Semiempirical Calculations of the Static Electric Hyperpolarizabilities of Benzene *

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Second hyperpolarizability values of benzene are calculated using the "finite perturbation theory" and the CNDO/2, MINDO/1 and MINDO/2 methods.

According to the "finite perturbation theory" [1–7] the static electric hyperpolarizabilities of a molecule in its electronic ground state are accessible from [8]

$$\mu_i = \mu_i^0 + \alpha_{ij} F_j + \tfrac{1}{2}\beta_{ijk} F_j F_k + \tfrac{1}{6}\gamma_{ijkl} F_j F_k F_l + \ldots, \quad i,j,k,l = x,y,z, \qquad (1)$$

where $\mu_i(\mu_i^0)$ are its dipole moment in the presence (in the absence) of an external uniform electric field F_i, α_{ij} its polarizability tensor, and β_{ijk} and γ_{ijkl} its first and second hyperpolarizability tensors.

From (1) in conjunction with the CNDO/2 [9], MINDO/1 [10], and MINDO/2 [10] method we have calculated the non-zero γ_{ijkl} components for benzene. They are listed in Table 1. For completeness, the Table further includes the obtained α_{ij} components. All β_{ijk} components vanish by symmetry. In addition, the mean values $\bar{\alpha}$ and $\bar{\gamma}$ defined as [11]

$$\bar{\alpha} = \tfrac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}), \qquad (2)$$

$$\bar{\gamma} = \tfrac{1}{5}(\gamma_{xxxx} + \gamma_{yyyy} + \gamma_{zzzz} + 2\gamma_{xxyy} + 2\gamma_{xxzz} + 2\gamma_{yyzz}) \qquad (3)$$

are given.

The comparison of the γ_{ijkl} values emerging from the various valence electron methods shows that values belonging together always agree in sign. The largest values are due to MINDO/1 and the smallest ones to CNDO/2. The same trend has been observed for the α_{ij} values [§] and for the first and second hyperpolarizabilities of a variety of molecules [12]. Experimental hyperpolarizabilities are scarce and rather uncertain. For benzene, two experimental estimates are known (cf. the Table). These values nicely join the MINDO ones. On the other hand, the striking discrepancy between the γ_{ijkl} values of Sen and Basu [13] (using a simple perturbational treatment in conjunction with a free-electron method) and both our and the experimental values must be noted. It is further worth mentioning that the γ_{xxxx} ($= \gamma_{yyyy}$) value previously derived by one of us [14] using the "finite perturbational" approach in the framework of a Pople π-electron treatment reasonably agrees with the new results arising from the valence electron procedures.

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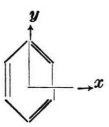
Table 1. Polarizabilities α_{ij} (in 10^{-24} cm^3) and second hyperpolarizabilities γ_{ijkl} (in 10^{-36} cm^7/esu^2) of benzene [a].



	CNDO/2	MINDO/2	MINDO/1	π-Electron methods Ref. [13]	Ref. [14]	Experimental	
$\alpha_{xx}=\alpha_{yy}$	5.46	9.98	14.14	3.7 [b]	6.84	12.31 [16]	11.12 [17]
α_{zz}	1.08	2.03	2.66			6.35 [16]	7.37 [17]
$\bar{\alpha}$	4.00	7.33	10.31			10.32 [16]	9.87 [17]
$\gamma_{xxxx}=\gamma_{yyyy}$	0.42	2.6	14.5	−111.89	1.4		
γ_{zzzz}	0.01	0.02	0.09	−40.57			
$\gamma_{xxzz}=\gamma_{yyzz}$	0.14	0.88	2.03	−37.25			
γ_{xxyy}	0.23	1.03	5.42	−37.30			
$\bar{\gamma}$	0.37	2.2	9.6	−97.59		6±3 [18]	−3±6 [19]

[a] Experimental bond lengths are used in the calculations. [b] Taken from Ref. [15].

* Part 17 of "Properties of Molecules in Electric Fields". Part 16: H. Meyer, K.-W. Schulte, and A. Schweig, Chem. Phys. Lett. **31**, 187 [1975].

§ see Ref. [4] and the Table in this paper.

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