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SYNTHESIS AND INVESTIGATION OF 4,5-DIMETHYL-1,3-DITHIOLYLIDENE-(4-DIMETHYLAMINOPHENYL)ACETONITRILE

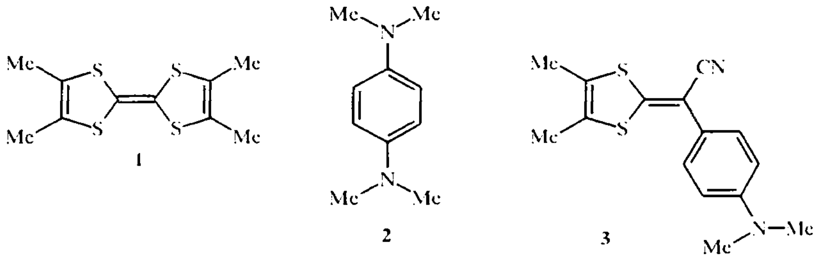
V. Kampars, V. Kokars, and A. Kaimin'sh

A method was developed for the synthesis of unsymmetrical strong electron donors. 4,5-Dimethyl-1,3-dithiolylidene(4-dimethylaminophenyl)acetonitrile was obtained, and its properties were investigated by electrochemical, spectroscopic, and quantum-chemical methods.

Keywords: Unsymmetrical electron donor, charge-transfer complexes, quantum-chemical calculations, cyclic voltammetry.

The most widely investigated electron donors are tetrathiafulvalene (**1**) or *p*-phenylenediamine (**2**) derivatives, and they are characterized by high symmetry [1]. The materials for nonlinear optics obtained on the basis of these donors cannot be centrosymmetrical [2], consequently the characteristics of these materials can be affected significantly by the symmetry of their components. In order to investigate this effect we synthesized 4,5-dimethyl-1,3-dithiolylidene(4-dimethylaminophenyl)acetonitrile (**3**), which can represent a strong unsymmetrical electron donor (scheme 1).

Scheme 1



Compound **3** was obtained from 4,5-dimethyl-1,3-dithiole-2-thione (**4**). Alkylation of compound **4** gives the reactive dithiolium cation **5**, which enters into reaction with 4-nitrobenzyl cyanide in the presence of pyridine as catalyst; the obtained 4,5-dimethyl-1,3-dithiolylidene(4-nitrophenyl)acetonitrile (**6**) is reduced by tin chloride to 4,5-dimethyl-1,3-dithiolylidene(4-aminophenyl)acetonitrile (**7**), which is alkylated by methyl iodide with subsequent decomposition of the formed trimethylammonium cation **8** (scheme 2).

The electron donor ability of compound **3** was evaluated by cyclic voltammetry and also by investigation of the charge-transfer complexes. The voltammograms of the nitrile **3**, like those of compounds **1** and **2**, each contain two well-defined anodic and cathodic peaks (Fig. 1). As demonstrated by their position, the first anodic peak corresponds to reversible one-electron oxidation and characterizes the donor ability of compounds **1-3**.

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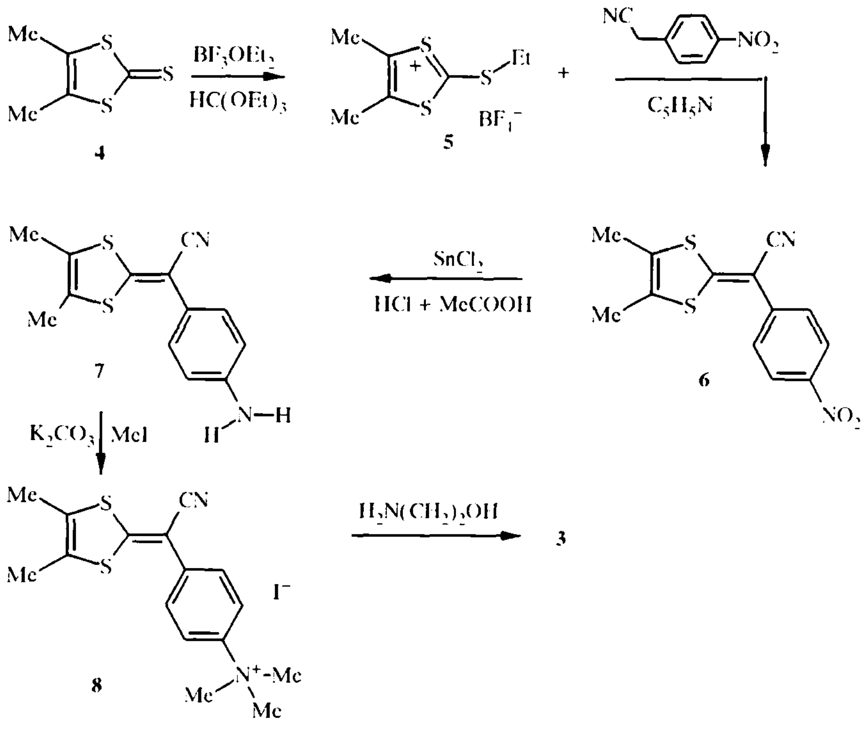
Scheme 2



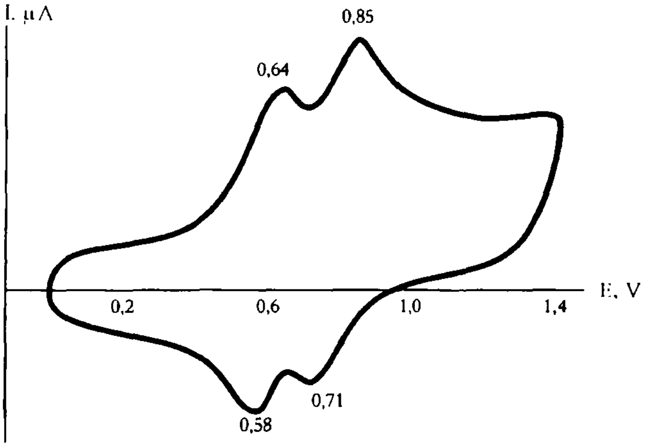


Fig. 1. The cyclic voltammogram of 4,5-dimethyl-1,3-dithiolylidene(4-dimethylaminophenyl)acetonitrile **3**.

The potentials of the anodic peaks relative to the Ag/AgCl electrode in acetonitrile solution

Donor	Peak potential, V
1	0.34
2	0.23
3	0.64

TABLE 1. The Characteristics of the Complexes and the Ionization Potentials

Donor	Energy of long-wave transition with charge transfer (eV) for the complexes		Ionization potential (IP), eV*
	with *p*-chloranil	with tetracyanoethylene	
I	1.09*	—	6.4
II	1.24*	—	6.55
III	1.53	1.30	6.85±0.05

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*The ionization potential was calculated on the basis of the energies of the charge-transfer transition according to the following equations: for the complexes with *p*-chloranil IP = $1.15(h\nu + 4.46)$; for the complexes with tetracyanoethylene IP = $1.22(h\nu + 4.28)$.

As follows from the presented data, the oxidation of the nitrile **3** takes place at higher potentials than that of the compounds **1** and **2** taken for comparison, i.e., the synthesized sample does not have such strong electron-donor characteristics. Its ionization potential can be expected to exceed that of tetrathiafulvalene **1** by approximately 0.3 eV.

The ionization potentials were determined by investigation of the charge-transfer complexes in chloroform solutions. *p*-Chloranil and tetracyanoethylene were used as acceptors. Well-defined charge-transfer bands were observed in the electronic absorption spectra of the mixed solutions of the donor and acceptor. Both in the case of the complex of the investigated compound **3** with the acceptor *p*-chloranil and in the case of its complex with tetracyanoethylene two charge-transfer bands were observed in the spectra. In both cases the difference between the transition energies amounts to 0.86 eV, indicating that the second ionization potential of the nitrile **3** exceeds the first by 0.86 eV. The obtained data are given in Table 1. The results of the ionization potential calculations coincide with the results of the electrochemical investigations of compounds **3** and **1** but do not coincide with those for compound **2**. The results of quantum-chemical calculations by the semiempirical CNDO/S method indicate that the highest occupied molecular orbital of the nitrile **3** is localized by 80% at the dithiolylidene fragment and at the carbon atom directly attached to this fragment. Consequently, the solvation of the cation radical, capable to affect the results of the electrochemical investigations, must be practically the same for compounds **3** and **1**, and so the apparent contradictions of the obtained experimental data can be explained. The results of quantum-chemical calculations of the model compounds also show that substitution of the cyano group in the nitrile **3** by hydrogen leads to decrease of 0.2 eV in the ionization potential of compound **3**, and the developed method can consequently be used for the production of stronger electron donors than compound **3**.

EXPERIMENTAL

The cyclic voltammograms were obtained using a three-electrode scheme with a PI-50-1 potentiostat. The working electrode was glassy graphite, and the reference electrode was of platinum. The supporting electrolyte was tetrabutylammonium perchlorate. The sweep rate was 200 mV/sec. The IR spectra were recorded on a Specord IR-75 spectrometer (vaseline oil). The electronic absorption spectra were recorded on a Specord UV-Vis spectrometer (solutions in chloroform). The PMR spectra were recorded on a Bruker WH-90/DS spectrometer for solutions in deuterochloroform with TMS as internal standard.

2-Ethylthio-4,5-dimethyl-1,3-dithiolium Tetrafluoroborate (5) was obtained by the well-known method [3].

4,5-Dimethyl-1,3-dithiolylidene(4-nitrophenyl)acetonitrile (6). Mixture of compound **5** (2.7 g, 0.01 mol) and 4-nitrobenzyl cyanide (1.62 g, 0.01 mol) was boiled in acetic acid (100 ml) containing pyridine (1 ml) for 2.5 h. Then the solvent (20-30 ml) was removed at reduced pressure. The mixture was cooled and filtered. The precipitate was washed with 1:1 aqueous solution of ethanol and recrystallized from acetonitrile.

Compound **6** was obtained. Yield 2.0 g (80%); mp 235-237°C. IR spectrum, cm^{-1}: 1545 (NO_2), 2198 (CN). Found, %: C 59.84; H 3.42; N 10.30. $C_{13}H_{10}N_2O_2S_2$. Calculated, %: C 60.43; H 3.90; N 10.84; S 24.82.

4,5-Dimethyl-1,3-dithiolylidene(4-aminophenyl)acetonitrile (7). To solution of $SnCl_2 \cdot 2H_2O$ (10 g) in acetic acid (8 ml) and concentrated hydrochloric acid (8 ml) compound **6** (2.9 g, 0.01 mol) was added. The reaction mixture was stirred at the same temperature for further 30 min, cooled, and filtered. The precipitate was shaken with 20% solution of potassium hydroxide (50 ml), filtered, dried, and recrystallized from ethanol. Compound **7** was obtained. Yield 2.2 g (85%); mp 165-167°C. Found, %: C 59.53; H 4.54; N 10.27; S 23.89. $C_{13}H_{12}N_2S_2$. Calculated, %: C 59.96; H 4.64; N 10.76; S 24.70.

4,5-Dimethyl-1,3-dithiolylidene(4-trimethylammoniophenyl)acetonitrile Iodide (7). To solution of compound **7** (2.61 g, 0.01 mol) in anhydrous ethanol (100 ml) anhydrous potassium carbonate (10.5 g, 0.075 mol) and methyl iodide (16 ml, 0.26 mol) were added. The mixture was boiled and stirred for 8 h. Half the solvent was then removed, and the residue was cooled. The precipitate was filtered off and recrystallized from ethanol. Compound **8** was obtained. Yield 3.4 g (80%). Found, %: C 44.54; H 4.24; N 6.48; S 14.65. $C_{16}H_{19}N_2S_2I$. Calculated, %: C 44.65; H 4.45; N 6.51; S 14.90.

4,5-Dimethyl-1,3-dithiolylidene(4-dimethylaminophenyl)acetonitrile (3). Mixture of the iodide **8** (4.3 g, 0.01 mol) and ethanolamine (0.6 ml, 0.01 mol) in ethanol (40 ml) was boiled for 1 h. The reaction mixture was cooled, and compound **3** was filtered off. The total amount of the compound was recrystallized from ethanol, and 2.3 g (78%) of compound **3** were obtained; mp 162°C. PMR spectrum (δ, ppm): 1.98 (3H, s, CH_3); 2.04 (3H, s, CH_3); 2.98 (6H, s, $2NCH_3$); 6.67 (2H, d, J = 8 Hz, *m*-H_{Ar}); 7.29 (2H, d, *o*-H_{Ar}). Found, %: C 62.46; H 5.59; N 9.70; S 22.42. $C_{15}H_{16}N_2S_2$. Calculated, %: C 62.63; H 5.64; N 9.71; S 22.23.

REFERENCES

1. M. Nazario, P. Ignacio, L. Sanchez, and C. Seone, *J. Org. Chem.*, **62**, 877 (1997).
2. N. J. Long, *Angew. Chem. Int. Ed. Engl.*, **34**, 21 (1995).
3. V. Yu. Khodorkovskii and O. Ya. Neiland, *Izv. Akad. Nauk Latv. SSR, Ser. Khim.*, No. 2, 131 (1982).