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Novel D-π-A Chromophores Based on the Fulvene Accepting Moiety

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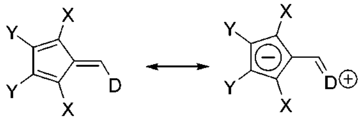
ABSTRACT



Novel D-π-A chromophores based on the fulvene accepting moiety and *p*-dimethylamino phenyl and 1,3-dithiole-2-ylidene donor moieties have been prepared. The X-ray structures of two representative derivatives have been determined. Examination of the UV−visible spectra and cyclic voltamperometry data revealed remarkable sensitivity of the electronic structure of these derivatives to substituents at the cyclopentadiene ring.

Conjugated donor−acceptor systems are currently the focus of numerous studies owing to their large hyperpolarizabilities and, therefore, the ability of second harmonic generation. A general trend in the design of second-order nonlinear optical materials involves tuning the donor and acceptor strength, and a variety of strong accepting groups, such as polycarbonyl, nitro, and cyano derivatives have been employed.[1] In particular, the high potential of polynitrofluorenes as the electron-accepting units have recently been demonstrated.[2] Fulvene derivatives[3] should exhibit higher polarizability than fluorene derivatives, which suggested the possibility of their use as accepting moieties in the above systems, and indeed, several fulvene compounds unsubstituted at the cyclopentadiene ring, showing nonlinear optic properties, have been described.[4] Derivatives substituted at the cyclopentadiene ring have received only scant attention. Recently, we have shown that fulvalene derivatives are strong proaromatic electron acceptors and their electron affinities (LUMO energies) are highly sensitive to substitution at the cyclopentadiene ring.[5]

Here we report on the synthesis of a series of novel 2,3,4,5-substituted fulvene derivatives and their spectroscopic and electrochemical properties. Three sets of fulvene derivatives were studied: tetrachloro-, 3,4-dimethoxy-2,5-dicyano-, and poly(methoxycarbonyl)-fulvenes (**5**−**8** and **10**, **11**). Fulvene derivatives[6] discussed here are unknown except the tetrachlorofulvenes **5a** and **6a**.[7] Derivatives **5**−**8** were synthesized by condensation of tetrachlorocyclopentadiene (**1a**),[8] 3,4-

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(6) All new fulvenes were characterized by spectroscopic means and HRMS. The molecular structure of cyclopentadiene **1b** and fulvenes **10** and **11** were determined by X-ray analysis and will be described elsewhere.

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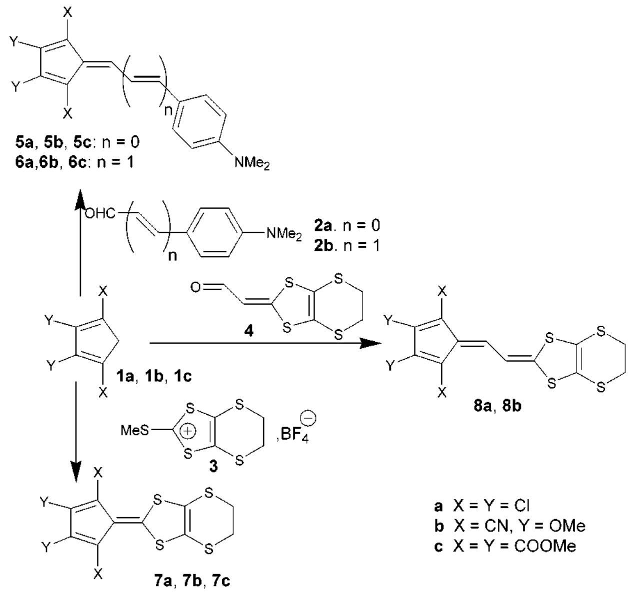
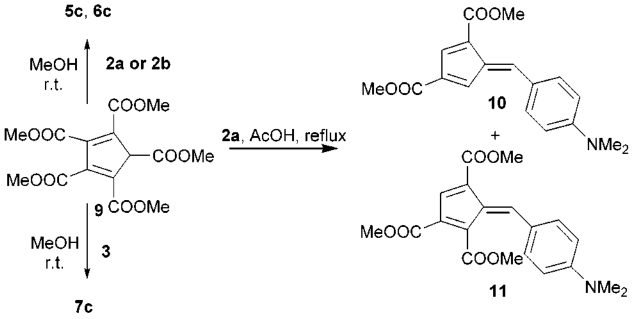
Scheme 1



dimethoxy-2,5-dicyanocyclopentadiene (**1b**), or tetrakis(methoxycarbonyl) cyclopentadiene (**1c**) (Scheme 1) with the corresponding aldehyde or 1,3-dithiole precursors.[9]

The synthesis of **1c** was achieved by reproducing the recently reported[10] partial hydrolysis/decarboxylation of pentakis (methoxycarbonyl) cyclopentadiene (**9**). The overall yield of **1c** did not exceed 5%, which makes its use as a precursor not practical. Alternatively, we found that derivative (**9**) reacts smoothly with aromatic aldehydes and 2-methylthio-1,3-dithiolium salt **3** in methanol at room temperature, providing an efficient one-pot synthesis of tetrakis(methoxycarbonyl) fulvenes (Scheme 2). The reaction of **9** with **2a** in refluxing acetic acid was accompanied by hydrolysis and decarboxylation, and di- and triesters **10** and **11** were isolated from the reaction mixture.

Scheme 2



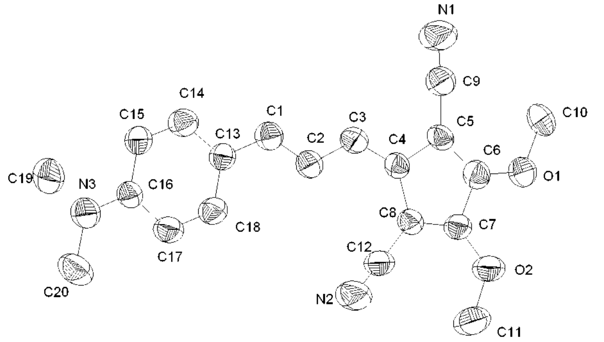


Figure 1. Molecular structure of **6b**. Selected bond lengths (in Å): 1.338(4) (C1–C2), 1.433(4) (C2–C3), 1.357(4) (C3–C4), 1.442(4) (C1–C13), 1.388(4) (C13–C14), 1.396(5) (C13–C18), 1.373(4) (C14–C15), 1.393(5) (C15–C16), 1.406(4) (C16–C17), 1.374(4) (C17–C18).

The crystal structures of derivatives **6b** and **7b** were determined by the X-ray experiments.[11] Both derivatives are planar in the solid state. The geometry of the conjugating bridge linking the donor and acceptor moieties within derivative **6b** (Figure 1) is close to that found for the corresponding 1,3-indanedione-2-ylidene analog: 1.363(4), 1.423(5), 1.352(4), and 1.439(4) Å for the bonds corresponding to C3–C4, C2–C3, C1–C2, and C1–C13.[12]

The length of the central double bond (1.380 Å) of derivative **7b** (Figure 2) is also close to that found in the corresponding 1,3-indandione-2-ylidene analog[13] (1.370 Å), and therefore the accepting ability of the 1,4-dicyano-2,3-dimethoxycyclopentadiene-2-ylidene moiety is close to that of 1,3-indandione-2-ylidene moiety.

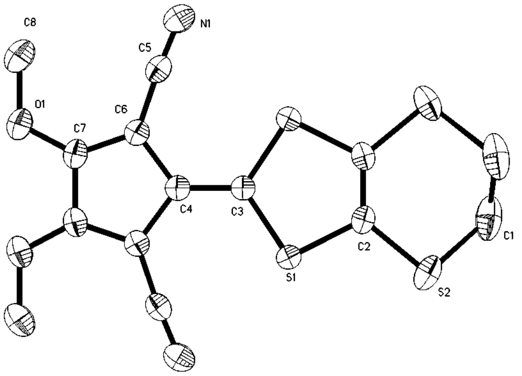


Figure 2. Molecular structure of **7b**. Selected bond lengths (in Å): 1.747(3) (S1–C2), 1.742(2) (S1–C3), 1.380(5) (C3–C4), 1.454(3) (C4–C6), 1.382(3) (C6–C7).

Results of the electrochemical and spectroscopic studies are collated in Table 1. All new derivatives undergo one-

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[9] Condensation of tetrachlorocyclopentadiene (**1a**) with aldehydes **2a** and **2b** was carried out in MeOH in the presence of a catalytic amount of DMF. Reaction of **1a** with 2-methylthio-1,3-dithiolium salt (**3**) was carried out in refluxing AcOH. Condensation of 3,4-dimethoxy-2,5-dicyanocyclopentadiene (**1b**) with **2a**, **2b** and **3** carried out in refluxing AcOH. Condensation of tetrakis(methoxycarbonyl) cyclopentadiene (**1c**) with **2a**, **2b**, and **2c** was carried out in methanol at room temperature. Cyclopentadienes **1a** and **1b** were condensed with aldehyde **4** in refluxing AcOH in the presence of catalytic amount of piperidine.

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Table 1. Redox Potentials (V vs Ag/AgCl) in CH_2Cl_2 Solution and Absorption Spectra (nm) for 10^{-5} mol L^{-1} Solutions

compound	E_{red}	E_{ox}	$\lambda_{max}{}^{b}$	$\lambda_{max}{}^{c}$	$\lambda_{max}{}^{d}$
7a			502	511	
7b	−1.07	1.11[a,e]	514	511	518
7c	−0.77[a]	1.41	520	519	521
8a	−0.99	1.04	541	550	545
8b	−0.93	0.95[a]	539	525	537
5a	−1.26	1.06	474	485	479
5b	−1.20	0.97[a]	485	479	489
5c	−0.87[a]	1.19[a]	523	562	556
6a	−1.05	0.85	511	527	518
6b	−1.07	0.79[a]	512	503	517
6c	−0.72	0.96[a]	600	633	625
10	−1.16[a]	1.04	506	522	518
11	−1.04	1.11	521	540	536

[a] Reversible. [b] In CH_3Ph. [c] In CH_3CN. [d] In CH_2Cl_2. [e] $E_{ox(2)} = 1.49$ V.

electron reduction at potentials between −1.26 (**5a**) and −0.72 V (**6c**) and one-electron oxidation between 1.41 (**7c**) and 0.79 V (**6b**). Derivatives **5c**, **7c**, and **10** undergo reversible reduction.

The reduction potentials within the series **a** (X = Y = Cl) and **b** (X = CN, Y = OMe) are very close and approximately 300 mV more negative than observed for the series **c** (X = Y = CO_2Me). Thus, the electron-withdrawing effect of four chlorine atoms is close to that of the two cyano and two methoxy groups and, expectedly, weaker than the effect of four methoxycarbonyl groups. The trend in oxidation potentials is more difficult to rationalize. All derivatives of the **b** series undergo reversible oxidation at considerably lower potentials than derivatives from **a** and **c** series (Table 1); two oxidation peaks were observed for derivative **7b**.

The position of the longest wave absorption bands of derivatives **5**−**8**, **10**, and **11** within the series undergoes shifts in agreement with the differences in redox potentials. Thus, the largest difference in redox potentials observed for **5a** (2.32 V) corresponds to the absorption at the shortest wavelength (479 nm), and the smallest difference observed for **6c** (1.68 V) corresponds to the absorption at 625 nm (all values for methylene chloride solutions). This observation supports indirectly the assignment of these bands as charge-transfer bands (HOMO → LUMO transitions). Derivatives of the **a** series exhibit moderate positive solvatochromism, which increases for derivative **10** and **11** and reaches its maximum in the case of the **c** series. However, the derivatives of the **b** series exhibit fully unexpected negative solvatochromism.

Indeed, whereas the positive solvatochromism is expected for the longest wave absorption band that should have a charge-transfer nature, the above behavior of derivatives of the **b** series is puzzling. Quantum mechanical calculations[14] were performed for derivatives **6a**, **6b**, and **6d** (X = Y = CN) to gain deeper insight into the remarkable sensitivity of the cyclopentadiene ring to the substituent effects. Geometry optimization on RHF/6-31G(p,d) level yielded planar structures, and a good agreement with the experimental geometry found for **6b** was obtained. All bond lengths were predicted within 0.01 Å, except the C1−C13 bond for which the length of 1.461 Å was calculated. The calculated dipole moments for compounds **6a**, **6b**, and **6d** were μ_g = 9.15 , 2.56, and 19.44 D, respectively. HOMOs of all three derivatives feature zero coefficients at 1,4-positions of the cyclopentadiene ring (see Figure 3 for an example), which means that the HOMO energies are not sensitive to the substituents mesomeric effect at these positions. This result accounts for the observed trend in oxidation potentials. Absorption spectra were calculated using TD B3LYP/6-31G-(d,p) (see, e.g., ref 15 and references therein), which gave excellent predictions for molecules of a similar type.[16] Strong charge-transfer bands at 431 nm (f = 1.27) and 490 nm (f =

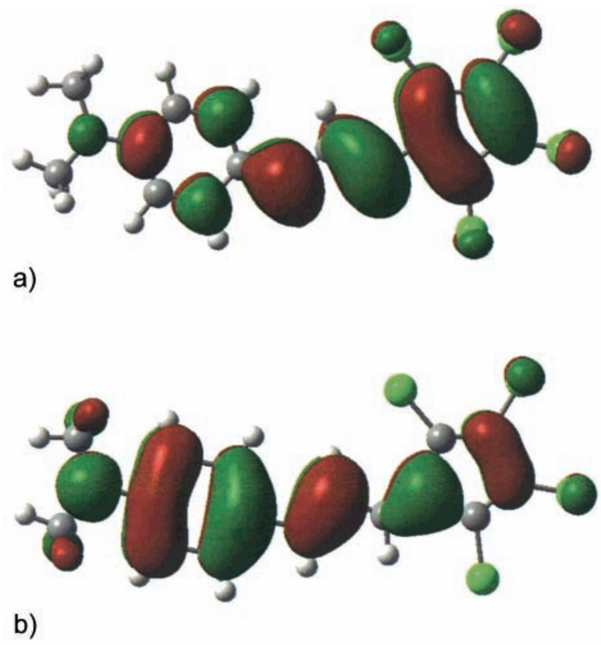

Figure 3. LUMO (a) and HOMO (b) diagrams for derivative **6a**.

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(11) **6a**: dark violet prism (0.4 × 0.4 × 0.1), monoclinic, $C_{20}H_{13}N_3O_2$, space group $C2/c$, $Z = 8$, at 294 K, $a = 21.474(6)$, $b = 13.828(1)$, $c = 15.723(7)$ Å, $V = 3565(3)$ Å^3, $\rho_{calcd} = 1.24$ Mg/m^3, $F(000) = 1408$; 3410 reflections were collected of which 1342 reflections were independent. Structure was refined to R1 = 0.044, wR2 = 0.057, GOF = 1.117. **7b**: dark ruby prism (0.5 × 0.2 × 0.2), orthorhombic, $C_{14}H_{10}N_2O_2S_4$, space group $Cmcm$, $Z = 4$, at 293(2) K, $a = 15.917(1)$, $b = 13.513(2)$, $c = 7.1891(7)$ Å, $V = 1546.4(3)$ Å^3, $\rho_{calcd} = 1.574$Mg/m^3, $F(000) = 752$; 6894 reflections were collected of which 1065 reflections were independent. Structure was refined to R1 = 0.0388, wR2 = 0.1013, GOF = 0.933. Atomic coordinates, bond lengths and angles, and anisotropic parameters have been deposited at the Cambridge Crystallographic Data Center.

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1.40) (HOMO → LUMO, $\pi \rightarrow \pi^*$ transition), which should undergo a red shift at increasing polarity of solvents, were predicted for derivative **6a** and **6d**, correspondingly. In contrast, two intense transitions in the visible part of the spectrum, 467 nm, $f = 1.0$ (HOMO → LUMO, $\pi - \pi^*$) and 323 nm, $f = 0.45$ (HOMO^{2-} → LUMO, $\pi \rightarrow \pi^*$), were predicted for derivative **6b**. This result is consistent with the observed asymmetric longest wave absorption bands of **6b** and other derivatives of the **b** series. The transition dipole moments for both transitions involve predominantly the X-component and have the opposite signs (charge transfer from NMe_2 donor moiety for the first transition and from 2 MeO donors for the second transition to the accepting moiety). The calculated energy and intensity of the first transition strongly depends on the conformation of the molecule. For instance, the intensity of the first transition for a nonplanar conformer of **6b** (with the C14−C13−C1−C2 dihedral angle of 45°) drops down considerably ($f = 0.60$), whereas the intensity of the second transition increases ($f = 0.67$). The nonplanar conformers of **6b** should always be present in solution at room temperature, since the rotation barriers around C1−C13 and C2−C3 bonds do not exceed 4 kcal/mol according to the results of RHF/6-31G(p,d) calculations. In contrast, HOMO^{2-} → LUMO transition does not depend on the conformation.[17] The above difference in the transition nature gives rise to the observed negative solvatochromism. Similar behavior was recently observed for the D-π-A systems involving a carbazole moiety for which negative solvatochromism and negative $\mu\beta_0$ values were found.[18]

In summary, we synthesized a series of D-π-A chromophores involving a substituted fulvene moiety as electron acceptor and studied their electrochemical and electronic spectra. These compounds exhibit a remarkable sensitivity to the substituents' nature and position. Fine-tuning of the substituents at the cyclopentadiene ring and the conjugating bridge can afford new dyes possessing a variety of solvatochromic effects and high hyperpolarizability. Indeed, the initial EFISH measurements performed for derivative **6a**[19] afforded a value of $\mu\beta_0 = 548 \times 10^{-48}$ esu, about two times larger than for the analogue of **6a** involving the 1,3-indandione accepting moiety.[20] Detailed studies of the donor−acceptor substituted fulvene derivatives are currently under way.

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[17] Calculations on the semiempirical (PM3) level provided essentially the same results. However, the energies of both transitions calculated at this level using CI are very close: 412 and 408 nm for the planar conformation. The second transition becomes the first (409 nm), whereas the first transition undergoes considerable hypsochromic shift (389 nm) for the above nonplanar conformation, which is less stable by 1.4 kcal/mol. The large energy gap between the first and the second transitions predicted by the TD DFT method stems probably from the propensity of this method to overestimate energies of the higher energy transitions, as it is the case with the HF-based methods.

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