Solvent Effects on the Second-Order Nonlinear Optical Response of π-Conjugated Molecules: A Combined Evaluation through Self-Consistent Reaction Field Calculations and Hyper-Rayleigh Scattering Measurements

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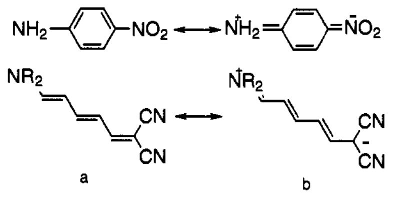
Recent experimental studies have pointed out the sensitivity of the nonlinear optical (NLO) response of π-conjugated molecules on solvent polarity.[1−4] Given this sensitivity, various theoretical approaches have been used to simulate the effect of solvent on the first hyperpolarizability, β: (i) by putting point charges around the molecule;[5] (ii) by considering a valence-bond charge transfer solvation model;[6] (iii) by taking account of a homogeneous external electric field;[1b,3,7] or (iv) by exploiting Onsager's reaction field theory in a simple form,[4,8] *i.e.*, considering the solute to occupy a spherical cavity within the solvent and/or restricting the solute/solvent interaction to the dipolar term. Although such a reaction field approach could be *a priori* considered to be well adapted to the problem, it must be borne in mind that most π-conjugated molecules possessing large second- or third-order NLO responses present a quasi-one-dimensional character and a complex pattern of their π-charge distribution;[7,9] accordingly, the use of a spherical cavity and the dipolar approximation can prove to be inadequate. Therefore, in this communication, we discuss and demonstrate the validity of a more refined approach to model the effects of solvent polarity on NLO properties: we use an expanded self-consistent reaction-field (SCRF) theory,[10] in which the self-consistent solute/solvent interactions are described by multipolar terms up to 2^6 poles and the solute is taken to occupy an ellipsoidal cavity.

We have examined p-nitroaniline (PNA, **I**), whose structure and NLO properties are only moderately sensitive to solvent polarity,[1c] and the push−pull polyene 1,1-dicyano-6-(dibutylamino)hexatriene (DCH, **II**), which is much more strongly affected by solvent effects.[3] The use of solvents of different polarity can modulate somewhat the structure of the molecule from a neutral (form a) to a charge-separated zwitterionic structure (form b) for which the degree of bond-length alternation δr (*i.e.*, the average difference in length between the single and double bonds within the polymethine chain) is completely reversed.

I

II



The theoretical β values for these molecules in solvents of different polarity are compared to experimental data from hyper-Rayleigh scattering (HRS)[11] measurements performed at 1064 nm in dichloromethane ($\epsilon = 9.08$); 1,4-dioxane ($\epsilon = 2.23$); and mixtures of these two solvents in 20/80, 40/60, 60/40, and 80/20 (v/v) proportions corresponding to ϵ values of 3.33, 4.47, 5.73, and 7.25, respectively. In the case of DCH, we have also performed HRS measurements in acetone ($\epsilon = 20.7$) and acetonitrile ($\epsilon = 37.5$).

The details of the expanded SCRF method have been presented in previous works, where it was successfully applied to conformational problems.[12] We simply briefly recall here that, within a Hartree−Fock approach, the electrostatic effect of the solvent is represented by an additional term to the Hamiltonian of the isolated molecule (H_0), which describes the electrostatic interaction energy between the molecule and the solvent through a multipolar expansion of the molecular charge distribution:

$$H' = H_0 - {}^1/_2 \sum_{l=0}^{6} \sum_{m=-l}^{l} \sum_{l'=0}^{6} \sum_{m'=-l'}^{l'} M_l^m f_{ll'}^{mm'} M_{l'}^{m'}$$

where $M_{l(l')}^{m(m')}$ represents the multipole of order $l(l')$ and the reaction field factor $f_{ll'}^{mm'}$ depends on the geometry of the cavity and the electric permittivity ϵ of the solvent.[12] The interaction is treated as a perturbation to the Hartree−Fock Hamiltonian, and the calculation is carried out until self-consistency is achieved.

For each value of the dielectric constant, the geometry optimization of the molecules and the second-order polarizability β calculations have been performed at the restricted Hartree−Fock *ab initio* level using a 3-21G split valence basis set (which was found earlier to be satisfactory to obtain reliable trends in β values).[13] Note that because of the size of the DCH molecule, we have considered the amino donor group in our calculations rather than the dibutylamino group. The components of β are calculated analytically via electric field derivatives of the total

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(13) Meyers, F.; Brédas, J. L.; Zyss, J. *J. Am. Chem. Soc.* **1992**, *114*, 2914. We have also performed 6-31G* SCRF ($l = 6$, ellipsoidal cavity) calculations on PNA: the results are fully similar to the corresponding 3-21G results (except that the 6-31G* β values are systematically *ca.* 25% smaller).

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Table 1. Evolution of the 3-21G Theoretical ($l = 6$, Ellipsoidal Cavity Shape) and Experimental β Values (in 10^{-30} esu) for PNA and DCH as a Function of the Solvent Dielectric Constant[a]

	PNA		DCH		
ϵ	β_v	β_{exp}	β_v	β_{exp}	λ_{max}
1	3.94		11.26		
2.23	6.67	16.9	19.18	34.2	472
3.33	8.06	18.2	22.40	39.8	475
4.47	8.99	19.6	23.66	42.3	477
5.73	9.70	20.1	24.06	46.8	479
7.25	10.29	21.2	24.10	49.8	479
9.08	10.78	21.6	23.51	47.4	480
20.7	12.04	25.9[b]	21.20	43.1	478
37.5	12.55	29.2[b]	20.22	35.1	476

[a] The λ_{max} values for DCH in solution are given in nanometers. [b] From ref 1c.

energy within a coupled perturbed Hartree–Fock approach.[14] We here report the vector part of the β tensor (β_v).[11]

In Table 1, we compare the theoretical static β_v values to the experimental HRS data for PNA and DCH for solvents with ϵ in the range 2.23–37.5. For DCH, we observe some β enhancement for the HRS measurements due to resonance effects as the experimental two-photon resonance occurs at 960 nm (twice λ_{max}) and is not far from the wavelength used in the HRS experiment (1064 nm). As a result, the corresponding HRS β data have been extrapolated to the zero frequency values using the dispersion factor of the two-state model,[15] as was done recently in a similar context.[11] Although the calculated values are somewhat smaller than the HRS data (which is expected due to the neglect of electron correlation contributions in the calculations),[16] there is excellent agreement with the experimental trends. In particular, for PNA, we find an increase in β within the range of solvent polarity. It is worth stressing that the β increase in passing from the gas phase ($\epsilon = 1$) to dioxane, characterized by a low dielectric constant ($\epsilon = 2.2$), is as strong as the β increase in passing from dioxane to acetonitrile, which is a much more polar solvent ($\epsilon = 37.5$). In the case of DCH, β exhibits a peak as a function of solvent polarity (see Figure 1), as was recently deduced from $\mu\beta$ determinations by EFISHG.[2] The calculations not only reproduce this peak behavior but also provide the same peak position ($\epsilon = 7.25$). Furthermore, the bond-length alternation (δr) at which this peak occurs, 0.05 Å , is in excellent agreement with predictions of the molecular structure providing an optimal β response[5] as well as with previous semiempirical calculations in which the molecule was polarized using a static homogeneous electric field.[7] We stress that the weak solvent sensitivity of the β value in PNA is due to the aromaticity of the benzene ring, which inhibits electron polarization in the ground state. In contrast, the ground-state structure and β of the DCH molecule are much more easily modulated by the polarity of the solvent.

In order to analyze the importance of taking account in the calculations of both an ellipsoidal shape of the cavity and a multipolar expansion of the interaction energy, we present, in Figure 1, the different curves of β as a function of ϵ in the case of DCH, as calculated by considering (i) an ellipsoidal cavity and a multipolar expansion ($l = 6$); (ii) an ellipsoidal cavity but a dipolar approximation ($l = 1$); and (iii) a multipolar expansion ($l = 6$) but a spherical cavity shape. We observe that the latter two types of calculations lead to β values which keep growing within the solvent dielectric constant range and do not provide the peak behavior of β . Actually, *both kinds of approximations underestimate the interaction energy* between the solvent and the molecule; as a result, even in very polar solvents, the medium-induced electronic and structural molecular changes remain too weak for the β peak to be reached (see inset of Figure 1): using a spherical cavity results in too large distances between the medium and the molecule in the directions perpendicular to the molecular long axis; restricting the interaction to the dipolar term is unable to account for the complex π-charge distribution (presenting charge alternation) along the polyene segment.[7]

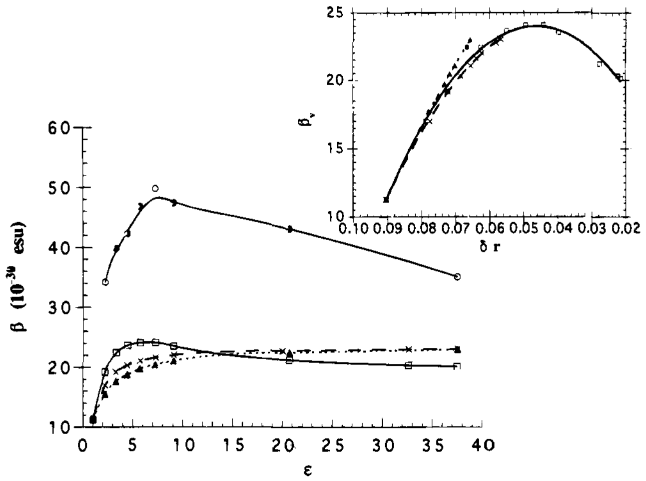

Figure 1. Evolution of β with ϵ in the case of the DCH molecule. The experimental β values extrapolated to zero frequency[11] are represented as open circles; the 3-21G SCRF β_v values are plotted for the following three cases: (i) open squares, $l = 6$, ellipsoidal cavity shape; (ii) crosses, $l = 1$, ellipsoidal shape; and (iii) filled triangles, $l = 6$, spherical shape. In the inset, the same three series of theoretical β values are given as a function of the degree of bond-length alternation δr (in Å), optimized in each case for the same range of ϵ values.

In conclusion, the very good agreement with experiment validates the expanded SCRF theory as a powerful theoretical tool to study the solvent dependence of β; we emphasize that both a multipolar expansion of the interaction energy and the use of an ellipsoidal cavity shape in the SCRF theory are necessary. It is especially relevant that this model is able to predict the nature of the solvent which maximizes the value of β; it is thus of particular interest to apply it for tuning of the NLO response in solution. Finally, we stress that our results confirm recent statements made on the effect of medium on hyperpolarizability–structure relationships.[2–7]

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Supporting Information Available: 3-21G optimized geometries of PNA and DCH and β_v 6-31G* SCRF results for PNA (3 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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