Tetrahedron Letters, Vol. 33, No. 48, pp. 7341-7344, 1992
Printed in Great Britain

0040-4039/92 $5.00 + .00
Pergamon Press Ltd

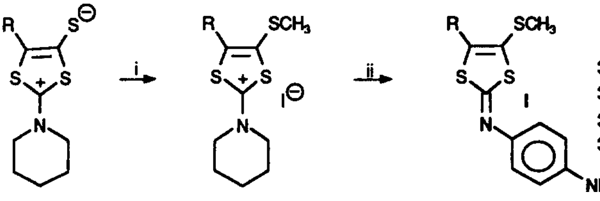
2(p-Dimethylaminophenyl) Imino-1,3-Dithioles : New Unsymmetrical Donors.

Dominique Lorcy [a,§], Albert Robert [a*], Smaïl Triki [b], Lahcène Ouahab[b], Philippe Robin[c] and Eveline Chastaing[c].

[a] Laboratoire de Physicochimie Structurale associé au CNRS, Campus de Beaulieu, 35042 Rennes, France
[b] Laboratoire de Chimie du Solide et Inorganique Moléculaire associé au CNRS, Université de Rennes I, 35042 Rennes, France
[c] Laboratoire Central de Recherche Thomson-CSF, Domaine de Corbeville, 91405 Orsay, France

Abstract - The synthesis, structure, electrochemical properties and second harmonic generation from the title compounds are presented.

Geometrical factors and intermolecular orbital overlaps in the solid state are parameters of fundamental importance for the design of materials useful for electronic or optoelectronic applications. For example, the structure of tetrathiafulvalene (TTF) is well suited for the preparation of organic metals as TTF derivatives are good donors able to give charge transfer complexes with acceptors. Furthermore, due to the high polarizability of the sulfur atoms and their large van der Waals radius, the oxidized TTF molecules can give segregated stacks in the solid state, leading to mono-, two-, or three - dimensional conducting salts. Of course, the efficiency of intermolecular interactions is directly linked to the substituents on the TTF core. That is the reason why many substituted TTF derivatives have been prepared and studied as components of organic metals.[1] These considerations prompted us to focus our attention on 2-arylimino-1,3-dithioles **3** which seemed to us to be of interest for the following three reasons. (i) A convenient choice of a good donor on the imino functionality could contribute to the donor character of the dithiole ring and give charge transfer complexes with appropriate acceptors. (ii) As the syn-anti isomerism of conjugated imines is a weakly energetic process, one can imagine that such molecules **3** could adopt the best geometry to fit the strongest intermolecular stabilizing interactions in the solid state. (iii) Such a syn-anti isomerism is also of interest for non-linear optical applications, for instance in **3** where R = electron-withdrawing group creating conjugated push-pull polarized molecules[2-4]. We report in this communication the preparation of several donors **3**, the characterization by X-ray crystal structure of **3b**, their electrochemical properties and their second harmonic generation.



3 a : R = CH_3 Yield % 75
3 b : R = $pMeC_6H_4$ 78
3 c : R = $pNO_2C_6H_4$ 75
3 d : R = $pClC_6H_4$ 80

1 **2**

Scheme 1 : i : CH_3I (excess in $(CH_3)_2CO$.
ii : N,N dimethyl p-phenylene diamine 1 eq. in CH_2Cl_2.

Results

Synthesis : The new donors **3** were prepared by reacting an amine with 1,3-dithiolium cations [5]. The synthesis of the amino dithiolium cation **2** was achieved by the reaction of methyl iodide with mesoionic-1,3 dithiolium-4-thiolates [6] **1** in acetone ; **2** was subsequently reacted with N,N-dimethyl-p-phenylenediamine to afford **3** in good yield (75-80% yield after purification by flash chromatography with diethyl ether) (scheme 1).

---

§ Present address : University of Tuscaloosa, Dept. of Chemistry, Box 870336, Tuscaloosa, Alabama 35487 .

<u>Structure</u> : The structure of compounds **3** was established by nmr and mass spectroscopies. Furthermore, the X-ray crystal structure of compound **3b** has been determined*. The molecular structure, selected bond lengths and selected bond angles are given in Figure 1. The molecule is not planar, as indicated by the dihedral angles between planes (a), (b) and (c) [See Figure 1; $\widehat{ab}$= 107.27(7)°, $\widehat{ac}$= 42.86(7)° and $\widehat{bc}$= 66.55(8)°]. In the solid state, **3b** adopts an anti configuration [(p-tol) and p-N-dimethylamino) phenyl are anti].

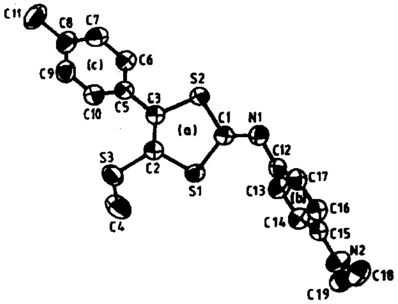


Figure 1. ORTEP view of **3b** ; selected bond lengths (Å) and angles (°): S1-C1 1.772(2), S1-C2 1.749(2), S2-C1 1.750(2), S2-C3 1.752(2), N1-C1 1.255(3), N1-C12 1.420(3),C2-C3 1.342(3), C1-S1-C2 96.1(1), C1-S2-C3 97.2(1), C1-N1-C12 118.4(2), S1-C1-S2 112.7(1), S1-C2-C3 117.8(2), S2-C3-C2 116.2(2).

The following characteristics of compounds **3** are worth noting.

i) The 2-iminodithioles **3** are good donors, as shown by the cyclic voltammetric data of donor **3a** in comparison with dimethyl dithiomethyl TTF (DMDTMTTF) given in figure 2. Indeed **3a** presents two perfectly one electron reversible waves showing the good stability of the first and second oxidation states of **3a**. It appears that changing R = CH_3 **3a** to R = p tol **3b** has no significant influence on the first and second ionization potentials. Having in mind the preferred conformation of **3b** in the solid state, (fig. 1), this result may arise from a non-coplanar preferential conformation of the p-tolyl and dithiole rings for **3b** in solution.

Donors	E_1 $^{1/2}$ (V)	E_2 $^{1/2}$ (V)	ΔE $^{1/2}$ (V)
DMDTMTTF	0.03	0.35	0.32
3a	0.27	0.52	0.25
3b	0.26	0.51	0.25

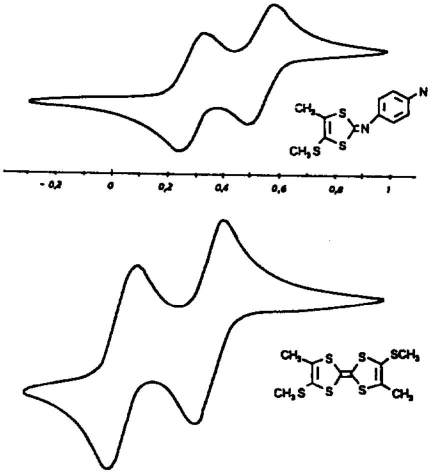
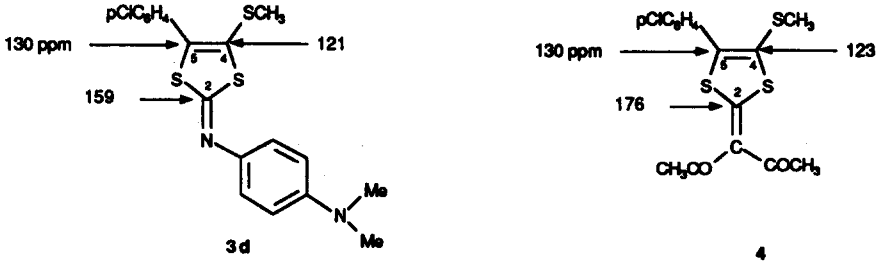


Figure 2. Cyclic Voltammograms of : a) compound **3a** and b) DMDTMTTF. The comparison of the potential values are given in (c). Experimental conditions: room temperature, Pt working electrode, Ag/AgNO3 reference electrode, n-Bu_4NPF_6 0.1M electrolyte in CH_3CN under N_2.

ii) The sulfur atoms of the dithiol rings are not efficient for the transmission of the conjugaison. In fact, it appears that the chemical shifts of C-4 and C-5 in compounds **3** are nearly the same that those of C-4 and C-5 of the analogs **4** (scheme 2).



Scheme 2 : Comparaison of ^{13}C nmr chemical shifts of the carbons 2, 4 and 5 in dithiols **3d** and **4**

The relative small value of λ max observed for **3c** (R = $pNO_2C_6H_4$)/EtOH (λmax = 342 nm, ε = 18000 to be compared for instance to the λmax = 404 nm EtOH of p-N-dimethyl nitro aniline), is also in agreement with a poor transmission of the conjugation through the dithiole ring.

iii) Spontaneous syn-anti isomerisation is observed by nmr for compounds 3 solubilized in $CDCl_3$ or C_5D_5N. As an exemple pure crystals **3b** (anti configuration in the solid stade fig. 1) dissolved in C_5D_5N show a 300 mHz ^1H nmr spectra characterized by two N<u>Me</u>$_2$ signals (2,79 and 2,77 ppm) ; two p<u>Me</u>C_6H_4 signals (2,18 and 2,10 ppm) ; two S<u>Me</u> signals (2,11 and 2,09 ppm) ; and complex signals for the aryl protons (7,56 - 6,80 ppm). The presence of a 50-50 % mixture of the syn-anti isomers is deduced from the relative intensity of the signals. Two sets of signals are also observed in the ^{13}C nmr spectra of 3.

<u>Non-linear optical characterization</u> : As syn-anti isomerisation is effective in solution, and as conjugation is not transmitted through the dithiol ring, two distinct dipoles may be colinearly oriented by an electric field using the corona method. Such a situation will be of interest for second harmonic generation (SHF) in the blue, because a second order non linear susceptibility is escounted, and furthermore the material will not absorb in the blue. As SHG in the blue is of practical interest, [7] we decided to evaluate the non-linear susceptibility of **3c** by using a doped polymer polymethylmetacrylate (PMMA).

The host polymer PMMA is dissolved (40 g/l) in methylisobutylketone (MIBC). The molecules are then added in PMMA at a concentration of 10 % by weight. The solution is filtered. Indium Tin Oxide (ITO) coated glass slides are then spin coated with the solution. The ITO coating supplied by Balzers is conducting and transparent. After annealing at 120°C during 1 hour, the solvent is evaporated and thicknesses of few microns are achieved for the doped polymer films. The molecules inside the polymer film are then aligned by corona poling (5 kv). As is explained in many previous papers an electric field is applied on the sample at a temperature above the Tg (glass transition temperature). Due to their dipolar momentum the molecules orient themselves along the electric field. By cooling the sample down to room temperature, the orientations of the molecules are frozen and the electric field can be removed.

The product of the non-linear hyperpolarizability β of the molecule by the dipolar moment can be calculated from the measurement of the non-linear hyperpolarizability d_{33} of the sample using the following relation

$$d_{33} = \frac{1}{2} N \ f^{2\omega} f^{\omega} f^{\omega} \beta \ f^{0} \frac{\mu E}{5\,kT} \qquad (8)$$

where μ is the dipolar moment of the molecule, E the electric field applied on the sample, N the volumic concentration of molecules, f^{ω} and $f^{2\omega}$ the local field factors at ω and 2ω [2].

The samples described above have been measured using a Nd : YAG laser. The wavelength is 1.06 mm, the power 400 mWatt, the pulse duration 250 ns and the repetition rate 1 KHz. From the second harmonic generation signal recorded when varying the incident angle of the fondamental beam, we can calculate the d_{33} coefficient.

Results

Molecule	λmax nm	N mole/cm^3	d33 esu	β^{μ} cm^5-D/esu
3c	342	1.4 10^{20}	2,07 10^{-9}	4.8 10^{-28}

Although, in a corona poling, we do not know exactly the electric field applied on the sample, we have taken 10^8V/m in the above calculations. The results have to be seen as an order of magnitude. They are similar to the ones found for the dimethylaminobiphenyl [9] which absorb at the same wavelength.

References and notes

1 Reviews : a) M. Narita, C.U. Pittman, *Synthesis*, 1976, 489. b) A. Krief, *Tetrahedron, 1986*, ***42***, 1209. c) G. Schukat, A.M. Richter, E. Fanghänel, *Sulfur reports*, 1987,**7**, 155. d) J.M. Williams, A.J. Schultz, U. Geiser, K.D. Carlson, A.M. Kini, H.H. Wang, W.K. Kwok, M.H. Whangbo, J.E. Schirber, *Science*, 1991, **252**, 1501.

2 "Non linear optical properties of organic molecules and crystals", J. Zyss, Eds, D.S. Chemla, *Acad. Press*, 1987.

3 M. Blanchard-Desce, I. Ledoux, J.M. Lehn, J. Malthête, J. Zyss, *J. Chem. Soc. Chem. Commun.*, 1988, 737.

4 H.E. Katz, K.D. Singer, J.E. Sohn, C.W. Dirk, L.A. King, H.M. Gordon, *J. Am. Chem. Soc.*, 1987, **109**, 6561.

5 K. Hiraï, H. Sugimoto and T. Ishiba, *Sulfur Reports* , 1983 , 3, 1-32.

6 A. Souizi and A. Robert, *Synthesis*, 1982, 1059.

7 M. Cross, New Scientist, July 1988, p. 38.

8 M. Eich, B. Reck, D.Y. Yoon, C.G. Willson, *J. Appl. Phys.*, 1989, **66**, 3241-3247.

9 I. Ledoux, J. Zyss, A. Jutand, Ch. Amatore, *Chem. Phys.*, 1991, **150**, 117-123 .

10 B.A. Frenz, & Associates Inc. 1985. *SDP structure Determination Package*. College Station, Texas, USA, and Enraf-Nonius, Delft, The Netherlands.

***Crystal Data of 3b.** A crystal measuring 0.3 x 0.15 x 0.15 mm was mounted on an Enraf-Nonius CAD4 diffractometer equipped with a graphite-monochromated Mo-Kα radiation source (λ = 0.71073Å). $C_{19}H_{20}N_2S_3$; M_r= 372.58, Triclinic, $P\bar{1}$, a = 8.439(6), b = 10.595(3), c = 11.634(6)Å, α = 111.71(4), β = 96.31(6), γ = 101.09(4)°, V = 929.4Å^3, Z = 2, d_{calc} = 1.331 g.cm^{-3}, μ = 3.85cm^{-1}, F(000)=392 . Data were collected in the range $2 \leq 2\theta \leq 50°$ with the θ–2θ scan mode. 3248 unique reflections observed of which 2597 were considered observed having $I \geq 3\sigma(I)$. Intensities were corrected for Lorentz and polarization effects. The absorption corrections were performed using DIFABS procedure.[10] The structure was solved by direct methods and successive Fourier difference syntheses. After refinement of positional and anisotropic (β_{ij}) thermal parameters for all non-hydrogen atoms, the positions of the H-atoms were calculated [d(C-H)= 1 Å; B_{eq}= 4 Å^2] and included as a fixed contribution to F_c. The refinement by Full-matrix least squares give a final R = 0.048 (R_ω= 0.064). Scattering factors and corrections for anomalous dispersion were taken from "*International Tables for X-ray Crystallography* 1974, *vol IV*". All the calculations were performed on a microvax 3100 computer using the SDP programs described by Frenz.[10] weights $\omega = 4Fo^2/[\sigma^2(I)+(0.06\,|Fo|^2)^2]$.

(Received in France 7 May 1992)