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2-(1,1-dicyanomethylene)rhodanine: A novel, efficient electron acceptor

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ABSTRACT

The push–pull behaviour of novel 2-(1,1-dicyanomethylene)rhodanines bearing an electron donor *N*,*N*-dimethylaniline or tetrathiafulvalene group on the C-5 of the heterocyclic ring was studied using experimental (electrochemical and spectroscopical analysis) and theoretical (DFT/B3LYP/631G**) methods. Calculations showed a remarkable push–pull trend with the HOMO mainly located on the donor moiety and the LUMO on the acceptor dicyanomethylene moiety. In agreement with the theoretical predictions, a solvatochromic, behavior intramolecular charge transfer band was observed in the visible region.

1. Introduction

The inter- and intra-molecular electronic communication between electron donor and acceptor units is an important topic in chemistry since it is a key issue in a wide variety of different areas such as electrically conducting materials, non-linear optics (NLO), molecular rectification, dyes, solvatochromism, photovoltaics (PV) [1], etc.

The linkage between both donor (D) and acceptor (A) fragments has been carried out by means of covalent saturated (sigma) bridge (D-σ-A) such as in the well-known Aviran and Ratner model single molecule [2], which according to its constitution could act as a molecular rectifier, thus opening the field to the so called molecular electronics [3]. The D and A moieties have also been connected through a π conjugated bridge to form D-π-A organic materials of interest in optical applications such as, for instance, modulation, molecular switching, optical memory and frequency doubling [4]. Finally, non-covalent interactions between the D and A moieties are increasingly being used for the preparation of well defined supramolecular architectures [5].

Rhodanine derivatives have been used as acceptor moiety in a variety of push–pull organic compounds of interest, for instance, in second order NLO [6], as analytical reagent [7], and, more recently, they have proven their utility as metal-free organic dyes in the fabrication of dye sensitized solar cells (DSSCs). For this purpose, the donor-rhodanine push–pull dyad is covalently connected to a carboxylic group to efficiently anchor to the mesoporous TiO_2 surface. The light absorbed by the dye inject electrons into de conduction band of the TiO_2, thus generating an electrical current, while the ground state of the dye is regenerated by the electrolyte [8].

2. Experimental

2.1. Materials and equipments

Commercially available starting materials, reagents and solvents were used as supplied. Solvents used in photochemical measurements were of spectroscopic grade. TLC analyses were performed on Merck TLC-plates aluminium silica gel 60 F254, melting points were determined in a Buchi Melting Point Apparatus and are uncorrected. The ^1H and ^{13}C NMR spectra were run on a Bruker AVANCE 400 spectrometer operating at 400 MHz and 100 MHz respectively, using dimethyl sulfoxide–d_6 as solvent and tetramethylsilane as internal standard. The mass spectra were scanned on

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a Shimadzu GCMS-QP 2010 spectrometer (equipped with a direct inlet probe) and operating at 70 eV. The elemental analyses have been obtained using a Thermo Finnigan Flash EA1112. CHN (STIUJA) elemental analyzer. UV–Vis spectra were recorded in a Shimadzu 1700 spectrometer.

2.2. *Electrochemical measurements*

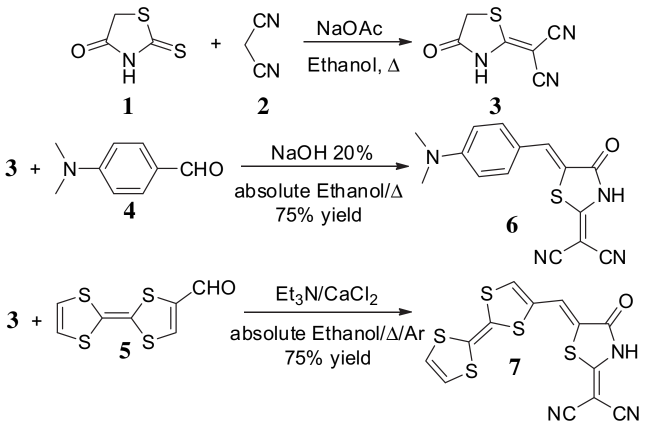
Electrochemical measurements were performed on an autolab PGStat 30 equipment using a three-electrode configuration system. The measurements were carried out using a CH_3CN solution 0.1 M in tetrabutylammoniun hexafluorophosphate ($TBAPF_6$). A glassy carbon electrode (3 mm diameter) was used as the working electrode, and a platinum wire and an $Ag/AgNO_3$ electrode were employed as the counter and the reference electrodes, respectively. Both the counter and the reference electrodes were directly immersed in the electrolyte solution. The surface of the working electrode was polished with commercial alumina prior to use. Solutions were deaerated by bubbling argon for a few minutes prior to each voltammetric measurement. Unless otherwise specified the scan rate was 100 mV s^{-1}.

2.3. *Preparation and characterization*

The preparation of the novel push–pull chromophores **6** and **7** was carried out in two steps using commercially available rhodanine **1**. The rhodanine derivative **3** was prepared by the Knoevenagel condensation of **1** with equivalent amounts of malononitrile **2**, under basic conditions as shown in Scheme 1.

2.3.1. *Procedure for the preparation of 2-(1,1-dicyanomethylene)-1,3-thiazol-4-one* **3**

An equimolar mixture of rhodanine **1** (500 mg, 3.8 mmol), malononitrile **2** (251 mg, 3.8 mmol) and sodium acetate (312 mg, 3.8 mmol) in absolute ethanol (15 mL) was refluxed for 12 h. The ensuing precipitate was filtered off and washed with water and ice cooled ethanol. The solid was purified by recrystallization from ethanol, 74% yield; mp = 225–227 °C; FT-IR (KBr): υ 3445 (N–H), 2212 and 2196 (2C≡N), 1647 (C═O) cm^{-1}; ^{1}H NMR (400 MHz, DMSO–d_6): δ 3.79 (s, 2H, CH_2) ppm; ^{13}C NMR (100 MHz, DMSO–d_6) δ 39.2 (C-5), 46.4(C-2′), 117.7 (C≡N), 119.0 (C≡N), 188.7 (C-2), 188.9 (C═O) ppm; HR-MS (EI) calculated for $C_6H_3N_3OS$ 164.9997, found: 164.9998. Anal. Calc. for $C_6H_3N_3OS$: C, 43.63; H, 1.83; N, 25.44. Found: C, 43.71; H, 1.87; N, 25.35.



Scheme 1. Synthesis of push–pull compounds **6** and **7**.

2.3.2. *Procedure for the preparation of (Z)-2-((1,1-Dicyanomethylene)-5-(4-dimethylamino)benzylidene)-1,3-thiazol-4-one* **6**

Equimolar quantities of dicyanorhodanine **3** (100 mg, 0.61 mmol) and 4-dimethylaminobenzaldehyde **4** (91 mg, 0.61 mmol) in EtOH (15 mL) was stirred under basic conditions (5 drops, 20% aq NaOH solution) at room temperature for 12 h. The crude reaction was purified by column chromatography on silica gel with $CHCl_3$ as eluent. The desired compound was obtained in 75% yield. mp > 350 °C. FT-IR (KBr): υ 3425 (NH), 2211 (2C≡N), 1637 (C═O) cm^{-1}; ^{1}H NMR (400 MHz, DMSO–d_6): δ 2.99 (s, 6H, CH_3), 6.82 (d, J = 8.92 Hz, 2H, H-*m*), 7.42 (d, J = 8.92 Hz, 2H, H-*o*), 7.40 (s, 1H, H-6) ppm; ^{13}C NMR (100 MHz, DMSO–d_6): δ 40.4 (2CH_3), 46.7 (C-2′), 112.6 (C-*m*), 117.5 (C≡N), 118.9 (C≡N), 121.9 (C-*ip*), 123.5 (C-5), 129.4 (C-6), 131.7 (C-*o*), 151.2 (C-*p*), 179.8 (C-2), 181.7 (C═O) ppm; HR-MS (IE) calculated for $C_{15}H_{12}N_4OS$ 296.0732, found 296.0732. Anal. Calc. for $C_{15}H_{12}N_4OS$: C, 60.79; H, 4.05; N, 18.91. Found: C, 60.75; H, 4.07; N, 18.88.

2.3.3. *Procedure for the preparation of (Z)-2-(1,1-Dicyanomethylene)-5-(tetrathiafulvalene-2-ylidene)-1,3-thiazol-4-one* **7**

Equimolar amounts of dicyanorhodanine **3** (100 mg, 0.61 mmol), 2-formyltetratiafulvalene **5** (141 mg, 0.61 mmol) and catalytic amounts of triethylamine (0.50 mL) and $CaCl_2$ (5 mg) in dry ethanol (15 mL) was heated under reflux for 24 h under argon. The crude reaction was purified by column chromatography on silica gel with CH_2Cl_2:MeOH (20:1) as eluent. The compound **7** was obtained in 41% yield. mp = 201 °C (d). FT-IR (KBr): υ 3423 (NH), 2212 (2C≡N), 1650 (C═O) cm^{-1}; ^{1}H NMR (400 MHz, DMSO–d_6): δ 6.72 (H-TTF), 6.79 (H-TTF), 7.33 (H-TTF), 7.38 (s, 1H, H-6) ppm; ^{13}C NMR (100 MHz, DMSO–d_6): δ 44.7 (C-2′), 113.7 (C≡N), 117.8 (C≡N), 119.4, 120.0, 120.1, 128.2 (C-6), 130.1, 132.7, 140.4, 178.5 (C-2), 179.7 (C═O) ppm; MS (ESI): 379 (M$^+$), 378 (M$^+$ − 1), 380 (M$^+$ + 1). Anal. Calc. for $C_{13}H_5N_3OS_5$: C, 41.14; H, 1.33; N, 11.07. Found: C, 41.20; H, 1.24; N, 11.11.

3. Results and discussion

In this paper we describe the straightforward synthesis of new rhodanine derivatives bearing the dicyanomethylene group, which significantly improves the electron acceptor character of the system. Furthermore, the further covalent linkage to two different electron donor moieties, namely *N*,*N*-dimethylaniline and the well-known tetrathiafulvalene (TTF) [9], has allowed preparing two new push–pull chromophores (**6**, **7**) exhibiting interesting photo- and electrochemical properties.

The preparation of the novel push–pull chromophores **6** and **7** has been carried out in two synthetic steps from commercially available rhodanine **1**. Firstly rhodanine derivative **3** was prepared by Knoevenagel condensation of **1** with equivalent amounts of malononitrile **2**, under basic conditions as shown in Scheme 1. The FT-IR spectrum for this compound showed the band corresponding to the NH group at 3445 cm^{-1}, and at 2212 and 2196 cm^{-1} the bands due to the CN groups. Compound **3** exhibits the band due to C═O group at 1647 cm^{-1}. The ^{1}H NMR spectrum for **3** only shows a signal at δ = 3.79 ppm, corresponding to the methylene protons. The ^{13}C NMR spectrum exhibited the signals due to cyano carbons at δ = 117.7 and 119.0 ppm, as well as the signal for the carbonyl group at 188.9 ppm as mainly signals. The MS spectrum and elemental analysis confirmed the proposed structure.

In the second stage of the synthesis, an equimolar mixture of **3** and 4-(*N*,*N*-dimethylamino)benzaldehyde **4** was stirred for 12 h in ethanol under basic conditions. The crude of the reaction was purified by column chromatography in silica gel, to obtain push–pull compound **6**. In the same way, a mixture with equimolar amounts of **3**, 2-formyltetrathiafulvalene **5** [10], and triethylamine

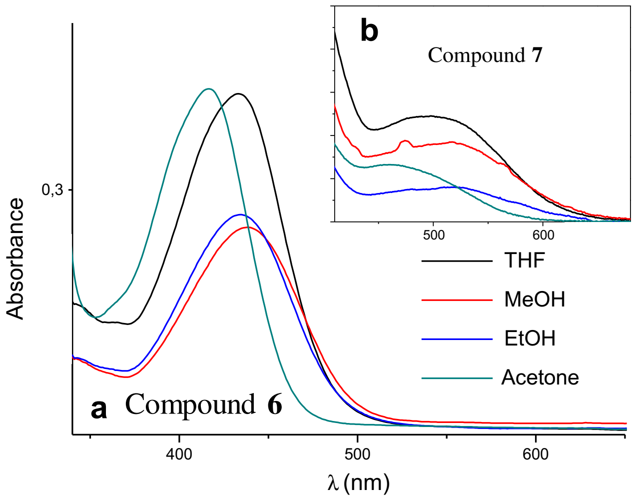


Fig. 1. Uv-Vis spectra for compounds **6** and **7** in different solvents.

was heated to reflux for 24 h in dry ethanol under argon. The crude of the reaction was purified by column chromatography in silica gel to obtain compound **7**. Dyes **6** and **7** were unambiguously characterized by spectroscopic techniques. In contrast to **3**, the FT-IR of **6** only shows a band due to the stretching vibration mode for the cyano group at 2210 cm^{-1}. In the ^{1}H NMR, in addition to the aromatic protons, dye **6** shows a singlet at $\delta = 2.99$ ppm for the methyl groups, as well as the olefinic proton which appears as a singlet at $\delta = 7.40$ ppm. In the ^{13}C NMR spectrum the signals for the cyano carbons appear at $\delta = 117.5$ and 118.9 ppm, the signal for olefinic carbon was observed at $\delta = 129.4$, and the carbonyl group appears at $\delta = 181.7$ ppm. The FT-IR of **7** shows a band at 2212 cm^{-1} due to the stretching vibration mode for the cyano groups. The ^{1}H NMR spectrum of **7** showed signals at $\delta = 6.72$, 6.79 and 7.33 ppm for the TTF protons, as well as the olefinic proton at $\delta = 7.38$ ppm. The ^{13}C NMR spectrum shows signals at $\delta = 119.4$, 120.0 and 120.1 ppm for the primary carbons of TTF, and the signals for the cyano groups appear at $\delta = 113.7$ and 117.8 ppm. The signal for the olefinic carbon was observed at $\delta = 128.2$, and the carbonyl group at $\delta = 179.3$ ppm.

In the absorption spectra of dyes **6** and **7** the broad band in the visible region, λ_{max} (THF) (ε) = 433 nm (1.68×10^{5} M^{-1} cm^{-1}) for **6** and λ_{max} (THF) (ε) = 498 nm (1.55×10^{3} M^{-1} cm^{-1}) for **7**, evidences the occurrence of a donor-acceptor intramolecular charge transfer (ICT). This finding was confirmed by solvatochromic studies using a variety of solvents of different polarity (Fig. 1).

This experiment reveals a positive solvatochromism since the observed λ_{max} for the ICT is slightly bathochromically shifted in different solvent polarity (Table 1). In order to confirm the ICT, emission spectra were measured in different solvents of dye **6** and using the same experimental conditions as that for the absorption spectra. A blue emitting laser at 473 nm was used for this experiment and the spectra showed a broad fluorescence band in the visible region at values: λ_f(acetone) = 510 nm, λ_f(THF) = 528 nm, λ_f (EtOH) = 529 nm and λ_f (MeOH) = 542. The band observed in the emission spectra stems from the intramolecular charge transfer state. Furthermore, in this study, the ICT state is reflected in the large and regular red shift of the fluorescence maxima, from 510 nm to 542 nm, with different solvent polarity.

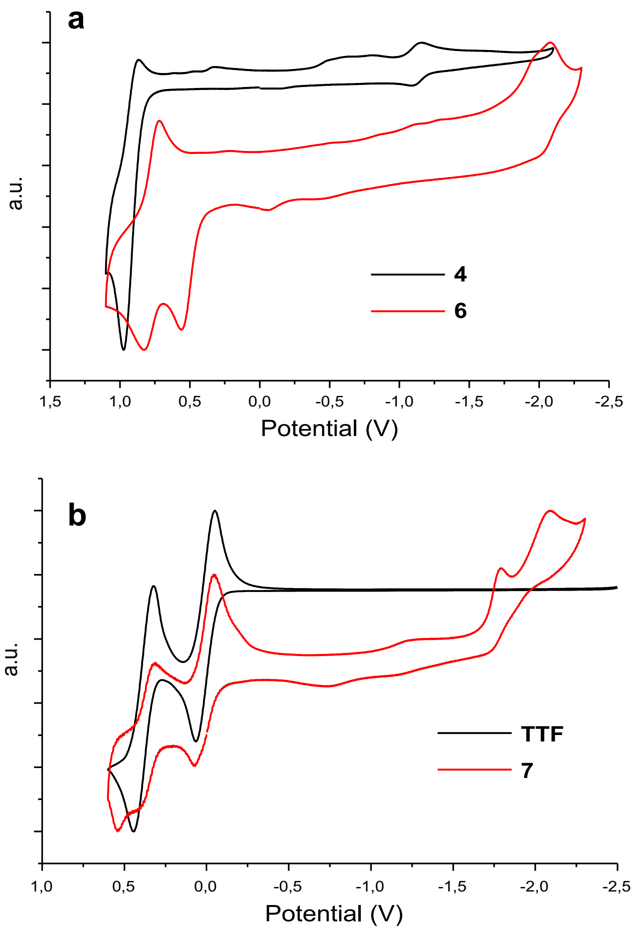


Fig. 2. Cyclic Voltammograms of compounds a) **4** and **6**; b) TTF and **7**.

Interestingly, the outcomes of λ_{max} of the ICT band showed above for dyes **6** and **7**, are very close to those reported for a similar molecular system (5-(*p*-dimethylaminobenzylidene) rhodanine) [7], where they test the push–pull behavior and the λ_{max} of the ICT band reported is 455 nm in THF. It should be noted that the value for λ_{max} of the ICT band of compound **7** is shifted at longer value in the same solvent.

The electrochemical properties of compounds **3**, **4**, **6**, **7** and **TTF** were studied by cyclic voltammetry (CV) at room temperature. Dye **6** bearing the electron-donating *N*,*N*-dimethylaniline group, showed two oxidation peak potential at +564 mV and +776 mV assigned to *N*,*N*-dimethylaniline sequential two-electron oxidation.

Table 1
Values of λ_{max} for dyes **6** and **7** in different solvents.

Solvent	λ_{max} (ε (M^{-1} cm^{-1}))	
	Dye 6	Dye 7
THF	433 nm (1.68×10^{5})	498 nm (1.55×10^{3})
Acetone	417 nm (1.68×10^{5})	461 nm (1.09×10^{3})
EtOH	435 nm (1.13×10^{5})	524 nm (1.15×10^{3})
MeOH	439 nm (1.09×10^{5})	516 nm (1.33×10^{3})

Table 2
Oxidation and reduction peak potentials for compounds **3**, **4**, **6**, **7** and TTF.

Compound	E^{1}_{ox}[a] (mV)	E^{2}_{ox}[a] (mV)	E^{1}_{red}[b] (mV)	E^{2}_{red}[b] (mV)
3	–	–	–	−1978
4	–	+927	–	–
TTF	+106	+386	–	–
6	+564	+776	–	−2086
7	+93	+367	−1801	−2085

[a] Anodic peak potentials are reported.
[b] Cathodic peak potentials are reported.

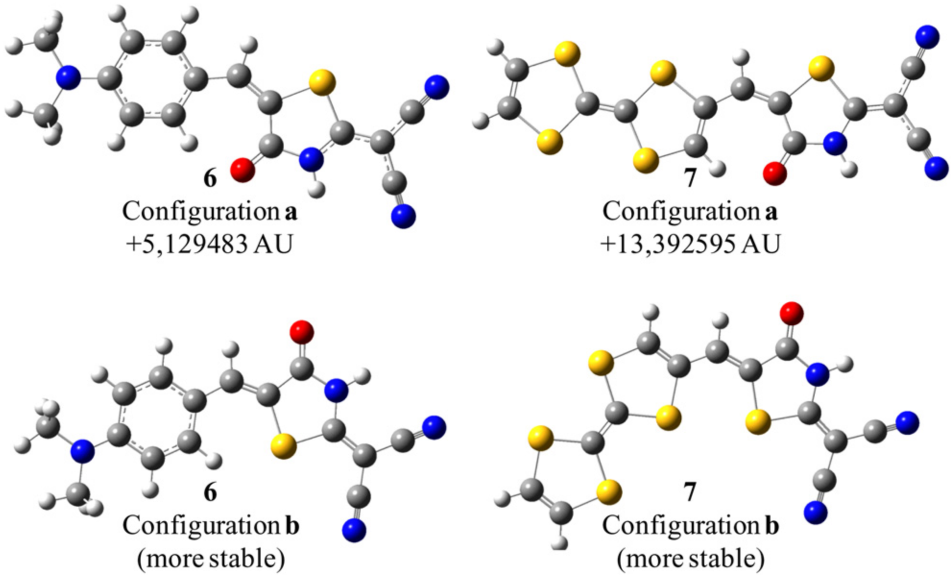


Fig. 3. Minimum-energy conformation calculated for **6** and **7** with energies in atomic units at the B3LYP/6-31G** level.

The second oxidation peak potential is shifted to slightly lower anodic potential compared to that of compound **4**.

These findings have been confirmed by means differential pulse voltammetry; this fact can be explained for the interaction of dicyanomethylenerhodanine electron acceptor moiety with the *N*,*N*-dimethylaniline unit. In the same way dye **7** bearing the electron-donating TTF fragment showed two oxidation peak potentials at +93 mV and +367 mV. Both peak potentials of **7**, shifts to slightly lower oxidation potentials compared to that of pristine TTF (Fig. 2).

As expected, dyes **6** and **7** showed an amphoteric redox behavior. In addition to the oxidation peak potential, these compounds show reduction peak potentials at −2086 mV for **6** and −1801 mV and −2085 mV for **7**, in contrast to compound **3** which shows a reduction peak potential at −1978 mV (Table 2). The stronger electron donor ability of TTF in **7** compared to the *N*,*N*-dimethylaniline in **6** could account for the shift observed in the reduction peak potential of the acceptor moiety. The above finding reveals that there is a significant electronic communication between the electron-donating units and the dicyanomethylenerhodanine ring through the π-conjugated core.

Theoretical calculations were carried out with the DFT approach using the C.02 revision of the Gaussian 03 program package [11].

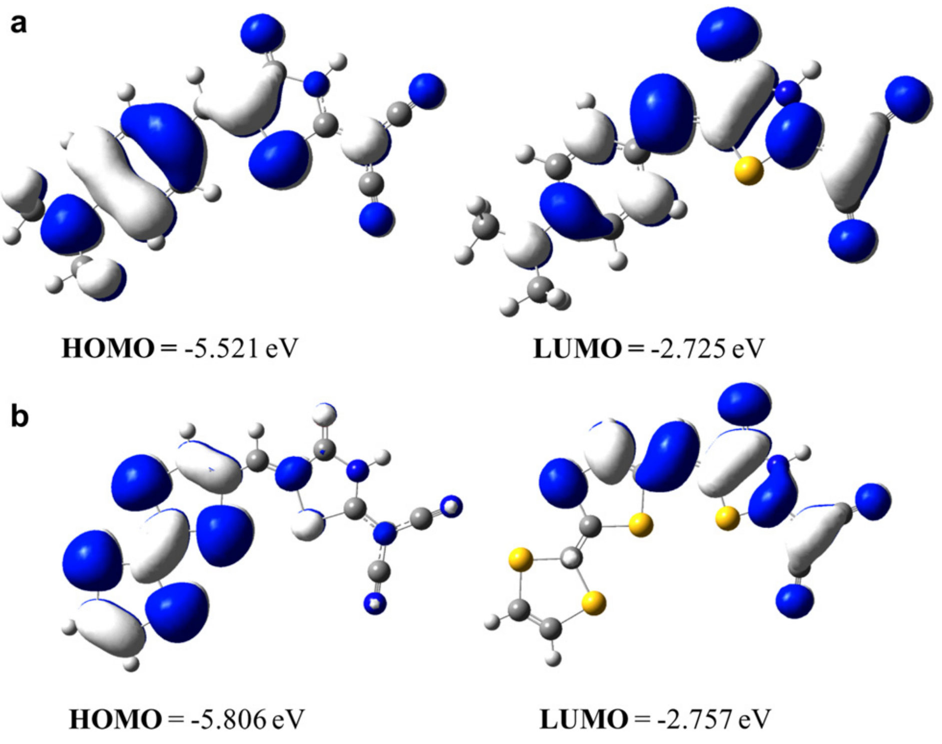


Fig. 4. a) Electron density contours (0.03 eBohr^{-3}) calculated for the HOMO and LUMO of **6**. b) Electron density contours (0.03 eBohr^{-3}) calculated for the HOMO and LUMO of **7**.

DFT calculations were performed using Becke's three-parameter B3LYP exchange-correlation functional and the 6-31G** basis set. The geometry of dyes **6** and **7** was theoretically optimized and the most stable conformation is depicted in Fig. 3. Although the found energy values for the configurations **a** and **b** in the dyes **6** and **7** are very close, the **b** configuration is slightly favored for both ((*Z*)-configuration). Previously have been reported that although arylalkylidenerhodanines may exists in both *Z* and *E* isomeric forms, the thermodynamically more stable *Z* isomer is the preferred [12]. In such reports, configuration on the exocyclic double bond was determined on the basis of NMR spectra. Our experimental NMR data showed that methine protons signals are in the range of 7.38–7.40 ppm, confirming that our dyes **6** and **7** were obtained as the single *Z* isomeric form. For compound **7**, also should be noted that intramolecular 1,5-S···S interaction would be expect to occur, which is usual in TTF systems. The geometry of both molecules was found to be near to planarity, thus favoring the intramolecular electronic communication between the electroactive units.

Fig. 4a shows the atomic orbital (AO) composition of the highest-occupied and lowest-unoccupied molecular orbitals (HOMO and LUMO) of **6**; the mentioned (AO) for compound **6** is delocalized on the whole molecule, however the LUMO shows a larger contribution from the dicyanomethylene group in the rhodanine moiety and the HOMO shows that the electronic density is mainly localized on the *N*,*N*-dimethylaniline donor group. In contrast compound **7** shows the frontier orbitals more clearly localized in their respective electroactive units (Fig. 4b). The last finding shows a better push–pull behavior for compound **7** than **6** in accord with the calculated (AO) composition. These results are in agreement with the previous experimental UV–Vis and CV findings, and the orbital overlapping between the HOMO and LUMO in both **6** and **7** support the push–pull nature of these new chromophores.

In summary, readily available push–pull chromophores (**6** and **7**) containing the new electron acceptor moiety dicyanomethylene rhodanine have been easily synthesized and their optical and electrochemical properties reveal a good electronic communication in the ground state. Theoretical calculations at the DFT level show the planar geometry of these chromophores and the push–pull features, thus supporting their redox amphoteric character. The potentials of the highest oxidation peak and the lowest reduction peak can be used to calculate the HOMO/LUMO energy levels according with equation (1) [13].

$$x(\mathrm{eV}) = -4.8 - \left[E_{\mathrm{reductionoroxidationpeak}} - E_{1/2}(\mathrm{ferrocene})\right] \quad (1)$$

The estimated electron affinity (LUMO level) values for dyes **6** and **7** were −2.46 eV and −2.55 eV respectively. The ionization potential (HOMO level) for dyes **6** and **7** were −5.11 eV and −5.48 eV respectively; these values are very close to the calculated DFT/B3LYP energy values.

4. Conclusions

In summary, two new "push–pull" derivatives **6** and **7**, were synthesized using Knoevenagel reactions between 2-(1,1-dicyanomethylene)rhodanine **3** and aldehydes bearing different donor units, namely 4-(*N*,*N*-dimethylamino)-benzaldehyde **4** and 2-formyltetrathiafulvalene **5**. The absorption spectra of dyes **6** and **7** exhibit an intamolecular charge transfer (ICT) band; which showed a positive solvatochromism by recording in different solvents. The emission spectra for **6** recorded under the same conditions confirm the ICT band character. The new "push–pull" compounds display a clear electrochemically amphoteric behavior. This finding reveals that there is a significant electronic communication between the electron-donating units and the dicyanomethylenerhodanine fragment through the π-conjugated core. Theoretical calculations at the DFT level for both compounds are in agreement with the experimental outcome and confirm the electronic communication in the ground state. Furthermore, these features of the dicyanomethylenerhodanine, confirm its behavior as a versatile, readily available and efficient acceptor unit.

Acknowledgements

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