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Tris(ethylenedithio)- and Tris(1,2-benzodithio)-substituted Trimethylenemethanes

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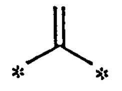
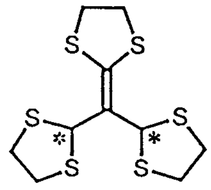
Trimethylenemethanes substituted with three ethylenedithio or 1,2-benzodithio groups were generated by electrochemical reduction of the corresponding dication salts, and investigated by ESR. For the latter diradical the triplet ESR spectrum was observed and the temperature dependence of the signal intensity established the ground triplet state. The ESR spectrum of the former diradical could not be detected because of its high reactivity so as to allow ring-closure to the methylenecyclopropane.

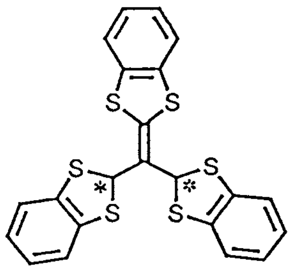
The continuous search for bulk ferromagnetism in the organic solid state is the current interest of many synthetic chemists and physicists. Recently, with guidance from a McConnell's model,$^{1)}$ in which the ferromagnetic interaction can be stabilized by admixing the lowest excited charge-transfer (CT) triplet state with the ground state in alternating donor-acceptor stacking, a ferromagnetic organometallic/molecular CT solid, decamethylferrocenium tetracyanoethylenide, was prepared.$^{2)}$ This success suggests that the McConnell model may also serve as a useful guiding principle for the production of purely organic s/p orbital-based ferromagnets.$^{3)}$ Tirmethylenemethane dication ($\underline{1}^{2+}$) is worthy to be considered as an acceptor model, since the two-electron reduced species of $\underline{1}^{2+}$, trimethylenemethane ($\underline{1}$), whose basic structure could participate in the excited state of the CT complex with a dianionic donor, has shown experimentally to be a



1^{2+}: * = +
1: * = ·



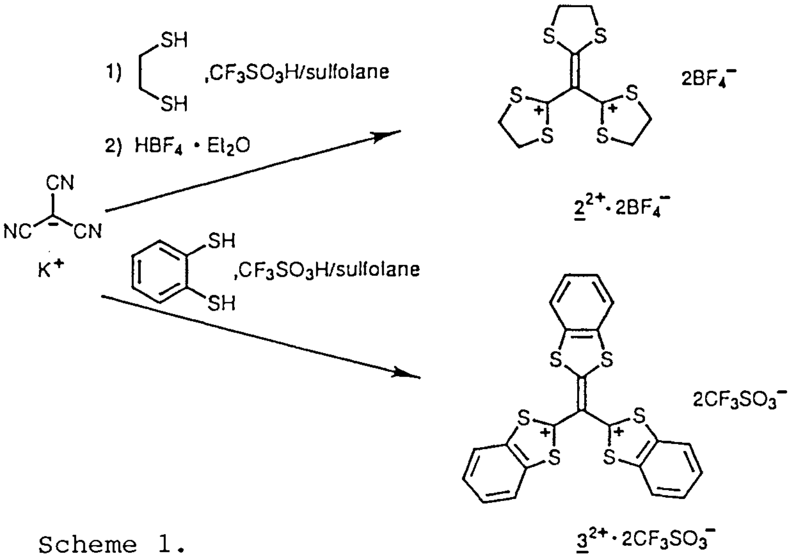
2^{2+}: * = +
2: * = ·



3^{2+}: * = +
3: * = ·

triplet in the ground state.[4)] MO calculations not only support the experimental conclusion, but also predict a large energy gap of ca. 20 kcal/mol between the ground state triplet and its higher-energy singlet.[5)] Of course, $\underline{1}^{2+}$ needs to be stabilized by appropriate substitution for the present purpose. We wish to report one-step synthesis of $\underline{1}^{2+}$ dications symmetrically substituted with three ethylenedithio or 1,2-benzodithio[6)] groups ($\underline{2}^{2+}$ and $\underline{3}^{2+}$) and chracteristics of their corresponding trimethylenemethanes ($\underline{2}$ and $\underline{3}$).

The bis(tetrafluoroborate) and bis(trifluoromethanesulfonate) salts of $\underline{2}^{2+}$ and $\underline{3}^{2+}$, respectively, ($\underline{2}^{2+}\cdot 2BF_4^-$ and $\underline{3}^{2+}\cdot 2CF_3SO_3^-$) were synthesized in one step as shown in Scheme 1. Thus, when a sulfolane solution of potassium tricyanomethanide and ethanedithio or 1,2-benzenedithiol (5 equiv.) was reacted with an excess of trifluoromethanesulfonic acid at r.t., and then the mixture was heated at 80 °C for 23 h, $\underline{2}^{2+}\cdot 2BF_4^-$ (after counter anion exchange with $HBF_4\cdot Et_2O$, orange needles from CH_3CN-$CHCl_3$, mp 237-238 °C (dec))[7)] and $\underline{3}^{2+}\cdot 2CF_3SO_3^-$ (red needles from CH_3NO_2-EtOAc, mp> 300 °C)[7)] were isolated in respectively yields of 27 and 35%. The ^{13}C NMR spectra of $\underline{2}^{2+}\cdot 2BF_4^-$ in CD_3CN and $\underline{3}^{2+}\cdot 2CF_3SO_3^-$ in CF_3CO_2D showed only 3 and 5 signals, respectively, suggesting that the molecular symmetry of $\underline{2}^{2+}$ and $\underline{3}^{2+}$ is C_3 or higher in solution.[8)] The chemical shifts of the central and exomethylene carbons of the trimethylenemethane moiety were δ 117.8 and 210.0 for $\underline{2}^{2+}\cdot 2BF_4^-$ and 105.1 and 184.3 for $\underline{3}^{2+}\cdot 2CF_3SO_3^-$, respectively. We infer that the positive charge is more localized on the trimethylenemethane moiety in $\underline{2}^{2+}$ than in $\underline{3}^{2+}$, where some charge delocalization on the aromatic 1,3-dithiolium moieties may take place.



Scheme 1.

The redox potentials of the two dication salts were measured in DMF at 0 °C by using cyclic voltammetry: ±0.00 and -0.55 V vs. Ag/AgCl for $\underline{2}^{2+}\cdot$

$2BF_4^-$, and -0.01 and -0.24 V for $\underline{3}^{2+}\cdot 2CF_3SO_3^-$, respectively. In view of their redox potentials, $\underline{2}^{2+}$ and $\underline{3}^{2+}$ can be two-electron reduced at comparatively low voltage to generate $\underline{2}$ and $\underline{3}$. Indeed, it was successful in the case of $\underline{3}$. The degassed CH_3CN solution containing $\underline{3}^{2+}\cdot 2CF_3SO_3^-$ and $(\underline{n}\text{-Bu})_4N^+\cdot ClO_4^-$, a supporting electrolyte at -40 °C was electrochemically reduced by gradually raising the potential. The signal began to appear from -1.6 V[9] and the intensity became maximum at -2.2 V.[9] The solution was immediately frozen and the ESR spectrum was measured. Figure 1 shows the ESR spectrum at -50 °C. The absorptions on each side of the central line (g=2.0050) are characteristic of randomly oriented triplet species, whose zero-field splitting parameters $|D'|$ and $|E'|$, are 0.00193 and ≈ 0 cm^{-1}, respectively. The axial symmetry of the D tensor ($|E'|=0$, also observed in $\underline{1}$: $|D'|=0.025$ cm^{-1} and $|E'|=0$) indicates that the two interacting unpaired electrons of $\underline{3}$ delocalize with at least C_3 symmetry. The smaller $|D'|$ value observed for $\underline{3}$ compared with that of $\underline{1}$ suggests delocalization of the two unpaired electrons not only over the trimethylenemethane moiety but also over the sulfurs.[10] In addition, a half-field resonance signal appeared at 1688 G.[11] The temperature change of the signal intensity obeyed a Curie law in the range of -50 to -196 °C, establishing that the triplet is in the ground state.[12] In the similar manner $\underline{2}^{2+}\cdot 2BF_4^-$ was electrochemically reduced in degassed C_2H_5CN at -90 °C and immediately frozen to -120 °C, but the triplet ESR spectrum of $\underline{2}$ could not be observed at all, because of so high reactivity of $\underline{2}$ as to allow rapid ring-closure to the methylenecyclopropane.

For preliminaries the CT complex formation was examined between the

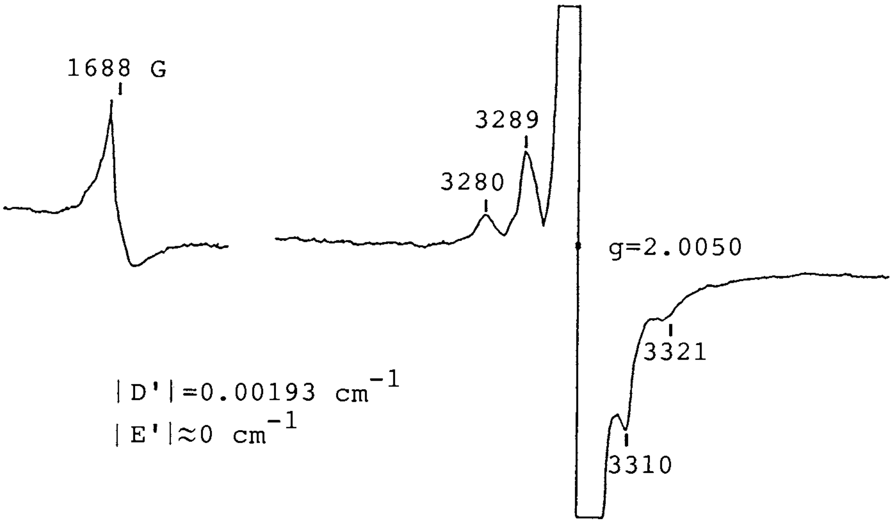


Fig. 1. The ESR spectrum of $\underline{3}$ frozen to -50 °C immediately after electrochemical reduction of $\underline{3}^{2+}\cdot 2CF_3SO_3^-$ at -40 °C in degassed CH_3CN (the microwave frequency used in the measurement: 9.26 GHz).

two dication and some anion salts. By the reaction with $2(\underline{n}\text{-Bu})_4N^+\cdot$(hexacyanotrimethylenecyclopropane)$^{2-}$ 12) and $K^+\cdot DDQ^{-\cdot}$ the 1:1 and 1:2 CT complexes were obtained, respectively. Their magnetic properties are now under investigation.

References

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6) The same dication salt already was synthesized in a different method from ours by Gompper et al.: F. Adams, R. Gompper, A. Hohenester, and H.-U. Wagner, Tetrahedron Lett., 1988, 6921; R. Gompper and H.-U. Wagner, Angew. Chem., 100, 1492 (1988); Angew. Chem., Int. Ed. Engl., 27, 1437 (1988); F. Closs, W. Breimaier, W. Frank, R. Gompper, and A. Hohenester, Synth. Metals, 29, E537 (1989).
7) The satisfactory elemental analyses were obtained for the new dication salts.
8) The ^{1}H NMR spectral data are as follows: δ 4.34 (s) for $\underline{2}^{2+}\cdot 2BF_4^-$, and δ 8.52 (m, 6H), 8.00 (m, 6H) for $\underline{3}^{2+}\cdot 2CF_3SO_3^-$.
9) The potential value is not corrected by using reference electrode.
10) Simple Hückel MO calculations show a large unpaired electron density distribution on the trimethylenemethane terminal carbons as well as on the sulfurs.
11) The signal is unusually broad. Presumably, this is due to anisotropy in the g value, which is induced by much residing of unpaired electrons on the sulfurs.
12) It is also possible that the ground state is singlet with its thermally-accessible triplet in higher energy by only 100 cal/mol.
13) T. Fukunaga, J. Am. Chem. Soc., 98, 610 (1976); T. Fukunaga, M. D. Gordon, and P. J. Krusic, ibid., 98, 611 (1976).

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