Push-pull 1,4-dithiafulvenes: a combined experimental and theoretical study

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Dedicated to Professor Enrique Meléndez on the occasion of his 70th birthday

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Abstract

Novel push-pull 6,6-disubstituted 1,4-dithiafulvenes have been synthesized and their electrochemical and spectral properties were recorded. The proaromaticity of the donor end of these alkenes lies at the origin of their strong dipolar character, confirmed by DFT calculations, and their second-order NLO properties.

Keywords: Dithiafulvenes, 1,3-dithioles, donor-acceptor, proaromaticity, DFT calculations

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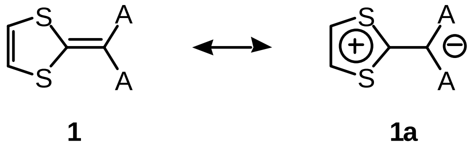
Introduction

Push-pull alkenes are substituted ethylenes containing electron-donor groups (D) at one end and electron-acceptor groups (A) at the other. These compounds have been widely studied on account of their low rotational barrier around the carbon–carbon double bond,[1] which is due to their high degree of polarization or, in valence-bond language, to the importance of zwitterionic limiting forms to the description of their ground states. Moreover, there is a renewed interest in this kind of compounds, since their high dipole moments and strong intramolecular charge-transfer (ICT) bands are at the origin of their first molecular hyperpolarizabilities (β) and, therefore, of their second-order nonlinear optical (NLO) responses.[2,3]

In this context, push-pull 1,4-dithiafulvenes of general formula **1** are expected to exhibit an increased dipolar character on account of the gain in aromaticity of the donor end on charge-transfer (Scheme 1).



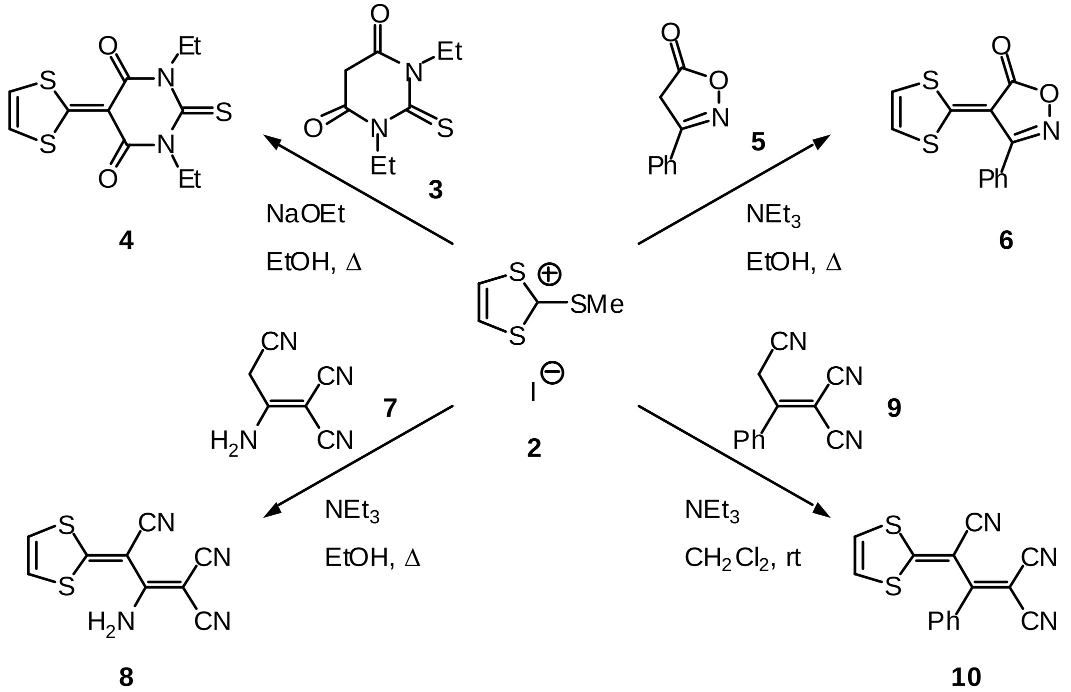
Scheme 1

In this work we report the synthesis, optical and electrochemical properties of a series of push-pull 6,6-disubstituted 1,4-dithiafulvenes. DFT calculations have been carried out in order to study their electronic structure.

Results and Discussion

Chemistry

The previously unreported compounds **4**, **6**, **8**, and **10** were envisaged as target molecules because of the strong electron-withdrawing character of their acceptor moieties. They were prepared by Knoevenagel-type reaction of dithiolium salt **2**[4] with active methylene compounds **3**, **5**, **7**, and **9**[5] in a basic medium (Scheme 2).[6] All of them have been fully characterised by standard spectroscopic techniques.



Scheme 2

Electrochemistry and optical spectroscopy

The electrochemical and optical properties of the synthesized compounds were studied by cyclic voltammetry and UV-vis spectroscopy, respectively, the most relevant results being collected in Table 1.

Table 1. Redox potentials [V] and absorption spectra [nm]

Compound	E_{ox}[a]	E_{red}[a]	λ_{max} (log ε)[b]	λ_{max}[c]
4	1.55	–1.48	403 (4.81)	405
6	1.60	–1.53	403 (4.35)	413
8	1.72	–1.20	403 (4.16)	398
10	1.74	–0.98 –1.49	467 (4.40)	474

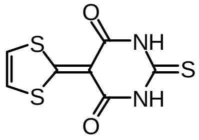
[a] In CH_2Cl_2 *vs*. Ag/AgCl, glassy carbon working electrode, 0.1 M $TBAPF_6$, 0.1 V s^{-1}. [b] In CH_2Cl_2. [c] In DMSO.

The higher anodic reduction potentials of the polycyano groups (present in **8** and **10**) indicate that they are stronger electron-withdrawing groups than the thiobarbituric and isoxazolone moieties. The higher oxidation potentials of the dithiafulvene moieties in **8** and **10**, when compared to those of **4** and **6**, confirm this fact. It is pertinent to note that the acceptor group in compound **10** is the only one to show two distinct reduction potentials.

The UV-vis spectra show that **10** has the longest wavelength ICT band among the newly prepared dithiafulvenes and that all, except **8**, show a weak positive solvatochromism.

Theoretical calculations: electronic properties

In order to get a deeper understanding of the structure and properties of these push-pull dithiafulvenes, theoretical calculations on model compound **4a** and compounds **6**, **8**, and **10** have been carried out at the B3P86/6-31G*// B3P86/6-31G* level as it has previously been demonstrated that geometries calculated at this level are in very good agreement with crystal structures for 1,3-dithiole derivatives.[7]



4a

The most relevant data for the target compounds are gathered in Table 2.

Table 2. Energies of the frontier orbitals (eV), Mulliken charges on the dithiole fragment (e), and dipole moments (D)

Compound	E_{HOMO}	E_{LUMO}	Charge	μ
4a	–6.93	–3.09	0.226	6.09
6	–6.62	–2.88	0.135	7.93
8	–6.99	–3.19	0.281	6.94
10	–6.94	–3.62	0.264	6.24

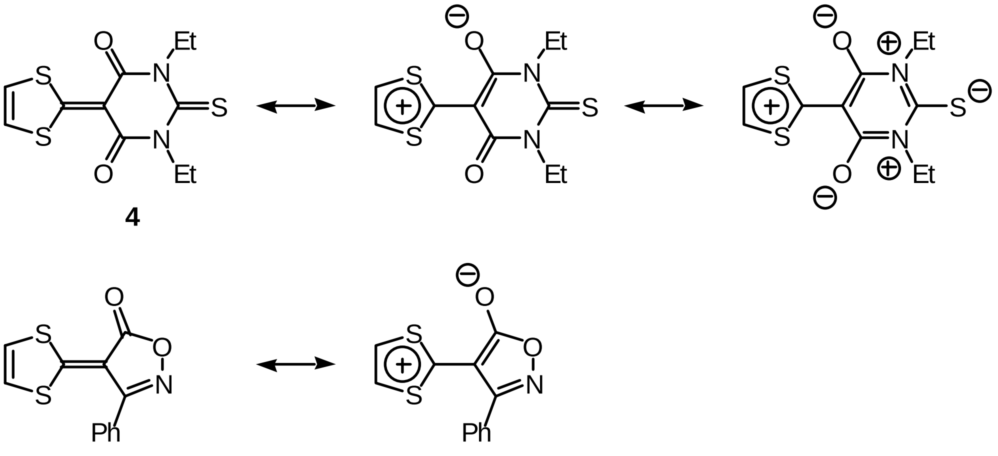
It can be seen that there is a good qualitative correlation between the calculated energies of the LUMOs and the experimentally determined reduction potentials. Both sets of values point to the fact that the isoxazolone group is the least electron-withdrawing fragment among those studied in this work. This is also confirmed by the smaller positive charge on the dithiole ring of **6** and by the higher energy of its HOMO.

The relatively high positive charge supported by the dithiole ring of all these dervatives suggests an important contribution of the charge-separated form (**1a**) to the ground state of these molecules, as confirmed by the high values of their ground state dipole moments.

Table 2 also shows that the HOMO–LUMO gap for compound **10** is smaller than for the other derivatives, in agreement with its experimentally determined λ_{max} value (Table 1). This fact lends support to the ICT character of this band.

The proaromaticity of the acceptor

In compounds **4** and **6** the exocyclic C=C bond links two proaromatic moieties, as revealed by the following canonical forms (Scheme 3):

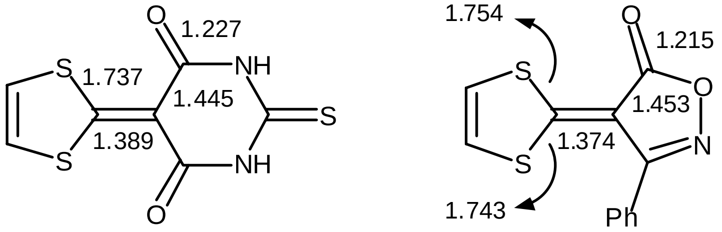


4

6

Scheme 3

This feature results in an important contribution of the zwitterionic limiting forms to the description of the ground state of these molecules, as confirmed by DFT calculations. Thus, selected bond lengths of compounds **4a** and **6** are shown in Figure 1.



4a **6**

Figure 1. Selected bond lengths (Å) of **4a** and **6** (B3P86/6-31G*).

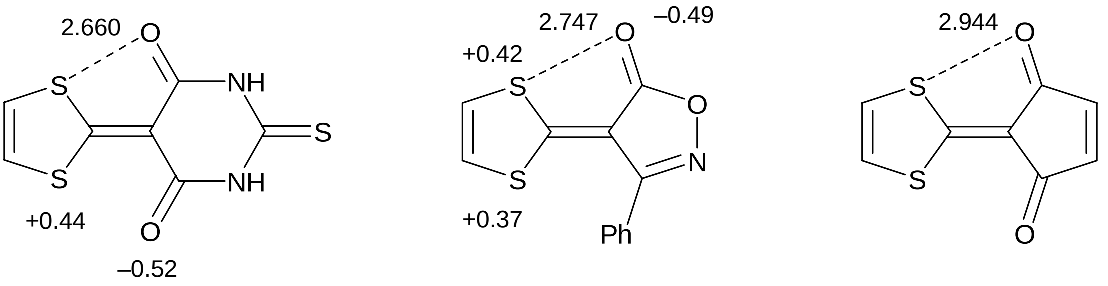
The short C–S bond (1.737 Å) of **4a** is nearly identical to the analogous one calculated for the cation-radical of tetrathiafulvalene (TTF),[7] which indicates that the dithiole ring supports a high degree of positive charge. Moreover, the C=O bond length of the thiobarbituric moiety is similar to those experimentally determined for 1,3-diethyl-5-(4-dimethylaminobenzylidene)thiobarbituric acid, a compound with a highly polarized structure.[8]

Similar features can be found in the optimized structure of **6**, although the C–S bonds are longer and the exocyclic C=C bond and the C=O bond are shorter than the corresponding ones in compound **4a**. This points to a weaker electron-withdrawing ability of the isoxazolone group, when compared to the thiobarbituric group, in agreement with cyclovoltammetric data. A comparison of the relevant bond lengths of **6** with those determined for a substituted 3-phenyl-4-pyridylidenisoxazol-5-one[9] seems to indicate that the 4-pyridylidene group is a stronger electron donor than the 1,3-dithiol-2-ylidene moiety.

1,5 S·····O interactions

The optimized geometry of compound **4a** reveals the presence of two 1,5-interactions between the dithiole sulfur atoms and the oxygen atoms, with S– –O distances of 2.660 Å, which are substantially less than the sum of van der Waals radii (3.32 Å) of both atoms, and are indicative of weak interactions[10,11] with a covalency ratio of $\chi = 0.420$. These attractive interactions result from the opposite charges of +0.44 e on the sulfur atoms and –0.52 e on the oxygen atoms (Figure 2).

A similar feature can be found in the structure of **6**, although the S– –O distance of 2.747 Å (resulting in a smaller covalency ratio, $\chi = 0.365$) is longer than those calculated for **4a**. The different geometries of the six- and five-membered acceptor rings account for the weaker interaction found for the latter. For the sake of comparison, the experimentally determined (X-ray diffraction) intramolecular S– –O distance in compound **11** is 2.944 Å (Figure 2).[12]

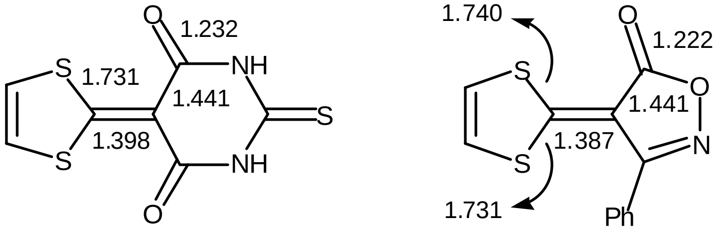


4a **6** **11**

Figure 2. Selected charges (e) and S– –O distances (Å).

The influence of the solvent

The geometry of very polar compounds, such as those reported in this work, is expected to be quite sensitive to a change in the polarity of the surrounding medium. In order to check this possibility, the geometries of compounds **4a** and **6** in DMSO were optimized, using the PCM-B3P86/6-31G* level (Figure 3).



4a **6**

Figure 3. Selected bond lengths (Å) of **4a** and **6** in DMSO (PCM-B3P86/6-31G*).

A comparison of the bond lengths in Figure 3 with those in Figure 1 reveals that, in a more polar environment, the contribution of the generalized zwitterionic limiting form **1a** to the description of the ground state of these molecules increases. This is also confirmed by the higher positive charge supported by the dithiole ring in DMSO than in vacuum (+0.307 e for **4a** and +0.274 e for **6**; *cf.* Table 2) and by the ^{1}H-NMR chemical shifts of the dithiole ring hydrogen atoms, which are progressively deshielded in solvents of increasing polarity: 7.60 ($CDCl_3$), 8.04 (acetone-d_6), and 8.11 (DMSO-d_6) for **4**; 7.31 and 7.05 ($CDCl_3$), 7.80 and 7.62 (acetone-d_6), and 7.85 and 7.65 (DMSO-d_6) for **6**. The chemical shift of the dithiole ring protons points to the proaromaticity of the ring.

Tricyano-containing dithiafulvenes

Compounds **8** and **10** can exist in two conformations, *s-trans* (**a**) or *s-cis* (**b**), around the C2–C3 bond (Figure 4).

a b

8: R = NH_2

10: R = Ph

Figure 4. *s-trans* and *s-cis* conformers of compounds **8** and **10**.

For compound **8** DFT calculations show that conformer **b** is 2.48 kcal/mol more stable than conformer **a**, and that the dihedral angle τ (C1–C2–C3–C4) is 43.0°. These structural features closely agree with the results of *ab initio* calculations on similar compounds bearing substituted benzylidene groups instead of the 1,3-dithiol-2-ylidene moiety.[13] In a similar vein, compound **10** also adopts conformation **b** (0.96 kcal/mol more stable than **a**), with a dihedral angle τ (C1–C2–C3–C4) = 43.2°. Nevertheless, the difference between the energy of the two conformers is small and the more polar conformer **a** can be the favored one in a polar environment, such as that found in the solid state.

NLO properties

Given their dipolar character, the dithiafulvenes herein reported are expected to show moderate second-order NLO properties. In fact, for compound **4** $\mu\beta = -12 \times 10^{-48}$ esu (measured at 1907 nm in CH_2Cl_2 using the EFISH technique). On the other hand, preliminary measurements indicate that compounds **6**, **8**, and **10** display low but positive μβ values. Taking into account that increasing the length of the conjugated spacer linking the two rings in **4** leads to a dramatic increase of the corresponding second-order NLO responses,[14] the synthesis and study of higher vinylogues of compounds **6**, **8**, and **10** are being actively pursued in our laboratory.

Conclusions

The dithiafulvenes herein reported are strongly polarized as a result of both the proaromatic character of the dithiolylidene moiety and the powerful electron-withdrawing ability of the acceptor groups present at C6. Cyclovoltammetric measurements and theoretical calculations indicate that the isoxazolone moiety is the weakest acceptor among those studied in this work. The title compounds show moderate second-order NLO properties and constitute the simplest derivatives of the corresponding dithiafulvene-based merocyanines, which are excellent candidates in the search for new NLO-phores.

Experimental Section

General Procedures. Melting points were obtained on an Olympus BH-Z polarizing microscope equipped with a hot stage or in a Gallenkamp apparatus and are uncorrected. Infrared measurements were carried out in nujol mulls using a Perkin-Elmer FTIR 1600 spectrometer. ^{1}H- and ^{13}C-NMR spectra were recorded on a Bruker ARX300 or a Varian Unity-300 spectrometers operating at 300 MHz and 75 MHz respectively; δ values are given in ppm (relative to TMS) and *J* values in Hz. EI Mass spectra were recorded with a VG Autospec at 70 eV. Microanalyses were performed with a Perkin-Elmer 2400 microanalyzer. Electronic spectra were recorded with a UV-Vis-NIR Cary 500 Scan spectrophotometer. Cyclic voltammetry measurements were performed with a μ-Autolab ECO-Chemie potentiostat, using a glassy carbon working electrode, Pt counter electrode, and Ag/AgCl reference electrode. The experiments were carried out under argon, in CH_2Cl_2, with Bu_4NPF_6 as supporting electrolyte (0.1 mol L^{-1}). Scan rate was 100 mV s^{-1}. Molecular orbital calculations were performed on Intel Pentium III and Pentium IV based computers running under Windows XP. DFT calculations were performed with the Gaussian 98w program.[15] Processing of the results of molecular orbital calculations was achieved with the MOLEKEL-4.3 program.[16]

1,3-Diethyl-2-thiobarbituric acid (**3**), 3-phenyl-5-isoxazolone (**5**), and 2-amino-1-propene-1,1,3-tricarbonitrile (**7**) are commercially available. Compounds **2**[4] and **9**[5] were prepared as previously described.

1,3-Diethyl-5-(1,3-dithiol-2-ylidene)-2-thiobarbituric acid (4). To a stirred solution of NaOEt (4.31 mmol) in absolute ethanol (20 mL) was added 1,3-diethylthiobarbituric acid (**3**) (750 mg, 3.75 mmol). and the mixture was refluxed for 30 minutes. Then, 2-methylthio-1,3-dithiolium iodide (**2**) (1.035 g, 3.75 mmol) was added, and refluxing was continued for 4-5 hours. The mixture was cooled to room temperature and ethanol was evaporated. Water was added and the product was extracted with CH_2Cl_2 (3x100 mL). The extracts were dried over $MgSO_4$, evaporated and purified by chromatography (silica gel) using CH_2Cl_2 as eluent, to give a yellow solid (290 mg, 26%). M.p. 278°C. IR (Nujol) ν cm^{-1}: 1627 (C=O), 1105 (C=S). ^{1}H NMR ($CDCl_3$, 300 MHz): δ= 7.60 (s, 2H), 4.65 (q, *J* = 6.9 Hz, 4H), 1.35 (t, *J* = 6.9 Hz, 6H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ= 180.3, 177.1, 158.9, 127.8, 101.5, 43.4, 12.3. MS (EI^{+}) m/z (%): 300 ($M^{+\bullet}$, 100), 267 (45), 212 (23), 143 (27), 142 (25), 69 (21). Anal. Calcd. for $C_{11}H_{12}N_2O_2S_3$ (300.42): C, 43.98; H, 4.03; N, 9.32; S, 32.02. Found: C, 44.22; H, 3.90; N, 9.22; S, 32.23.

General procedure for 6, 8

To a stirred solution of corresponding acceptor (**5**, **7**) (1 mmol) in absolute ethanol (20 mL) triethylamine (0.16 mL, 1.1 mmol) was added. The solution was stirred for 5 minutes, and then, 2-methylthio-1,3-dithiolium iodide (**2**) (276 mg, 1 mmol) was added. The mixture was refluxed under argon atmosphere with exclusion of light for 2-2.5 hours, then cooled, and the resulting products isolated as outlined below.

4-(1,3-Dithiol-2-ylidene)-3-phenyl-5-isoxazolone (6). The precipitated solid was filtered off, washed with cold ethanol and dried.Yellow solid. (190 mg, 73%). M.p. 227-230ºC (dec.). IR (Nujol) ν cm^{-1}: 3108 (=C-H), 1694 (C=O), 1499 (C=C, Ar). ^{1}H NMR ($CDCl_3$, 300 MHz): δ= 7.60-7.48 (m, 5H), 7.31 (d, *J* = 6.3 Hz, 1H), 7.05 (d, *J* = 6.3 Hz, 1H). ^{13}C NMR ([d_6]-DMSO, 75 MHz):δ= 174.9, 169.9, 160.0, 130.8, 129.2, 128.9, 128.7, 127.1, 126.1, 97.8. MS (EI$^+$) m/z (%): 261 ($M^{+\bullet}$,100), 203 (27), 145 (20). Anal. Calcd. for $C_{12}H_7NO_2S_2$ (261.32): C, 55.15; H, 2.70; N, 5.36; S, 24.54. Found: C, 55.25; H, 2.54; N, 5.55; S, 24.33.

3-Amino-2-cyano-4-(1,3-dithiol-2-ylidene)-2-pentenedinitrile (8). The solid and the evaporated filtrate were purified by chromatography (silica gel) using diethyl ether as eluent. Finally, precipitation in CH_2Cl_2 and vacuum filtration afforded the product as a yellow solid (58 mg, 25%). M.p. 241-245°C (dec.). IR (Nujol) ν cm^{-1}: 3306, 3212 (NH_2), 3094 (=C-H), 2207 (CN), 1639 (C=C). ^{1}H NMR ([d_6]-DMSO, 300 MHz): δ= 8.80 (s, 2H), 7.41 (s, 2H). ^{13}C NMR (CD_3COCD_3, 75 MHz):δ= 176.41, 164.68, 125.08, 122.97, 116.05, 114.98, 114.58, 82.50, 52.61. MS (EI$^+$) m/z (%): 232 ($M^{+\bullet}$,100), 206 (23), 190 (21), 167 (42), 58 (27). Anal. Calcd. for $C_9H_4N_4S_2$ (232.29): C, 46.54; H, 1.74; N, 24.12; S, 27.61. Found: C, 46.75; H, 1.66; N, 23.93; S, 27.64.

2-Cyano-4-(1,3-dithiol-2-ylidene)-3-phenyl-2-pentenedinitrile (10). To a stirred solution of 2-cyano-3-phenyl-2-pentenedinitrile (**9**) (386 mg, 2 mmol) in dry CH_2Cl_2 (20 mL) triethylamine (0.28 mL, 2 mmol) was syringed. The solution was stirred for 5 minutes, and then, 2-methylthio-1,3-dithiolium iodide (**2**) (276 mg, 1 mmol) was added. The mixture was stirred at room temperature under argon atmosphere for 2 hours. Then, it was washed with HCl 1N (3x75 mL) and water (2x75 mL). The extract was dried over $MgSO_4$, evaporated and purified by chromatography (silica gel) using CH_2Cl_2 as eluent, to give an orange solid. (176 mg, 60%).
M.p. 217-220°C. IR (Nujol) ν cm^{-1}: 2188, 2216 (CN). ^{1}H NMR ($CDCl_3$, 300 MHz): δ= 7.66-7.48 (m, 5H), 7.06 (br s, 1H), 6.91 (br s, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz):δ= 180.22, 164.16, 133.27, 131.69, 130.39, 130.12, 127.85, 126.33, 123.02, 115.61, 114.18, 112.61, 88.13. MS (EI$^+$) m/z (%): 293 ($M^{+\bullet}$,100), 228 (25), 203 (18), 141 (26), 84 (27). Anal. Calcd. for $C_{15}H_7N_3S_2$ (293.37): C, 61.41; H, 2.41; N, 14.32; S, 21.86. Found: C, 61.63; H, 2.37; N, 14.45; S, 21.54.

Acknowledgments

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