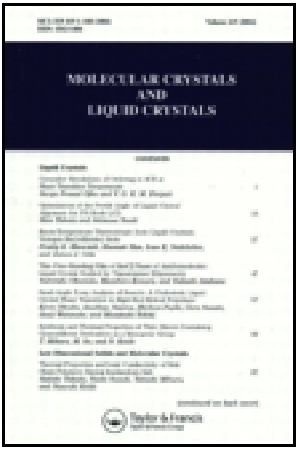

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ESR, UV-Visible and Infrared Spectroscopies of Hexakis(Alkylthio)Benzene Cations with C_3 Symmetry

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ESR, UV-VISIBLE AND INFRARED SPECTROSCOPIES OF HEXAKIS(ALKYLTHIO)BENZENE CATIONS WITH C_3 SYMMETRY

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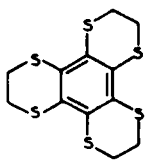
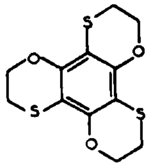
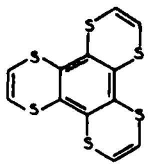
Abstract The cations of the new series of hexakis(alkylthio)benzenes with C_3 symmetry have been studied in solution as well as in solid state. Dications are more stable in acidic medium and the second redox potential appears to be higher than for hexamethoxytriphenylene (HMT). Electronic spectra of monocations show molecular excitation bands without evidence for dimer species. ESR spectra present sometimes an hyperfine structure indicating a mean C_3 symmetry. Dications are chemically less stable and we have not been able to detect a triplet state. We suspect that a Jahn-Teller distorsion could cause the dication to have a singlet ground state. In solid state crystals of triethylenedithiobenzene-tetrafluoroborate $(tEDT\text{-}B)_2BF_4$ have a charge transfer band corresponding to a mixed valence state. The complexation with tetrafluorotetracyanoquinodimethane gives crystals of $(tEDT\text{-}B)_2TCNQF_4$ which present stacking columns of alternating donor dyads and acceptor monads (DAD units) with an intense charge transfer band at 10 000 cm^{-1}.

INTRODUCTION

Three mechanisms have been proposed for achieving ferromagnetic coupling in molecular solid.[1] One of the most attractive suggested by McConnell involves the admixing of a virtual triplet state with the ground state for a chain of alternating radical cation donors and radical anion acceptors. Previously, we have synthetized hexakis(alkylthio)benzenes whose dications, owing to their presumed C_3 symmetry, could be in a ground or thermally accessible triplet state.[2] We have published some results on the magnetic properties of their radical cation salts and charge transfer complexes.[3,4]


tEDT-B (I)


tEOT-B (II)


tVDT-B (III)

In order to verify if the above molecules are possible precursors for ferromagnet compounds, we have (i) to ascertain if the radical cations and dications in solution retain the same symmetry, (ii) to check if a triplet state can be reached and (iii) to achieve molecular association with a magnetic interaction in solid state.

MONO AND DICATIONS IN SOLUTION : EXPERIMENTS AND RESULTS

Redox potentials

Cyclic voltammetry of I - III in acetonitrile or dichloromethane shows only one reversible wave corresponding to the radical monocation formation.[2,4] In trifluoroacetic acid two reversible waves appear (Fig. 1). In this solvent the dication is more stable and we have the redox sequence :

$$p0 \underset{+e}{\overset{-e}{\rightleftharpoons}} p^{.+} \underset{+e}{\overset{-e}{\rightleftharpoons}} p^{++}$$

The redox data are listed in Table I. They are comparable to the results reported by Bechgaard and Parker for (HMT).[5] The second oxidation potential appears slightly higher than the observed potential for HMT and suggests a very weak chemical stability. The difference between the first and the second oxidation potential is minimal with III (0.5 V) but much higher than for HMT. In solution it appears that the dismutation of monoradical cations in dications and neutral species is less favorable for the studied compounds than for HMT.

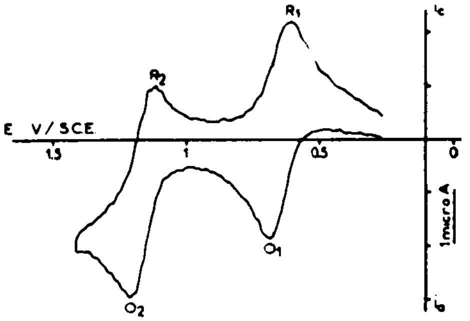


Figure 1 Cyclic voltammetry of tVDT-B in CF_3COOH

TABLE I Redox potentials in V *vs* SCE. Electolyte support : Bu_4NBF_4 (0.2 M) in CF_3COOH.

compound	$E_{1/2}^1$	$E_{1/2}^2$
tEDT-B	0.59	1.16
tVDT-B	0.64	1.16
tEOT-B	0.54	1.19

Electronic spectra

Radical monocation solutions have been obtained in concentrated H_2SO_4, trifluoroacetic acid or in a mixture of CH_2Cl_2-CF_3COOH (9:1). For the last two cases additions of bromine or nitrosium tetrafluoroborate ($NOBF_4$) are necessary to oxidize the compounds.

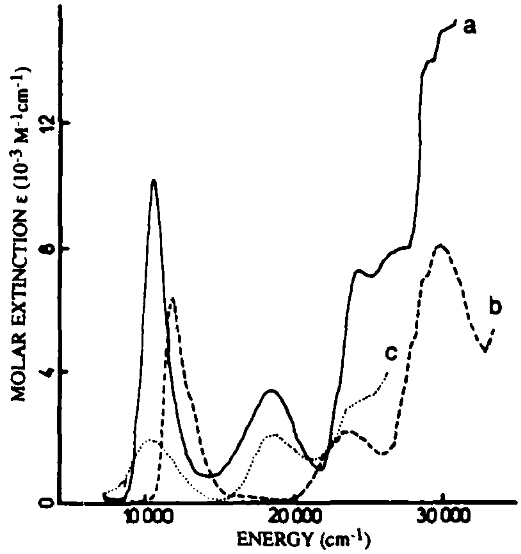


Figure 2 Electronic spectra of : a- tEDT-B; b- tEOT-B; c- TVDT-B

The radical cations are stable and exhibit absorption bands in the UV-visible region (Fig. 2). For concentration between 10^{-4} to 10^{-5} M the wavelength and the relative intensity of the bands do not change, indicating that radical dimerisation is not extensive under these conditions. The UV-visible absorption is also unaffected by the presence of the neutral donors so that charge transfer association is not important. All the bands can then be attributed to intramolecular excitations of the radical cation salts.

ESR experiments

i/ Radical cations of tEDT-B and tVDT-B

The 10^{-4} M solutions were prepared as described for the electronic spectra. The oxygen was removed by freezing, pumping and thawing. We have detected an hyperfine structure for tEDT-B$^{\cdot+}$ and tVDT-B$^{\cdot+}$, and only a broad ESR line for tEOT-B$^{\cdot+}$.

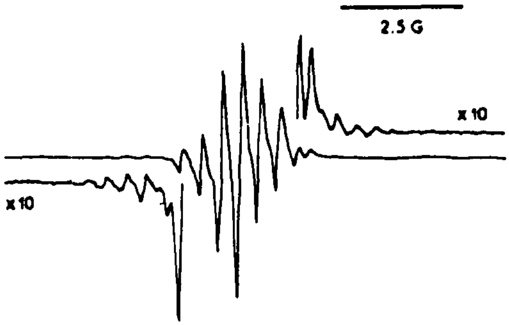


Figure 3 ESR Hyperfine spectrum at -40°C of tVDT-B

A rather strong signal was observed for tVDT-B$^{\cdot+}$ (Fig. 3), which can be separated in two parts. A central part composed of seven lines whose intensities are in agreement with the theoretical prediction for an hyperfine coupling due to six equivalent protons. Satellite lines in the wings which can be tentatively associated with the hyperfine coupling ^{13}C and ^{33}S as for the radical cations derived from the TTF moiety.[6]

We observed for tEDT-B$^{\cdot+}$ (Fig. 4a), a weak signal (g = 2.0099) which is the superposition of a broad ESR line and a complex hyperfine structure. Similar broad background has be noticed in radical cations of naphthalenic derivatives[7] and attributed to aggregates. This broad line can be substracted and the resulting hyperfine spectrum which is revealed has no intense center line (Fig. 4b). The hyperfine structure could result from coupling with axial and equatorial protons of two conformers as already observed by Morihashi *et al.*[8] on tetra(alkylthio)-benzenes. More experiments are necessary to interpret the complex hyperfine spectrum.

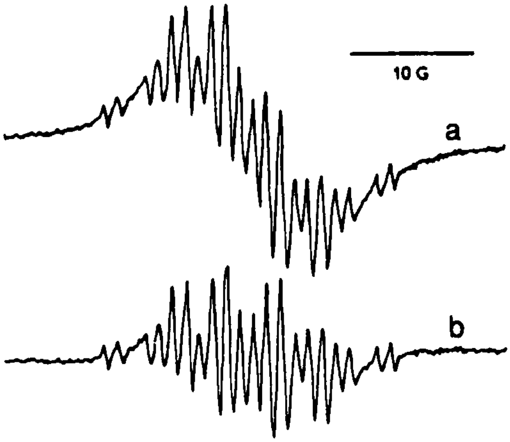


Figure 4 ESR Hyperfine spectra at -40°C of tEDT-B

In order to attribute the observed hyperfine coupling constant for tVDT-B$^{\cdot +}$, we made a standard Huckel calculation assuming that the molecules have a C_3 symmetry which leads to a degenerate highest occupied molecular orbital. Then we calculated the π spin density distribution on each atom without electron correlation (no McLachlan type correction[9]). Assuming a proportionnality constant between the spin density and the hyperfine constant as proposed initially by McConnell[10] and using the values recently applied by Cavara *et al.*[6] [proton (Q_H = 29 G); ^{13}C (Q_C = 38.6 G); and ^{33}S (Q_S = 32 G)], we have evaluated the coupling constants. The results are presented on Table II.

TABLE II Hyperfine splitting constant (G) of tVDT-B (g = 2.0084)

	calculated*	observed
a_H =	0.77	0.75
a_S =	1	0.80
a_C =	$\left\{ \begin{matrix} 0.11 \\ 0.41 \end{matrix} \right.$	

* with $\Sigma\rho_\pi$ = 0.5 for degenerated orbital

ii/ Dications of tEDT-B and tVDT-B

Recently, it has been shown that a large π donor system with sulfur heterocycles presents a thermally accessible triplet state.[11] Chemical oxidations of a trifluoroacetic solution of I - III (10^{-3} M), were achieved with an excess of $NOBF_4$. To obtain only the monocation, the solution is rapidly frozen and the EPR signal recorded. On raising the temperature to 10°C, the signal intensity decreases without evidence for a triplet state.

When the temperature was quickly lowered down to 100 K, we did not observe a triplet state signature. We have therefore to conclude that in solution, either the dications are in a singlet ground state with an excited triplet state which is not thermally accessible, or they are decomposed. Since the dication is in a triplet state only due to its symmetry, any molecular distorsion like a Jahn-Teller effect as found on $HAOC^{2+}$ could cause the dication to have a singlet ground state.[12] The molecular deformation which is, may be, already present in the radical cations but masked by a dynamical interconversion, would be predominant for these dications.

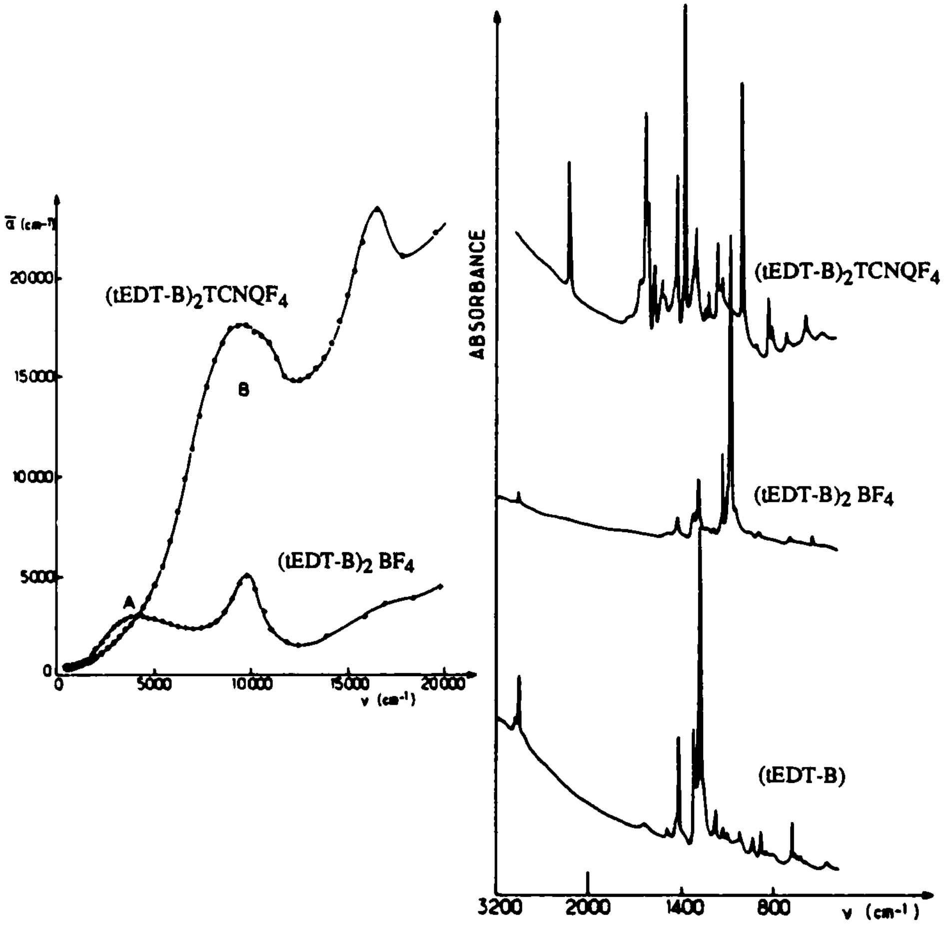


Figure 5 Dispersed powders of $(tEDT\text{-}B)_2BF_4$ and $(tEDT\text{-}B)_2TCNQF_4$ in KBr pellets : a- electronic spectra; b- vibrational spectra

SOLID STATE PROPERTIES

We focused our attention on two compounds : $(tEDT\text{-}B)_2BF_4$ and $(tEDT\text{-}B)_2TCNQF_4$. The crystal structure of the radical cation salt has been published[3] and we found that the unit cell is orthorhombic (space group $Pca2_1$) with the presence of tEDT-B stacks. Along the stacks, there are two independent tEDT-B molecules which do not form a centrosymmetric dimer, besides each molecule has lost the C_3 symmetry. The charge transfer complex $(tEDT\text{-}B)_2TCNQF_4$ crystallizes in the triclinic system with stacking columns of alternating donor dyads and acceptor monads (DAD units).[13]

Electronic spectra

In Figure 5a, we show the UV-visible bands of $(tEDT\text{-}B)_2BF_4$ and $(tEDT\text{-}B)_2TCNQF_4$ as dispersed powders in KBr pellets. We observed for the BF_4^- salt a new charge transfer band in the infrared range (namely A following the Torrance's classification[14] which is characteristic of a mixed valence system. For $(tEDT\text{-}B)_2TCNQF_4$ we can see an intense B band at 10 000 cm^{-1} which is a back charge transfer band between acceptor and donor if they are in a ionic fondamental state, or a real charge transfer band if we are in presence of a neutral ground state.[14]

Vibrational spectra

They are observed from the same pellets and presented in Figure 5b. For $(tEDT\text{-}B)_2BF_4$, we do not detect any vibronic line resulting from electron-molecular vibration coupling as for usual organic conductors. From the known crystal structure, it appears that we are not in presence of centrosymmetrical dimers as required by Rice's model.[15] This is a new situation which needs more detailed investigations.

CONCLUSION

Our results indicate that mono and dications forms of the studied compounds are certainly perturbated by a Jahn-Teller distorsion like $HAOC^{2+}$ which preclude the formation of a stable triplet state,[16] a necessary but not sufficient condition to obtain organic ferromagnet compounds. Another approach put forward by Chiang *et al.*[17] on a similar charge transfer complex, has been to start from a C_3 symmetry compound, to prepare a weak charge transfer complex and then initiate a triplet state by diffusion of a donor (acceptor) in solid state. Under these circumstances, the lattice rigidity decreases the Jahn-Teller distorsion and stabilize the induced triplet state. We are currently investigating $(tEDT\text{-}B)_2TCNQF_4$ along these lines.

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