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Comparative Study of Optical Nonlinearities in Substituted Polyynes versus the Corresponding Polyenes and Polyphenyls

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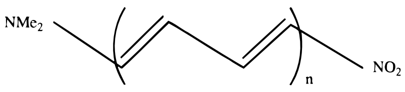
The frequency-dependent polarizability, hyperpolarizability, and second hyperpolarizability of a series of donor−acceptor polyynes (**III**) have been calculated by the correction vector approach, using both singly and doubly excited configurations. The results are compared with those obtained for the corresponding polyenes (**I**) and polyphenyls (**II**). Both the SHG and THG coefficients of the polyynes (**III**) are predicted to be significantly larger than those of the polyphenyls (**II**) but inferior to those of the polyenes (**I**) at this level of theory. The inclusion of doubly excited configurations in the evaluation of the hyperpolarizability tensor for the polyynes increases the absolute value relative to calculations which include singly excited configurations alone, but the reverse is true for the polyenes where the absolute value decreases with the inclusion of doubly excited configurations.

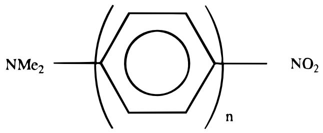
Introduction

Molecules and materials possessing large nonlinear optical (NLO) properties are of interest in materials science and technology because of their potential optoelectronic applications.[1] While the ultimate suitability of a molecule or material can only be decided by actual experiment, the theoretical calculation and analysis of the desired properties at the microscopic level can be a powerful tool for aiding basic design and may help narrow the area of search when developing a material for specific applications. This approach has led to a considerable number of theoretical studies on the nonlinear optical properties of organic molecules, using a variety of methods.[2−13]

In earlier papers we examined the first hyperpolarizabilities of donor/acceptor substituted polyenes (**I**),[14] polyphenyls (**II**),[14] and polyynes (**III**)[15] using a singly excited configuration interaction treatment. The NLO coefficients were calculated by the sum-over-states (SOS) method[16,17] using a large number of singly excited configurations generated in order of increasing energy with the ground state represented by a CNDO Hartree−Fock determinant. This level of theory has been generally accepted to be adequate for computing the electronic spectra and NLO properties of these systems. However, the inclusion of higher-order configurations is necessary to get a good description of the second hyperpolarizability, and our recent studies[18,19] have confirmed that it is also essential for many organic compounds if an adequate representation of the electronic spectrum is to be obtained. This is particularly true in the study of the electronic spectra and nonlinear optical properties of unsubstituted polyenes where it is known that the electron correlation contributions are strong.[18] In these systems the effect of the large electron correlations has been seen in both the electronic spectra, where it manifests itself in lowering one of the dipole-unallowed states (2^1A_g) below the lowest dipole-allowed state (1^1B_u) and in the nonlinear optical properties, where the sign of the THG coefficients from calculations which include the electron correlations are different from those which do not.[18] It is to be expected that the effects of electron correlation observed in the unsubstituted systems will also be present in the substituted molecules.



I



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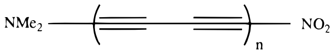

III

In this paper we have reexamined the linear and nonlinear optical properties of the donor−acceptor polyynes (**III**) and compared the results with those obtained previously for the polyenes (**I**) and the polyphenyls (**II**) using singly and doubly excited configuration interaction (SDCI) calculations. The NLO coefficients reported in this paper have been computed using the correction vector method, which is much more efficient than the conventional SOS procedure used in earlier studies. Details of the computational procedure are briefly described in the next section (for details see ref 18).

Computational Scheme

The CNDOVSB method,[14,17] which is based in part on the CNDO/S[20] and CNDO/UV[21] methods, was used in the present study because it gives a good description of the dipole moment, transition energies, and the corresponding oscillator strengths of a wide range of conjugated organic molecules. Limited correlations are included by including all possible singly and

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doubly excited configurations generated from an active space formed by six occupied π-orbitals and four unoccupied π^*-orbitals. Such an active space has been used in our earlier calculations on the NLO properties of organic systems and has been proven to be adequate.[19] The linear and nonlinear optical properties reported in this paper are the frequency-dependent polarizability, the first hyperpolarizability $\beta(2\omega,\omega,\omega)$, and the second hyperpolarizability $\gamma(3\omega,\omega,\omega,\omega)$. The NLO coefficients have been computed using the correction vector approach briefly described below.

The first-order correction to the ground state eigenfunction, $|\mathrm{G}\rangle$, obeys the equation

$$(H - E_{\mathrm{G}} \pm \hbar\omega)\phi_i^{(1)} = -\mu_i|\mathrm{G}\rangle \qquad (1)$$

where $|\mathrm{G}\rangle$ represents the ground state eigenfunction after the CI calculation, E_{G} is the corresponding ground state energy, and μ_i is the component of the dipole operator. The solution of the above equation can be obtained by expanding the first-order correction vector $\phi_i^{(1)}$ in terms of the same set of configurations used as the basis for the calculation of the unperturbed ground and excited states. Since this set of configurations forms a linearly independent basis, it is possible to match the set of coefficients and obtain a set of linear inhomogeneous equations. Solving the equations gives the first-order correction vector $\phi_i^{(1)}$. The polarizability and the first hyperpolarizability can be written in terms of the first-order correction vector as

$$\alpha_{ij} = \langle\phi_i^{(1)}(\omega)|\mu_j|\mathrm{G}\rangle + \langle\mathrm{G}|\mu_i|\phi_j^{(1)}(-\omega)\rangle \qquad (2)$$

$$\beta_{ijk} = {}^1/_8 P\,\langle\phi_i^{(1)}(-2\omega)|\mu_j|\phi_k^{(1)}(-\omega)\rangle \qquad (3)$$

where P is the permutation operator implying the addition of terms generated when the coordinates and the frequencies are permuted. In order to compute the second hyperpolarizability, γ, one has to solve for the second-order correction to the ground state which obeys the following equation,

$$(H - E_{\mathrm{G}} \pm \hbar\omega)\phi_{ij}^{(2)}(\omega,\omega) = -\mu_j\phi_i^{(1)}(\omega) \qquad (4)$$

Solution to eq 4 is exactly analogous to the solution of eq 1. The second hyperpolarizability γ can now be written in terms of the first- and second-order correction vectors $\phi_i^{(1)}$ and $\phi_{ij}^{(2)}$ as

$$\gamma_{xxxx}(3\omega;\omega,\omega,\omega) - {}^1/_8[\langle\phi_x^{(1)}(-3\omega)|\mu_x|\phi_{xx}^{(2)}(-2\omega,-\omega)\rangle + \omega \rightarrow -\omega] \qquad (5)$$

where $\omega \rightarrow -\omega$ indicates the same matrix elements with new arguments. The linear inhomogeneous equations were solved using the Gauss−Seidel iterative procedure for positive ω, and the scheme due to Ramasesha[22] has been used to solve the equations for negative ω's. The molecular geometries of the donor acceptor polyynes (**III**) used in the present calculation were those adopted previously in our earlier studies.[14,15] The crystallographic data from which the polyphenyl structures were derived indicate that the rings lie in one plane, the most favorable arrangement for high hyperpolarizabilites.[14] If different conformations exist in solution or in other phases, the effect should be to further reduce their values.

Results and Discussion

We have used 325 singly and doubly excited configurations in our calculations, generated between 10 active π-orbitals in all the molecules. The justification for this selection is based on earlier work where it has been demonstrated that the electronic and nonlinear optical properties of most conjugated systems such as the polyenes (**I**), polyphenyls (**II**) are dominated by the π-electron contributions from the p_z orbitals on each atom. In contrast to the polyenes (**I**) and polyphenyls (**II**), which contribute one π-orbital per atom, the polyynes (**III**) belong to a different category where each of the carbon atoms donates two π-orbitals, the p_y and p_z orbitals. However to be consistent with previous studies, we have chosen an active space of 10 π-orbitals and generated all singly and doubly excited configurations within the chosen active space. While the active space in the case of polyenes (**I**) and polyphenyls (**II**) contains only the p_z π-orbitals, the active space in the case of polyynes (**III**) contains both p_y and p_z orbitals. It would therefore be desirable to make a further systematic examination of larger active spaces, but this is not at present possible because of the rapid escalation of the number of configurations with the number of orbitals. The present choice is sufficiently large to allow for the inclusion of some interaction between the orthogonal sets of π-orbitals. Such a calculation has been found to be adequate for obtaining reliable values of the NLO coefficients of most donor-acceptor chromophores.[19,23]

TABLE 1: Frequency-Dependent Polarizability (in 10^{-23} esu), SHG Hyperpolarizability (in 10^{-30} cm^{-5} esu), and THG Hyperpolarizability (in 10^{-36} esu) of Polyenes (I), Polyphenyls (II), and Polyynes (III) at an Excitation Energy of 0.65 eV[a]

	polyenes			polyphenyls			polyynes		
n	α	β_{vec}	γ	α	β_{vec}	γ	α	β_{vec}	γ
1	3.5	18.1	3.9	2.0	11.4	1.7	2.7	17.6	3.7
2	10.4	105.2	104.6	4.1	34.8	8.7	7.0	58.0	25.0
3	21.3	326.9	1 566.9	5.8	65.0	28.5	12.2	107.5	74.1
4	35.8	874.3	−11 554	7.0	95.7	49.1	17.7	168.3	151.2
5	54.0	1970.1	−10 486	8.9	106.7	75.5	22.9	236.8	257.1
6	76.1	4072.2	−18 833	10.4	117.1	92.6	27.6	313.6	394.1
7	98.4	7289.7	−51 021	11.7	140.0	121.2	31.7	393.4	553.7
8	122.6	12038	91 129	11.2	191.4	219.4	35.1	477.4	735.9
9				15.7	152.3	165.2	38.0	564.6	939.0
10							40.3	655.2	1161.8

[a] The values for the polyenes and polyphenyls from ref 19 have been included for completeness.

The computed values of $\alpha(\omega,\omega)$, $\beta(2\omega,\omega,\omega)$, and γ-$(3\omega,\omega,\omega,\omega)$ for the donor acceptor polyynes (**III**) with varying chain lengths are given in Table 1. The quantities given in the table represent the dominant component of the frequency-dependent polarizability, the vector component of the SHG hyperpolarizability defined by

$$\beta_i = \beta_{iii} + {}^1/_3\sum_{j\neq i}(\beta_{ijj} + 2\beta_{jji}) \qquad (6)$$

and the scalar component of the THG hyperpolarizability defined by

$$\langle\gamma\rangle = {}^1/_5\Big[\sum_i \gamma_{iiii} + {}^1/_3\sum_{i\neq j}(\gamma_{iijj} + \gamma_{ijij} + \gamma_{ijji})\Big] \qquad (7)$$

First Hyperpolarizabilities

There have been a number of previous comparisons of the SHG hyperpolarizabilities of donor acceptor polyynes (**III**) versus polyenes (**I**) at the sum-over-states level but all have used singly excited configurations only.[15,24,25] In an AM1 study on closely related structures containing the amino group in place of the dimethylamino group, it was found that the polyenes had calculated SHG values which were only 2−3 times larger than those calculated for the corresponding polyynes at extended chain length. For example, for the polyene where $n = 4$, the

TABLE 2: Dipole Moments and Excitation Energies of Polyenes (I), Polyphenyls (II), and Polyynes (III)[a]

	polyenes		polyphenyls		polyynes	
n	μ_g	λ_{max}	μ_g	λ_{max}	μ_g	λ_{max}
1	11.93	392.5	9.03 (6.4)	333.4 (376)	9.79	330.0
2	15.47	503.6	9.72 (5.5)	369.5 (390)	11.07	383.6
3	17.95	600.5	9.96	382.8	11.68	407.4
4	19.78	658.6	10.13	384.0	12.01	414.9
5	21.14	712.5	10.19	390.2	12.19	415.6
6	22.55	759.3	10.22	390.0	12.36	415.0
7	23.88	790.9	10.24	390.1	12.43	413.4
8	24.03	816.6	10.33	377.0	12.49	410.1
9	25.58		10.34	391.7	12.52	406.3
10	24.97				12.54	400.7

[a] The values in parentheses are the experimental values from ref 26. The values of n are to be interpreted in terms of structures **I**, **II**, and **III** in Chart 1. μ_g is the ground state dipole moment in debye; λ_{max} is the absorption maximum in nanometers of the first allowed optical transition.

value was calculated to be 2.64 times larger than the related polyyne.[24] In contrast, in a different study by one of us using the CNDOVSB method, the SHG coefficients for the polyenes (**I**) were calculated to be considerably larger than those calculated for the corresponding polyynes (**III**) at extended chain length.[15] For a similar case where $n = 4$, the polyene (**I**) has a calculated value which is 11 times larger than the polyyne (**III**), and this difference increases with increasing chain length so that when $n = 6$ the SHG coefficient is some 40 times larger.[15]

The inclusion of doubly excited states in these calculations would be expected to dramatically improve the quality of the calculated results for reasons given earlier. A comparison of the β_{vec} values of the polyynes (**III**) versus the polyenes (**I**) and polyphenyls (**II**) obtained in the present studies as a function of the number of double bonds, n, shows that at short chain lengths with $n = 1$, there is little to differentiate between the aliphatic systems, but the value for the aromatic system is smaller. However, on chain extension, the values for the polyynes (**III**) increase in a gradual fashion and exceed those calculated for the polyphenyls by a factor of 2−3 (Table 1). The corresponding values for the polyenes (**I**), however, increase sharply with increasing chain length partly because of their large red shift in the λ_{max} values (Table 2), as discussed previously. There is only one dominant charge transfer state for the donor−acceptor polyenes (**I**) and polyphenyls (**II**), but as has been noticed previously,[15,24] in the polyynes there is more than one state with large oscillator strength. These additional states are known to reduce the NLO coefficients of the polyynes by contributing negatively to the overall value by opposing the usual direction of charge transfer along the chain from donor to acceptor. The absorption maximum of the longer polyynes tends to reduce at longer chain lengths because of saturation effects.

The inclusion of doubly excited configurations in the evaluation of the hyperpolarizability tensor for the polyynes (**III**) has little impact on the overall value at short chain lengths with values for $n = 2$ of 61.2 (singly excited configurations only)[15] versus 58.0 (Table 1; singly and doubly excited configurations). However, at longer chain length their inclusion and effect is more noticeable with corresponding values for $n = 6$ of 171 for the former[15] versus 314 for the latter (Table 1). The calculations involving singly excited states only therefore appear to *underestimate* the hyperpolarizabilities of the polyynes. The values for the corresponding polyenes (**II**), however, show an entirely different trend with the inclusion of doubly excited states . Thus for $n = 6$, the SHG coefficient of the polyene (**I**) obtained with singly excited configurations only,[15] reduces from 6810 to 4072 with the inclusion of doubly excited configurations (Table 1). It follows that calculations involving singly excited states *overestimate* the hyperpolarizability of the polyenes, and the differences between the hyperpolarizabilities of the polyenes (**I**) and polyynes (**III**) are therefore reduced with the inclusion of doubly excited states.

Second Hyperpolarizabilities

The calculated THG coefficients of donor acceptor polyynes (**III**) have not previously been reported though it is well-known that important related systems such as the polyacetylenes and diacetylenes show very large third-order effects.[1] The results obtained show that the polyynes (**III**) have much larger hyperpolarizabilities than the polyphenyls (**II**) at all chain lengths explored with values at least 3 times larger, but substantially smaller values than the polyenes (**I**) (Table 1). A direct comparison of the polyynes (**III**) with the polyenes (**I**), however, is not straightforward because some of the polyene coefficients are strongly affected by resonance effects. For example, at $n = 4$, the tripled photon energy ($3\omega = 1.95$ eV) is comparable to the excitation energy from the ground state of the polyene to the charge transfer state ($\omega_{ng} = 659$ nm or 1.88 eV, Table 2), with the consequence that the denominator of eq 5 which contains expressions such as ($\omega_{ng} - 3\omega$) becomes very small and negative and the corresponding hyperpolarizability becomes very large and also negative in this case (Table 1). This effect does not occur in the polyynes because the longest predicted excitation energy from the ground state to the charge transfer state is far from resonance (ω_{ng} is a maximum for $n = 4 - 6$ with a value of 415 nm or 2.98eV; Table 2). However, a comparison of the off-resonance values of the polyenes at short chain lengths of $n = 1-3$ (where $\omega_{ng} \gg 3\omega$) shows that the THG coefficients are comparable to the donor polyphenyls (**I**) and r-acceptor polyynes when $n = 1$, but thereafter the values are an order of magnitude larger.

To conclude, we have demonstrated from semiempirical calculations involving both singly and doubly excited configurations that the donor−acceptor polyynes (**II**) are much more efficient SHG and THG systems than the corresponding polyphenyls (**I**) but less efficient than the corresponding polyenes (**I**) partly because there is no appreciable resonance enhancement of the hyperpolarizability in the former case.

References and Notes

(1) See for example: (a) *Chem. Rev.* **1994**, *94*, 1−278. (b) *Nonlinear Optical Properties of Organic Molecules and Crystals;* Chemla, D. S., Zyss, J., Eds.; Academic: New York, 1987. (c) *Nonlinear Optical Effects in Molecules and Polymers*; Prasad, P. N., Williams, D. J., Eds.; Wiley: New York, 1991.

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