130. Solution Structures of One-Electron Reduced and Oxidized Molecules with Twisted Donor and Acceptor Moieties

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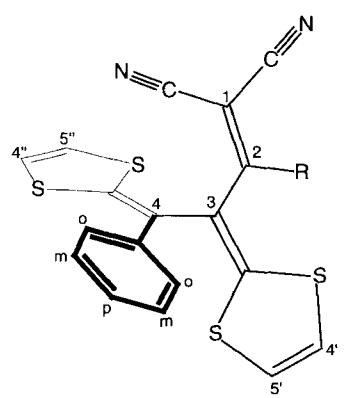
The solution structures of the radical anion and the radical cation of the donor-acceptor molecules 3,4-di(1,3-dithiol-2-ylidene)-4-phenylbut-1-ene-1,1-dicarbonitrile (**1**) and 3,4-di(1,3-dithiol-2-ylidene)-4-phenylbut-1-ene-1,1,2-tricarbonitrile (**2**) are discussed based on cyclovoltammetric and ESR/ENDOR measurements. It is shown that the spin population of the radical anions is limited to the di- and tricyanoethene moiety and the coplanar 1,3-dithiole at C(3), whereas that of the radical cations resides mainly inside the two 1,3-dithiole rings. The energies of the long-wave bands in the electronic-absorption spectra of **1** and **2** correspond to the differences between the oxidation and reduction potentials and thus point to a charge-transfer character of these transitions.

Introduction. – Organic materials indicating charge-transfer interactions are playing an important role in the development of conductors [1] or opto-electronic devices [2]. Whereas one class of such compounds involves charge-transfer complexes [3] of donors (*e.g.*, tetrathiafulvalene, TTF) and acceptors (*e.g.*, tetracyanoquinodimethane, TCNQ), recently synthesized molecules comprise both functionalities in a geometry allowing spiroconjugation [4]. Compounds **1** (3,4-di(1,3-dithiol-2-ylidene)-4-phenylbut-1-ene-1,1-dicarbonitrile) and **2** (3,4-di(1,3-dithiol-2-ylidene)-4-phenylbut-1-ene-1,1,2-tricarbonitrile) [5] are composed of efficient acceptor and donor fragments. The electron-accepting part of these molecules is the di- or tricyanoethene whereas the 1,2-di(1,3-dithiol-2-ylidene)ethane moiety serves as the electron donor.



1 R = H
2 R = CN

The crystal structure of **2** indicates that the tricyanoethenyl group and the 1,3-dithiole at C(3) are coplanar but almost orthogonal to the second part of the molecule, *i.e.*, the Ph substituent and the second 1,3-dithiole [5]. A very similar geometry should also hold for **1**.

Here, we investigate the influence of the restricted geometry, *i.e.*, the close proximity but twisted arrangement of the donor and acceptor moieties within the molecule, on the electron-transfer behavior of **1** and **2**. Moreover, we shed some light onto the solution structure of the one-electron reduced and oxidized stages of **1** and **2** on the hyperfine time-scale provided by ESR spectroscopy.

Compound ($^2H_5$)-**1** in which the H-atoms of the Ph ring are replaced by ^2H is also included [5][1]). The analysis of the ESR spectra of (($^2H_5$)-**1**)$^{-\cdot}$/(($^2H_5$)-**1**)$^{+\cdot}$ in comparison to **1**$^{-\cdot}$/**1**$^{+\cdot}$ and **2**$^{-\cdot}$/**2**$^{+\cdot}$ allows to substantiate the assignment of the proton-hyperfine coupling constants, and thus helps to gain a conclusive information about electron delocalization.

Experimental. – Cyclovoltammograms were recorded on a *Metrohm* instrument (Polarecord *E 506*, VA scanner *E 612*, VA stand *663*); working electrode: Pt disk; counterelectrode: Pt wire; reference electrode: Ag/AgCl (3M KCl); solvent: MeCN; supporting electrolyte: $Bu_4N^+ClO_4^-$ (0.1M); scan rate 300 mV · s^{-1}.

ESR Spectra were taken on a *Varian E9* spectrometer equipped with a *Marconi Instruments 2440* microwave counter and a *Bruker ER 035 M* NMR gaussmeter for the determination of the g factors. ENDOR and TRIPLE measurements were performed on a *Bruker ESP 300* spectrometer system.

Results. – *Electrochemistry. Fig. 1* shows the cyclic voltammograms of **1** and **2**. Both compounds are able to take up two electrons. Whereas both reduction waves indicate reversible redox processes for the tricyano derivative **2** ($E_{1/2}^{-1} = -0.55$ V and $E_{1/2}^{-2} = -1.21$ V *vs.* Ag/AgCl) only the first reduction step is reversible for the dicyano derivative **1**. The potentials of **1** are shifted to more negative values ($E_{1/2}^{-1} = -1.12$ V and $E_P^{-2} = -1.88$ V *vs.* Ag/AgCl).

Reversible oxidation waves are detected for **1** and **2**; the potentials, $E_{1/2}^{+1}$ are rather similar (0.76 and 0.85 V *vs.* Ag/AgCl, respectively).

ESR Spectroscopy. Radical Anions. Reduction of **1** with K metal in 1,2-dimethoxyethane (DME) led to the ESR spectrum indicated in *Fig. 2*. The signal is split into two sets of lines due to a hyperfine-coupling constant of one proton ($a_H = -0.776$ mT). The set at high field possesses narrower lines than that at low field, but the linewidths inside those two sets follow the opposite way. The coupling constants and the g value are given in *Table 1*. The ESR spectra of (($^2H_5$)-**1**)$^{-\cdot}$ and **1**$^{-\cdot}$ are very much alike and the ENDOR technique confirms that the ESR parameters for (($^2H_5$)-**1**)$^{-\cdot}$ and **1**$^{-\cdot}$ are identical (*Table 1*).

As a consequence of the replacement of the proton in the electron-accepting moiety of the molecule by the CN group on going from **1** to **2**, the a_H of –0.776 mT is replaced by a ^{14}N coupling constant of *ca.* 0.15 mT; thus the ESR signal of **2**$^{-\cdot}$ consists of one signal group. Again, this ESR signal displays a marked anisotropy (broader lines at high field) which diminishes at higher temperatures. Three a_H can be detected in the ENDOR spectrum (–0.048, –0.025, and +0.011 mT). The simulation of the ESR spectrum establishes that all a_H are due to one proton, and that the ^{14}N-coupling constants, a_N, are 0.1 (2 N) and 0.15 (1 N) mT (*Table 1*).

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[1]) Preparation of **1**, ($^2H_5$)-**1**, and **2** will be published elsewhere [5b].

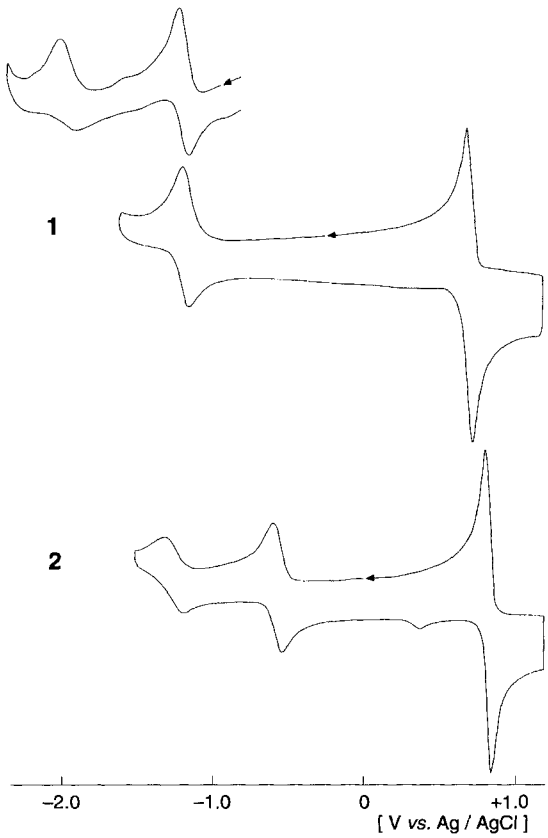


Fig. 1. *Cyclovoltammograms of* **1** *and* **2**. The insert above the cyclovoltammogram of **1** indicates the irreversible reduction to $\mathbf{1}^{2-}$.

Table 1. *Experimental and Calculated Proton- and Nitrogen-Hyperfine-Coupling Constants* [mT] *as well as g Factors of the Radical Anions of* **1**, ($^2H_5$)-**1**, *and* **2**

Assignment	H–C(2)	H–C(4')	H–C(5')	H–C(4" or 5")	H_o	H_m	H_p	CN–C(1)	CN–C(1)	CN–C(2)	g Factor
Exper.											
$\mathbf{1}^{\cdot-}$	–0.776	–0.076	–0.027	+0.014	–	–	–	0.075	0.061	–	2.0039
$(^2H_5)$-$\mathbf{1})^{\cdot-}$	–0.776	–0.076	–0.027	+0.014	–	–	–	0.075	0.061	–	2.0039
$\mathbf{2}^{\cdot-}$		–0.048	–0.025	+0.011	–	–	–	0.10	0.10	0.15	2.0040
Calc. (HMO)[a])											
$\mathbf{1}^{\cdot-}$	–0.76	–0.03	–0.03	0.0	0.0	0.0	0.0	0.09	0.09	–	
$\mathbf{2}^{\cdot-}$		–0.04	–0.04	0.0	0.0	0.0	0.0	0.09	0.09	0.18	

[a]) Parameters for heteroatoms: $h_S = 1.0$, $k_{CS} = 0.7$, $h_N = 1.0$, $k_{CN} = 2.0$, $k_{C(3)C(4)} = 0.2$. Coupling constants calculated using first-order spin populations, $Q_H = -2.5$ mT, $Q_N = 1.9$ mT.

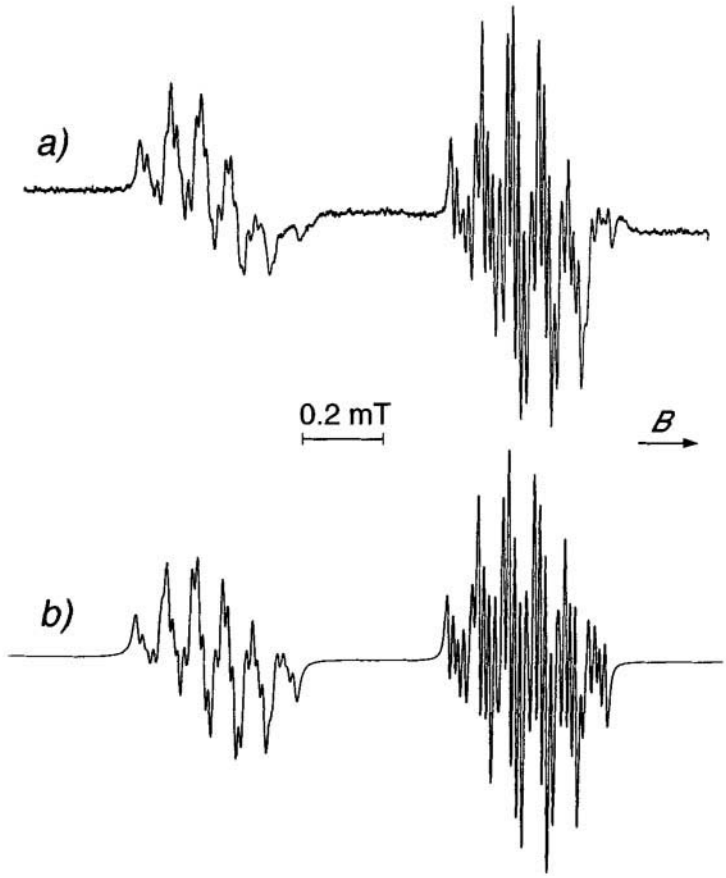


Fig. 2. *ESR Spectrum of* $\mathbf{1}^{+\cdot}$ (*a*, solvent: DME, counterion: K^+, temp.: 223 K) *and its simulation* (*b*)

Radical Cations. The radical cations of **1**, ($^2H_5$)-**1**, and **2** were accessible by oxidation with tris(4-bromophenyl)ammoniumyl hexachloroantimonate [6] in CH_2Cl_2 as the solvent. The ESR spectra of $\mathbf{1}^{+\cdot}$ and $\mathbf{2}^{+\cdot}$ are unresolved having a width of *ca.* 1 mT; that of (($^2H_5$)-**1**)$^{+\cdot}$ is split into three lines spaced by *ca.* 0.15 mT (spectral width *ca.* 0.6 mT). ENDOR spectroscopy allows the determination of the proton-coupling constants (*Fig. 3*). For $\mathbf{1}^{+\cdot}$, the a_H of 0.178, 0.121, 0.099, 0.079, 0.053, 0.041, and 0.028 mT are determined (*Table 2*). The ENDOR spectrum of (($^2H_5$)-**1**)$^{+\cdot}$ is identical except the missing signals for the a_H of 0.099, 0.079, and 0.041 mT showing that the latter a_H are replaced by deuterium-coupling constants (*Fig. 3*). In the case of $\mathbf{2}^{+\cdot}$, the a_H are 0.180, 0.111, 0.091, 0.073, and 0.035 mT (*Table 2*). The ENDOR signals belonging to the latter a_H centered at 15.1 and 14.0 MHz are rather broad but cannot be resolved further; comparison with the a_H of $\mathbf{1}^{+\cdot}$ implies that the a_H of *ca.* 0.053, 0.041, and 0.028 mT are enveloped inside these lines. From the simulations of the ESR spectra, a_N can be estimated to be <0.05 mT.

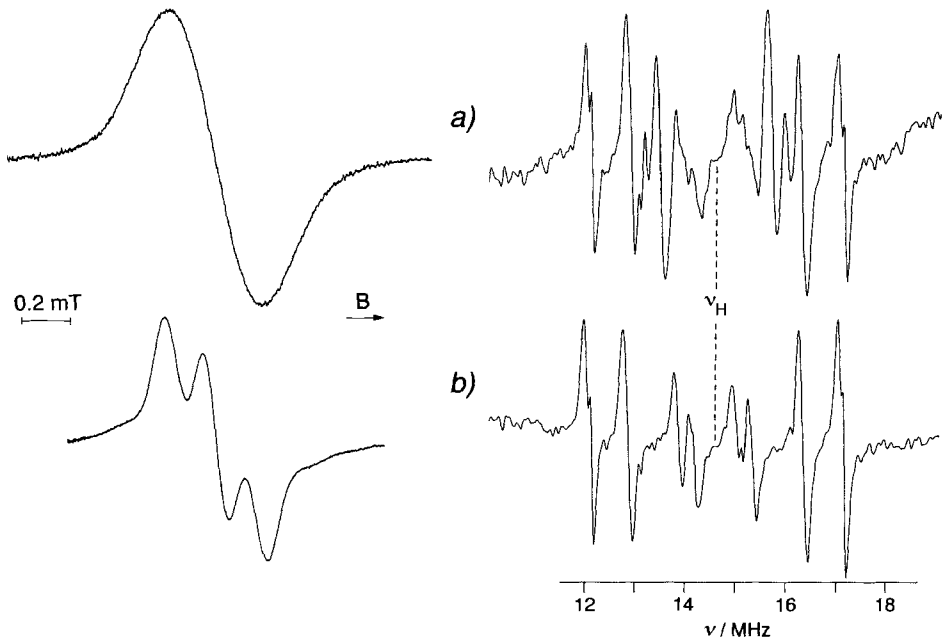


Fig. 3. *ESR Spectra* (left) *of* $\mathbf{1}^{+\bullet}$ (***a***) *and* $((^2H_5)\text{-}\mathbf{1})^{+\bullet}$ (***b***) *and the corresponding ENDOR spectra* (right). Solvent: CH_2Cl_2, counterion: $SbCl_6^-$, temp.: 243 K.

Table 2. *Experimental and Calculated Proton-Hyperfine-Coupling Constants* [mT] *as well as g Factors of the Radical Cations of* **1**, $(^2H_5)$-**1**, *and* **2**

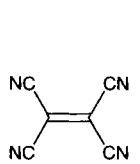
Assignment	H–C(4'')[a]	H–C(5'')[a]	H_p[b]	H_o[b]	H–C(4')[c]	H_m	H–C(5')[c]	g Factor
Exper.								
$\mathbf{1}^{+\bullet}$	0.178	0.121	0.099	0.079	0.053	0.041	0.028	2.0072
$((^2H_5)\text{-}\mathbf{1})^{+\bullet}$	0.180	0.124				0.053	0.029	2.0072
$\mathbf{2}^{+\bullet}$	0.180	0.111	0.091	0.073	0.035[d]	0.035[d]	0.035[d]	2.0072
Calc. (HMO)[e]								
$\mathbf{1}^{+\bullet}$ and $\mathbf{2}^{+\bullet}$	0.17	0.17	0.10	0.10	0.07	0.04	0.07	

[a])[c]) Assignment based on comparison with the data in [11]; however, these a_H may be interchanged. [b])These a_H may be interchanged.[d]) Broad ENDOR signal which presumably comprises three coupling constants of comparable size. [e]) Parameters for heteroatoms: $h_S = 1.0$, $k_{CS} = 0.7$, $h_N = 1.0$, $k_{CN} = 2.0$, $k_{C(3)C(4)} = 0.2$., $k_{C(2)C(3)} = k_{C(4)Ph} = 0.7$. Coupling constants calculated based on spin populations using the *McLachlan* procedure, $Q_H = -2.5$ mT, $Q_N = 1.9$ mT.

Discussion. – *Radical Anions.* The first reduction potentials of –1.12 and –0.55 V *vs.* Ag/AgCl of **1** and **2**, respectively, represent the enhanced electron accepting capability on replacing one H-atom by a CN group. Still, **1** and **2** are worse electron acceptors than tetracyanoethene (**3**; $E_{1/2}$ = –0.24 V *vs.* Ag/AgCl [7]).

The results of the cyclovoltammetric measurements only represent thermodynamic and kinetic stabilities; structural features and the amount of spin delocalisation in $\mathbf{1}^{-\cdot}$ and $\mathbf{2}^{-\cdot}$ are provided by the ESR/ENDOR/TRIPLE spectroscopies.

The ESR spectra of $\mathbf{1}^{-\cdot}$ and $((^2H_5)\text{-}\mathbf{1})^{-\cdot}$ indicate identical hyperfine data (*Table 1*). This means that no detectable spin population resides in the phenyl substituent. The assignment of the a_H of –0.776 mT[2]) to the single proton at C(2) is straightforward, and, thus, the a_H of –0.076, –0.027, and +0.014 mT must belong to the four non-equivalent H-atoms at the two 1,3-dithiols. The two negative a_H with the higher values are ascribed to the H-atoms at the 1,3-dithiole ring at C(3) which, according to the X-ray structure of **2**, is oriented coplanar to the dicyanoethene moiety. The remaining coupling constant of +0.014 mT (1 H) consequently must be allotted to one of the protons at the second 1,3-dithiole at C(4); the other proton carries no detectable spin population. As presented in *Table 1*, HMO calculations predict only very roughly the spin distribution in $\mathbf{1}^{-\cdot}$ and $\mathbf{2}^{-\cdot}$, presumably because the standard parameters for the S-atom do underestimate the ability of S-atoms for the delocalisation of the negative charge[3]). The g factors of $\mathbf{1}^{-\cdot}$, $((^2H_5)\text{-}\mathbf{1})^{-\cdot}$, and $\mathbf{2}^{-\cdot}$ are in the same range as those of related electron acceptors as tetracyanoethene [8], tetracyanoquinodimethane [9], or 2,2'-(furan-2,5-diyldimethylidene)bispropanedinitrile [10] (g = 2.0026, 2.0027, 2.0039, respectively).



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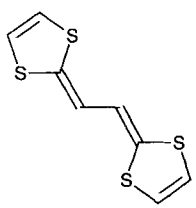

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Radical Cations. The oxidation potentials of **1** and **2** are considerably higher (*Fig. 1*) than those of the related donor 1,2-di(1,3-dithiol-2-ylidene)ethene (**4**; 0.24 V *vs.* Ag/AgCl [11]). Two factors should be responsible for these diminished donor properties of **1** and **2**: *i*) electron density is withdrawn from the π system of the 1,2-di(1,3-dithiol-2-ylidene)ethane fragment by the electron accepting (1,1-dicyano- or 1,1,2-tricyanoethene) moiety and/or *ii*) the geometry of $\mathbf{1}^{+\cdot}$ and $\mathbf{2}^{+\cdot}$ in solution resembles that of **2** in the solid state and thus impairs delocalisation inside the entire donor π system. An answer to this assumptions is given by the ESR data of $\mathbf{1}^{+\cdot}$, $((^2H_5)\text{-}\mathbf{1})^{+\cdot}$, and $\mathbf{2}^{+\cdot}$.

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[2]) The negative sign of this coupling constant can directly be derived from the observation of the broadened low-field line which is characteristic of negative coupling constants. On the other hand, the broadened high-field lines inside these two line groups point to a positive ^{14}N-coupling constant.

[3]) It is, in our eyes, not appropriate to change the HMO parameters as long as a perfect match between experimental and calculated coupling constants is reached. This certainly leads to an overinterpretation of the simple HMO model for the heteroatom-rich and non-planar molecules **1** and **2**.

The marked difference between the ESR spectra of radical anions $\mathbf{1}^{-\cdot}$ and $\mathbf{2}^{-\cdot}$ is missing for the radical cations $\mathbf{1}^{+\cdot}$ and $\mathbf{2}^{+\cdot}$. The a_H detected for $\mathbf{1}^{+\cdot}$ and $\mathbf{2}^{+\cdot}$ are very similar. This mirrors that the electron-accepting di- (tri-)cyanoethene moieties have no influence on the spin distribution in $\mathbf{1}^{+\cdot}$ and $\mathbf{2}^{+\cdot}$.

In contrast to the radical anions, the ESR/ENDOR spectra of $\mathbf{1}^{+\cdot}$ and $((^2H_5)\text{-}\mathbf{1})^{+\cdot}$ are different: the a_H of 0.099, 0.079, and 0.041 mT are missing for $((^2H_5)\text{-}\mathbf{1})^{+\cdot}$ and must, therefore, be ascribed to the *ortho* (2 H), *para* (1 H), and *meta* (2 H) protons of the Ph substituent. Consequently, the remaining a_H reflect the spin distribution inside the 1,2-di(1,3-dithiol-2-ylidene)ethane moiety. In respect to the a_H found for $\mathbf{4}^{+\cdot}$ [11], the a_H of 0.178 and 0.121 mT must be assigned to the two protons in the 1,3-dithiole at C(4) which carries the major part of the spin population leaving the a_H of 0.053 and 0.028 mT to the 1,3-dithiole at C(3). The a_H-ratios 0.178/0.121 and 0.053/0.028 of 1.5 and 1.8 are in very good agreement with the corresponding ratio in $\mathbf{4}^{+\cdot}$ (a_H = 0.123 and 0.082 mT; ratio = 1.5, see [11]). It is noteworthy that the sum of the four a_H of $\mathbf{1}^{+\cdot}$ ($((^2H_5)\text{-}\mathbf{1})^{+\cdot}$, $\mathbf{2}^{+\cdot}$) is very close to that of $\mathbf{4}^{+\cdot}$, *i.e.*, 0.38 *vs.* 0.41 mT, respectively, thus pointing out that spin population is indeed concentrated inside the 1,2-di(1,3-dithiol-2-ylidene)-1-phenylethane fragment of $\mathbf{1}^{+\cdot}$ ($((^2H_5)\text{-}\mathbf{1})^{+\cdot}$, $\mathbf{2}^{+\cdot}$). This spin population is, however, unevenly distributed between the two 1,3-dithioles. The 1,3-dithiole at C(4) of $\mathbf{1}^{+\cdot}$ ($((^2H_5)\text{-}\mathbf{1})^{+\cdot}$, $\mathbf{2}^{+\cdot}$) bears *ca.* four times the amount of spin as that at C(3).

An additional indicator for the spin distribution, particularly for radical ions possessing heavy (*e.g.* second row) heteroatoms carrying a high spin population, is the g factor. The g factor of radical cation $\mathbf{4}^{+\cdot}$ is 2.0081 [11]. For $\mathbf{1}^{+\cdot}$, $((^2H_5)\text{-}\mathbf{1})^{+\cdot}$, and $\mathbf{2}^{+\cdot}$ a g factor of 2.0072 was determined. This values are clearly distinct from the g factor of the free electron, 2.0023. The deviation is grounded on a high spin population at the S-atoms [12]. For related donors possessing four S-atoms, the relationship:

$$g = 2.00379 + 0.03564\rho_S$$

where ρ_S is the spin population at one S-atom, has been developed [11], and for $\mathbf{4}^{+\cdot}$ ρ_S = 0.121 was established. Based on the above formula using the observed g-factor shifts, the spin population inside the 1,2-di(1,3-dithiol-2-ylidene)ethane moiety of $\mathbf{1}^{+\cdot}$, $((^2H_5)\text{-}\mathbf{1})^{+\cdot}$, and $\mathbf{2}^{+\cdot}$ is *ca.* 80% of that of $\mathbf{4}^{+\cdot}$. The remaining 20% of the spin population must be predominately delocalized inside the Ph substituent because the substitution of the H-atom in the acceptor moiety by a CN group does not alter the a_H and the g factor. About the same spin distribution was found for Me-substituted and Ph-annelated derivatives of **4** [11].

Calculations and Structural Considerations. AM1 [13] calculations of **1** starting from a geometry corresponding to that found for **2** in the solid state indicate a shallow energy surface, *e.g.*, a considerable amount of twist around the C(3)–C(4) bond is possible without a considerable change of energy. Furthermore, the Ph group at C(4) can rotate almost freely within a range of *ca.* 20°. Without a well defined geometry of **1**, **2** and their radical ions it is impossible to gain insightful hyperfine parameters by a semiempirical SCF procedure. *Fig. 4* shows the highest occupied (HOMO) and the lowest unoccupied molecular orbital (LUMO) of **1** calculated by the HMO procedure. For the HMO model, the squares of the coefficients in the singly occupied molecular orbital are proportional, in first order, to the hyperfine-coupling constants [14]. The HMO-calculated HOMO and

LUMO offer only an incomplete picture of the π-electron distribution in **1**, **2** and their radical anions and cations (*Tables 1* and *2*). However, the comparison between the theoretical (HMO) and the experimental a_H allows some useful qualitative structural considerations.

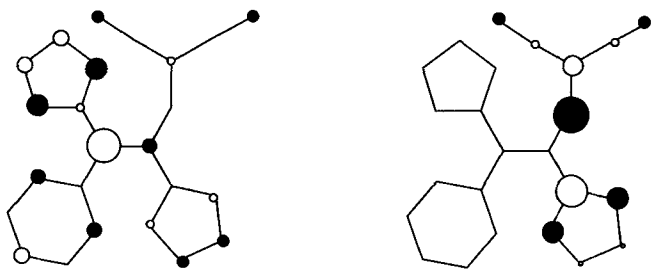

Fig. 4. *HOMO and LUMO of* **1** *calculated by the HMO method* (for parameters, see *Tables 1* and *2*)

In the LUMO of **1**, the singly occupied orbital of the radical anion, the coefficients at the 1,3-dithiole and the Ph substituent at C(4) remain almost zero irrespective of the parameters used to model the torsion around the C(3)–C(4) bond. Consequently, also the a_H predicted by the HMO model are zero; therefore, no clear evidence about a higher degree of planarity of $\mathbf{1}^{-\cdot}$ and $\mathbf{2}^{-\cdot}$ compared to the neutral molecules can be gained based on the calculations. Experimentally, however, spin delocalisation into the 1,3-dithiole ring at C(4) of $\mathbf{1}^{-\cdot}$ and $\mathbf{2}^{-\cdot}$ is established (*Table 1*); the only indication about the conformation around the C(3)–C(4) bond of $\mathbf{1}^{-\cdot}$ and $\mathbf{2}^{-\cdot}$ is the positive sign of the a_H of 0.014 mT which we assign to one proton at the 1,3-dithiole attached to C(4). Because of the very small MO coefficients in this 1,3-dithiole it is not probable that the positive sign is caused by a π-π spin-polarisation mechanism [15]. A conceivable rationalisation for the small a_H is a through-space spin transfer (homohyperconjugation) from a π-orbital of the close but not directly bound atom of one cyano group. This assumption implies a geometry closer to planarity than established for neutral **2**.

The considerably higher oxidation potentials of **1** and **2** compared to **4** bear out a hindered interaction between the two 1,3-dithioles. If this situation is accounted for by $k_{C(3)C(4)} = 0.2$ in the HMO model, the spin distribution represented by the ESR data and predicted by the model show a good agreement (*Table 2*). The two non-coplanar (almost perpendicular) 1,3-dithioles, however, still form a delocalised π system.

Conclusions. – The cyclovoltammetric and ESR/ENDOR investigations have shown that the donor-acceptor molecules **1**, $(^2H_5)$-**1**, and **2** resemble distinct characteristics specific of the two different redox stages.

In the radical anions the spin population is confined to the di- (tri-)cyanoethene moiety of the molecule and the coplanar 1,3-dithiole at C(3). Presumably, the geometries of $\mathbf{1}^{-\bullet}$, $((^2H_5)\text{-}\mathbf{1})^{-\bullet}$, and $\mathbf{2}^{-\bullet}$ are very similar to that of **2** in the solid state with a slightly more planar arrangement of the substituents at C(3) and C(4).

On the other hand, the radical cations $\mathbf{1}^{+\bullet}$, $((^2H_5)\text{-}\mathbf{1})^{+\bullet}$, and $\mathbf{2}^{+\bullet}$ indicate spin delocalisation across the C(3)–C(4) bond which divides these molecules into two (almost) orthogonal moieties. Despite the divergence from planarity, a considerable amount of spin (*ca.* 20%) can be found in the unfavorably arranged (in terms of π-conjugation) 1,3-dithiole at C(3).

The UV/VIS spectra of **1**, $(^2H_5)$-**1**, and **2** are identical [5] except the long-wave band which has to be considered as a HOMO-LUMO charge-transfer transition [16]. The bathochromic shift of this band from 462 to 525 nm on going from **1** ($(^2H_5)$-**1**) to **2** agrees very well with the HOMO-LUMO gaps reflected by the differences between the first oxidation and reduction potentials ($\Delta E_{1/2}$): the higher excitation energy for **1** is anticipated by $\Delta E_{1/2} = 1.88$ V, whereas the longer-wave absorption of **2** is in line with $\Delta E_{1/2} = 1.40$ V. These energy differences are particularly grounded on the less negative reduction potential of **2**.

Such charge-transfer transitions are important factors for nonlinear optical properties of molecules. Therefore, based on our results, the investigation of the electron- and charge-transfer behavior of **1** and **2** in the solid state should present further interesting insights.

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