2p1d] and (5s1p)/[3s1p] sets for carbon and hydrogen, respectively. The functional units were the methyl and methylene groups, with the origin at the carbon atom. The polarizabilities were calculated using our CPHF program which uses the necessary transformed two-electron integral blocks produced by either a non-standard link after a closed-shell SCF run of GAUSSIAN 92 [13], or by the MOLCAS-2 suite of programs [15]. Because our CPHF code can take advantage of Abelian point group symmetries, handled by MOLCAS, we were able to treat symmetrical conformations of alkanes up to heptane with relatively limited hardware resources. The occupied/virtual one-electron integral blocks of the distributed moments were generated by a modified version of the PROAIM program [16].

In order to test the validity of the polarizability model a number of low-symmetry conformations of hexane and heptane also were generated, keeping the bond lengths and bond angles at the values optimized for the all-*trans* conformation, and overall molecular polarizabilities were calculated for these structures. Molecular polarizabilities were also calculated for the all-*trans* isomers of n-octane and n-nonane.

3. Results and discussion

We localized the polarizabilities using the technique of Le Sueur and Stone [17]. For the reasons explained above, we localized only the dipole polarizabilities and not the charge-flow polarizabilities. The results obtained by this procedure are given in table 1. Only unique polarizability values are shown, and components which can be derived from these by appropriate symmetry operations are omitted. In practice the calculated numbers were not strictly symmetrical, because of errors in the numerical integration procedure, which led to differences of about 0·01–0·03 au between localized group dipole polarizabilities that should be equal by symmetry. Such differences have been averaged out in the tabulated numbers. The local dipole polarizabilities are expressed in a local coordinate frame for each methyl or methylene unit, in order to facilitate comparison and assess the degree of transferability (figure 1). For a terminal methyl group C_1, the local z axis is along the bond from the next carbon atom, C_2, the y axis is perpendicular to the plane of C_1, C_2 and C_3, and the x axis completes a right-handed set with C_3 lying at positive x. For a methylene group C_k the z axis bisects the C_{k-1}—C_k—C_{k+1} angle, the y axis is perpendicular to the C_{k-1}, C_k C_{k+1} plane, and the x axis completes a right-handed set with C_{k+1} lying at positive x.

There is evidently a substantial degree of transferability between corresponding elements of the polarizability tensors, but it is necessary to distinguish between

Table 1. The unique distributed polarizabilities left after localization of all non-local polarizabilities except charge flows, for the saturated hydrocarbons C_2H_6, C_3H_8, C_4H_{10}, C_5H_{12}, C_6H_{14} and C_7H_{16}. Note that $\alpha_{00}^{ii} = -\Sigma_{j\neq i}\alpha_{00}^{ij}$. Local axes for C_1: z along bond from C_2; x in C_1, C_2, C_3 plane, with C_3 at positive x. Axes for atom i, i ≠ 1: z bisecting C_{i-1}—C_i—C_{i+1} angle, x in C_{i-1}, C_i, C_{i+1} plane, in the direction from C_{i-1} to C_{i+1}.

	i j	C_2H_6	C_3H_8	t-C_4H_{10}	g-C_4H_{10}	tt-C_5H_{12}	tg-C_5H_{12}	gg-C_5H_{12}	C_6H_{14}	C_7H_{16}
α_{00}^{ij}	1 2	−1·021	−0·807	−0·798	−0·799	−0·798	−0·793	−0·793	−0·797	−0·797
	2 3			−0·661	−0·672	−0·655	−0·656	−0·666	−0·655	−0·655
	3 4						−0·666		−0·650	−0·649
	4 5						−0·799			
	1 3		−0·247	−0·168	−0·156	−0·164	−0·164	−0·154	−0·163	−0·164
	2 4					−0·141	−0·102	−0·089	−0·139	−0·140
	3 5						−0·151			−0·138
	1 4			−0·092	−0·112	−0·034	−0·062	−0·083	−0·032	−0·032
	2 5						−0·077		−0·001	−0·000
	1 5					−0·065	−0·042	−0·040	−0·037	−0·035
	2 6									−0·027
	1 6								−0·031	−0·011
	1 7									−0·025
α_{zz}^{ii}	1	10·189	10·463	10·933	10·267	11·005	11·054	10·254	11·183	11·251
	2		9·477	9·270	9·929	9·202	8·791	9·660	9·083	9·096
	3					8·802	9·414	10·136	8·695	8·655
	4						10·136			8·700
	5						10·297			

α^{ii}_{xx}	1	12·764	12·759	12·682	12·505	12·750	12·574	12·403	12·804	12·831
	2		3·426	2·973	3·250	3·168	2·755	3·150	3·076	3·120
	3					2·465	2·747	3·040	2·636	2·552
	4						3·256			2·861
	5						12·759			
α^{ii}_{yy}	1	12·764	12·444	12·339	11·953	12·262	12·249	12·035	12·242	12·231
	2		10·447	10·100	10·392	9·971	9·588	9·993	9·915	9·908
	3					9·702	10·008	10·352	9·601	9·601
	4						10·338			9·575
	5						11·916			
α^{ii}_{xz}	1	0	− 0·429	− 0·721	− 0·675	− 0·847	− 0·742	− 0·742	− 0·985	− 1·041
	2		0	0·273	0·058	0·362	− 0·445	0·138	0·392	0·409
	3					0	0·239	0	0·071	0·105
	4						0·273			0
	5						− 0·804			
α^{ii}_{yz}	1	0	0	0	− 0·172	0·007	0·120	− 0·292	0	0·007
	2		0	0	0·328	0·004	− 0·341	0·623	0	− 0·003
	3					0	0·330	0	0	− 0·019
	4						− 0·441			− 0·058
	5						− 0·233			
α^{ii}_{xy}	1	0	0	0	− 0·130	− 0·006	− 0·051	0·088	0	− 0·003
	2		0	0	− 0·004	0·001	− 0·211	− 0·107	0	− 0·006
	3					0	− 0·008	0·007	0	0·011
	4						− 0·110			0
	5						0·014			

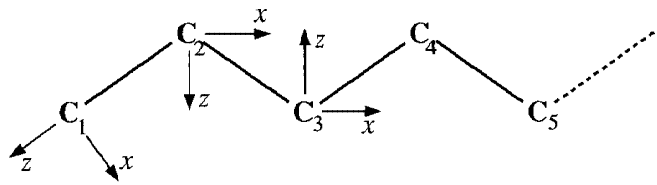


Figure 1. Local axes for atomic polarizabilities.

Table 2. Approximate transferable local dipole polarizabilities for (*a*) a terminal methyl group in a normal alkane, (*b*) a methylene group attached to one methyl and one methylene, and (*c*) a methylene attached to two methylenes. Axes as specified in table 1.

	(*a*)			(*b*)			(*c*)		
	x	*y*	*z*	*x*	*y*	*z*	*x*	*y*	*z*
x	12·7	0·0	− 0·9	3·1	0·0	0·0	2·6	0·0	0·0
y	0·0	12·25	0·0	0·0	9·9	0·0	0·0	9·6	0·0
z	− 0·9	0·0	11·0	0·0	0·0	9·1	0·0	0·0	8·7

methylene groups according to whether they are attached to two methyl groups (i.e., in propane), to one methyl and one methylene, or to two methylenes, as Bader *et al.* found [10]. Ethane is a special case, since it is the only molecule to feature methyl bonded to methyl, but for the other molecules we can assign approximate transferable polarizabilities as in table 2. These have not been obtained by any kind of fitting procedure, but merely by a rough averaging of the values in table 1.

The charge-flow polarizabilities also show a high degree of transferability, but do not lend themselves so easily to a simple description. They can be classified according to whether the functional groups concerned are methyl or methylene, and by the topological distance between them, that is, the number k of intervening C—C bonds. Thus we have the values $\alpha_{00}^{CH_3,CH_3}(k)$, $\alpha_{00}^{CH_3,CH_2}(k)$ and $\alpha_{00}^{CH_2,CH_2}(k)$. The polarizabilities in table 1 are listed in order of increasing k, and they decrease with increasing k as one would expect. However, the contribution of a charge-flow polarizability to the overall dipole polarizability depends on the square of the geometrical distance (i.e., through space) between the sites. Although this is not the same as the topological distance k, it tends to increase with k, so it is helpful to tabulate the quantity $k^2\alpha_{00}(k)$ (table 3).

From these values we extract the average values listed in table 4. We have used only the values for the all-*trans* alkanes, so that the other molecules can be used to test the resulting set of parameters. There is very little pattern to be discerned in the numbers in table 4, except that the methyl–methyl values are close to − 1·0 and show little sign of decreasing as k increases. The remaining values show a marked alternation in magnitude between odd and even k, and appear to decrease somewhat in magnitude as k increases. Note that because the distributed polarizabilities are accurate only to about 0·001 au, the numbers in table 4 have an error of about 0·001 k^2 au.

The values in tables 2 and 4 have been used as a model to calculate the overall mean polarizability $\bar{\alpha}$ and the polarizability anisotropy γ for all the molecules studied, including those conformers of hexane and heptane for which distributed polarizabilities were not calculated, and the all-*trans* conformers of octane and nonane. (γ is defined in terms of the polarizability tensor $\alpha_{\alpha\beta}$ by $\gamma^2 = \frac{1}{2}(3\alpha_{\alpha\beta}\alpha_{\alpha\beta} - \alpha_{\alpha\alpha}\alpha_{\beta\beta})$ [18].) For this purpose the values in table 4 were extrapolated, somewhat arbitrarily, by

Table 3. Values of $(i-j)^2\,\alpha_{00}^{ij}$ for the saturated hydrocarbons C_2H_6, C_3H_8, C_4H_{10}, C_5H_{12}, C_6H_{14} and C_7H_{16}. A square bracket '[' to the left of the value indicates that region i is a methyl group, and ']' to the right that region j is a methyl group.

i j	C_2H_6	C_3H_8	t-C_4H_{10}	g-C_4H_{10}	tt-C_5H_{12}	tg-C_5H_{12}	gg-C_5H_{12}	C_6H_{14}	C_7H_{16}
k = j − i = 1									
1 2	[−1·021]	[−0·807	[−0·798	[−0·799	[−0·798	[−0·793	[−0·793	[−0·797	[−0·797
2 3			−0·661	−0·672	−0·655	−0·656	−0·666	−0·655	−0·655
3 4						−0·666		−0·650	−0·649
4 5						−0·799]			
k = j − i = 2									
1 3		[−0·988]	[−0·672	[−0·624	[−0·656	[−0·656	[−0·616	[−0·652	[−0·656
2 4					−0·564	−0·408	−0·356	−0·556	−0·560
3 5						−0·604]			−0·552
k = j − i = 3									
1 4			[−0·828]	[−1·008]	[−0·306	[−0·558	[−0·747	[−0·288	[−0·288
2 5						−0·693]		−0·009	−0·000
k = j − i = 4									
1 5					[−1·040]	[−0·672]	[−0·640]	[−0·592	[−0·560
2 6									−0·432
k = j − i = 5									
1 6								[−0·775]	[−0·275
k = j − i = 6									
1 7									[−0·900]

Table 4. Approximate average values of $k^2 \alpha_{00}^{ab}(k)$ for the saturated hydrocarbons. k is the topological distance between a and b, i.e., the number of C—C bonds separating them. Values in parentheses are extrapolated for use with larger alkanes.

a	b	k =	1	2	3	4	5	6	7	8
CH_3	CH_3		−1·0	−1·0	−0·8	−1·0	−0·8	−0·9	(−1·0)	(−1·0)
CH_3	CH_2		−0·8	−0·66	−0·3	−0·57	−0·3	(0·0)	(0·0)	—
CH_2	CH_2		−0·66	−0·56	−0·1	−0·4	(−0·1)	(0·0)	—	—

Table 5. Values of mean polarizability and anisotropy calculated using coupled perturbed Hartree–Fock theory and using the model described in the text.

	Mean polarizability		Anisotropy	
Molecule	CPHF	Model	CPHF	Model
C_3H_8	38·065	37·710	5·566	7·808
g-C_4H_{10}	48·975	48·650	6·746	6·898
t-C_4H_{10}	49·431	49·167	10·561	11·707
gg-C_5H_{12}	59·891	59·450	7·596	6·391
tg-C_5H_{12}	60·422	60·058	12·510	12·159
tt-C_5H_{12}	60·873	60·596	15·211	15·419
ggg-C_6H_{14}	70·430	70·229	11·062	9·941
tgg-C_6H_{14}	71·045	70·763	12·322	9·576
gtg-C_6H_{14}	71·064	70·895	13·767	11·402
ttg-C_6H_{14}	71·727	71·607	16·284	14·429
tgt-C_6H_{14}	71·862	71·746	18·910	18·432
ttt-C_6H_{14}	72·418	72·545	21·139	21·676
ggg′g′-C_7H_{16}	81·673	81·018	11·625	6·653
tgg′t-C_7H_{16}	83·328	82·855	17·904	15·518
gttg-C_7H_{16}	83·383	83·719	19·271	19·146
tttg-C_7H_{16}	83·928	84·521	23·784	25·582
tttt-C_7H_{16}	84·424	84·834	26·326	28·119
ttttt-C_8H_{18}	95·688	95·266	33·227	29·583
tttttt-C_9H_{20}	107·392	107·288	39·407	35·595

supplying the values shown in parentheses. The results are shown in table 5 and figure 2. The notations g and g' are used to distinguish between dihedral angles of 60° and −60°. Although the values obtained from the model are not in exact agreement with the values calculated directly by CPHF theory, the trends are reasonably well reproduced. The variations in mean polarizability among the conformers of each molecule are reproduced quite well (RMS error 0·35 au), and the variations in γ are echoed qualitatively though rather exaggerated in magnitude, so that γ generally is too small for the *gauche* conformers. The RMS error in the γ values is 2·2 au.

The same model was used to calculate the induction energy of *gg*-pentane in the presence of a unit charge. Values were calculated for a grid of point-charge positions, some 1·2 Å and some 2·0 Å from the van der Waals surface. The induction energy was also calculated using the full set of distributed polarizabilities for *gg*-pentane, and figure 3 shows a plot of the model energy against the accurate value. The RMS error for the points at 1·2 Å from the van der Waals surface is 2·4%, and the maximum deviation is 5·7%. The errors are somewhat smaller for the points at 2·0 Å from the surface: 2·2% and 4·7%, respectively.

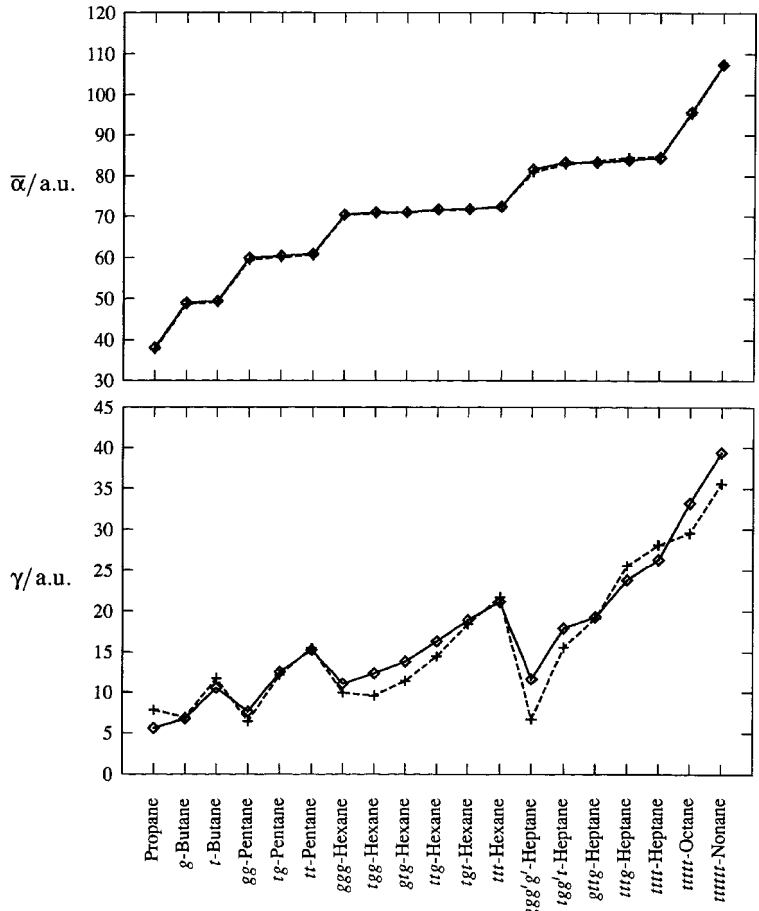


Figure 2. Mean polarizabilities (top) and anisotropies (bottom) for the normal alkanes. The diamond symbols show the CPHF values, and the crosses the values obtained from the localized model.

4. Conclusion

Distributed polarizabilities have been calculated for the normal alkanes C_nH_{2n+2} for n up to 7, and the dipolar polarizabilities have been transformed into a localized representation referred to local axes of coordinates for each carbon atom. The charge-flow polarizabilities have not been localized, because previous work [17] has shown that the resulting description in terms of local dipolar polarizabilities would not be transferable. When the charge-flow polarizabilities are left unlocalized, as in the present calculations, the localized dipole polarizabilities are highly transferable. The charge-flow polarizabilities are also transferable between similar environments, but they do not show any simple pattern with increasing distance between the sites.

We have extracted from the all-*trans* alkanes a set of charge-flow and local dipole polarizabilities. When used to determine the overall polarizabilities of a set of conformers of the alkanes up to $n = 7$, including a number of *gauche* conformers, the mean polarizabilities agree well with values obtained directly from coupled perturbed Hartree–Fock calculations on the same molecules. The values derived from the model are all slightly too low; this could be rectified by tweaking the parameters slightly, but

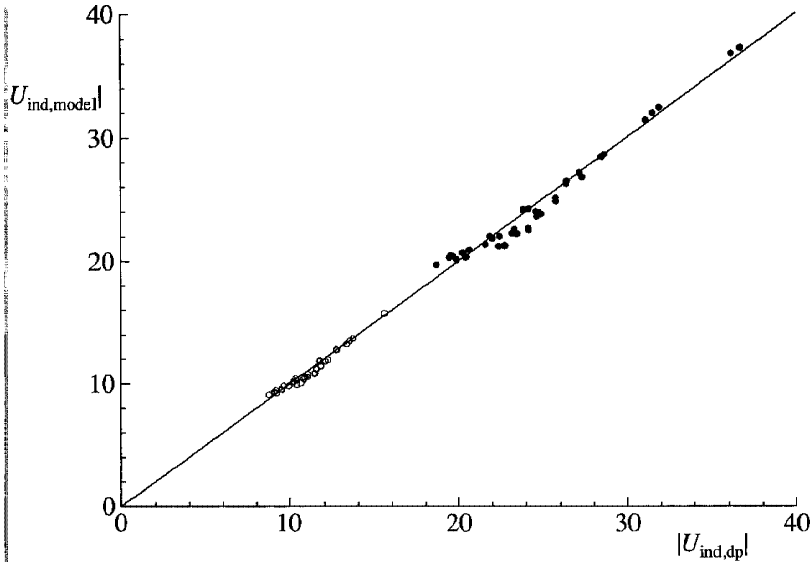


Figure 3. Induction energies in kJ mol^{-1} of *gg*-pentane in the presence of a unit point charge (i.e., a proton) at points 1·2 Å (filled circles) and 2·0 Å (open circles) from the van der Waals surface. Values calculated using full distributed polarizabilities are compared with values calculated using the simplified model described in the text.

the quality of the calculations probably does not justify attempts to fit the data more closely. The induction energies in the presence of a point charge also agree well with those calculated from the full set of distributed polarizabilities.

The polarizability anisotropy is less well described, being generally too small for those conformers that have many *gauche* bonds. We believe that this happens because although the model rolls up the secondary polarizations into the local polarizabilities, it is derived from the all-*trans* conformers and so fails to take into account the additional through-space secondary polarizations that arise in the sterically crowded *gauche* conformers. One way to improve the description might therefore be to use the localized distributed-multipole picture to describe the secondary interactions involving atoms separated by up to two or three bonds, but to use a formalism of the Applequist type to describe longer-range secondary effects. However, we have not yet had an opportunity to explore such an approach.

This paper is dedicated to Professor A. D. Buckingham on the occasion of his 65th birthday, and in acknowledgement of his profound contributions to the theory and measurement of polarizabilities and other molecular properties.

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