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Conformation-dependent molecular optical nonlinearities in bisnaphthol derivatives

Anna Gussoni ^a, Giuseppe Zerbi ^a, J.J.G.S. van Es ^b, H.A.M. Biemans ^b, E.W. Meijer ^b

^a Dipartimento di Chimica Industriale, Politecnico di Milano, piazza Leonardo da Vinci 32, Milan 20133, Italy

^b Laboratory of Organic Chemistry, Eindhoven University of Technology, PO Box 513, 5600 MB Eindhoven, Netherlands

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Abstract

The 'vibrational technique' has been applied to measure first-order and second-order molecular nonlinearities β and γ of bisnaphthol derivatives constrained in a non-coplanar conformation and containing electron donor and acceptor groups. The vibrational chemical shifts observed in the IR spectra of model molecules show that in solution a conformational equilibrium exists with only one conformer favouring electron injection by the oxygen lone pair into the aromatic ring, with the consequent increase of the weight of a quinoid structure. It follows that the hyperpolarizabilities are conformationally dependent and may show temperature dependence. The same spectroscopic approach to the bisnaphthol derivatives shows that the conformationally dependent role of the electron injecting property of the oxygen is more relevant than the inter-ring electron hopping between p_z orbitals.

Keywords: Bisnaphthol; Nonlinear optical properties

1. Introduction

Because of the potential applications in new technologies the interest in nonlinear optical (NLO) properties of organic molecules has grown very rapidly in the past few years. Systematic studies have been made on a series of homologous molecules with the aim of developing a structure–property relationship for use in the new synthesis of materials with improved properties [1,2].

Depending on the techniques used in the measurements, groups of workers focus mainly on bulk susceptibilities of first and second order ($\chi^{(2)}$ and $\chi^{(3)}$, respectively), while others aim first at molecules and measure molecular hyperpolarizabilities of first and second order (β and γ , respectively).

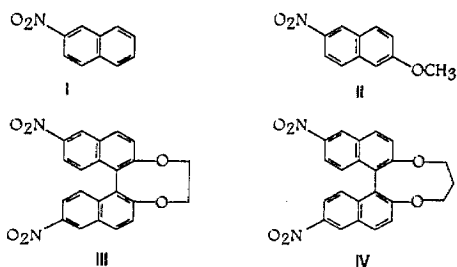
Among the techniques of measuring molecular nonlinearities the use of absolute vibrational IR intensities and Raman cross sections has been recently shown to be applicable either on theoretical grounds [3] or from experiments [4–6] on many molecules in which large electron–phonon coupling takes place. This happens mostly in low bandgap polyconjugated systems [7–9].

The basic phenomenon which determines NLO responses in such systems is the delocalization of π electrons along a delocalization path determined by the topology of p_z orbitals

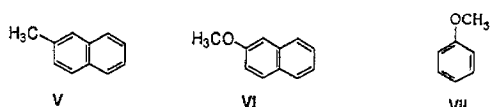
within the molecule [4–6]. Moreover, in β active systems a separation of charges induced by electron donating (push) and electron accepting (pull) groups is needed, while for obtaining large γ values a large delocalization path is necessary. The many data available in the literature have already allowed us to develop a preliminary structure–property relationship [4–6,10–12]. However, since device technology is strictly related to the bulk NLO properties, the detailed understanding of the effects of the supermolecular organization of single molecules becomes the next essential step. Recently, bichromophoric systems based on bisnaphthol have gained considerable interest to study push–pull aromatic systems in which the planes of the aromatic moieties are constrained to form a certain dihedral angle [13–15]. The purpose of our work is to ascertain and possibly evaluate the contributions by intermolecular and/or intramolecular electronic interactions to NLO responses.

2. Materials and experiments

We have measured β and γ of the following molecules in chloroform solutions (approx. 5–10 mg/ml):



The syntheses of **I** through **IV** are described elsewhere [15]. Model molecules such as 2-methyl naphthalene (**V**), 2-methoxy naphthalene (**VI**) and anisole (**VII**) have been used for a better understanding of the vibrational spectra:



The static hyperpolarizabilities β and γ (at $\omega=0$) were measured with the 'vibrational method' fully described and discussed in [3–6]. Such a method is based on the measurements of the absolute IR absorption intensities and of the absolute off-resonance Raman cross sections. According to the theory, contributions to vibrational β mostly arise from the vibrational modes which show an appreciable intensity both in IR and Raman; γ is determined by the off-resonance Raman spectrum which shows the effects of electron-phonon coupling [8,9].

IR spectra were recorded with a Nicolet 7000 FT-IR interferometer and the Raman spectra with a Nicolet 910 FT-Raman interferometer with excitation in the near IR ($\lambda_{\text{exc}} = 1.064 \mu\text{m}$ of a NdYag laser) with backscattering geometry and parallel polarization.

The measured values of β and γ are reported in Table 1.

Table 1
Molecular NLO properties, β_{yyy} and γ , of naphthalene and its derivatives (β_{yyy} and γ values are, respectively, in units of 10^{-30} and 10^{-26} e.s.u.)

Molecule	β_{yyy}	γ
	– ^a	1.9
	5.7	4.4
	11.7	7.6
	30.2	11.8
	39.2	17.2

^a Since naphthalene is centro-symmetric, $\beta=0$.

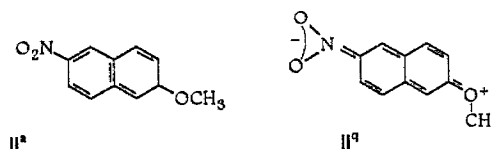
3. Results and discussion

In the study of the electronic structure of aromatic systems considered in this work it is immediately necessary to describe the actual molecular electronic configuration Ψ as a linear combination of several canonical structures ψ_i :

$$\Psi = \sum a_i \psi_i \quad (1)$$

where the coefficients a_i describe the weights of each canonical configuration.

In this work among the very many canonical structures we consider the two certainly of low energy, generally defined as 'aromatic' and 'quinoid', which are sketched below and labeled as Π^a and Π^q :



The structural features of the molecules studied in this work and which are strongly relevant to NLO properties need to be analyzed.

Molecule **I** can be considered mostly in the aromatic structure a_1 (of the type Π^a), while in molecule **II** the weight a_2 of the canonical 'quinoid' structure Π^q becomes larger because of the intramolecular push-pull effect by the methoxy and nitro groups, with the consequent increase of the value of the molecular electric dipole moment μ .

The increase of the measured values of β from **I** to **II** is an experimental proof of the obvious increase of the weight of ψ_2 with respect of ψ_1 .

The extent of either interaction could be in principle evaluated by the measured values of the hyperpolarizabilities, namely, if no interaction takes place the values of β and γ of **III** and **IV** should turn out to be the tensorial combination of hyperpolarizabilities relative to two units **II** tilted at a given angle θ . The evaluation of θ is usually done by molecular mechanics calculations. Another approximate way is to use the angular-dependent relation between the dipole moment change obtained from the infrared intensities of model molecule **II** and that from the measured infrared intensities of molecules **III** and **IV**. The β values obtained for **III** and **IV** (Table 1) indicate that no strong interactions take place.

In an attempt to understand the trend of the values of β and γ measured in this work, an additional problem of general validity has to be considered, namely, the role played by the orientation in space of the lone pair with respect to the p_z orbitals of the aromatic unit [13]. The orientation of the lone pair is determined by the overall conformation of the aliphatic ring which contains the oxygen atom.

The role by the oxygen lone pair is first studied on the IR spectrum of methoxybenzene **VII** taken as a model molecule.

Using 'vibrational chemical shifts' (VCS) and intensity spectroscopy (IS) [16,17], Villa et al. [18] suggested that in the gas and liquid (and solution) phases a sample of **VII**

may consist of a mixture of two conformational isomers obtained by the rotation of the $\text{CH}_3\text{-O-}$ group about the O-C(arom.) bond [18], in agreement with a few quantum chemical calculations [19]. In one of the two conformers the -O-CH_3 group is coplanar with the ring (in-plane model, IP) while in the second conformer the methoxy group is tilted out of the aromatic plane (OPLA model).

The concept of conformational-dependent hyperpolarizability needs then to be introduced, namely, in IP the lone pair can interact with the π electrons by injecting electronic charge into the ring, thus raising the weight of the quinoid structure (larger a_2). In the second rotamer (OPLA) the charge injection is strongly reduced or practically canceled with the generation of electronic back-donation towards the CH_3 group. Back-donation can occur only when the oxygen lone pair is not engaged in 'conjugation' with the aromatic ring [20].

The contributions to the hyperpolarizabilities by the two conformations are certainly different because of the different values taken up by a_2 . Thus, the values of β and γ measured in solution either in this work or with any other method have to be considered an average value which should be also temperature dependent.

Evidence of IP and OPLA conformations in the series of naphthalene derivatives studied in this work (**II** and **VI**) can be derived from VCS+IS in the C–H stretching range. VCS+IS in the CH_3 stretching region should allow us to distinguish the normal modes of the methyl group in the two rotamers. Indeed the spectral pattern of **VI** is quite complicated. Starting from the IR spectrum of **V** (with no oxygen) the stretching of the aromatic C–H is identified by the doublet labeled as A and B in Fig. 1(a), while the triplet CDE originates from the two antisymmetric stretches and the symmetric C–H stretch of the CH_3 group. In the IR spectrum of **II** the aromatic 'doublet' A' and B' is observed with different splitting and relative intensity if compared with A and B. Such differences are associated with the existence of the charge transfer structure. In going from **V** to **VI** the vibrational spectrum of **VI** (Fig. 1(b)) becomes more complex possibly because it is the result of the superposition of two triplets: one originating from the fraction of molecules with the IP conformation, and the other one associated with the OPLA fraction. This situation in **VI** is identical to what has been observed in the case of methoxybenzene [18]. Possible evidence of the OPLA conformer in **VI** is the vibrational sharp line at 2841 cm^{-1} associated with the antisymmetric stretching of the C–H bonds perturbed by back-donation by the oxygen atom.

A similar spectral pattern is observed in the IR spectrum of **II** (Fig. 1(c)).

An indirect effect of the extent of electron injection by the oxygen lone pair can be found also in compounds **III** and **IV** from the measured values of β and γ . In **III** the two oxygen atoms are constrained in a rigid ring where the dihedral angle C(arom.)-O-C-C is distorted from the coplanar conformation. Because of the conformational rigidity the measured values of β and γ of **III** can no longer be an average between

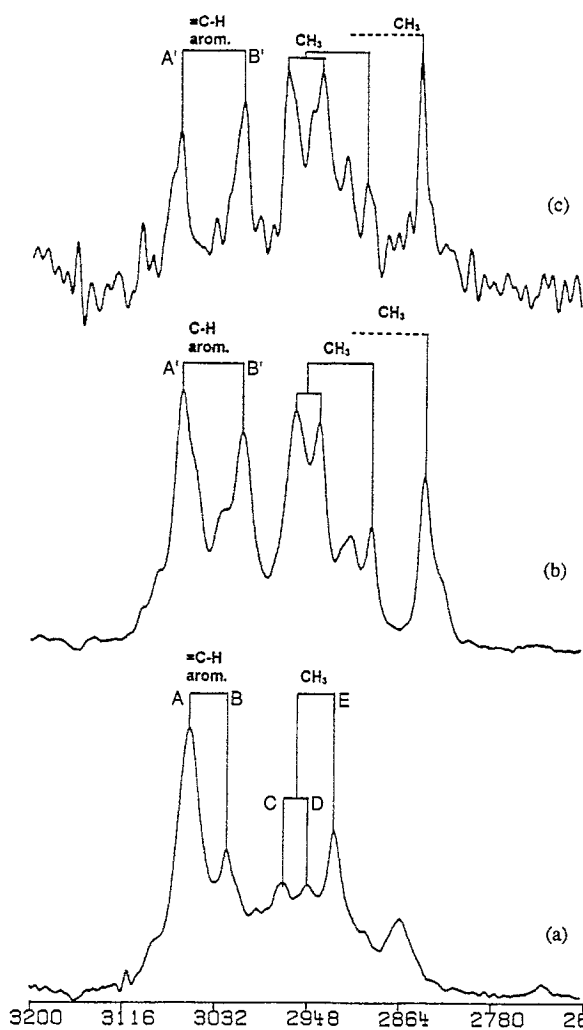


Fig. 1. IR spectra in the C–H stretching range of (a) 2-methyl-naphthalene, (b) 2-methoxynaphthalene and (c) 2-methoxy,6-nitro-naphthalene. The band at 2845 cm^{-1} in (b) and (c) is associated with one of the two antisymmetric stretchings of the CH_3 group in OPLA conformation (see text).

different rotamers, but a measure of a property intrinsic to a molecule in a fixed structure. The fact that the measured values are approximately the tensorial combination of those of the two units **II** proves that the charge injection by the oxygen atoms in each naphthalene ring is not very large and is certainly smaller with respect to the optimal coplanar conformation because of the conformational distortion.

The fact that in **IV** both β and γ increase slightly if compared with **III** indicates a tendency opposite to what is discussed for **III**, namely, the conformation of the ring containing two oxygens and three CH_2 groups is such that the lone pair may find a geometrical configuration more favorable for electron injection, as described by ψ_2 .

The question raised at the beginning can now be answered, namely, the tilting angle between the two rings which is thought to modulate inter-ring delocalization turns out not to be the only geometrical parameter relevant in affecting molecular hyperpolarizabilities. An important role is played by the oxygen whose electron donating strength is modulated by the geometry of the external moiety to which it is attached.

A final comparison of the values of γ can be made with the parent molecule naphthalene [21] and molecules **I** and **II** (Table 1). The measured γ of naphthalene is low and slowly increases in **I** and **II** because of the increasingly larger contribution by the quinoid structure. The results found here are in agreement with EFISH and HRS experiments on the same series of molecules and will be addressed in an forthcoming paper.

4. Conclusions

The results of this work indicate that molecular hyperpolarizabilities of aromatic systems depend mostly on the intraring polarizing effects of the push–pull groups and not much by the ‘supermolecular’ organization which may affect π electron hopping along a certain delocalization path. However, the relevant message which cannot be overlooked is that the conformation of the push–pull groups with respect to the p electron skeleton may play an important role in the generation of the electron transfer across polyenic or aromatic polyconjugated networks. This introduces a temperature dependence of molecular hyperpolarizabilities.

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