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Second Order NLO Properties of Novel Dicyanovinylthiophene Derived Chromophores

Ana I. de Lucas, Nazario Martín,* Luis Sánchez and Carlos Seoane*

Departamento de Química Orgánica I, Facultad de Química, Universidad Complutense de Madrid, E-28040, Madrid (Spain)

Javier Garín and Jesús Orduna

Departamento de Química Orgánica, ICMA, Universidad de Zaragoza-CSIC, E-50009, Zaragoza (Spain)

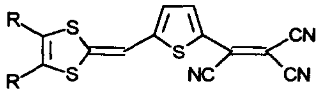
Rafael Alcalá and Belén Villacampa

Departamento de Física de la Materia Condensada, ICMA, Universidad de Zaragoza-CSIC, E-50009, Zaragoza (Spain)

Abstract: Novel compounds containing the dicyanovinylthiophene moiety conjugated with different substituted dithiafulvenyl electron-donor chromophores exhibit efficient molecular nonlinearities; the presence of additional sulfur atoms leads to an increase of the nonlinear optical response.

The electronic and structural properties of donor-acceptor substituted π-conjugated organic compounds are of considerable interest due to the nonlinear optical (NLO) properties they can exhibit with potential applications in optical communications.[1] A wide variety of structural modifications on the donor, acceptor and spacer moieties have been carried out[2] and, in relation to the π-conjugated spacer, experimental[3] and theoretical[4] studies reveal that the presence of a conjugated thiophene ring results in higher hyperpolarizabilities (β), in comparison with the benzene ring, due to the lesser aromatic resonance energy of the thiophene molecule.[5] Consequently, the preparation of novel thiophene-containing D-π-A systems is of great interest and, recently, several papers with different donor and acceptor chromophores attached to the thiophene ring have been published.[6]

In the search for more efficient electron-donating groups, Jen *et al.*[7] have recently investigated the effect of the electron-donating dithiafulvenyl group in combination with the thiophene spacer. Highly efficient second-order nonlinearities were obtained using a tricyanovinyl chromophore as electron acceptor (**1**). Other tricyanovinylthiophene derivatives with different donors (**2**) have also led to high second-order NLO susceptibilities.[8] In these compounds (**1**, **2**) the tricyanovinyl group is attached to the thiophene ring in a one-step procedure by reaction of the donor-substituted thiophene with tetracyanoethylene (TCNE).[7,8]



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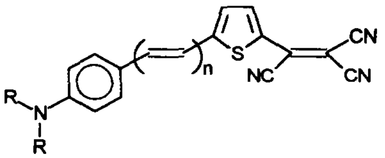

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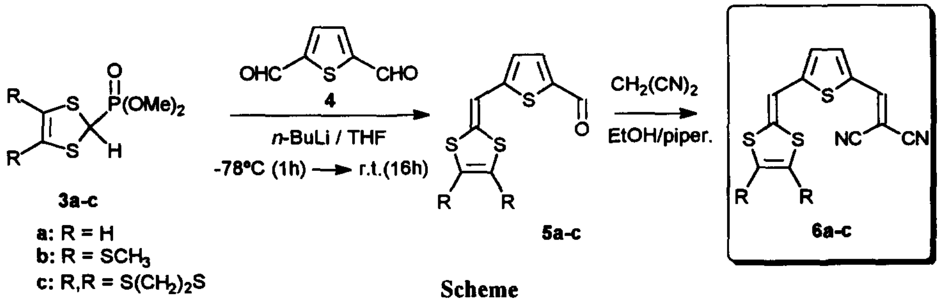
It has been recently reported that the presence of stronger acceptors can diminish the nonlinear optical response in simple donor-acceptor polyenes.[9] In order to evaluate the effect of a milder electron-acceptor chromophore on the "unconventional" dithiafulvenyl electron-donor covalently linked to a thiophene ring, we have prepared the novel D-π-A compounds (**5a-c** and **6a-c**) bearing carbonyl or dicyanovinyl groups as acceptor chromophores respectively and determined their NLO properties both by experimental (EFISH) and theoretical calculations.

The novel compounds were synthesized from 2,5-diformylthiophene (**4**) by Wittig-Horner reaction with the carbanion generated from phosphonate esters (**3a,c**),[10] in the presence of *n*-BuLi. Thus, the stoichiometric reaction of compounds **3** and **4** (1:1) leads to the formation of the monocondensed compounds **5a-c** (30-38%) bearing a free formyl group. A further Knoevenagel reaction of formylthiophenes **5a-c** with malononitrile under basic conditions (piperidine) afforded to compounds **6a-c** in 70-90% yield[11] (Scheme).



Scheme

The stretching cyano band of compounds **6a-c** appears at 2210 cm^{-1}, thus indicating the large conjugative effect in these molecules. The UV-Vis spectra of compounds **5** and **6** show a low energy charge-transfer band in the visible region which is bathochromically shifted in compounds **6a-c** as a consequence of the stronger electron-acceptor character of the dicyanovinyl chromophore, in comparison with the carbonyl group in **5a-c** (Table).

Table UV-Vis, μβ and redox potentials for **5** and **6**

Comp.	λ_{max} (nm)[a]	μβ[b]	$\mu\beta_0$[b]	$E^{1,ox}_{c\ a.p.}$	$E^{1,red}_{c\ c.p}$
5a[d]	432	115	62.9	0.74	-1.57
5b[d]	446	140	103.3	0.78	-1.53
5c[d]	447	115	59	0.76	-1.57
6a[e]	550	320	195.8	0.73	-1.51
6b[e]	565	500	295.7	0.80	-1.52
6c[e]	549	500	306.3	0.81	-1.53

[a] Measured in dioxane. [b] All μβ values are given in (. 10^{-48} esu) units. [c] In volts *vs*. SCE; solvent: CH_2Cl_2; supporting electrolite: NBu_4ClO_4; working electrode: GCE; scan rate: 0.2 Vs^{-1}. [d] In dioxane at 1378 nm. [e] In $CHCl_3$ at 1907 nm.

Compounds **5** and **6** showed an oxidation wave which is only slightly influenced by the substitution on the 1,3-dithiole ring. Thus, the presence of methylthio or ethylenedithio as substituents results in a more positive value of the first oxidation potentials which reveals a slightly poorer donor behaviour. The CV data also seems to show the better acceptor ability of the dicyanovinyl chromophore, compared to the carbonyl group. These findings are more clearly observed by their electronic spectral data (Table).

The molecular hyperpolarizabilities (μβ) of compounds **5** and **6** were measured in dioxane or chloroform as solvent using the electric-field-induced second harmonic generation (EFISH) technique at 1378 nm for **5a** and 1907 nm for the rest of compounds to minimize a possible resonance enhancement which could exagerate the measured values. The zero-frequency hyperpolarizability ($\mu\beta_o$) values were obtained from a two level dispersion model[12] and are shown in the Table.

The change of the formyl group by the dicyanomethylene as acceptor chromophore results in higher $\mu\beta$ values. The presence of additional sulfur atoms in the substituents on the 1,3-dithiole ring leads to an enhancement of the $\mu\beta$ values, in agreement with that previously observed for the tricyanovinyl analogues.[7]

Semiempirical calculations have been frequently used to predict trends in $\mu\beta_o$ values. Nevertheless, a conformational study of compounds **5** and **6** revealed that the PM3 method (in contrast to AM1) fails to locate the correct geometries for these derivatives since the C=C (or C=O) bonds of the substituents at the 2- and 5- positions of the thiophene ring are predicted to be *anti* with respect to the thiophene sulfur atom. It is well known that the C=O bond of 2-formylthiophene exists in the *syn* conformation[13] and that the dithiole rings in 2,5-bis(1,4-dithiafulven-6-yl)thiophene show a *syn-syn* relationship as demonstrated by X-ray diffraction data.[14] More recently, the X-ray structure of 2-chloro-5-tricyanovinylthiophene also reveals the presence of the *syn* conformation in the single-crystal.[15] Given that similar failures of PM3 have already been noted in the study of other compounds showing intramolecular S...S interactions,[16] the geometry optimization of the model compounds **5a** and **6a** was carried out by *ab initio* methods[17] at the 3-21G* level, which incorporates polarization functions on the sulfur atoms, a necessary requisite to treat adequately the compounds under study. These calculations revealed that the most stable conformers are those depicted in the Scheme, in agreement with the above-mentioned observations on related compounds. CPHF calculations at the 6-31+G* level afforded $\mu\beta_o$ values of 57.10^{-48} and 307.10^{-48} esu for **5a** and **6a**, respectively, in reasonably good agreement with the experimental values.

In summary, the experimental and theoretical $\mu\beta_o$ values obtained for compounds **5** and **6** indicate that the combination of dithiafulvenyl donors and dicyanovinyl acceptors conjugated through a thiophene ring results in nonlinear optical chromophores exhibiting good molecular nonlinearities which, however, are not so dramatically enhanced as those tricyanovinylthiophene-containing derivatives.[7]

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11. All compounds gave satisfactory spectral and analytical data. **6a**: ^{1}H NMR (DMSO-d_6): 7.84 (d, 1 H, J=4.4 Hz), 7.40 (s, 1 H), 7.19 (s, 2 H), 7.11 (d, 1 H, J=4.4 Hz), 5.46 (s, 1 H); ^{13}C NMR (DMSO-d_6): 153.0, 150.6, 148.3, 141.8, 131.8, 124.7, 121.8, 121.4, 115.5, 114.8, 113.2, 105.4; MS (m/z); 274 (100%). **6b**: ^{1}H NMR (DMSO-d_6): 8.50 (s, 1 H), 7.85 (d, 1 H, J=4.2 Hz), 7.34 (s, 1 H), 7.14 (d, 1 H, J=4.2 Hz), 3.37 (s, 6 H); ^{13}C NMR ($CDCl_3$): 152.2, 149.0, 143.2, 139.1, 132.7, 124.8, 115.0, 114.1, 106.4, 19.1, 18.9; MS (m/z); 366 (79%).**6c**: ^{1}H NMR (DMSO-d_6): 8.53 (s, 1 H), 7.86 (d, 1 H, J=4.0 Hz), 7.40 (s, 1 H), 7.15 (d, 1 H, J=4.0 Hz), 3.63 (s, 4 H); ^{13}C NMR ($CDCl_3$): 151.3, 151.2, 141.7, 138.5, 133.3, 126.1, 115.2, 114.6, 114.5, 112.9, 107.5, 29.1, 29.0; MS (m/z); 364 (35%).
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