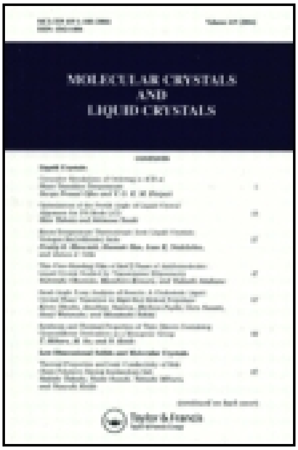

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

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To cite this article: Toyonari Sugimoto , Yohji Misaki , Zen-Ichi Yoshida & Jun Yamauchi (1989): Design of Purely Molecular/Organic Ferromagnets by Use of Odd-Numbered [N]Radialenes, Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 176:1, 259-270

To link to this article: http://dx.doi.org/10.1080/00268948908037485

Mol. Cryst. Liq. Cryst., Vol. 176, pp. 259–270
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Printed in the United States of America

DESIGN OF PURELY MOLECULAR/ORGANIC FERROMAGNETS BY USE OF ODD-NUMBERED [n]RADIALENES

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Abstract Two electron-donating odd-numbered radialenes, tris(thioxanthen-9-ylidene)cyclopropane and pentakis(1,3-benzodithiol-2-ylidene)cyclopentane, were synthesized as a donor component for the preparation of purely molecular/organic ferromagnets, since their dications can be a ground state triplet, assuming that the molecular symmetries are C_3 and C_5, or their highers, respectively. The magnetic properties of the dication and charge-transfer complex salts obtained from the new donors are discussed on the basis of results of ESR spectra and magnetic susceptibility.

INTRODUCTION

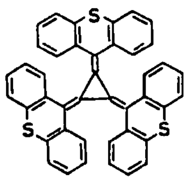
In contrast to the considerable developments that have occurred in organic materials with electrical conductivity, and especially superconductivity, ferromagnetism, another very important and useful physical property, has not yet surely been achieved in organic materials. Ferromagnetism is a special state of complete spin alignment throughout the bulk. Several theoretical models have already been proposed for achieving a linear-chain ferromagnetic coupling in an organic solid. The most attractive of these are two models proposed by McConnell, based respectively on Heitler-London spin exchange between positive spin density on a radical and negative spin density on another,[1] and on configurational mixing of a virtual triplet excited state with the ground state for a chain of alternating radical cation donors and radical anion acceptors,[2] and a ferromagnetic superexchange model proposed by Soos.[3] Very recently, Miller et al. have developed an extended McConnell model leading to the spin alignment throughout the bulk that is necessary for bulk ferromagnetism.[4]

Guided by the theoretical background, current experimental programs are very actively concentrated in two directions, starting from polymeric systems and molecular solids, respectively. For the latter types of organic ferromagnets with which are concerned, particularly those based on the CT solids, the second McConnell model can serve as a reliable initial guide. To give ferromagnetic behavior the donor or acceptor component needs to occupy at least one pair of degenerate highest occupied (HO) or lowest unoccupied (LU) molecular orbitals (MO's). This situation appears very often in d and f orbitals of transition metals, but very rarely in organic molecules, except for the case where there is an odd-fold axis of symmetry. Breslow[5] and Miller[4] are continuing their efforts to prepare organic ferromagnets based on a mixed stack of CT complexes of a donor and acceptor as above. On the other hand, Torrance[6] and Wudl et al.[7] are investigating the possibility of organic ferromagnets in a stack of either all donors or all acceptors, as commonly found in electrical conducting radical ion salts.

Until now all the attempts have been directed toward the CT complex and radical cation salts of organic donors such as hexaazatritetralin,[8] hexakis(alkylthio)-,[9] tris(ethyleneoxythio)-,[9] tris(ethyleneaminothio)-[10] and tris(ethyleneoxyamino)benzenes,[10] and hexaazaoctadecahydrocoronene.[10] Unfortunately, for all CT complex and radical cation salts was not observed ferromagnetism. The cause is due to the molecular symmetry lowering of the donors by Jahn-Teller distortion in the solid environment. In order to achieve unprecedented molecular organic ferromagnets we are rather concerned to odd-numbered [n]radialenes, which have a pair of degenerate HOMO's of comparatively high energy, assuming that the molecular symmetry is C_n or higher. With this assumption two electron-donating [3]- and [5]-radialenes were synthesized, and the magnetic properties of their dication and/or charge-transfer (CT) complex salts were investigated.

SYNTHESIS OF TRIS(THIOXANTHEN-9-YLIDENE)CYCLOPROPANE AND PENTAKIS(1,3-BENZODITHIOL-2-YLIDENE)CYCLOPENTANE

So far, there is not any report on odd-numbered radialenes having electron-donating substituents, although some electron-withdrawing [3]radialenes have been already synthesized.[11] Now, we attempted the synthesis of electron-donating [3]- and [5]-radialenes by use of different methods. In consequence, tris(thioxanthen-9-ylidene)-cyclopropane (1)[12] and pentakis(1,3-benzodithiol-2-ylidene)cyclopentane (2)[13] were successfully obtained by



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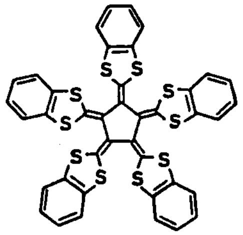

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the reaction of hexachlorocyclopropane with lithium thioxanthenide and by the reaction of tetrakis(1,3-benzodithiol-2-ylidene)cyclopentanylium tetrafluoroborate obtained from the LAH reduction and subsequent $HBF_4 \cdot Et_2O$ treatment of tetrakis(1,3-benzodithiol-2-ylidene)cyclopentanone[14] with (1,3-benzodithiol-2-ylidene)triphenylphosphorane, respectively. For both radialenes we do not still get their single crystals being suitable for X-ray structure analysis. However, their structures can be supposed from known X-ray structures of [3]- and [5]-radialenes.[15] Thus, it is most likely that 1 has a planar three-membered ring attached by three thioxanthen-9-ylidene groups in a twist state each other, while the five-membered ring of 2 is in a half-chair conformation or its near resemblance. Assuming that the propeller structure twisted in the same direction (that is, C_3 symmetry) is also adopted in the dication state of 1 (1^{2+}), it is expected that 1^{2+} is a ground state triplet. On the other hand, 2 must be at least subjected to a gross change from the half-chair to planar conformations of five-membered ring in the dication state of 2 (2^{2+}), whose ground spin state is triplet. As discussed later, the conformation tends to increasingly become planar with progress of oxidation, thus providing a possibility of a ground state triplet of 2^{2+}.

REDOX PROPERTY

The redox property of 1 and 2 was investigated by cyclic voltammetry. The cyclic voltammogram of 1 measured in CH_2Cl_2 at room temperature, showed two pairs of reversible waves at +0.67 and +0.80 V vs. Ag/AgCl, each of which involves one-electron transfer.[12] In PhCN solvent the two pairs of waves overlapped each other and apparently one pair of waves appeared at +0.70 V vs. Ag/AgCl. The first and second potentials are comparatively high in consequence of not so strong electron-donating ability of thioxanthenyl groups. On the other hand, for the cyclic voltammogram of 2 measured in PhCN at room temperature, very interestingly only one pair of reversible waves was observed at +0.36 V vs. Ag/AgCl.[13] This was quite surprising, if it is taken into consideration that such a multi-electron redox system as 2 usually exhibits several pairs of redox waves due to sequential redox processes at separate potentials. The peak current change by sample concentration indicated involvement of four-electron transfer in the pair of waves. From the more detailed analysis by digital simulation method the four-electron transfer was proved to be really due to two-step two-electron transfer in very small potential difference of -14 - +2 mV. To our knowledge, this provides the first case of apparently one-step four-electron transfer in organic redox systems. This unusual redox behavior can be understood as follows. Thus, intramolecular on-site Coulomb repulsion really increases as the oxidation progresses. Simultaneously, the gradual change of five-membered ring into the planar structure is accompanied with. In particular, for the trication radical and dication states the five-membered ring becomes nearly planar, and energetically favorable cyclopentadienide structure can participate. This special stabilization effect makes up for energy increase due to the on-site Coulomb repulsion.

TRIS(THIOXANTHEN-9-YLIDENE)CYCLOPROPANE RADICAL CATION ($1^{+\cdot}$) AND DICATION ($1^{2+\cdot}$) SALTS

No CT complex salt was formed even between $\underline{1}$ and a strong electron acceptor. Now, the preparation of $\underline{1}^{+\cdot}$ and $\underline{1}^{2+}$ salts was attempted. The tribromide salt of $\underline{1}^{+\cdot}$ ($\underline{1}^{+\cdot}\cdot Br_3^-$) was isolated by the reaction of $\underline{1}$ with Br_2 in CCl_4. Unfortunately, this salt is fairly unstable, and decomposes gradually in air. This circumvents characterization on the magnetic property of $\underline{1}^{+\cdot}\cdot Br_3^-$. In contrast with this, the bis(trifluoroacetate) salt of $\underline{1}^{2+}$ ($\underline{1}^{2+}\cdot 2CF_3CO_2^-$) obtained from the reaction of $\underline{1}$ with $Tl(CF_3CO_2)_3$ in CH_2Cl_2, was comparatively stable even in air. By use of ESR spectroscopy the magnetic property of $\underline{1}^{2+}\cdot 2CF_3CO_2^-$ was investigated.[12] The ESR spectrum at 298 K showed one sharp signal with a linewidth of 0.55 mT at g=2.00509. At cooling to 77 K a fine structure appeared together with a

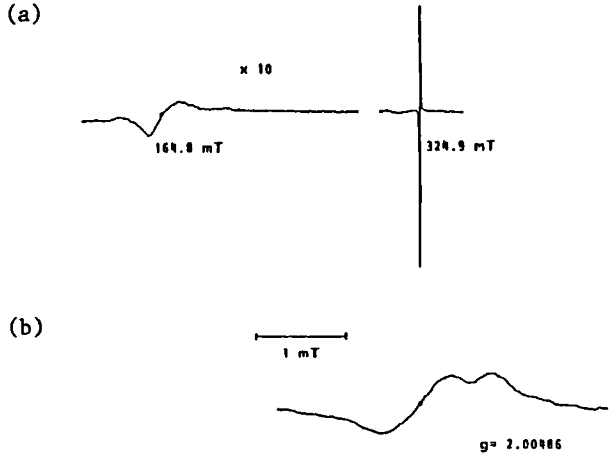
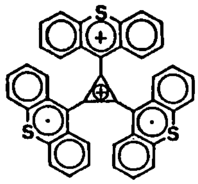


Figure 1. The ESR spectrum of $\underline{1}^{2+}\cdot 2CF_3CO_2^-$ at 77 K: (a) the whole spectrum (the half-field ($\Delta m_s = \pm 2$) ESR signal was measured with the 10-fold amplitude); (b) the width-expansion of the central signal at 324.9 mT.

half-field resonance signal at 164.8 mT (Figure 1). From analysis of the spectrum only one of the zero-field splitting parameters, D was determined to be ca. 0.7 mT. The very small value strongly suggests that the radical pair distantly resides at the thioxanthenyl groups. Furthermore, the intensity of the central signal gradually decreased with lowering temperature. From the quantitative analysis on the temperature change of the signal intensity in the range of 298-77 K, it is concluded that triplet state lies 0.07 eV higher in energy. As discussed in pentaarylcyclopentadienyl cations, whose ground state is a singlet with a triplet lying 0.002-0.04 eV higher,[16] it is likely also for $\underline{1}^{2+}$ that the singlet is favored because the



large π electron system decreases electron correlation and the complex structure allows easy Jahn-Teller distortion.

CT COMPLEX SALTS OF PENTAKIS(1,3-BENZODITHIOL-2-YLIDENE)-CYCLOPENTANE WITH 2,3-DICHLORO-5,6,-DICYANO-p-BENZOQUINONE, TRIS(DICYANOMETHYLIDENE)CYCLOPROPANE, AND TETRAFLUOROTETRA-CYANOQUINODIMETHANE

In contrast with 1, 2 formed CT complex salts with comparatively strong electron-acceptors, i.e., 2,3-dichloro-5,6,-dicyano-p-benzoquinone (DDQ), tris(dicyanomethylidene)-cyclopropane (3), and tetrafluorotetracyanoquinodimethane (TCNQF$_4$) etc.. The composition of 2 and acceptor components in the CT complex salts was not 1:1: 2:DDQ=1:2, 2:3=1:2, and 2:TCNQF$_4$=1:4 for the respective acceptors of DDQ, 3, and TCNQF$_4$. The IR spectra in KBr pellet showed the CN stretching bands at 2221 cm^{-1} for $2\cdot(\mathrm{DDQ})_2$, 2215 and 2166 cm^{-1} for $2\cdot(3)_2$, and 2201 cm^{-1} for $2\cdot(\mathrm{TCNQF}_4)_4$, respectively, which are almost the same to those of the anion radical of DDQ ($\mathrm{DDQ}^{-\bullet}$), the dianion of 3 (3^{2-}), and the anion radical of TCNQF$_4$ ($\mathrm{TCNQF}_4{}^{-\bullet}$). In considering the IR results together with the redox potentials of 2 (+0.36 V vs. Ag/AgCl) and the acceptors (DDQ: +0.46 and -0.42 V; 3: +1.14 and +0.29 V; TCNQF$_4$: +0.54 and -0.09 V), the CT complex salts $2\cdot(\mathrm{DDQ})_2$, $2\cdot(3)_2$, and $2\cdot(\mathrm{TCNQF}_4)_4$, are actually in the close form to $2^{2+}\cdot(\mathrm{DDQ}^{-\bullet})_2$, $2^{4+}\cdot(3^{2-})_2$, and $2^{4+}\cdot(\mathrm{TCNQF}_4{}^{-\bullet})_4$, respectively. This result is important on understanding the magnetic properties of the salts. The magnetic susceptibility of each salt was measured and subjected to temperature change in the range of 298-4.5 K. Figures 2-4 show the plots of the observed (χ_{obs}) or the reverse paramagnetic susceptibility ($\chi_{para} = \chi_{obs} - \chi_{dia}$, where χ_{dia} is the diamagnetic susceptibility) vs. temperature for $2\cdot(3)_2$, $2\cdot(\mathrm{DDQ})_2$, and $2\cdot(\mathrm{TCNQF}_4)_4$, respectively. For $2\cdot(3)_2$ there was almost no change of χ_{obs}, but at very low temperature region a slight increase was observed.

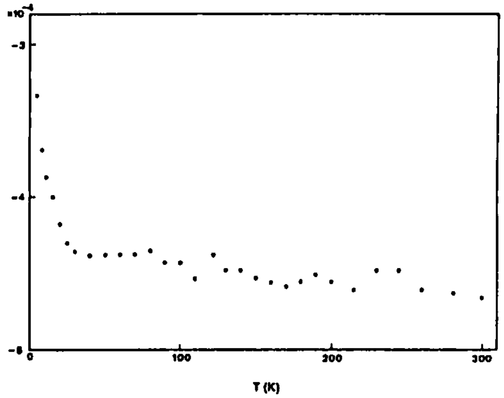


Figure 2. The temperature change of the χ_{obs} for $\underline{2}\cdot(\underline{3})_2$.

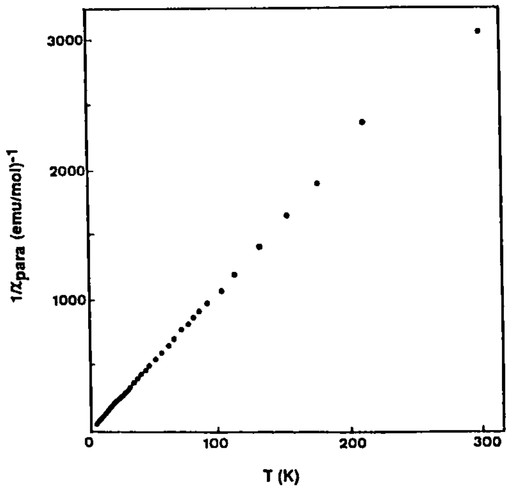


Figure 3. The temperature change of the reverse χ_{para} for $\underline{2}\cdot(DDQ)_2$.

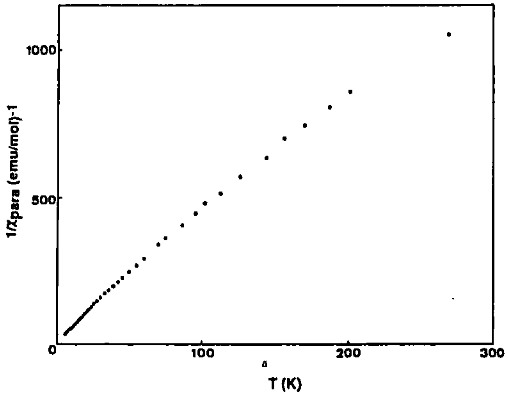


Figure 4. The temperature change of the reverse χ_{para} for $\underline{2}\cdot(TCNQF_4)_4$.

This salt is undoubtedly diamagnetic even if an impurity of triplet (and also doublet) species is contaminanted. In correspondence with this, the ESR spectrum at 298 K showed one very-weak signal with a fine structure (D'=0.00096 cm^{-1}, E'=0.00011 cm^{-1}) characteristic of a triplet, which is likely enough due to a contaminanted 2^{2+} (Figure 5). On the other hand, for the other two salts a temperature dependence on the χ_{para} obeyed a Curie Weiss law in the whole measured temperature range. The Weiss constant (Θ) was ca. -2 K. While for $2 \cdot (TCNQF_4)_4$ the dependence of the reverse χ_{para} on temperature exhibited a slightly complicated behavior, and Θ was obtained to be also -2 K from a Curie-Weiss plotting in the low temperature region of 170-5 K. Accordingly, for these salts it is concluded that the radical species of 2 and DDQ, and of 2 and $TCNQF_4$ are weak-antiferromagnetically coupled with each other, respectively. In addition, the experimental χ_{para}'s at 298 K are $3.3x10^{-4}$ and $9.5x10^{-4}$ emu/mol, for $2 \cdot (DDQ)_2$ and $2 \cdot (TCNQF_4)_4$, respectively, and their values are equal to only few percents of those calculated with use of mutally non-interacting spin systems of 2^{2+} (S=1 if it is a ground state triplet) and two $DDQ^{-\cdot}$ (S=1/2) species, and of four $TCNQF_4^{-\cdot}$ (S=1/2) species. These results indicate the presence of a small amounts of doublet and triplet species surviving in the salts presumably as a result of a Jahn-

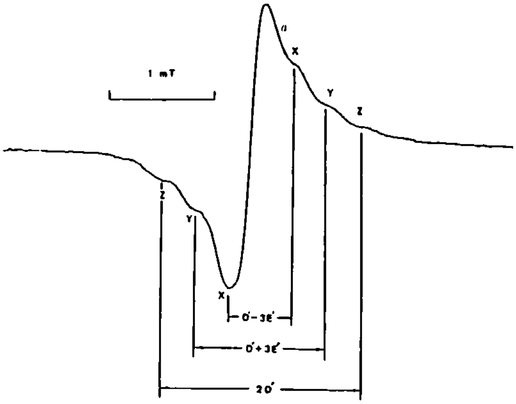


Figure 5. The ESR spectrum of $2 \cdot (3)_2$ at 298 K.

Teller distortion of $\underline{2}^{2+}$ and a strong-antiferomagnetic interaction between a pair of DDQ$^{-\bullet}$'s or TCNQF$_4^{-\bullet}$'s. Nevertheless, the ESR measurement of $\underline{2}\cdot(\mathrm{DDQ})_2$ demonstrated involvement of a ground state triplet, which is most conceivably due to a non Jahn-Teller distorted $\underline{2}^{2+}$, albeit in a very small amount. Thus, a weak half-field resonance signal due to $\Delta m_s=\pm 2$ transition appeared at 163.9 mT together with a strong signal at 327.6 mT (g=2.00523) in the ESR spectrum at 298 K, as shown in Figure 6. The signal intensity measured at each temperature in the range of 298-4.5 K, obeyed a Curie law (Figure 7). The fine structure was not observed at any temperature. In consid-

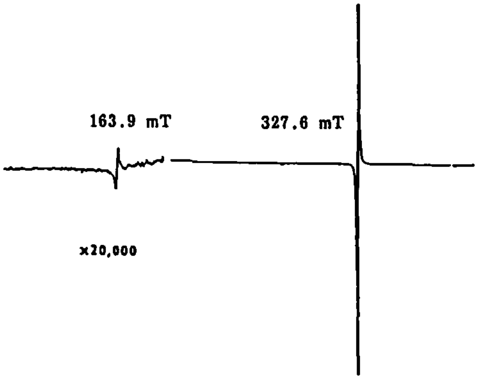


Figure 6. The ESR spectrum of $\underline{2}\cdot(\mathrm{DDQ})_2$ at 298 K.

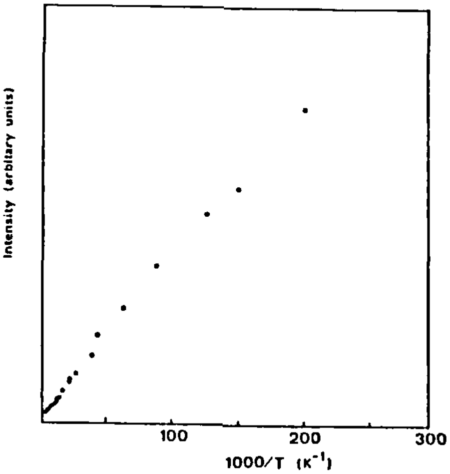
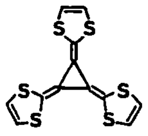


Figure 7. The temperature change of the intensity of half-field ($\Delta m_s=\pm 2$) ESR signal for $\underline{2}\cdot(\mathrm{DDQ})_2$.

eration of very small zero-field splitting parameters of $\underline{2}^{2+}$ observed in $\underline{2}\cdot(\underline{3})_2$, it is probable that the parameters are very small also in $\underline{2}\cdot(\mathrm{DDQ})_2$ and the fine structure is hidden by the strong central signal.

CONCLUDING REMARKS

The [3]- and [5]-radialenes with appropriate electron-donating substituents are still in much expectation of use as a donor component for the preparation of CT types of organic ferromagnets. In particular, tris(1,3-dithiol-2-ylidene)cyclopropane ($\underline{4}$), and hexa(dimethylamino)trimethylenecyclopropane ($\underline{5}$), which has been proposed by Miller and Epstein,[17] are most promising donor. Their preparation is now our most urgent objective. On the other hand, the 1:1 CT complex salts of $\underline{2}$ with appropriate acceptors might exhibit favorable magnetic properties, if $\underline{2}^{2+}$ remains its ground state triplet in the salts, as is the case in the $\underline{2}\cdot(\mathrm{DDQ})_2$ salt.



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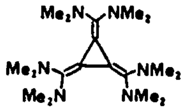

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ACKNOWLEDGEMENT

We are deeply grateful to Messrs. T. Kajita, T. Nagatomi, H. Hatakeyama, H. Oka, M. Sakaguchi, and Y. Hosotani for experimental assistance, to Prof. Y. Maruyama and Dr. T. Inabe for ESR measurement, and to Prof. T. Shinjo and Dr. N. Hosoito for magnetic susceptibility measurement.

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