Pergamon

Tetrahedron Letters 39 (1998) 6853–6856

TETRAHEDRON
LETTERS

Push-Pull Azulene-Based Chromophores with Nonlinear Optical Properties

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Received 21 May 1998; accepted 15 July 1998

Abstract

A new chromophore 6-methoxy-1-[2-(4-nitrophenyl)ethenyl]-azulene was synthesized and tested for the Second Harmonic Generation (SHG) in solid state by the Kurtz powder technique. This compound was six times more efficient (58 times than the urea standard) than the unsubstituted compound 1-[2-(4-nitrophenyl)ethenyl]-azulene (10 times than the urea).

Keywords: Azulene, Chromophore, Second Harmonic Generation, Nonlinear Optics

There has been considerable interest in recent years in the development of new organic materials with nonlinear optical (NLO) properties [1,2]. The majority of organic molecules which exhibit high efficiency in Second Harmonic Generation (SHG) contain a strong electron donor and acceptor groups connected at the ends of a conjugated system [3]. Semi-empirical and *ab initio* calculations have suggested that azulene itself or suitably substituted azulenes should possess large hyperpolarizabilities, which are comparable to those of molecules like 4-nitroaniline [4,5].

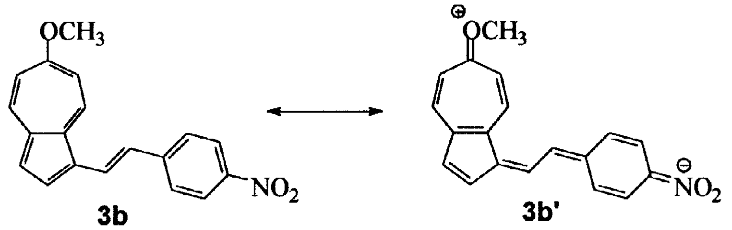
Surprisingly, the only report on the NLO activity of azulene push-pull derivatives was published by Asato *et al.* only in 1996. These compounds contain azulene or guiazulene as electron donor groups and dicyanovinyl or 1,3-diethyl-2-thiobarbituric acid as electron acceptor groups [6]. The $\beta\mu$ values, determined by the electric field induced second harmonic generation (EFISH) are comparable to those of NLO chromophores with N,N-diethylaniline as the donor group. To date, no measurements were reported in the solid state, where a non-centrosymmetric arrangement of the chromophores is an essential prerequisite, if the molecular NLO response is to contribute to an observable bulk nonlinearity [3]. We wish to report here our preliminary results on second order nonlinear properties in solid state of azulene-containing NLO

PII: S0040-4039(98)01495-6

chromophores with a 4-nitrophenyl electron acceptor group (**3**).

The electron-donating property of azulene was explained by the participation of a zwitterionic resonance form, stabilized by the formation of an aromatic azulenylium carbocation [7]. We expected that the presence of a π-electron donor in 6-position of azulene (OCH_3 in compound **3b**) would favor the formation of the zwitterionic form (**3b'**) as proposed in Scheme 1. A decrease in the energy gap between the ground (**3b**) and the excited state (**3b'**) should result from this substitution. This is normally associated with an enhanced hyperpolarizability (β) of the molecule [3].

Scheme 1



6-Methoxy-azulene (**1b**) was obtained in 4 steps starting from 4-pyrone, by modifications to old procedures [8]. The azulene-1-carboxaldehydes **2a** [8] and **2b** [9], have been synthesized from azulene and 6-methoxy-azulene respectively, by Vilsmeier-Haack formylation (Scheme 2). The 1-styryl-substituted azulenes (**3**) were obtained by a modified Wittig procedure [10], by treating the carboxaldehydes **2** with an excess of *p*-nitrophenylmethyl-triphenylphosphonium bromide [11] in boiling toluene and using *t*-BuOK as a base. This method provided both **E** and **Z** isomers (**E**:**Z** > 78:22) in good yield (>90%). The **E** and **Z** isomers were separated by column chromatography or by fractionated crystallization (Scheme 2).[1] Synthesis of compound **E-3a** was previously reported but under different conditions to give only a 15% yield [12].

The electronic absorption spectra of compounds **3** show the expected charge-transfer absorption bands in the visible region (Table 1). Substitution of azulene with the 2-(4-nitrophenyl)ethenyl group resulted in a significant blue shift of the long-wave absorption bands (from 576 mn in **1a** to 454 nm in **E-3a**). This phenomenon has been observed for other

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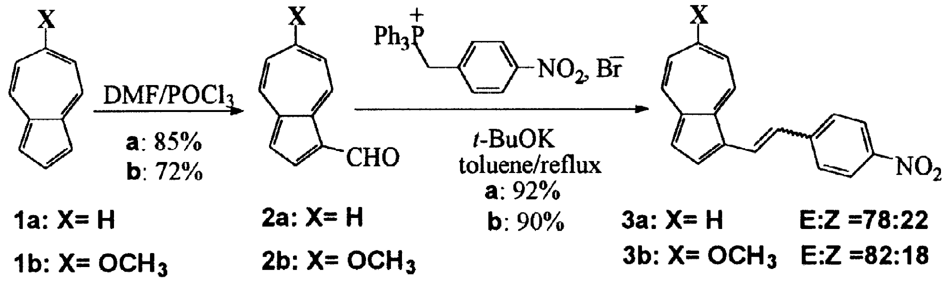
[1] **Experimental.** The compound **2b** was reported in a recent publication [9] but no synthetic details and characterization were reported. We obtained it following the same procedure as for the **2a** [8]. The purification was done by chromatography on alumina with petroleum ether-diethyl ether (72% yield). **^{1}H-NMR:** ($CDCl_3$): 10.29 (s, 1H, CHO); 9.47 (d, J=11.2Hz, 1H); 8.35 (d, J=11.2Hz, 1H); 7.98 (d, J=4.1Hz, 1H); 7.21 (d, J=4.1Hz, 1H); 7.16 (m, 2H); 4.01 (s, 3H, CH_3). **^{13}C-NMR:** ($CDCl_3$), δ (ppm): 186.9; 169.2; 141.6; 138.3; 138.1; 137.5; 135.6; 126.9; 119.5; 116.7; 114.9; 56.3. Found: C, 74.98; H, 5.27%. Calcd. for $C_{12}H_{11}O_2$: C: 74.64; H, 5.29%. **Compounds 3a.** 0.77g (1.6 mmol) of *p*-nitrophenylmethyl-triphenylphosphonium bromide and 0.23 g (2.05 mmol) of *t*-BuOK were suspended under argon in 15 ml of dried toluene. 12 ml of toluene were distilled in one hour. After cooling to the room temperature to this red mixture was added a solution containing 0.10 g (0.64 mmol) of aldehyde **2a** in 10 ml of dried toluene. The mixture was heated and in 30 min were distilled 10 ml of toluene, then refluxed for one additional hour. After the usual workup, the purification of the crude compound (**E**:**Z**=78:22) by fractionated precipitation with methylene chloride-petroleum ether, gave the **E** isomer pure. The filtrate contained a mixture of both isomers which were separated by chromatography on alumina (petroleum ether-diethyl ether). The global amounts: 0.127 g of isomer **E** and 0.035 g isomer **Z** (global yield 92%). **Isomer E-3a: mp**: 187-188° (lit.: 188° [12]). **MS** (70eV, m/*z*): 275 (M^+). **^{1}H-NMR:** ($CDCl_3$): 8.50 (d, J=9.8Hz, 1H); 8.26 (m, 2H); 8.18 (d, J=8.8Hz, 2H); 7.85 (d, J=16.0Hz, 1H); 7.63 (d, J=8.8Hz, 2H); 7.58 (t, J=9.9 Hz, 1H); 7.41 (d, J=4.3Hz, 1H); 7.21 (m, 2H); 7.16 (d, J=16.0Hz, 1H). **^{13}C-NMR:** ($CDCl_3$), δ (ppm): 145.9; 145.2; 143.7; 138.7; 137.3; 136.8; 133.7; 133.6; 126.4; 126.0; 125.1; 124.9; 124.3; 123.9; 123.7; 119.7. **Isomer Z-3a: mp**: 112-113°. **MS** (70eV, m/*z*): 275 (M^+). **^{1}H-NMR:** ($CDCl_3$): 8.33 (d, J=9.8Hz, 1H); 8.25 (d, J=9.3Hz, 1H); 8.06 (d, J=8.7Hz, 2H); 7.74 (d, J=3.9Hz, 1H); 7.59 (t, J=9.8Hz, 1H); 7.48 (d, J=8.7Hz, 2H); 7.26 (d, J=3.9Hz, 1H); 7.24 (d, J=12.1Hz, 1H); 7.18 (t, J=9.5Hz, 1H); 7.16 (t, J=9.8Hz, 1H); 6.62 (d, J=12.1Hz, 1H). **^{13}C-NMR:** ($CDCl_3$), δ (ppm): 146.4; 145.7; 142.4; 138.3; 137.1; 136.9; 134.1; 129.2; 126.8; 125.6; 124.8; 124.6; 123.6; 123.5; 118.4. Compounds **3b** were obtained by a similar procedure. The isomer **Z** could not be obtained in a pure form and was not characterized. **Isomer E-3b: mp**: 179-180°. **MS** (70eV, m/*z*): 305 (M^+). **^{1}H-NMR:** ($CDCl_3$): 8.38 (d, J=11.0Hz, 1H); 8.21 (d, J=8.8Hz, 2H); 8.13 (d, J=10.5Hz, 1H); 7.97 (d, J=4.1Hz, 1H); 7.84 (d, J=15.9Hz, 1H); 7.64 (d, J=8.8Hz, 2H); 7.31 (d, J=4.1Hz, 1H); 7.16 (d, J=15.9Hz, 1H); 6.89 (d, J=11.0Hz, 1H); 6.76 (d, J=10.5Hz, 1H); 3.97 (s, 3H, CH_3). **^{13}C-NMR:** ($CDCl_3$), δ (ppm): 168.3; 145.9; 145.5; 139.1; 136.9; 133.1; 129.4; 127.5; 126.1; 125.6; 124.4; 123.4; 120.9;117.4; 113.1; 110.0; 56.2.

substituted azulene derivatives [6,13]. The presence of the methoxy group resulted in a slight bathochromic shift of 9 nm (**E-3a** *vs* **E-3b**). Solvatochromic behaviour was observed for the compounds **E-3a** and **E-3b**, which is strongly indicative of changes in dipole moment upon electronic transition, and hence a sizable molecular hyperpolarizability.[2]

Scheme 2



The second-order NLO properties for all compounds were determined by the Kurtz-powder test at the fundamental wavelength of 1.907 μm to avoid absorption at the second-harmonic frequency [14]. Surprisingly for non chiral molecules, compounds **3** all exhibit SHG activity in solid state (Table 1), indicating non-centrosymmetric packing. The chromophore **E-3a** exhibits an efficiency 10 times larger than that of urea. The **Z-3a** isomer was about 3 times less efficient than the **E-3a**. The new compound (**3b**) is the first example of an azulene-based conjugated push-pull chromophore with the azulene moiety in the conjugation path, to be described as being efficient for SHG. **E-3b** exhibits a SHG signal that is 58 times larger than that of urea.

Table 1

Electronic absorption (λ_{max}), Dipole Moments (μ) and Efficiencies for Compounds **3**.

Compound	λ_{max} (nm)^a	μ (D)^b	$I^{2\omega}/I^{2\omega}$ (urea)^c
Z-3a	436	----	3
E-3a	454	7.5	10
E-3b	463	5.8	58

a. in CHCl$_3$. *b.* measured by a classical method based on the Guggenheim theory [15] (+/- 1 D). *c.* measured at 1.907 μm.

There are probably two main factors that determine the increased efficiency of this compound when compared to the unsubstituted compound **E-3a**. First, **E-3b** may possess a higher hyperpolarizability than **E-3a** because of the methoxy group on the azulene moiety, as suggested by the slight red shift. The second factor is the relative arrangement of molecules in the solid state. It is currently assumed that decreasing the ground-state dipole moment is a suitable strategy to favor crystallization in noncentrosymmetric space groups [16]. The dipole moment of **E-3b** (5.8 D) was found to be lower than the dipole moment of **E-3a** (7.5 D). This is indicative of a possibly more favorable arrangement of molecules **E-3b** in the crystal (Table 1). Unfortunately we could not obtain good quality single crystals of this compound, so that we can not confirm this hypothesis. The particular feature of compound **E-3b** (six times more efficient

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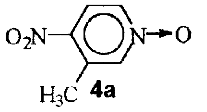
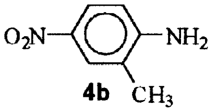
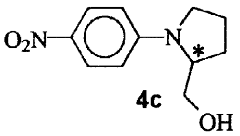
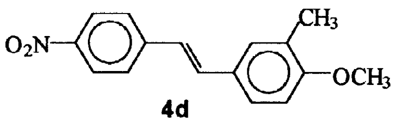
[2] Solvatochromism (λ_{max}, nm) **E-3a**: 444 (ethyl acetate); 447 (toluene); 454 (chloroform). **E-3b**: 453 (ethyl acetate); 456 (toluene); 463 (chloroform). The long-wave transition of azulene **1a** in chloroform appears as a broad band with several sharp absorptions (λ_{max}= 690 nm and the most intense maximum at 576 nm). Both of these bands showed only low solvatochromism in toluene and ethyl acetate (+/- 2 nm). See also ref. [13].

than **E-3a**) is that the introduction of the methoxy group probably resulted in a gain of efficiency at both the molecular and the solid state levels.

Table 2
SHG powder efficiencies of selected neutral compounds relative to urea.

 **4a**	13	ref. [16]	 **4b**	22	ref. [17]
 **4c**	70	ref. [18]	 **4d**	1250	ref. [19]

This is the first time that the efficiency of azulene-based chromophores for the SHG in solid state has been reported. For comparison, some of the most known neutral molecules (**4**) with their SHG powder efficiencies are listed in the Table 2.

In conclusion, our preliminary results have demonstrated the potential interest of azulene derivatives with the 4-nitrophenyl as the electron acceptor group for SHG. An efficiency as high as 58 times larger than that of urea was observed for the 6-methoxy substituted compound (**E-3b**). We are currently investigating other types of azulene-based chromophores, with the aim of optimizing the structures for high NLO efficiencies.

Acknowledgments: We gratefully acknowledge financial support from the Romanian Academy and Centre National de la Recherche Scientifique (CNRS).

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