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ScienceDirect
Mendeleev Commun., 2008, **18**, 265–267

Mendeleev Communications

Conformational dependence of the first molecular hyperpolarizability in the computational design of nonlinear optical materials for optical switching

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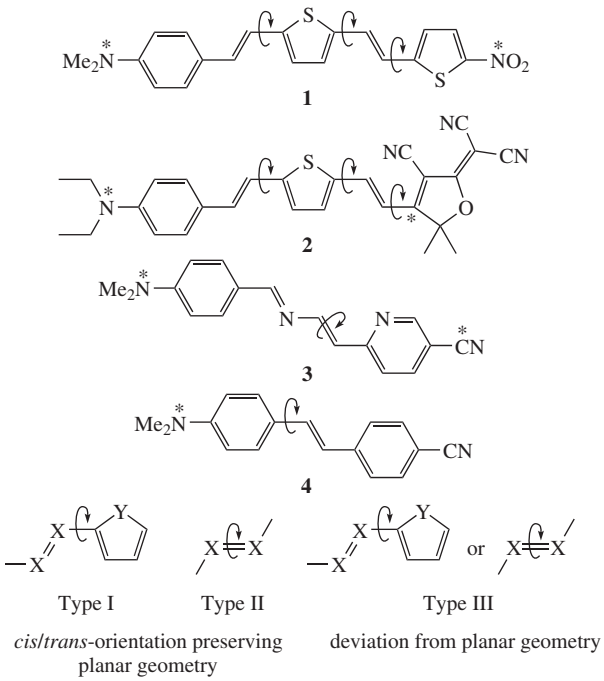
DOI: 10.1016/j.mencom.2008.09.013

In certain cases for conjugated molecules, which can often be found in several conformations close in energy, hyperpolarizabilities of the rotamers differ by less than 20%, which is comparable to uncertainty in experimental data and this makes it possible to consider only one representative conformation in the process of computational design.

It has long been recognized that molecules with nonlinear optical (NLO) properties often contain a π-conjugated system substituted at the termini with donor and acceptor (D/A) groups (so-called D-π-A molecules).[1–4] Crystals formed by these molecules can be used to build optical transistors and for other optoelectronic applications. The π-system usually contains aromatic and $–(X=X)_n–$ fragments (where X = CH, N). Molecular first hyperpolarizability strongly depends on the length of π-system and shows a significant (factor of 2–3) increase with elongation of the π-conjugated bridge.[5,6] In the computational design of materials for NLO applications at molecular level, a compromise between first hyperpolarizability (β) and optical transparency is required. Elongation of π-system in D-π-A molecule increases β but narrows the optical transparency range and decreases the thermal stability of the compound.[6–8] To balance these characteristics, NLO molecules of interest are usually built up of π-systems with 2–10 double bonds endcapped with D/A groups. Predictions of nonlinear optical properties using methods of quantum chemistry are becoming an important component in the design of materials with improved properties. While molecules with π-system tend to be planar, the rotamers along single bonds are often close in energy and their β need to be predicted for proper statistical averaging. In addition, intermolecular interactions in a solid can stabilize the rotamer that was not the most stable in a gas phase. This further complicates NLO material design.

This work is focused on the conformational dependence of the first molecular hyperpolarizability for four NLO molecules (Scheme 1), some of which were previously studied theoretically and experimentally.[9–12] We aim to answer the following question: would it be sufficient to consider only one conformation to predict hyperpolarizability at semiquantitative level of accuracy?

We distinguish three types of conformational transitions according to Scheme 1. The first one is a rotation of the aromatic ring relative to the $–(X=X)_n–$ chain (rotation about a single bond). The second type is *cis*/*trans* isomerization of $–(X=X)_n–$ chain (rotation about a double bond). For both types of conformations, the planar (or nearly planar) structure is assumed. The third type is deviation from planarity. The decrease of β when π-system deviates from planarity is well recognized.[13] We will also show to which extent the π-system of the molecule can deviate from a planar geometry to result in



Scheme 1

a no more than 20% decrease of β. For instance, it was recently shown that planarization of the NR_2 group in D/A-substituted benzenes and stilbenes leads to only a 5–10% decrease in β.[14] Taking into account the ambiguity of experimental data,[15–17] an error of 20% in β can be described as a semiquantitative level of accuracy.

For all considered molecules, optimization without symmetry constraints leads to nearly planar structures (torsion angles of the π-system do not deviate by more than 1–5°), which allow us to treat them as planar. The BMK/6-31+G* level of theory (with the Gaussian03 program[18]) was used for both optimization and static hyperpolarizability calculation (keyword Freq=Raman) throughout this study. The latter was estimated as the numerical negative derivative of the energy with respect to the applied electric field, and then vectorial part of β was estimated as

$$\beta_{\text{vect}} = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{1/2}, \text{ where } \beta_j = 1/3\sum_{i=1}^{3}(\beta_{jii} + \beta_{iji} + \beta_{iij}),\ i, j = x, y, z.$$

Table 1 Relative energies (ΔE), hyperpolarizabilities (β) and D/A separation distances (r) for eight conformers of **1** and **2**; S and A mark relative orientation of double bonds according to Scheme 1 (S for *syn*, A for *anti*).

Conformer	**1**			**2**		
	ΔE/ kcal mol^{-1}	β (a.u.)	r/Å	ΔE/ kcal mol^{-1}	β (a.u.)	r/Å
SSS	4.11	72864	18.315	3.40	94513	14.409
SSA	3.04	69843	17.678	3.06	99206	14.421
SAS	2.54	65870	17.555	1.12	88377	14.002
SAA	1.39	67432	17.812	1.83	90966	13.963
ASS	2.87	69888	18.017	2.35	94060	14.167
ASA	1.87	65880	17.049	1.97	100186	14.172
AAS	1.16	58955	16.635	0.00	83778	13.375
AAA	0.00	64072	17.289	0.48	85326	13.356

Molecules **1** and **2** were used to study the type I of conformational transition, molecule **3** – for type II, and for molecule **4** stepwise rotation about single bond was studied. For **1** and **2** eight planar conformations were considered. Table 1 presents energies, β values and D/A separation distances for all conformers. We used distances between atoms marked with stars in Scheme 1 as D/A separation distance.

For both molecules, the energies of all conformers do not differ significantly. When D/A separation distance varies within 10%, the differences in hyperpolarizability do not exceed 20% (smaller than uncertainty in the experimental data). This allows us to consider only one conformation for estimation of hyperpolarizability for such molecules, significantly saving computational time. The correlation between β values and D/A separation distance is presented in Figure 1. While single D/A groups (**1**) demonstrate a good correlation ($R = 0.93$), for molecule **2** the correlation is more approximate ($R = 0.87$) due to ambiguity in the choice of the acceptor center.

Note that no correlation was found between hyperpolarizability and relative energy of the conformers. It appears that the more energetically preferable conformer does not necessarily have stronger π-electron delocalization.

Two conformers of **3** (*trans* and *cis*) are related by type II transition. While for different conformers of **1** and **2**, variation of D/A separation is within 10%, in the case of **3** this distance for *cis*-conformer is 23% shorter than that for *trans*-conformer

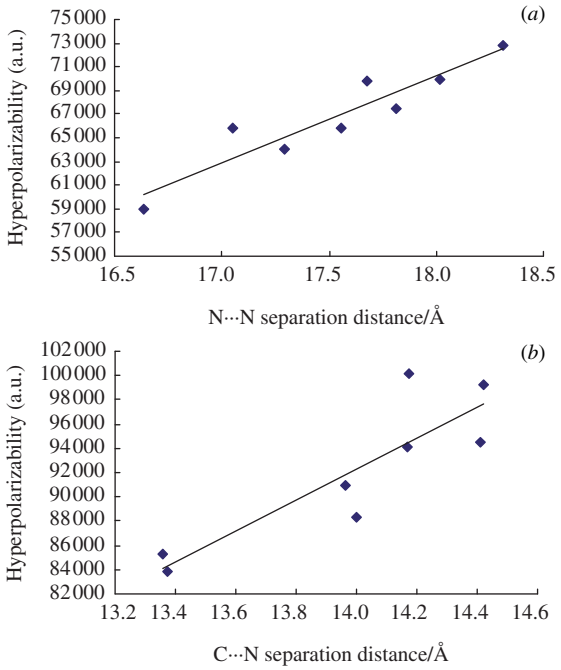


Figure 1 Dependence of hyperpolarizability on D/A separation for molecules (*a*) **1** and (*b*) **2**.

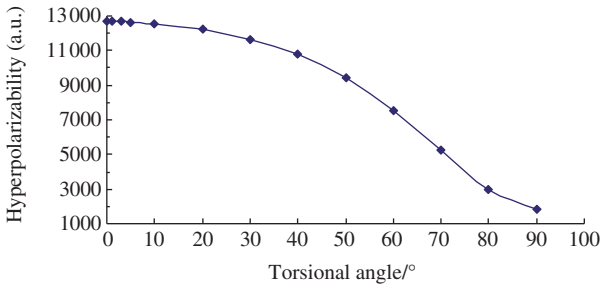


Figure 2 Dependence of hyperpolarizability on rotation about C–C bond for molecule **4**.

(11.05 and 14.35 Å). This results in a significant decrease of hyperpolarizability by 42% (12677 for *cis*- and 21566 a.u. for *trans*-conformer), and continues the trend observed in Figure 1: for each 10% decrease in D/A separation distance, the β value decreases nearly twice as much. The difference in energy between *cis*- and *trans*-isomers is also sizable (6.6 kcal mol^{-1}).

The dependence of β on the torsion angle for molecule **4** is presented graphically in Figure 2. The region of 0–10° was studied in more detail (with a 2–5° step) while for the region 10–90°, the step was increased to 10°. In the region of 0–10°, molecular hyperpolarizability is nearly constant. The 20% decrease is observed when torsion angle is rotated by 45°. Therefore, this value can be used as a criterion to consider a molecule as planar.

Our study leads to the following conclusions. Type I rotamer transition does not result in sizable variation of energy and molecular hyperpolarizability. Therefore, it may be sufficient to consider only one representative conformation in the process of computational design of the advanced nonlinear optical materials. In contrast, type II *cis*/*trans*-conformational transition leads to nearly 2-fold decrease of β. Simple criteria based on D/A separation distance can be used to predict the conformational effect on hyperpolarizability: the relative change in β is nearly twice larger then the relative change in D/A distance. Deviation from planarity up to 45° is shown to decrease of β value by less than 20% that makes it possible to treat such molecules within planar constraints.

This work was supported in part by the UCF (start-up grant), the US National Science Foundation (grant no. CCF 0740344) and the Russian Foundation for Basic Research (project no. 06-03-32557-a). We are grateful to US DOE NERSC and UCF I2Lab for the generous donation of computer time.

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Received: 13th March 2008; Com. 08/3101