

Nonlinear Susceptibilities of Conjugated Organic Systems: Fused-ring Oligomers*

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Abstract

The finite-field modified neglect of diatomic overlap (MNDO) molecular orbital technique has been used to calculate the second hyperpolarisability (the molecular counterpart to the macroscopic nonlinear susceptibility tensor χ_3) for selected fused-ring oligomers. The fused-ring segments are the active electro-optic units in ladder polymers and rigid-rod/flexible-chain copolymers that are under current investigation as polymeric materials with applications in ultrafast optoelectronic devices.

1. Introduction

Organic materials with conjugated π -electron systems can exhibit an ultrafast and very large nonlinear optical (NLO) response (Chemla and Zyss 1987; Messier *et al.* 1989). An additional attractive feature of organic materials is that their structural features may be varied to optimise adjunct properties, such as thermal stability, processibility and linear optical properties, whilst maintaining the electronic interactions responsible for the nonlinear optical effect. The third order nonlinear susceptibility χ_3 is of particular interest in nonlinear optics as it gives rise to a number of important third order nonlinear optical effects such as stimulated Brillouin scattering, third harmonic generation, stimulated Raman scattering and the instantaneous a.c. Kerr effect (degenerate four-wave mixing) (Fisher 1983).

The Kerr-like effects are characterised by an intensity-dependent refractive index (responsible for phenomena such as self-focusing and self-defocusing) and may be exploited in the construction of ultrafast nonlinear optical devices (Soileau *et al.* 1985; Messier *et al.* 1989). Some recent experimental studies (Yu and Dalton 1989*a*; Dalton 1989) have been directed toward the synthesis of ladder polymers and rigid-rod/flexible-chain copolymers which incorporate fused-ring conjugated systems. The planar conformation of fused-ring optimises the overlap of the π -electrons, and thus enhances the electron delocalisation responsible for large nonlinear optical effects. It has also been recognised that the third order NLO effects will saturate at a finite conjugation length due to electron-phonon and electron-electron interactions (de Melo and Silby 1988; Heflin *et al.* 1988; Beratan *et al.* 1987), and as a consequence it is not always

* Dedicated to Professor Ian McCarthy on the occasion of his sixtieth birthday.

necessary to have a large conjugated system within the polymer. On this basis Yu and Dalton (1989*a*) and Dalton (1989) have synthesised copolymers with fused-ring segments and flexible aliphatic chain segments. The advantage of the copolymer over traditional electro-optic active polymers is that it has improved processibility and a well defined absorption band edge. In previous studies (Williams 1987*a*, 1987*b*, 1990) the finite-field MNDO molecular orbital technique was used to investigate the second hyperpolarisability for a series of conjugated systems including polydiacetylene oligomers and small bandgap derivative polypyrrole and polythiophene oligomers. The second hyperpolarisability γ is the molecular counterpart to the macroscopic third-order nonlinear susceptibility χ_3 and can be directly related to the macroscopic susceptibility through local field effects for isotropic media. In this paper the technique is extended to the investigation of the second hyperpolarisability for a series of fused-ring oligomers, which are the active electro-optic units in ladder polymers and rigid-rod flexible-chain copolymers.

2. Theory

For a molecule in an external electric field E , the dipole moment μ is given by

$$\mu = \mu_0 + \alpha E + \frac{1}{2}\beta EE + \frac{1}{6}\gamma EEE + \dots,$$

where μ_0 is the permanent dipole moment, α the linear polarisability, and β and γ the first and second hyperpolarisability respectively.

The finite-field technique, in conjunction with the MNDO molecular orbital method (Dewar and Thiel 1977), has been used to compute values of the second hyperpolarisability. In this technique, the standard Hartree-Fock matrix elements $F_{\mu\nu}^0$ are modified by the inclusion of a perturbation term, arising from the application of a finite electric field to the molecule:

$$F_{\mu\nu} = F_{\mu\nu}^0 + \sum_i E_i D_{\mu\nu}^i,$$

where E_i is the i th component of the electric field and $D_{\mu\nu}^i$ is the i th component of the dipole moment matrix element. Alternating the sign and magnitude of E_i allows one to calculate the appropriate elements of the hyperpolarisability tensor in an efficient manner. In the limit of a vanishing field, the finite-field method is equivalent to the analytical coupled Hartree-Fock (CHF) method, where the perturbed wavefunctions are required to be solutions of the perturbed Hartree-Fock equations (Cohen and Roothaan 1965). The finite-field approach provides a practical way to perform the CHF calculations.

It should be noted that in this work we are concerned only with the calculation of the static polarisabilities and hyperpolarisabilities, as these are the quantities of major interest when investigating the broadband (nonresonant), nonlinear optical characteristics of materials.

The calculations reported in this study are based on the semi-empirical MNDO molecular orbital method (Dewar and Thiel 1977). The parameters in the MNDO method are chosen to optimise the predictive capabilities of the scheme

for molecular geometrics and heats of formation. An effective treatment of electron correlation is very important if accurate results are to be obtained for a number of molecular properties, such as heats of formation. The ability of the MNDO method to predict with some accuracy heats of formation (Dewar and Storch 1985) indicated that the MNDO parameters effectively build in some allowance for electron correlation neglected by standard Hartree-Fock theory.

Further details of this procedure, together with explicit expressions for the tensor elements, were given previously (Williams 1987*a*). The mean (isotropic) value of the γ tensor is defined in terms of its cartesian component as

$$\gamma = \frac{1}{5}(\gamma_{xxxx} + \gamma_{yyyy} + \gamma_{zzzz} + 2\gamma_{xxyy} + 2\gamma_{yyzz} + 2\gamma_{zzxx}).$$

3. Results and Discussion

The fused-ring oligomers studied in this work are shown in Fig. 1, together with the MNDO calculated value of the second hyperpolarisability in esu ($1 \text{ esu} \equiv 7.4279 \times 10^{-25} \text{ C}^4 \text{ m}^4 \text{ J}^{-3}$). The vinylamine-derivatised oligomer (I) forms the planar conjugated backbone of a ladder polymer (Yu and Dalton 1989*b*; Dalton 1989) and the triphenodioxazine oligomer (II) forms the rigid-rod structure of a rigid-rod flexible-chain copolymer (Yu and Dalton 1989*a*). Also shown in Fig. 1 for comparison are derivatives of the fused-ring oligomers which illustrate the effects of substitution, variation of heteroatoms and of the quinoid character of the oligomer backbone. The calculated magnitudes of the hyperpolarisabilities for the 20 π -electron fused-ring oligomers (I to IV) lie in the range 22×10^{-35} to 40×10^{-35} esu.

As a comparison, other conjugated systems with hyperpolarisabilities within this general range of magnitude (Williams 1987*a*, 1987*b*, 1990) are the 10 π -electron polyacetylene oligomer $\text{C}_{10}\text{H}_{12}$ ($\gamma = 25 \times 10^{-35}$ esu), the 12 π -electron polydiacetylene oligomer C_{12}H_8 ($\gamma = 35 \times 10^{-35}$ esu) and the 12 π -electron polythienylenevinylene oligomer $\text{C}_{12}\text{H}_{10}\text{S}_2$ ($\gamma = 31 \times 10^{-35}$ esu). These latter oligomers have a more extended or open-chain structure, and are thus able to achieve the same effective delocalisation length as the 20 π -electron fused-ring oligomers with a smaller number of π -electrons. However, the fused-ring oligomers have a structural advantage over the open-chain systems by enforcing a planar conformation on the backbone structure which optimises the π -electron overlap. This avoids many of the problems of polymer branching and disorder encountered with open-chain polymers which leads to a degradation of their nonlinear optical properties. The fused-ring polymers and copolymers can also lead to improved processibility and well defined absorption band edge.

The results presented in Fig. 1 also illustrate a number of other features which relate the molecular structure of the oligomer to the calculated magnitude of the hyperpolarisability. Substitution of functional groups, such as the hydroxyl group, onto the terminal phenyl rings can lead to an enhancement of the hyperpolarisability (structures I and III) and the introduction of second-row heteroatoms into the fused-ring structure (structures II and IV) can be further used to increase the magnitude of γ . It is observed from Fig. 1 that the largest value calculated for the series of oligomers studied occurs in structure IV where sulfur replaces oxygen in the rigid-rod structure and where the terminal

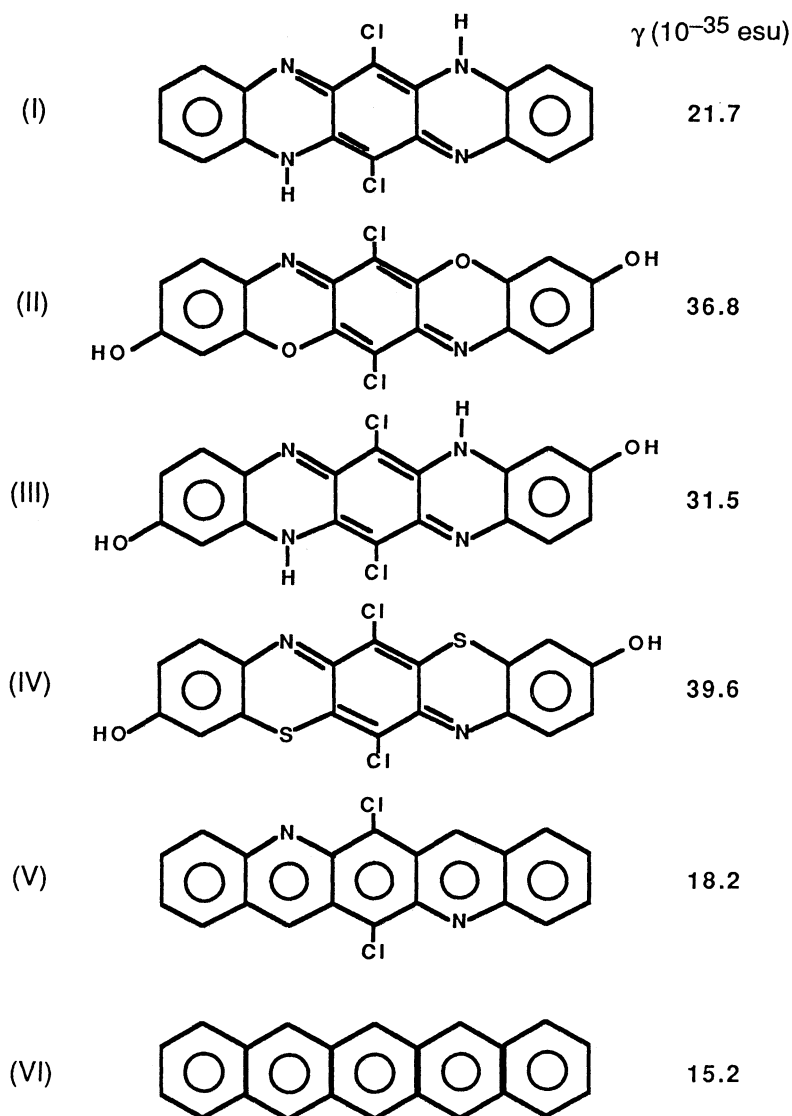


Fig. 1. Fused-ring oligomers and calculated hyperpolarisabilities γ .

phenyl groups are substituted with electron donating hydroxyl groups. It is also of interest to note that the magnitude of γ is enhanced for the 20 π -electron systems I to IV, where the central rings exhibit a distinctive quinoid character with the bonds alternating strongly between a single and a double bond (as reflected in their optimised MNDO bondlengths), compared with the 22 π -electron systems (V) and (VI), where the rings are essentially aromatic in nature with very little bond alteration.

4. Conclusions

The hyperpolarisability results obtained in this study would suggest that the fused-ring oligomers provide a structurally effective planar π -electron backbone for the construction of NLO polymers and copolymers. Furthermore, the results indicate that by incorporating heteroatoms such as sulfur into the backbone structure, utilising ring substitution and maximising the quinoid character of the backbone, the magnitude of γ (and hence χ_3) may be enhanced to optimise nonlinear optical properties.

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