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Azulene-Containing Donor-Acceptor Compounds as Second-Order Nonlinear Chromophores

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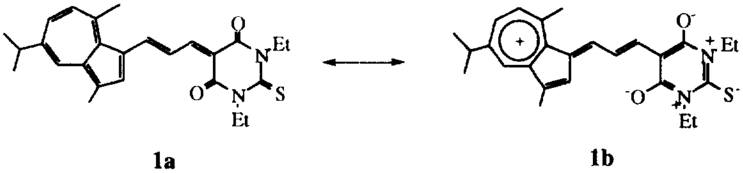
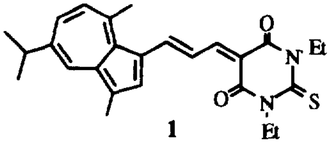
Abstract: Several novel, thermally stable azulene-containing donor-acceptor molecules were synthesized and their second-order nonlinear optical properties determined by the EFISH method. The βμ-values for these new compounds featuring azulene as the pi-electron donor were comparable with NLO compounds containing para-N,N-diethylaniline as the electron-donor.

Organic donor-acceptor molecules with highly polarizable pi-electrons are of great interest currently for their potential applications in nonlinear optical (NLO) devices.[1, 2] Recent studies indicate that the first molecular hyperpolarizability, β, of a conjugated NLO molecule such as **1** can be correlated to the relative contributions of its neutral and charge-separated resonance forms, **1a** and **1b**, respectively as shown below.[3, 4] Enhanced β-values have been reported for NLO compounds containing strong pi-electron donors like the ketene dithioacetal group,[5] electron deficient acceptors like the tricyanovinyl moiety,[6] or pi-electron heteroaromatic bridging units such as thiophene.[7, 8] In addition, donors or acceptors that are stabilized by aromatization also exhibit large hyperpolarizabilities.[4]

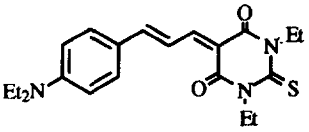


1a **1b**

We now wish to report on the preparation, NLO activity and thermal stability of several novel donor-acceptor compounds **1-4** that contain azulene or a substituted azulene (guaiazulene) as the pi-electron donor. The unique property of azulene in its role as an electron donor is that upon charge delocalization from the neutral to the zwitterionic resonance form, the disruption of aromaticity in azulene is more than offset by the gain of resonance energy upon formation of the aromatic azulenylium carbocation.[9] The pi-electron donor properties of azulene have been previously reported for long-wavelength light absorbing azulenic carbocyanine dyes[10] and azulene-containing analogs of bacteriorhodopsin.[11]



1



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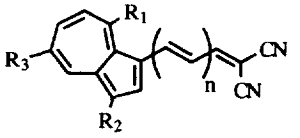
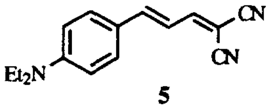


2: $n = 0$; $R_1 = R_2 = R_3 = H$
3: $n = 0$; $R_1 = R_2 = CH_3$; $R_3 = {}^{i}C_3H_7$
4: $n = 1$; $R_1 = R_2 = CH_3$; $R_3 = {}^{i}C_3H_7$



5

Dicyano derivatives **2** and **3** were prepared in high yield from azulene-1-carboxaldehyde and guaiazulene-1-carboxaldehyde, respectively,[12] by condensation with malononitrile in the presence of β-alanine. The more highly conjugated compounds **1** and **4** were obtained by condensation of 3-(1-guaiazulenyl)-propenal[13, 14] with 1,3-diethyl-2-thiobarbituric acid and malononitrile, respectively. All compounds were purified by recrystallization or column chromatography and characterized spectroscopically.[15] The electronic absorption (λ_{max}), nonlinear optical ($\beta\mu$) and thermal stability (T_d) properties for **1-4** and for the known N,N-diethylaniline derivatives **5** and **6** are listed in Table 1.

Table 1. Electronic Absorption, Second-Order NLO Properties and Thermal Stability Data for Azulenic NLO Compounds

Compounds	λ_{max}(nm)[a]	$\beta\mu$ (10^{-48} esu)[b]	T_d (°C)[c]
1	582	1323	247
2	425	153	360
3	470	216	289
4	513	911	290
5	477	906	280
6	555	1400	214

a. in dioxane; b. at 1.907 μm; c. Reference 16.

The azulenic derivatives **1-4** all possess an intense charge-transfer absorption band in the visible region of their electronic absorption spectra. The presence of alkyl groups on azulene (**2** vs **3**) resulted in a significant bathochromic shift of 45nm. Likewise, extending conjugation by a double bond (**3** vs **4**) and using a stronger acceptor (**4** vs **1**) produced large bathochromic shifts of 43 and 69 nm, respectively. Positive solvatochromism, (λ_{max} = 567 nm in cyclohexane to 639 nm in methanol) indicative of an enhanced contribution by the zwitterionic resonance form in the excited state, was observed for thiobarbituric acid derivative **1**.

The second-order NLO properties for all compounds were determined by the dc-electric field induced second harmonic generation (EFISH) method in dioxane at a fundamental wavelength of 1.907 μm.[7] At this wavelength, the second harmonic generated at a wavelength of 0.954 μm would be suitably distant from the lowest energy electronic transitions to minimize resonance enhancement.

The $\beta\mu$-values (150-1350 x 10^{-48} esu) obtained for azulenic derivatives **1-4** reveal the strong electron-donating ability of the azulene moiety. The guaiazulene derivative **3** possesses enhanced molecular nonlinearity relative to the corresponding azulene derivative **2**, due to the influence of electron-donating alkyl substituents on the ring. For compounds **3** and **4** increasing conjugation length substantially enhanced molecular nonlinearities by a factor of ~4. The $\beta\mu$-value (1323 x10^{-48} esu) obtained for the thiobarbituric acid derivative **1** clearly indicates that concomitant aromatization of both the donor and acceptor groups results in dramatic enhancement of NLO properties.

The molecular nonlinearities of the known N,N-diethylaniline derivatives **5** and **6** were also measured and compared to their respective guaiazulene derivatives **4** and **1**. The $\beta\mu$-values for dicyanovinyl compounds **4** and **5** were essentially identical (911 and 906, respectively) although **4** was considerably red-shifted (36 nm). For thiobarbituric acid derivatives **1** and **6**, $\beta\mu$-values were both similar and quite large (1323 and 1400, respectively) even though **1** absorbs 27 nm to longer wavelength. These data indicate that the NLO properties of guaiazulene-containing compounds are quite comparable to NLO chromophores with N,N-diethylaniline as the pi-electron donor.

The inherent thermal stability (T_d) behavior of compounds **1-6** were also examined using differential scanning calorimetry (DSC).[16] All the azulenic derivatives possess excellent inherent thermal stability ranging from 240°C-360°C. Extending the pi-conjugation by one double bond (**3** vs. **4**) had no effect on thermal stability. However, alkyl substituents on the azulene nucleus lowered thermal stability by about 70°C (**2** and **3**). The dicyanovinyl group conferred additional thermal stability relative to the thiobarbituric acid acceptor group for both the guaiazulene and N,N-diethylaniline series of compounds. For the thiobarbituric acid derivatives **1** and **6**, decomposition occurred immediately after the melting transition. The excellent thermal stability of the dicyanovinyl compounds **4** (290°C) and **5** (280°C) suggest that both azulene and substituted azulenes offer similar advantages as substituted aniline pi-electron donor groups for the design of NLO chromophores.

In conclusion, the important role of azulene and its alkylated derivative, guaiazulene, as both thermally stable and highly effective pi-electron donors in conjugated chromophores has been demonstrated for several representative NLO compounds. The observation that electron-donating alkyl substituents on azulene enhances molecular nonlinearity suggests that even more efficient NLO compounds can be designed by incorporating stronger electron-donating substituents such as amino or alkoxyl groups into the azulenic donor.

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15. ^{1}H-NMR data (300 MHz, $CDCl_3$, TMS) for **1-4**: Compound **1**: δ 1.30 and 1.34 (6H, 2 t, J = 7 Hz, 2-$NCH_2C\underline{H}_3$), 1.38 (6H, d, J = 6.9 Hz), 2.55 (3H, d, J = 0.7 Hz, C2'-CH_3), 3.12 (3H, s, $C_{8'}$-CH_3), 3.17 (1H, m), 4.58 (4H, J = 7 Hz, 2-$NC\underline{H}_2CH_3$), 7.37 (1H, d, J = 10.7 Hz), 7.56 (1H, dd, J = 2.2 and 10.7 Hz), 8.14 (1H, J = 1.9 Hz), 8.23 (1H, s), 8.24 (1H, d, 12.9 Hz), 8.45 (1H, d, J = 14.1 Hz) and 8.59 (1H, dd, J = 12.6 and 13.8 Hz) ppm.

    Compound **2**: δ 7.56 (d, J = 4.5 Hz), 7.65 (t, J = 9.9 Hz), 7.68 (7, J = 10 Hz), 7.96 (t, J = 9.8 Hz), 8.54 (d, J = 9.6 Hz), 8.62 (d, J = 9.85 Hz) and 8.93 (d, J = 4.5 Hz) ppm.

    Compound **3**: δ 1.31 (6H, d, J = 7 Hz), 2.51 (3H, s, C_3-CH_3), 3.02 (3H, s, C_8-CH_3), 3.10 (1H, m, J = 7 Hz), 7.43 (1H, d, J = 10.9 Hz, C_7-H), 7.61 (1H, dd, J = 2.0 and 10.9 Hz, C_6-H), 8.23 (1H, d, J = 2.0 Hz, C_4-H), 8.41 and 8.52 (1H each, s, C_2-H and vinyl H) ppm.

    Compound **4**: δ 1.32 (6H, d, J = 6.9 Hz), 2.59 (3H, s, $C_{2'}$-CH_3), 3.07 (3H, s, $C_{8'}$-CH_3), 3.13 (1H, m, J = 7 Hz), 7.13 (1H, dd, J = 12.2 and 13.9 Hz, C_3-H), 7.28 (1H, d, J = 10.7 Hz, $C_{7'}$-H), 7.53 (1H, dd, J = 1.6 and 10.7 Hz, $C_{6'}$-H), 7.55 (1H, d, J = 12 Hz, C_2-H), 8.03 (1H, s, $C_{4'}$-H), 8.16 (1H, s, $C_{2'}$-H) and 8.18 (1H, d, J = 14.7 H, C_4-H) ppm.
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