Third order NLO properties of modified azo-azulenes

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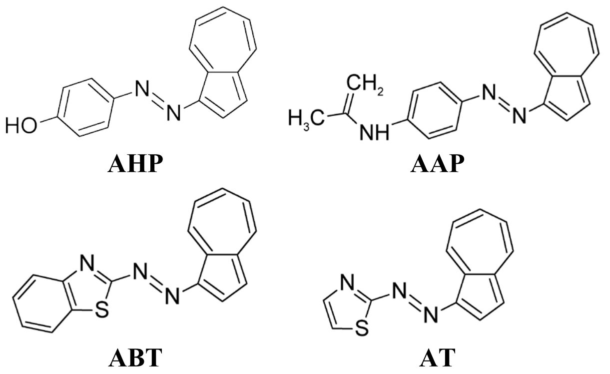
Abstract— In this work there are reported third order nonlinear optical properties of some new azo- functionalized azulene derivatives. They were studied using standard methods - degenerate four waves mixing and third harmonic generation and nonlinear optical absorption. The obtained results allow us to conclude that NLO properties of an azulene molecule can be significantly enhanced by substitution with an electron accepting an acetamidophenyl group.

For the last three decades organic nonlinear optical materials (NLO) have gained considerable interest because of their flexibility in tailoring the properties required in optoelectronics and in optical information processing [1]. Designing new molecules of enhanced NLO features most often exploits the so-called push-pull strategy. It comes down to or begins with donor and acceptor moieties bound together by a π-conjugated organic system. Most often, the last one is a benzenoid-like ring or alkene chain [2]. Recently more attention has been paid to other systems, for example, azulene and its derivatives [3]. Azulene is a naphthalene isomer, often met in nature. Brilliantly blue dyed, it is also the source of anomalous fluorescence of azulene $S_2 \rightarrow S_0$ [4], the first reported violation of Kasha's rule. It was shown that by the perturbation of HOMO and LUMO molecular orbitals, the fingerprint blue colour can be altered in a systematic manner to cover the entire visible spectrum. Due to a spontaneous drift from the seven-membered to five-membered ring, the azulene molecule possesses both electron donating and electron accepting character depending on the extremity [5]. Semi-empirical and *ab initio* calculations have suggested that a pristine or substituted azulene molecule should represent large hyperpolarizability, comparable to that of molecules reputable in the domain of NLO [6]. Following this idea, there were compounds reported containing azulene moieties in combination with donors like ferrocene[5] or different acceptors [7-8]. In this work this concept was further developed. There were synthesized four different molecules based on azulene moiety (playing role of the donor) linked through the azo (-N=N-) group to different planar acceptors, which were either hydroxyphenyl, acetamidophenyl, thiazole or benzothiazole. This design extended the conjugation length between the donor and the acceptor (which enhances hyperpolarizability). In addition, the rule of thumb predicts improved thermal stability of compounds modified with azo- bond. In Fig.1 are pictured structures of the studied molecules. Extensive description of a related synthetic routine has already been published elsewhere [9].



AHP **AAP**

ABT **AT**

Fig. 1. Structures of the studied molecules AHP - azulene-1-azo-(4-hydroxyphenyl) AAP - azulene-1-azo-(4-acetamidophenyl) ABT - azulene-1-azo-(2-benzothiazole), AT - azulene-1-azo-(2-thiazole).

Samples were prepared either as solutions in THF (tetrahydrofurane) or solid-state film blends with poly(methyl metacrylate). Usually the dye content in a blend is limited by crystallisation (or other forms of aggregation), appearing when a certain threshold of the dye load is exceeded. On the other side, NLO properties of blends are proportional to the dye content. By means of optical microscopy it was concluded that in the case of studied azulene derivatives, the optimum load was as much as 20% wt.

The absorption spectra of the studied samples are plotted in Fig. 2. In the case of phenyl substituted molecules the Soret peak appeared at c.a 485 nm. The replacement of the phenyl ring by thiazol, shifted this peak by c.a. 30 nm towards shorter wavelengths. Weaker maxima appeared at c.a. 350 nm. Generally, recorded spectra were very similar. This may support the assignment of observed maxima to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions. The latter one, although symmetry-forbidden for *trans*-azobenzene and then hardly visible, was observed to be strong in

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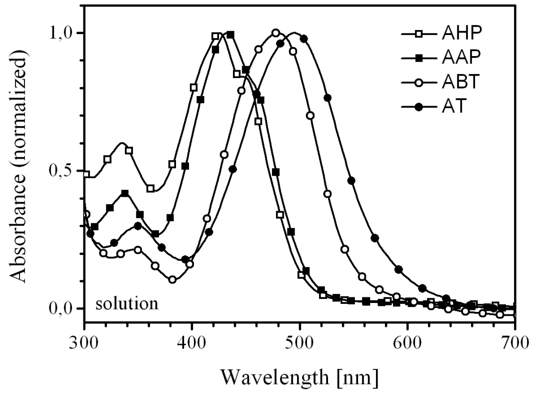
numerous derivatives due to vibrational coupling and some induced nonplanarity [10]. In addition, characteristic absorption of an azulene group lies outside this band [11]. A possible explanation can be internal charge transfer through –N=N- linkage.



Compound	λ_{max} [nm]	Compound	λ_{max} [nm]
AHP	488	ABT	461
AAP	485	AT	453

Fig. 2. Uv-vis absorption spectra of the studied compounds in solution.

A common technique for studying nonlinear optical properties of completely anisotropic media such as liquids is to degenerate four wave mixing (DFWM) [12]. It allows to deduce four not vanishing terms of the $\chi^{(3)}$ tensor. The data found for solutions can serve as a qualitative tool to compare different dissolved species. This is provided by the direct link between molecular second hyperpolarizability and macroscopic $\chi^{(3)}$ unless the solution is very concentrated [13]. The experimental setups and measurement routines have been described in detail elsewhere [13] and adopted for this work without major changes. Third order nonlinear susceptibility may be expressed as a linear combination of different contributions as shown in equation (1)

$$\chi^{(3)}_{ijkl} = \chi^{(3)el}_{ijkl} + \chi^{(3)mol}_{ijkl} + \chi^{(3)th}_{ijkl} + \chi^{(3)et}_{ijkl} + \ldots \qquad (1)$$

where *el*- electronic, *mol* – molecular, *th* – thermal, *et* – electrostrictive contributions, indices i,j,k,l denotes polarizations of each of four interacting waves (*s* or *p* relatively to the incidence plane). In the used setup, excitation light was delivered by a 30 ps, 532 nm pulse laser working at a frequency of 1Hz. At such low pulse repetition, the sum on the right hand of equation (1) may be limited to the first two terms arising from electronic cloud deformations and molecule reorientation. This assumption can be confirmed by the inspection of Fig. 3(a). The observed temporal dependence of the recorded signal corresponds exclusively to the laser pulse. If there had been accounted additional features like electrostriction, this fact would have been reflected by an additional signal lagging after that of the pulse. The graph in Fig. 3(b) proves perfect cubic dependence of signal intensity (outgoing beam) on pumping beam intensity. Theoretically, they are mutually related [14] as expressed in equations (2a) and (2b).

$$\chi^{(3)el}_{ssss} = 3\chi^{(3)el}_{psps} = 3\chi^{(3)el}_{sspp} = 3\chi^{(3)el}_{pssp} \qquad (2a)$$

$$\chi^{(3)mol}_{ssss} = 8\chi^{(3)mol}_{psps} = 8\chi^{(3)mol}_{sspp} = \tfrac{4}{3}\chi^{(3)mol}_{pssp} \qquad (2b)$$

Table 1 contains calculated components of $\chi^{(3)}$. Table 2 summarizes electronic and molecular contributions in $\chi^{(3)}$, estimated with the help of equations (2a) and (2b). It is evident from these tables that higher values of $\chi^{(3)}$ were found in compounds bearing thiazole or phenylthiazole moieties. Analysis of these data may lead to the conclusion that in the case of compounds AHP and AAP, electronic contribution to $\chi^{(3)}$ prevails, contrary to compounds AT and ABT, where the molecular factor is more pronounced. This can be explained by longer conjugation extent in molecules AHP and AAP, favouring electron delocalization. On the other side molecules AT and ABT are stabilised owing to more important steric hindrance and resulting larger dipole moments.

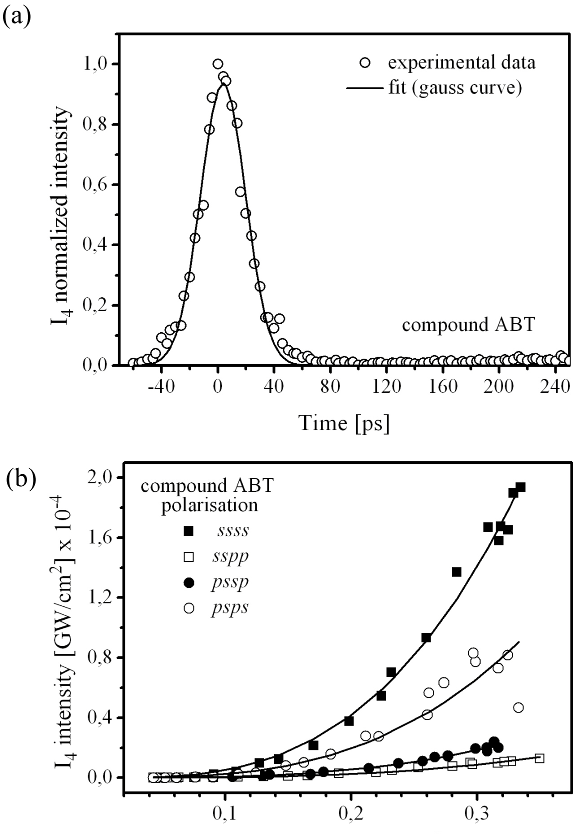


Fig. 3 (a) Temporal dependence of the intensity of the outgoing fourth wave (I_4) produced using DFWM method, (b) Correlation between intensities of this wave and the pumping beam (I_1). It is cubic as theoretically predicted.

Table 1. Solutions containing azo-azulene derivatives. Non-vanishing terms of the third order susceptibility tensor found by DFWM technique.

Polarization	$\chi^{(3)}\times10^{-20}$ [m^2/V^2]				
	Compound				
	THF	AHP	AAP	ABT	AT
ssss	0.079	0.166	0.210	6.546	5.068
sspp	0.020	0.038	0.230	1.552	1.265
psps	0.052	0.130	0.130	1.628	3.534
pssp	0.019	0.058	-	2.640	1.835

Table 2 Electronic and molecular contribution in third order susceptibility of azo-azulene derivatives

Compound	$\chi^{(3)el} / \chi^{(3)}$	$\chi^{(3)mol} / \chi^{(3)}$
AHP	$\chi^{(3)}_{ssss} = 1.27\chi^{(3)}_{psps} = 2.85\chi^{(3)}_{pssp} = 4.39\chi^{(3)}_{sspp}$	
	1.37	2.86
AAP	$\chi^{(3)}_{ssss} = 1.57\chi^{(3)}_{psps} = \ldots\cdot\chi^{(3)}_{pssp} = 0.91\chi^{(3)}_{sspp}$	
	2.6	6.94
ABT	$\chi^{(3)}_{ssss} = 4\chi^{(3)}_{psps} = 2,76\chi^{(3)}_{pssp} = 1,43\chi^{(3)}_{sspp}$	
	1.94	1.31
AT	$\chi^{(3)}_{ssss} = 4,22\chi^{(3)}_{psps} = 2,48\chi^{(3)}_{pssp} = 4,02\chi^{(3)}_{sspp}$	
	2.36	0.89

In blends consisting of physically dispersed NLO dye molecules and a host polymer, bulk NLO second order susceptibility is induced through a corona-poling technique [12]. Such a blend represents C∞v symmetry and the tensor of third order susceptibility reduces to one independent term, briefly referred as $\chi^{(3)}$ [12].

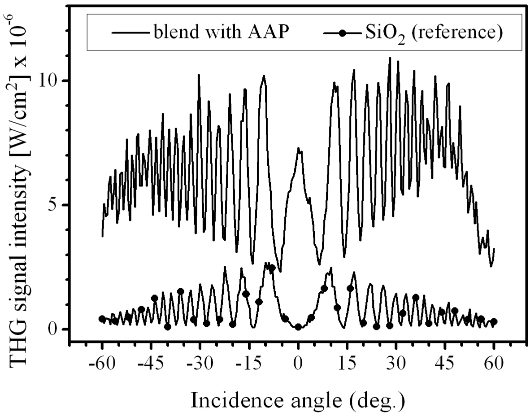


Fig. 4. Example of THG Maker fringes recorded for blend containing compound AAP. As reference SiO$_2$ was used.

Standard experimental tools used for $\chi^{(3)}$ determination are third harmonic generation (THG) and non-linear optical absorption [15]. Accordingly, they provide real part and imaginary part of the $\chi(3)$. The experimental arrangement used in this work was like the one described in [15]. Numerical recipes were taken from Kajzar *et al.* [16]. In Table 3 there are collected results of both experiments.

Table 3. Real and imaginary part of $\chi^{(3)}$.

Blend containing:	Re($\chi^{(3)}$) [m^2/V^2] $\times10^{-22}$	Im($\chi^{(3)}$) [m^2/V^2] $\times10^{-20}$
AHP	33.1	0.73
AAP	360	1.75
ABT	22.5	7.60
AT	41.4	14.30

It can be concluded that according to the experimental data, the most important values of $\chi^{(3)}$ represent azulene-1-azo-(4-acetamidophenyl) (compound AAP), which may be attributed to the strongest electron accepting character of the acetamidophenyl substituent. It should be stressed that in the case of the blend containing AAP compound, the measured THG signal was threefold larger than for quartz reference, already considered as a material of large $\chi^{(3)}$ as shown in Fig.4. Comparison between AT and ABT suggests a decreasing role in the electron accepting character of an additional phenyl group.

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