

Influence of Sequential Nitrogen Substitution on the Redox Properties of Bis(thiazolylidene)hydrazine and on the Charge Transfer of TCNQ Complexes

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Various extended π -donor molecules incorporating an azino spacer between two heterocyclic moieties, either dithiole or thiazole rings, are described. As evidenced by cyclic voltammetric studies, the donor ability of these derivatives can be modulated depending on the nature of the two heterocycles. Three similar crystalline complexes were obtained with TCNQ and the donors **4**, **7** and **8**. Crystal structures and magnetic susceptibility data of these complexes are presented and the degree of charge transfer within these complexes has been correlated with the redox properties. © 2002 Elsevier Science (USA)

INTRODUCTION

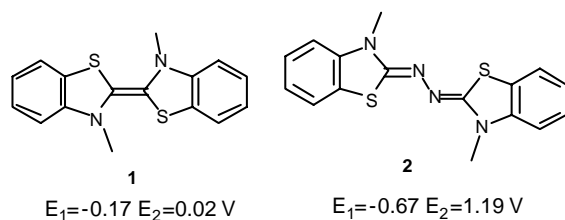
Among the various heterocycles used as precursors for the synthesis of charge transfer salts, dithiadiazafulvalenes (DTDAF) have shown recently an excellent ability to form molecular materials (1–4). On the one hand, due to their high electron donor properties, DTDAFs reduce almost all the traditional acceptors used in this research area. Indeed, when TCNQ is used for the formation of charge transfer salts, DTDAF dicationic salts are obtained with this acceptor (4). On the other hand, this property gives rise to donor molecules which are highly air sensitive and more difficult to handle than tetrathiafulvalenes (TTF) (1, 5). One possibility to modulate the redox properties, which has been extensively used in the TTF family, consists in the introduction of a conjugated spacer between the two heterocyclic five-membered rings (6). For example, the insertion of a vinyl spacer group induces an increase of the donor properties (7) of the molecule while the insertion of a conjugated spacer with nitrogen atoms leads to the opposite effect (8). Therefore we chose to explore the second possibility in DTDAF derivatives and introduced an azino spacer group between the thiazole moieties. The

first derivatives of this family, *N,N'*-dialkyl-bis(benzothiazolylidene)hydrazine (**2**, Scheme 1) have been prepared by Hünig *et al.* who first observed this stabilization effect of the azino spacer group compared to benzoDTDAF (**1**, Scheme 1) (9). Actually, to our knowledge, a cation radical salt of such extended donors, isolated in a pure form and crystallographically characterized, has not been reported yet. In this paper, we present the synthesis of alkyl substituted bis(thiazolylidene)hydrazine and investigate the influence of sequential nitrogen substitution in the redox properties of our donors. Complexes obtained with three different donors in the presence of TCNQ were fully characterized by X-ray structure determination and static and dynamic magnetic studies.

RESULTS AND DISCUSSION

The synthesis of the conjugated donors was accomplished using thiazolium salt **3** as the starting material (4). As previously described by Hünig *et al.* for the benzo analog (9), this salt reacts in basic medium with hydrazine monohydrate to afford *N,N'*-bis-(3,4,5-trimethyl-3H-thiazol-2-ylidene)-hydrazine **4** (Scheme 2). Two strategies can be used to form **4**, either directly by simply refluxing half equivalent of hydrazine with salt **3** or in a two-step procedure by first preparing the hydrazino derivative **5** in the presence of an excess of hydrazine (Scheme 2). This last pathway offers the possibility to form also unsymmetrical donors. Indeed, reaction of (3,4,5-trimethyl-3H-thiazol-2-ylidene)-hydrazine **5** with the dithiolium salt **6** gave the disymmetrical donor **7**. We also isolated another derivative which was formed in the medium in low yield with a longer conjugated system between the two thiazole rings while we were synthesizing **4**. Under alkaline conditions, thiazole ring rearrangement might occur which could explain the formation of **8**. The *N,N'*-bis-(4,5-dimethyl-dithiol-2-ylidene)-hydrazine **9** was also prepared

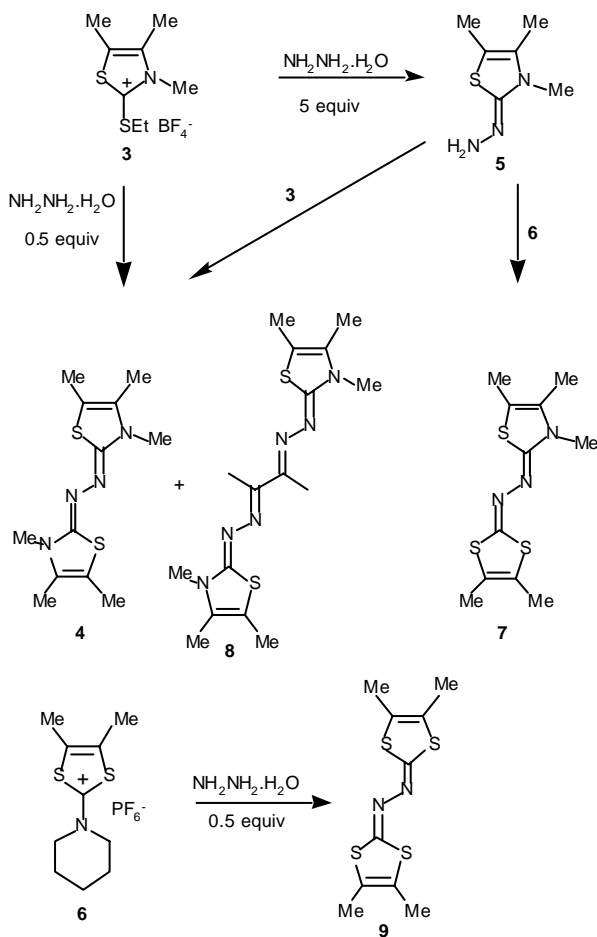
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SCHEME 1.

starting from the dithiolium salt using the one step procedure described for **4**.

In order to get information on the redox properties of these novel donor molecules **4**, **7**, **8** and **9**, cyclic voltammetry investigations were performed. Concerning the donors with an azino spacer group between the two heterocyclic rings (e.g., **4**, **7** and **9**), two reversible monoelectronic oxidation waves are observed. The data collected in Table 1 clearly indicate that for **4**, compared



SCHEME 2.

TABLE 1
Oxidation Potentials of Donors^a

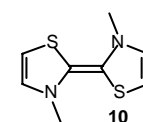
	E_{pa}^1	E_{pa}^2	ΔE
4	0.09	0.74	0.65
7	0.48	0.99	0.51
8^b	0.44 (E_1°)	0.48 (E_2°)	
9	0.87	1.24	0.37
10¹⁰	-0.54	-0.41	0.13

^a E in V vs SCE, Pt working electrode with *n*-Bu₄NPF₆ 1 M in CH₂Cl₂, scanning rate 0.1 V/s.

^b Scanning rate for TLCV 5 mV/s.

with DTDAF (**10** Scheme 3) (**10**), the insertion of an azino spacer between the thiazole cores shifts the oxidation potentials towards more positive values. This potential displacement is even more pronounced when a thiazole ring in **4** is replaced by one dithiole rings as in **7** or with two dithiole rings as in **9**. The fact that **4** and **7** exhibit such oxidation potentials suppresses the well-known oxygen sensitivity of DTDAF, and these derivatives are thus much easier to handle than DTDAF. Another interesting feature is the larger potential difference between the two oxidation waves ($\Delta E = E_{pa}^2 - E_{pa}^1$) which indicates that for **4** and **7** the cation radical specie is stable in a wider potential window than the DTDAF. Actually, the azino spacer group does not modify the electronic coupling between the two heterocyclic rings. For example, the ΔE value observed for tetramethyl TTF (380 mV) is similar to the one obtained for the azino-TTF **9** (370 mV). In fact, in the case of DTDAF **10** the small ΔE value (130 mV) is due to reduced coulombic interactions associated with conformational modifications upon electron transfer (4). On the other hand, **8** shows a peculiar redox behavior which was examined using thin-layer cyclic voltammetry (TLCV). Indeed two close reversible monoelectronic processes are observed on the voltammogram (11). This behavior is reminiscent of what is usually observed when two heterocyclic rings are linked together with a longer conjugated system and where coalescence of the two monoelectronic redox waves into one bielectronic redox wave is detected (8).

In order to form charge transfer salts of those three donor molecules with TCNQ, we mixed at room temperature a solution of the donor (**4**, **7** and **8**) with a solution of TCNQ in acetonitrile. Deep purple shiny single crystals



SCHEME 3.

TABLE 2
Crystallographic Data for (4)(TCNQ), (7)(TCNQ) and (8)(TCNQ)

	(4) (TCNQ)	(7) (TCNQ)	(8) (TCNQ)
Formula	C ₂₄ H ₂₂ N ₈ S ₂	C ₂₃ H ₁₉ N ₇ S ₃	C ₂₈ H ₂₈ N ₁₀ S ₂
Formula mass	486.62	489.63	568.72
<i>a</i> (Å)	6.8557(16)	6.8439(16)	7.9710(17)
<i>b</i> (Å)	8.367(2)	8.138(2)	8.2849(16)
<i>c</i> (Å)	11.089(3)	11.213(3)	12.549(3)
α (deg)	95.63(3)	94.85(3)	76.48(2)
β (deg)	101.99(3)	102.23(3)	89.64(3)
γ (deg)	100.59(3)	97.51(3)	64.98(2)
<i>V</i> (Å ³)	605.5(3)	601.0(3)	726.1(3)
Space group	<i>P</i> -1	<i>P</i> -1	<i>P</i> -1
<i>Z</i>	1	1	1
<i>D</i> _{calc} (g cm ⁻³)	1.335	1.353	1.301
Dimensions(mm)	0.54 × 0.06 × 0.06	0.42 × 0.11 × 0.05	0.48 × 0.09 × 0.015
μ (mm ⁻¹)	0.249	0.334	0.220
Data collected	5834	6208	7175
Independent data	2190	2213	2656
Observed data (<i>I</i> > 2 σ (<i>I</i>))	1008	936	1122
Parameters refined	154	163	181
<i>R</i> (<i>F</i>), <i>wR</i> (<i>F</i> ²)	0.068, 0.174	0.044, 0.111	0.064, 0.163
GOF	0.871	0.816	0.838
Residuals	+0.60, -0.28	+0.18, -0.19	+0.34, -0.28

were obtained in the case of **4** and **7**, deep green crystals in the case of **8** (Table 2). The crystal structure determinations reveal a stoichiometry of one donor for one TCNQ in each case (Fig. 1) with very similar structural organizations. The donor and TCNQ molecules are located on inversion

centers. In the specific case of the unsymmetrical donor **7**, the S and NMe moieties are disordered on the same positions with a 50:50 occupation distribution. In the three complexes, donor and TCNQ molecules form alternated stacks along the *a*-axis.

Within these mixed columns, the interplanar separations between the donor and the acceptor do not vary much with the nature of the donor, 3.420(7), 3.418(5) and 3.37(2) Å for (4)(TCNQ), (7)(TCNQ) and (8)(TCNQ), respectively. The donor/acceptor overlap is shown in Fig. 2 for (4)(TCNQ) and (8)(TCNQ). The replacement of one thiazole ring by a dithiole one in (7)(TCNQ) does not modify it.

The degree of charge transfer in the three complexes can be inferred from the analysis of the bond lengths in the TCNQ skeleton (Table 3). Using the empirical formula of Kistenmacher which correlates the bond lengths to the formal charge of the TCNQ in various charge transfer salts, we found the value of -0.96 for the (4)(TCNQ) and no charge transfer for (7)(TCNQ) and (8)(TCNQ) (12). This is supported by the nitrile stretching absorption band in the FTIR spectra of each complex. For example we found $\nu_{\text{CN}} = 2224 \text{ cm}^{-1}$ for neutral TCNQ and $\nu_{\text{CN}} = 2216 \text{ cm}^{-1}$ for (7)(TCNQ) and (8)(TCNQ) which confirms that those complexes are neutral. Contrariwise, a nitrile stretching absorption band at $\nu_{\text{CN}} = 2174 \text{ cm}^{-1}$ was observed for (4)(TCNQ), a value which is close to the one observed for TCNQ⁻¹ ($\nu_{\text{CN}} = 2183 \text{ cm}^{-1}$) in its Na⁺TCNQ⁻ salt (13). Both the bond lengths within the

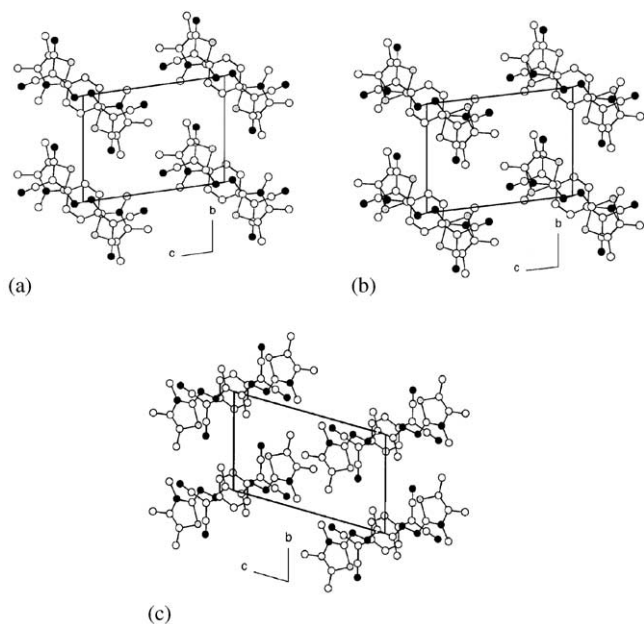


FIG. 1. Projection of the alternate stacks along *bc* plane (a) (4)(TCNQ), (b) (7)(TCNQ) and (c) (8)(TCNQ).

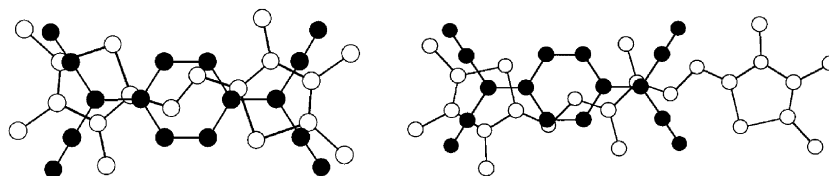


FIG. 2. Molecular overlap a) (4)(TCNQ), b) (8)(TCNQ).

TCNQ molecules and the IR stretching frequencies indicate that a full charge transfer in (4)(TCNQ), formulated now as $[4^+][TCNQ^-]$ while at the opposite (7)(TCNQ) and (8)(TCNQ) are simply neutral donor/acceptor complexes. This peculiar behavior, particularly between the complexes with 4 and 7 finds its origin in the anodic shift of the oxidation potentials thanks to the substitution of one dithiole ring for one *N*-methyl-thiazole ring, as discussed above in Table 1. Indeed, the bis(thiazole) derivative 4 oxidizes at 0.09 V, far below the reduction potential of TCNQ (0.18 V) while the (dithiole)(thiazole) molecule 7 oxidizes at 0.48 V, far above the reduction potential of TCNQ, as also for molecule 8.

Magnetic properties

In (8)(TCNQ) no EPR signal was observed from room to liquid helium temperature. This result is consistent with the presence of a neutral complex. This is also confirmed by the diamagnetic behavior found in the whole temperature range by SQUID susceptibility measurements, as also observed in (7)(TCNQ).

Contrariwise, in (4)(TCNQ) the EPR spectrum consists of one symmetric line. The EPR measurements were performed for the largest crystal available in two crystal orientations only. The spectrum shows the anisotropy of both *g* factor and linewidth. The averaged *g* factor value is 2.0036. However, there is another, much less intense signal in the EPR spectrum of the crystal. The line is the most clearly seen in Fig. 3, in the plane perpendicular to the long axis of the crystal. In this orientation the main line has a Lorentzian lineshape at $g=2.0035$ and a linewidth of 0.24 mT. Much less intense

line has a Gaussian lineshape at $g=2.0042$ with 0.15 mT linewidth in the crystal plane perpendicular to the long axis of the crystal. There is no indication of the interaction between these two centers. The Lorentzian line is characteristic for organic radical crystals. The Gaussian component is rather the impurity line of isolated donor molecule. Such line is characteristic of a defect in conjugated double-bond systems. The Gaussian lineshape can be due to the unresolved hyperfine interactions of the unpaired electron delocalized over the molecule of donor. The temperature dependence of the Lorentzian line intensity shows that spin susceptibility follows Curie law from room temperature to about 50 K (Fig. 4a). The linewidth narrowing (Fig. 4b) and the decrease of *g* factor (Fig. 4c) accompany the deviation of spin susceptibility from Curie law. At 10 K there is a distinct decrease of spin susceptibility (Fig. 4a).

Quantitative investigation was performed by SQUID magnetic susceptibility of (4)(TCNQ) (Fig. 5). The temperature dependence of magnetic susceptibility confirms the EPR result. The susceptibility monotonically increases with decreasing temperature down to 10 K, then below 10 K the susceptibility decreases. The SQUID data can be properly fitted in the high-temperature regime ($T > 30$ K) with $\chi_{mol} = \chi_0 + C/(T-\theta)$ with $\theta = -19.4$ K and

TABLE 3
Averaged Distances (*a-d*) in TCNQ Complexes

	<i>a</i>	<i>b</i>	<i>c</i>	<i>d</i>
(4)(TCNQ)	1.353	1.415	1.414	1.418
(7)(TCNQ)	1.342	1.436	1.372	1.427
(8)(TCNQ)	1.338	1.442	1.363	1.445

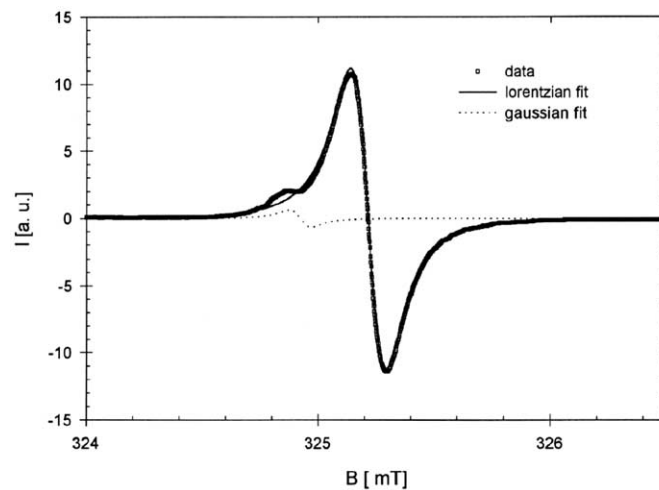


FIG. 3. The EPR spectrum of (4)(TCNQ) monocrystal at 4.2 K.

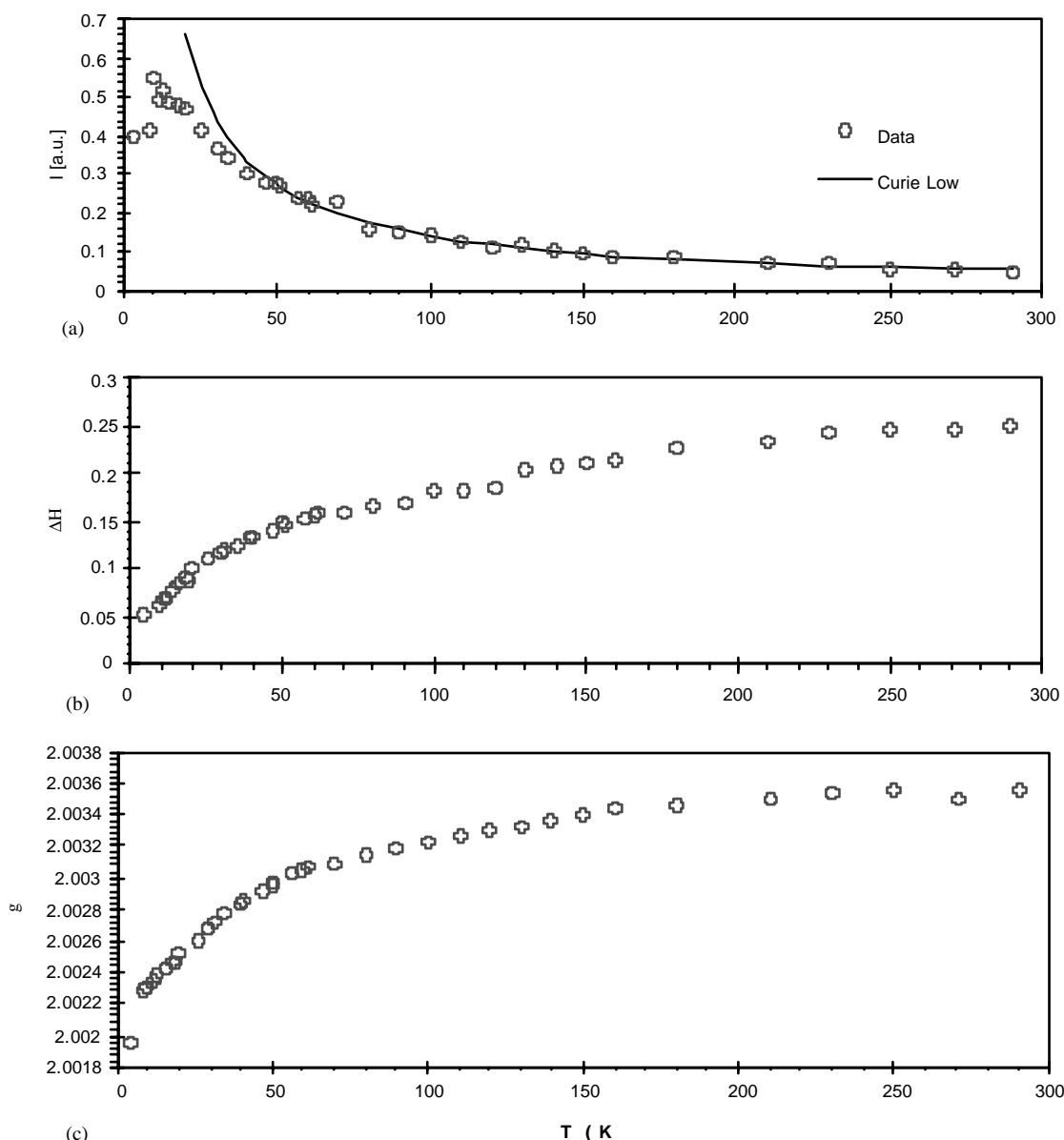


FIG. 4. The EPR parameters of (4)(TCNQ) spectrum (Lorentzian line) versus temperature: a) spin susceptibility, (b) line width and (c) g value.

$C = 0.75 \text{ K cm}^3 \text{ mol}^{-1}$, a value consistent indeed with the presence of two non-interacting spins, attributable to the two 4^{+} and TCNQ^{-} moieties. The large value of θ as well as the susceptibility decrease below 10 K, observed both in the EPR and the SQUID measurements traduce the presence of relatively strong intermolecular antiferromagnetic interactions. Susceptibility measurements at different fields did not exhibit any change, running out the possibility of a transition to an antiferromagnetic ground state. On the other hand, the SQUID data can be properly fitted in the whole temperature range by the sum of a Curie law and a Heisenberg linear chain

system with $J/k = -21 \text{ K}$. Indeed a close examination of the X-ray crystal structure of (4)(TCNQ) shows the presence of short S-S contacts (3.87 \AA) between (4^{+}) molecules pertaining to neighboring mixed stacks (Fig. 6). These S-S interaction in the bc plane might very well be the origin of the chain-like behavior of the (4^{+}) species while the TCNQ will independently contribute to the Curie-Weiss behavior. Because the EPR spin susceptibility derived from the Lorentzian line matches the SQUID magnetic susceptibility, it confirms that the EPR signal is a dynamically narrowed line due to (both radicals) delocalized electrons.

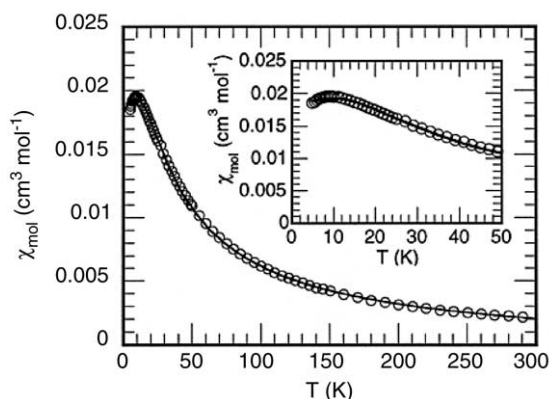


FIG. 5. Temperature dependence of the magnetic susceptibility in (4)(TCNQ).

CONCLUSION

Conjugated donors containing an azino spacer group between heterocyclic rings have been studied. Compared to DTDAF, the introduction of the azino spacer shifts the oxidation potentials towards more positive values and therefore these derivatives are easier to handle under atmospheric conditions. The wider difference between the two oxidation potentials is also an interesting effect of this spacer, increasing the window potential stability of the cation radical specie. Sequential nitrogen substitution decreases the redox properties towards less donor molecules. The X-ray determination of three complexes obtained with TCNQ reveals similar mixed stack structures. Among them, only the azino-DTDAF formed a charge transfer complex as confirmed by magnetic studies. Azino-DTDAF is of particular interest for its readily accessible redox potentials and the stability range of the radical, thus opening various possibilities to form molecular materials, either with different acceptors or by electrocrystallization.

EXPERIMENTAL SECTION

Synthesis

N,N'-Bis-(3,4,5-trimethyl-3H-thiazol-2-ylidene)-hydrazine (4)

To a solution of thiazolium salt **3** (3.63 mmol, 1 g) in acetonitrile (20 mL) triethylamine (7.26 mmol, 1 mL) and

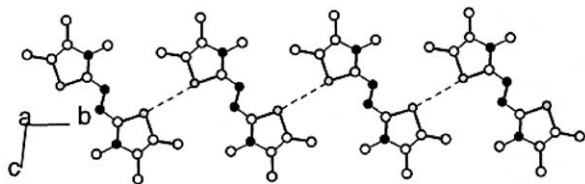


FIG. 6. S-S interactions in the bc plane in (4)(TCNQ).

hydrazine monohydrate (1.82 mmol, 90 μ L) were added. The reaction mixture, under inert atmosphere, and in the dark was stirred for 12 h at room temperature. The yellow precipitate formed in the medium was then filtered and washed with acetonitrile. Chromatography of this precipitate on silica gel column with CH_2Cl_2 - Et_2O 80/20 as eluent afforded **4** as a yellow powder, yield 16%, m.p. $>260^\circ\text{C}$ and **8** as a yellow powder, yield 8%, m.p. $>260^\circ\text{C}$. Only one isomer is observed by ^1H NMR.

4: ^1H NMR (CDCl_3) δ 1.94 (s, 6H, CH_3), 1.97 (s, 6H, CH_3), 3.24 (s, 6H, CH_3N). ^{13}C NMR (CDCl_3) δ 11.24, 12.24, 31.25, 103.75, 128.96, 157.10. Anal. Calcd for $\text{C}_{12}\text{H}_{18}\text{N}_4\text{S}_2$: C, 51.03; H, 6.42; N, 19.84; S, 22.70. Found: C, 50.61; H, 6.33; N, 19.66; S, 23.29; HRMS Calcd for $\text{C}_{12}\text{H}_{18}\text{N}_4\text{S}_2$: 282.0973. Found: 282.0979.

8: ^1H NMR ($\text{CDCl}_3/\text{CF}_3\text{CO}_2\text{H}$) δ 2.19 (s, 6H, CH_3), 2.23 (s, 6H, CH_3), 2.35 (s, 6H, CH_3), 3.73 (s, 6H, CH_3N). ^{13}C NMR ($\text{CDCl}_3/\text{CF}_3\text{CO}_2\text{H}$) δ 11.92, 12.23, 13.14, 34.69, 114.93, 132.99, 156.83, 170.26; HRMS FAB ($\text{M}+\text{H}$) $^+$ Calcd for $\text{C}_{16}\text{H}_{24}\text{N}_6\text{S}_2$: 365.1582. Found: 365.1579.

(3,4,5-Trimethyl-3H-thiazol-2-ylidene)-hydrazine (5). To a solution of 2-ethylthiothiazolium salt **3** (3.63 mmol, 1 g) in acetonitrile (20 mL) and 5 equivalents of hydrazine monohydrate (18.2 mmol, 0.9 mL) were added under inert atmosphere. The reaction mixture was stirred at room temperature for 2 h. After removal of the solvent in vacuum, CH_2Cl_2 (50 mL) was added. The organic phase was washed with water (3×100 mL), dried over Na_2SO_4 and evaporated. The residue was chromatographed on silica gel column using methanol as eluent. Recrystallization of the white solid using petroleum ether/ether 80:20 as the solvent afforded **5** as a white powder, yield 70%, m.p. 99°C . This compound should be kept under inert atmosphere in order to avoid decomposition. ^1H NMR (CDCl_3) δ 1.93 (s, 3H, CH_3), 2.00 (s, 3H, CH_3), 3.14 (s, 3H, CH_3N), 4.11 (s, 2H, NH_2). ^{13}C NMR (CDCl_3) δ 11.68, 12.61, 31.42, 103.24, 129.82, 162.52.

N-(4,5-Dimethyl-[1,3]dithiol-2-ylidene)-*N'*-(3,4,5-trimethyl-3H-thiazol-2-ylidene)-hydrazine (7). To a solution of dithiolium salt **6** (1.4 mmol, 500 mg) in acetonitrile (20 mL) **5** (1.4 mmol, 220 mg) was added under inert atmosphere. The medium was refluxed for 2 h. Then, the reaction mixture was stirred for 12 h at room temperature under inert atmosphere. After removal of the solvent, 50 mL of CH_2Cl_2 was added, washed with water and dried over Na_2SO_4 and condensed under vacuo. The residue was chromatographed on silica gel column with CH_2Cl_2 as eluent and afforded **7** as a white powder, yield 30%, m.p. 248°C . ^1H NMR (CDCl_3) δ 2.00 (s, 9H, CH_3), 2.03 (s, 3H, CH_3), 3.31 (s, 3H, CH_3N); ^{13}C NMR (CDCl_3) δ 11.69, 12.50, 14.17, 14.52, 31.85, 105.99, 120.14, 122.46, 129.57,

156.93, 164.30. Anal. Calcd for $C_{11}H_{15}N_3S_3$: C, 46.29; H, 5.30; N, 14.72; S, 33.70. Found: C, 46.31; H, 5.29; N, 14.69; S, 33.70.

Two-Step Procedure for the Synthesis of 4. Same procedure as the one described above for 7 but using the thiazolium salt 3 instead of the dithiolium salt 6.

Crystallography (14)

Experimental details for the three salts are collected in Table 2. Data collections were performed on a Stoe Imaging Plate Diffraction System at room temperature with graphite mono-chromatized $MoK\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). No absorption corrections were applied. Structures were solved by direct methods (SHELXS) and refined by full-matrix least-squares procedures (SHELXL). Hydrogen atoms were introduced at calculated positions (riding model), included in structure factor calculations but not refined. In (7) (TCNQ), the sulfur and NMe moiety are disordered on the same position with a 50:50 occupation parameter.

Magnetic Studies

The EPR studies were carried out on single crystals with an X band EPR spectrometer equipped with liquid helium cryostat. Magnetic susceptibility measurements were performed on a Quantum Design MPMS5 SQUID magnetometer operating in the range 5–300 K with polycrystalline samples. Data were corrected for Pascal diamagnetism and sample holder contribution.

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14. Full crystallographic details have been deposited at the Cambridge Crystallographic Data Center (CCDC). Any request to the CCDC for this material should quote the reference numbers 174406–174408.