The second hyperpolarizability of 1-nitronaphthalene

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We have decided to study the electronic contribution γ^e to the total second hyperpolarizability γ of 1-$C_{10}H_7NO_2$ for the following reasons:

(i) It has been argued that γ^e of 1-$C_{10}H_7NO_2$ is expected to be small and thus its contribution to γ can be neglected.[1] In many cases, including $C_6H_5NO_2$, this is a good approximation. However an examination of nine monosubstituted benzene derivatives—including the following substituents: F, Cl, Br, I, NO$_2$ CN, NH$_2$ N(CH$_3$)$_2$ and OH—has shown that γ^e of the derivative is larger than γ^e of the parent (unsubstituted) molecule.[2] It should also be noted that γ^e of the parent (unsubstituted) molecule.[2] It should also be noted that γ^e of $C_{10}H_8$ (naphthalene) is 61 900 a.u. while γ (at 110 °C) for 1-$C_{10}H_7NO_2$ is 222 000 a.u.[1]

(ii) There are few experimental data available for γ^e of organic molecules.[2–5] Furthermore the experimental determination is associated with various uncertainties of which the most significant is the choice of the appropriate local field model.[4] However, quantum mechanical computations of isolated systems may be useful for the establishment of a reliable and, if possible, generally applicable local field model.

(iii) Substituent effects on the electric properties of multiring aromatic systems have received very little attention. The most notable case is Bethea's study.[1]

For the computations reported here the CHF-PT-EB-CNDO procedure has been employed.[6–8] This method has been demonstrated to succesfully predict the polarizabilities and hyperpolarizabilities of some alkanes, polyenes, and aromatics.[6–8] The following basis set has been used for the calculations herein:

C: 2s(1.325), 2p(1.325),

H: 1s(0.8), 2s(0.4), 2p(0.4),

N: 2s(1.95), 2p(1.95),

O: 2s(2.275), 2p(2.275).

The exponents for C and H allowed a reasonable description for the charge polarization of some unsaturated systems[7] while the exponents, for N and O, are given by the Slater rules.[9]

The suitability of this basis for the proposed problem has been checked by using $C_6H_5NO_2$ as a test case. The reasonably accurate description of μ, α, and γ^e for $C_6H_5NO_2$ denotes that the essential characteristics of both the unperturbed and the perturbed charge cloud are appropriately considered (Table I). It is also observed that the values of the dipole moment for 1-$C_{10}H_7NO_2$ and 2-$C_{10}H_7NO_2$ are in remarkably good agreement with the experimental values (Table II). This is a further indication that the wave function provides a balanced description of the charge cloud.

It is noted that the ratio

$$\gamma^e/\gamma$$

TABLE I. The dipole moment (in D), polarizability, and hyperpolarizability (in a.u.) of $C_6H_5NO_2$.[a]

Property[b]	CHF-PT-EB-CNDO	Experiment
μ	4.1	4.1[c]
α	91.3	87.0[d]
γ^e	49 400	46 000[e]

[a] Conversion factors of a.u. to e.s.u. and SI are given in (Ref. 6–8).
[b] The geometry of $C_6H_5NO_2$ is from (Ref. 13).
[c] Reference 11.
[d] Reference 10.
[e] Reference 2.

has the values 0.15,[3] 0.11,[2] and 0.06[10] (this value is determined by employing a bond additivity estimate for γ^e) for $C_6H_5NO_2$, while for 1-$C_{10}H_7NO_2$ the values are 0.55 (383 K) and 0.48 (355 K) (Table II, and Ref. 1). That is, the present computations show that γ^e of 1-$C_{10}H_7NO_2$ makes quite an essential contribution to its total hyperpolarizability.

An interesting consequence of this γ^e value is the change in the value of β which will be only half (approximately) compared to that which has been reported.[1] Thus from the equation[1]

$$\gamma = \gamma^e + \frac{\mu\beta}{5KT},$$

where K is Boltzmann's constant and T the absolute temperature, we find $\beta = 116$ a.u. for $\mu = 4.1$ D[1] and $\beta = 139$ a.u. for $\mu = 3.3$ D, using the experimental γ ($T = 355$ K).

It is known that straightforward comparison of theoretical β values with experimental ones does not make sense, due to the pronounced sensitivity of this nonlinearity on environmental interactions.[16]

However, the reported β values contain the local field effects (since they are determined employing the experimental γ) and thus they are directly comparable with an experimentally determined one.

The hyperpolarizability γ^e being a very sensitive property, can be used to probe the effect of ring B[12] on the electron cloud of the remaining nitro substituted fragment. It is, thus, observed that ring B has a considerable effect on the

TABLE II. The dipole moments (in D), the polarizabilities and the electronic contribution to the second hyperpolarizabilities of 1-$C_{10}H_7NO_2$ and 2-$C_{10}H_7NO_2$ in a.u.

Molecule[a]	μ	α	γ_e
1-$C_{10}H_7NO_2$	3.3, 3.3[b], 4.1[c]	164	122 000
2-$C_{10}H_7NO_2$	4.6, 4.4[b]	167	129 000

[a] The geometry of 1-$C_{10}H_7NO_2$ and 2-$C_{10}H_7NO_2$ is from Ref. 13.
[b] Reference 14.
[c] Reference 1.

perturbed (by the uniform electric field) charge cloud of the other fragment. The remarkable difference between γ^e of $C_6H_5NO_2$ and 1-$C_{10}H_7NO_2$ (Tables I and II)—much larger than the difference between γ^e of C_6H_6 and $C_{10}H_8$ which is $\sim 35\ 000$ a.u.[1,8,10]—indicates that the induced moment in ring B increases the charge transfered from ring A to the nitro group. The results of Table II show that remarks similar to that for γ^e also apply to α.

Finally, the comparison of the properties of 1-$C_{10}H_7NO_2$ and 2-$C_{10}H_7NO_2$ demonstrates that isomerism has a small effect on the magnitude of γ^e and an even smaller effect on α. The difference in sensitivity between α and γ^e can be understood by perturbation theory arguments according to which γ^e is proportional to the inverse of the third power of state energy differences while α is inversely proportional to the first.[14]

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On the spherical representation of the polarizability tensor of an ensemble of interacting molecules within the DID model. Comparison with previous results

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The electric polarizability of a system of N correlated molecules is not restricted to the simple sum of the polarizabilities of all N molecules. Their mutual interactions give rise to changes in the polarizational properties of the system as a whole.[1] The interaction-induced contribution ΔA to the polarizability tensor within the dipole-induced dipole (DID) model has been widely and successfully applied to the description of absorption and scattering of electromagnetic radiation[2–9] as well as other processes in which the interactions of atoms and molecules are significant. In the lowest-order DID, the contribution ΔA for an N-molecular sample has the form (in Cartesian representation)[1–4]:

$$\Delta \mathbf{A} = \sum_{i}^{N} \sum_{j \neq i}^{N} {}^{i}\boldsymbol{\alpha} \cdot \mathbf{T}(\mathbf{r}_{ij}) \cdot {}^{j}\boldsymbol{\alpha}, \tag{1}$$

where ${}^{i}\boldsymbol{\alpha}$ denotes the ith molecule's intrinsic polarizability tensor and $\mathbf{T}(\mathbf{r}_{ij})$ the tensor of interaction of two electric dipoles distant by $\mathbf{r}_{ij}$.

The spherical tensor representation of ΔA has been given in several recently published papers.[3–7] However, the formulas proposed there are mutually divergent. Moreover, in some cases their analytical forms have been derived inconsistently or even incorrectly.

In our opinion, because of the generally accepted importance and applicability of the DID model[3,4,8] (e.g., numerical simulation of a fluid of interacting molecules), the spherical representation of ΔA should be reanalyzed.

The l,λ ($|\lambda| \leqslant l$) component of the spherical tensor $\Delta A^{(l)}$ is obtained by direct transformation of Eq. (1) into spherical basis

$$\Delta A_{\lambda}^{(l)} = 5^{1/2} \sum_{\substack{i,j \\ (i \neq j)}}^{N} \sum_{l_1,l_2,h} (-1)^{l+h} [l_1\, l_2\, h]\begin{Bmatrix} l_1\, l\, h \\ 1\, 1\, 1 \end{Bmatrix}$$
$$\times \begin{Bmatrix} 2\, l_2\, h \\ 1\, 1\, 1 \end{Bmatrix} \{ {}^{i}\boldsymbol{\alpha}^{(l_1)} \otimes (\mathbf{T}^{(2)}(\mathbf{r}_{ij}) \otimes {}^{j}\boldsymbol{\alpha}^{(l_2)})^{(h)} \}_{\lambda}^{(l)}. \tag{2a}$$

This natural automatic coupling scheme of the tensors is inconvenient when separation of the translational and orientational degrees of freedom is required. However, by some recoupling algebra, we obtain from Eq. (2a):

$$\Delta A_{\lambda}^{(l)} = 5^{1/2} \sum_{\substack{i,j \\ (i \neq j)}}^{N} \sum_{l_1,l_2,H} (-1)^{l_1+l+H} [l_1\, l_2\, H] \begin{Bmatrix} l\, 2\, H \\ 1\, 1\, l_2 \\ 1\, 1\, l_1 \end{Bmatrix}$$
$$\times \{ \mathbf{T}^{(2)}(\mathbf{r}_{ij}) \otimes ({}^{i}\boldsymbol{\alpha}^{(l_1)} \otimes {}^{j}\boldsymbol{\alpha}^{(l_2)})^{(H)} \}_{\lambda}^{(l)}, \tag{2b}$$

In the above expressions

$$\begin{Bmatrix} abc \\ def \end{Bmatrix} \text{ and } \begin{Bmatrix} abc \\ def \\ ghi \end{Bmatrix}$$

denote 6j and 9j coefficients, respectively, and

$$[ab...f] = \{ (2a+1)(2b+1)...(2f+1) \}^{1/2}.$$

The tensors ${}^{i}\boldsymbol{\alpha}^{(l)}$, $\mathbf{T}^{(2)}(\mathbf{r}_{ij})$, and ${}^{j}\boldsymbol{\alpha}^{(l)}$ are the spherical equiv-