

THIRD-ORDER NONLINEAR OPTICAL PROPERTIES OF PSEUDOAZULENES

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and Zdzisław Ruziewicz on the occasion of their 70th birthdays†*

The hyperpolarizabilities of several pseudoazulenes are evaluated using a semiempirical quantum chemistry package MOPAC-93 and compared with hyperpolarizabilities of simple molecules like chloroform, benzene, naphthalene and azulene. The third-order hyperpolarizability γ is measured for a derivative of 1,2-5,6 dibenzoxalene using a femtosecond Z-scan method at 800 nm. The resulting hyperpolarizability of 1.7×10^{-34} esu corroborates the theoretical prediction that pseudoazulene structures behave similar to other aromatic molecules provided the experiments are carried out in a non-resonant regime.

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1. Introduction

There is a continuing interest in development of optical materials which would be suitable for manufacturing of photonic switches and other devices. One of possible approaches is utilizing third-order nonlinear optical properties of such materials, in particular, the ability of these materials to change the value of the refractive index under the action of the optical field. This property is usually described in terms of the degenerate third-order susceptibility $\chi^{(3)}(-\omega; \omega, -\omega, \omega)$

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or the nonlinear refractive index n_2 . Large values of these parameters can be achieved in certain classes of materials, one of them being organics [1] with delocalised π -electrons such as π -conjugated polymers (often referred to as conducting polymers, although they are often only conducting when doped) and organic dyes. While there are still many unsolved problems, certain rules concerning nonlinearities of such structures have been formulated which, albeit not precise, are helpful in the choice of materials for investigations of their nonlinear optical properties. One such rule is that macroscopic nonlinear susceptibility of a material can be approximately expressed in terms of microscopic molecular properties, i.e. that an oriented gas model is applicable. In the case of third-order nonlinear susceptibility of an isotropic liquid or glass the approximate relation allowing one to compute the susceptibility is

$$\chi^{(3)} = L^4 \sum_i N_i \gamma_i,$$

where γ_i stand for third-order hyperpolarizabilities of molecules forming the material, N_i are their number densities and L is the local field factor. The quest for high third-order nonlinearities necessary to build useful nonlinear optical materials can be therefore thought of as the search for highly nonlinear molecules and ways of incorporating them into technologically viable structures having to fulfil additional criteria such as low one-photon and multiphoton absorption losses, low scattering, capability of forming wave guide structures, environmental stability etc.

Among interesting structures of organic molecules, there are chain structures such as those of polyenes, macrocycle structures such as porphyrins or phthalocyanines, metalorganics and also dyes with certain types of charge distribution which seem to be favoured for high nonlinearity. One example of a such a class of dyes is squaraines [2]. We address in this note a problem of nonlinear properties of pseudoazulenes — that is compounds having a backbone structure isoelectronic with azulene [3]. These compounds are known to have interesting spectroscopic properties [4] similar to those of azulene for which a striking phenomenon is fluorescence occurring from the second excited singlet state and not from the first excited singlet as for most organic molecules. Since the distribution of charges in pseudoazulene molecules is quite asymmetric one can wonder if these features are helpful in achieving a high nonlinearity of a conjugated π -electron system. It is known that azulene itself has relatively high second-order optical nonlinearity [5].

We attempted therefore a pilot study of third-order nonlinearity in selected pseudoazulene molecules using two approaches which are standard in such studies, i.e. firstly trying to evaluate theoretically the third-order hyperpolarizability of several molecules and then trying to measure such a hyperpolarizability using a carefully tested experimental technique.

2. Theoretical studies

We selected for the preliminary evaluation of nonlinearity of pseudoazulenes the well-known semiempirical quantum chemistry package MOPAC-93 [6]. This program allows one to compute the polarizability (α) and second-order as well

as third-order hyperpolarizabilities (β and γ , respectively) of a molecule using an approach known as time-dependent coupled-perturbed Hartree-Fock technique [7].

Table contains results of computations for the static hyperpolarizability for several pseudoazulene molecules chosen from those investigated in Ref. [4], and, for comparison, simple molecules like benzene, naphthalene and azulene. The computations were performed using two quantum chemical methods: AM1 and PM3.

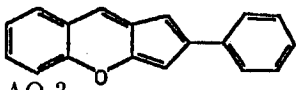
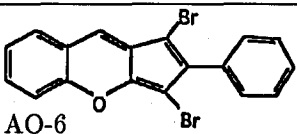
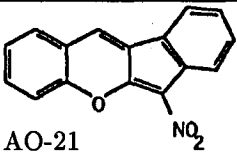
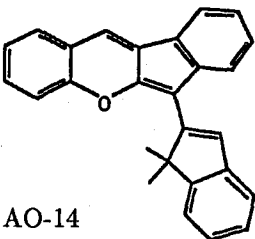
All the values in Table are given in atomic units. Rather than converting these values to electrostatic units (esu) commonly used in experimental studies, we compare them to the well-known standards: benzene and chloroform molecules and to naphthalene and azulene. This avoids numerous uncertainties deriving from various ways of defining hyperpolarizabilities. A comparison of results for various molecules brings several conclusions. We note that the third-order nonlinearity of azulene and naphthalene appear to be very similar despite their different electronic structure. Bigger molecules of substituted pseudoazulenes have higher nonlinearities reaching about two orders of magnitude bigger nonlinearity than that of benzene, however, the values are not high enough to be comparable with those predicted by MOPAC for e.g. squaraines. A slight nonplanarity was predicted by MOPAC for molecule AO-3, forcing the molecule to be strictly planar does not change the nonlinearity to a marked degree. However, a dibromosubstituted molecule AO-6 is strongly nonplanar because of steric hindrances and in result its nonlinearity is weaker than that of molecule AO-3. It should be finally noted that all the computed zero frequency hyperpolarizability values are positive, unlike in the case of squaraines where negative hyperpolarizabilities are consistently obtained from calculations [2].

3. Nonlinear optical measurement by Z-scan

The measurements of third-order nonlinear optical properties of model molecules can be performed in a variety of ways, however, the results may depend to a marked degree on factors such as the choice of the light wavelength and the duration of laser pulses used in the measurements. In general, in order to avoid contribution of resonant processes it is essential to perform measurements in the wavelength region where the material absorption is negligible and with laser pulses as short as possible. Our measurements were performed at 800 nm using 100 fs pulses generated in an amplified Ti-sapphire laser system at Laser Physics Centre, ANU, Canberra. This system contains a Coherent Mira Ar-pumped Ti-sapphire femtosecond laser and a home-built Ti-sapphire regenerative amplifier pumped with frequency-doubled Q-switched pulsed YAG laser at 30 Hz. The amplifier uses the technique of chirped pulse amplification, i.e. the pulses from the Mira laser are first stretched about 10^3 times and after amplification (by up to 10^6 times) are recompressed in a grating compressor. This system is mostly used in investigations of nonlinear optical properties of materials by several techniques. We have chosen a technique of Z-scan for this investigation because of its ability to provide the sign of the nonlinear optical susceptibility.

Z-scan is a measurement in which a sample is scanned along the path of a laser beam which is being focussed by a lens and the far-field on-axis light inten-

TABLE
MOPAC-93 computed values of the orientationally averaged polarizability (α), vector part of the second-order hyperpolarizability (β) and orientationally averaged third-order hyperpolarizability (γ). All values are in atomic units. Two values for each compound refer to AM1 and PM3 techniques, respectively.

Compound	α	β	γ (a.u.)	
chloroform	AM1	26.6	18	1458
	PM3	32.2	15	5431
benzene		49	0	1480
		46	0	1530
naphthalene		89	0	9855
		84	0	10008
azulene		101	174	8812
		95	158	10409
 AO-3		197	432	159292
		183	396	137293
AO-3 flat		198	457	176317
		186	417	162516
 AO-6		211	566	91868
		205	530	127333
AO-8		173	406	76175
		162	404	76750
 AO-21		190	120	73545
		177	161	74363
 AO-14		281	303	253592
		264	101	245995

sity is monitored with a detector with an aperture in front of it. The nonlinear behaviour of the sample is equivalent to the formation of an induced positive or negative lens in the case of positive (self-focussing) or negative (self-defocussing) third-order nonlinearity, respectively. Since the light intensity varies due to focussing, the lens strength varies, too, with the position of the sample with respect to the focussed beam waist. It is apparent that placing a positive induced lens before the waist will bring the waist closer and therefore will reduce the far-field on-axis intensity while placing the same induced lens after the waist will induce some focussing on the divergent beam and therefore increase the on-axis intensity. The S-shape resulting from scanning the sample can be analysed using calculation techniques described by Sheikh-bahae et al. [8] and nonlinear properties of the sample can be derived.

The major difficulty in performing the measurement of nonlinearity is that the pseudoazulenes have to be prepared in the form suitable for optical measurements — dissolving them in a solvent of known nonlinearity is a preferred choice since the nonlinear response of the solution can be compared to that of the solvent and the solute nonlinearity can be deduced. Theoretically predicted two orders of magnitude (at the most) difference between a pseudoazulene and benzene indicates that solutions with concentrations of the order of 1% are needed if benzene or a solvent with similar nonlinearity is to be used. We selected chloroform as a solvent. Figure 1 shows a comparison of Z-scans taken on pure chloroform (in a 1 mm glass cell) and on solution of the compound AO-14 in chloroform (1.2% by weight which corresponds to the molar fraction of 0.004). Both curves show the behaviour characteristic for positive nonlinearity, the magnitude of the effect being slightly but beyond experimental uncertainty bigger in the solution. This

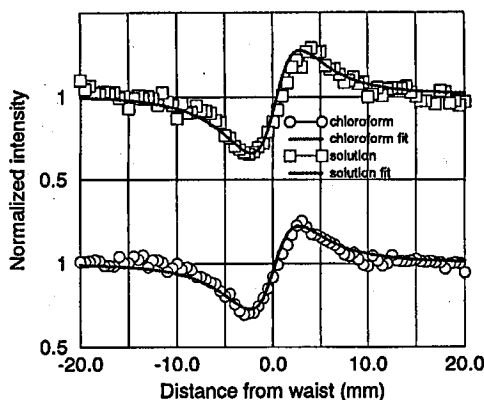


Fig. 1. A comparison of Z-scans performed at the same input power for a 1 mm cell of chloroform and 1 mm cell of a solution of the compound AO-14 in chloroform. The data were collected with 100 fs pulses at 800 nm with the pulse energy on the order of about $1 \mu\text{J}$ using a 25 cm focal length lens.

immediately indicates that the compound AO-14 possesses a positive third-order hyperpolarizability. The magnitude of the hyperpolarizability of the compound AO-14 can be calculated from the increase of the nonlinear phase change due to the presence of the solute. When the hyperpolarizability of chloroform is assumed to be 3×10^{-36} esu (an average from many literature data and own determinations), the hyperpolarizability of AO-14 comes to be 1.7×10^{-34} esu. This is not a very high hyperpolarizability — slightly less than two orders of magnitude higher than the solvent hyperpolarizability. In view of many factors influencing both the theoretical estimates of hyperpolarizability and its experimental determinations, we conclude that the experimental result is in reasonable agreement with the theoretical prediction.

We also conclude that pseudoazulene structures behave similar to other aromatic molecules of similar sizes and peculiarities of excited state properties of these molecules do not seem to have a profound effect on the values of their third-order hyperpolarizabilities.

References

- [1] E.g. D.S. Chemla, J. Zyss, *Nonlinear Optical Properties of Organic Molecules and Crystals*, Vols. 1 and 2, Academic Press, Orlando 1987; P.N. Prasad, D.J. Williams, *Introduction to Nonlinear Optical Effects in Molecules and Polymers*, Wiley, New York 1991; K.-S. Lee, M. Samoć, P.N. Prasad, in: *Comprehensive Polymer Science*, Ed. G. Allen, First Suppl., Pergamon Press, Oxford 1992, p. 407.
- [2] C.W. Dirk, L-T. Cheng, M.G. Kuzyk, *Int. J. Quantum Chem.* **43**, 27 (1992).
- [3] H.J. Timpe, A.V. Eltsov, *Adv. Heterocycl. Chem.* **33**, 185 (1983).
- [4] A. Olszowski, S.E. Bucher, U.P. Wild, *Chem. Phys.* **120**, 139 (1988); A. Olszowski, *Pr. Nauk. Inst. Chem. Org. Fiz. Politech. Wrocław* **24**, 3-181 (1981) (in Polish).
- [5] D. Li, T.J. Marks, M.A. Ratner, *J. Phys. Chem.* **96**, 4325 (1992).
- [6] H.A. Kurtz, J.J.P. Stewart, K.M. Dieter, *J. Comput. Chem.* **11**, 82 (1990).
- [7] M. Dupuis, S. Karna, *J. Comput. Chem.* **12**, 487 (1991).
- [8] M. Sheikh-bahae, A.A. Said, T. Wei, D.J. Hagan, E.W. van Stryland, *IEEE J. Quantum Electron.* **26**, 760 (1990).