On the Hyperpolarisabilities of Some Alkylbenzenes

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The first and second hyperpolarisabilities of 12 methylbenzenes and five methyl derivatives of t-butylbenzene have been computed by employing the CHF-PT-EB-CNDO method. The effect of isomerism on these properties is discussed and a model has been defined to estimate and analyse the contribution to the second hyperpolarisability, γ, due to intramolecular interactions (between the substituents and the ring).

The hyperpolarisabilities β and γ of organic molecules are of current interest.[1–4] Particularly important is the problem of understanding the factors which influence the values of these properties, since the answer to such a question would provide valuable information concerning two fundamental molecular constants and would increase the possibility of synthesising materials with predefined non-linear electrical properties.

Two such factors are considered in detail in this work: the effect of structural changes and intramolecular interactions. For this study we have chosen several alkylbenzenes (methylbenzenes and methyl derivatives of t-butylbenzene). The various isomers considered clearly demonstrate the effect of varying the structure (and in particular its geometric elements) on β and γ. The great sensitivity of β to the above variations is also discussed.

The methyl group repels electrons and is an electron donor, thus the intramolecular interactions between this group and the benzene ring are important since the charge-transfer process has been instrumental in the analysis of several abnormally large non-linearities.[5–7] These interactions are discussed by defining a simple model.

The analysis reported in this work is based on computations of the hyperpolarisability components using our CHF-PT-EB-CNDO method.[8,9] Further, an approximation for γ, which leads to considerable savings of computer time, has been examined.

Computational Method

The computations of the hyperpolarisability components were performed using the CHF-PT-EB-CNDO method,[8,9] which relies on an extended basis (EB) CNDO wavefunction.[10] This is perturbed using the coupled Hartree–Fock perturbation theory (CHF-PT) of McWeeny *et al.*[11] An essential element in this computational approach is the use of basis sets which have been optimised with respect to property (polarisability and/or hyperpolarisability) values of some judiciously chosen compounds or models of them.

This method has given reasonable results for a large variety of molecules.[8,12–14] The present results have been calculated by employing for the benzene ring the orbitals[15] C: 2*s* (1.625), 2*p* (1.625); H: 1*s* (0.9), 2*s* (0.4223), 2*p* (0.4223), which have been optimised with respect to α (polarisability) and γ of benzene.[15] The adequacy of these functions has been confirmed in the case of naphthalene, for which there is good agreement between the computed (α = 128; γ = 48 300 a.u.)[3] and the experimental values (α = 112; γ = 61 900 ± 12 400 a.u.).[16,17] Furthermore these orbitals have given satisfactory results in several other cases.[3,8d] For the methyl and t-butyl groups the set[8a] C: 2*s* (1.625), 2*p* (1.625); H: 1*s* (1.0), 2*s* (0.5), 2*p* (0.5), was used. These functions gave polarisability and hyperpolarisability values in reasonably good agreement with the experimental results, for a series of alkanes.[8a] The underlying principle of the definition of the above basis set is a working hypothesis according to which it is possible to develop basis sets for complex molecules employing functions suitable for describing the properties of appropriately defined molecular fragments or models of them.[12] This rule helped to obtain good results on a number of occasions.[8d,12,14]

The mean first- and second-hyperpolarisability values are given by equations (1) and (2)[18]

$$\gamma = \tfrac{3}{5}(\beta_{zzz} + \beta_{zxx} + \beta_{zyy}) \qquad (1)$$

$$\gamma = \tfrac{1}{5}(\gamma_{xxxx} + \gamma_{yyyy} + \gamma_{zzzz} + 2\gamma_{xxyy} + 2\gamma_{xxzz} + 2\gamma_{yyzz}) \qquad (2)$$

where the suffixes *x*, *y*, and *z* denote cartesian components. The molecules are rotated so that their dipole moments coincide with the *z*-axis.

We have also used approximation (3) for γ. This approximate

$$\gamma \simeq \tfrac{1}{3}(\gamma_{xxxx} + \gamma_{yyyy} + \gamma_{zzzz}) = \gamma_d \qquad (3)$$

formula, which has been applied to more than 200 molecules, allows considerable savings in computer time [because it requires 50% less time than does equation (2)] without a major loss of accuracy. For example for the 19 compounds investigated, the properties of which are presented in the Table, the average difference between γ and γ_d is 2.6%. For completeness it is added that the range of applicability of equation (3) does not cover molecules in which the diagonal terms differ in sign. For such cases a suitable approximation has been proposed in ref. 19.

For the first hyperpolarisability we report values normalised with respect to toluene, since the basis sets used were optimised with respect to the polarisability and second hyperpolarisability values only. Such normalised values diminish the significance of any systematic error, while they allow the study of existing trends.

The convergence criteria for the iterative calculation of the zeroth-order density matrix $\boldsymbol{R}^{(0)}$, as well as the first- and second-order corrections to the density matrices, $\boldsymbol{R}^{(1)},\boldsymbol{R}^{(2)}$, have been given elsewhere.[9]

Results and Discussion

It can be seen from the Table that isomerism may have a large effect on the first hyperpolarisability. For example β′ values of 1,2,3- and 1,2,4-trimethylbenzene differ by a factor of 25 and in sign, while the β′ values of *m*-methyl-t-butylbenzene and *p*-methyl-t-butylbenzene have, approximateley, the same mag-

Table. The first and second hyperpolarisabilities of 12 methylbenzenes, t-butylbenzene, and 5 methyl derivatives of t-butylbenzene (in a.u.)

Compound[a]	β'^{b}	γ^{c}	γ_d	$\bar{\gamma}^{d}$	γ_a	$\bar{\gamma} - \gamma_a{}^{e}$
Benzene	0.0	$22\,300^{f,15}$ $24\,500 \pm 596^{g,22}$ $12\,800 \pm 6\,410^{g,23}$ $18\,600 \pm 2\,790^{g,24}$	23 500 (5.4%)	22 300	22 300	
Methylbenzene	1.00	28 500	30 000 (5.3%)	28 500	24 500	4 000 (14%)
1,2-Dimethylbenzene	11.7	37 400	37 700 (0.8%)	36 300	26 700	9 600 (26%)
1,3-Dimethylbenzene	9.38	38 100	39 800 (4.5%)			
1,4-Dimethylbenzene	0.0	33 500	34 900 (4.2%)			
1,3,5-Trimethylbenzene	0.02	41 700	43 300 (3.8%)	38 800	28 900	9 900 (26%)
1,2,3-Trimethylbenzene	−0.25	36 700	37 400 (1.9%)			
1,2,4-Trimethylbenzene	0.01	38 100	39 200 (2.9%)			
1,2,4,5-Tetramethylbenzene	0.0	41 900	42 700 (1.9%)	41 700	31 100	10 600 (25%)
1,2,3,4-Tetramethylbenzene	−0.91	40 300	40 900 (1.5%)			
1,2,3,5-Tetramethylbenzene	−1.09	42 800	43 900 (2.6%)			
t-Butylbenzene	1.71	43 200	44 400 (2.8%)	43 200	37 100	6 100 (14%)
Pentamethylbenzene	−1.19	44 500	44 100 (0.9%)	44 500	33 300	11 200 (25%)
Hexamethylbenzene	−0.34	47 700	48 400 (1.5%)	47 700	35 500	12 200 (26%)
o-Methyl-t-butylbenzene	1.35	51 500	52 500 (1.9%)	51 000	39 300	11 700 (23%)
m-Methyl-t-butylbenzene	0.45	50 100	50 800 (1.4%)			
p-Methyl-t-butylbenzene	−0.44	51 400	52 000 (1.2%)			
3,4-Dimethyl-t-butylbenzene	1.10	56 000	56 400 (0.7%)	56 250	41 500	14 750 (26%)
3,5-Dimethyl-t-butylbenzene	1.58	56 500	59 000 (4.4%)			

[a] The co-ordinates of the molecules were determined from data given in refs. (25) and (26). [b] These values were normalised with respect to the first hyperpolarisability value of toluene. [c] 1 a.u. of second hyperpolarisability = $0.503\,717 \times 10^{-39}$ e.s.u. = $0.6235\,97 \times 10^{-64}$ $C^4\,m^4\,J^{-3}$. [d] The values for $\bar{\gamma}$ were determined by taking the average of the γ values for the various isomers of the compound. [e] The numbers in parentheses represent the percentage of $\bar{\gamma} - \gamma_a$ in $\bar{\gamma}$. [f] This is a theoretical value determined by the CHF-PT-EB-CNDO method. The employed basis set is given in the text. [g] This is an experimental value.

nitude although differing in sign. On the other hand the results for the second hyperpolarisability show that this property is not greatly affected by isomerism. Thus the largest change observed is between the property values of 1,3,5- and 1,2,3-trimethylbenzene (*ca.* 5 000 a.u.).

We have defined $\bar{\gamma}$ as the average γ value of all the isomers of the same compound. Several functional forms have been tried to correlate $\bar{\gamma}$ with n (the number of methyl groups in a given methylbenzene). Thus we obtained:

$$\bar{\gamma} = 0.403 \times 10^4 n + 0.251 \times 10^5 \qquad (4)$$

$$\bar{\gamma} = -0.495 \times 10^3 n^2 + 0.700 \times 10^4 n + 0.227 \times 10^5 \qquad (5)$$

where the first function is associated with an average error of 5.1%, and the second with 2.5%. Further noted is the small change in γ, observed between the various isomers of the methyl derivatives of t-butylbenzene. It is also seen (Table) that progressive methylation of benzene leads to an increase in $\bar{\gamma}$, whereas the behaviour of β' is more complicated.

We have defined a simple model, which allows an estimate of the intramolecular interactions between the functional (methyl and t-butyl) groups and the benzene ring to be determined. Thus taking the experimental γ value of CH_4 as 2 890 a.u.,[20] we approximate the γ value of CH_3 as being three-quarters of the above value, that is *ca.* 2 200 a.u., while for the t-butyl group we note that γ for $CH(CH_3)_3$ is 15 500 a.u. (theoretical estimate determined by the CHF-PT-EB-CNDO method). Thus γ-$[(CH_3)_3C]$ = (15 500 − 700) a.u. = 14 800 a.u., where 700 a.u. (this is a quarter of the methane hyperpolarisability value) is the approximate γ value for the C–H bond. Employing the above second hyperpolarisability values for the substituents, γ_i, and the benzene value for the ring, $\gamma(C_6H_6)$, we approximate the hyperpolarisability, γ_a, of the substituted benzenes by:

$$\gamma_a = \gamma(C_6H_6) + \sum_i \gamma_i \qquad (6)$$

The difference $\bar{\gamma} - \gamma_a$ gives a measure of the effect of the intramolecular interactions on the hyperpolarisability. In particular it is noted that since the methyl group is electron-repelling and a weak donor[21a] a considerable part of $\bar{\gamma} - \gamma_a$ is likely to be due to charge-transfer interactions.

From the results given in the Table it can be observed that the contribution $(\bar{\gamma} - \gamma_a)/n$, which is associated with each methyl group, has a maximum value at dimethylbenzene and then decreases. The results (Table) show that $\bar{\gamma} - \gamma_a$ for the methyl-t-butylbenzene has a value between that of $C_6H(CH_3)_5$ and $C_6(CH_3)_6$, while this property for the dimethyl-t-butylbenzenes is larger than that of $C_6(CH_3)_6$, demonstrating the larger changes induced in the charge distribution by $(CH_3)_3C$ compared with CH_3. It was also found that the average relative second hyperpolarisabilities of CH_3 and $(CH_3)_3C$ are 0.34 ± 0.3 and 3.19 ± 2.36, respectively.[21b] Furthermore it is known that the inductive effect of a t-butyl group is larger than that which corresponds to CH_3.[21c] The above indices and the inductive effect may be used to rationalise the larger effect of $(CH_3)_3C$ compared with that of CH_3 on the hyperpolarisability values of the molecules containing these groups.

Conclusions

The present results demonstrate the effect of progressive methylation of benzene on the first and second hyperpolarisabilities. It has been shown that $\bar{\gamma}$ increases with increasing n, while the emerging pattern for the first hyperpolarisability results is more complicated. This illustrates the considerable sensitivity of β to changes in structure. It has been observed that isomerism has, in general, a rather small effect on γ, but its effect on the first hyperpolarisability is remarkable. Overall it is noted that changes in geometry may have a profound effect on the first hyperpolarisability, while they have a rather small effect, in general, on the second hyperpolarisability. The above observations may be rationalised by invoking the scalar nature of γ, while β is a component of a vector.

It is shown that the effect of the intramolecular interactions, which are associated with each methyl group and the ring, reaches a maximum when $n = 2$ (two methyl groups) and then continuously decreases as n increases. It has been estimated that $\bar{\gamma} - \gamma_a$ (which represents the effect of the intramolecular interactions between the substituents and the ring) varies between 23 and 26% of $\bar{\gamma}$, except for toluene, in which it is 14%.

In summary, an attempt has been made to correlate, semi-quantitatively, the variations of molecular structure with the induced changes in the molecular hyperpolarisabilities. Understanding of these relationships is very useful for the design of appropriate materials for devices in non-linear optics.

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