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Electron Spin Resonance of the Quartet State of 1,3,5-Tris(diphenylamino)benzene

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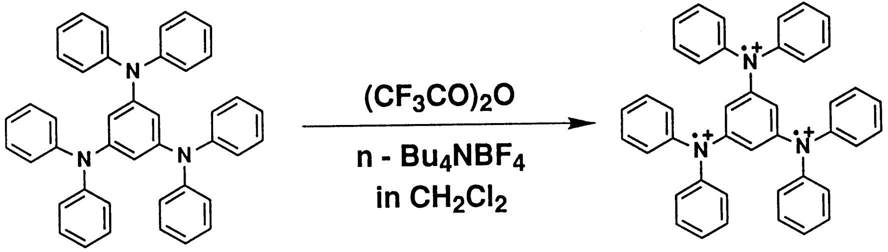
The electron spin resonance (ESR) of the quartet state of 1,3,5-tris(diphenylamino)-benzene (TDAB) is reported. The orange-colored cationic radical is prepared by oxidation of TDAB with trifluoroacetic anhydride in a tetrabutylammonium tetrafluoroborate-CH_2Cl_2 solution. The ESR spectrum reveals that the cationic radical shows a typical quartet signal and that it is extremely stable at room temperature.

Recently an organic ferromagnet, γ-phase crystal of *p*-nitrophenyl nitronyl nitroxide with Curie temperature (T_c) of 0.65 K has been reported by Kinoshita et al.1) In our attempt to synthesize a ferromagnetic polymer, poly(*m*-aniline) has been prepared from *m*-chloro- or *m*-bromoaniline using the Ullmann reaction.2-4) In this polymer ferromagnetic interaction between a few of spins has been observed from ESR and magnetic-susceptibility measurements.5)

The magnetic properties of cationic radicals of 1,3,5-tris(diisopropylamino)benzene (TDIAB) has been examined by Chiang et al.6) For stabilization of the radicals of this type of molecule, conjugation between π-electrons of the benzene rings and unpaired electrons of the nitrogens is important. In our previous paper,7) we have described the synthesis, the molecular and crystal structures, and the characterizations of 1,3,5-tris(diphenylamino)benzene (TDAB) based on IR, UV-vis, ^{1}H-NMR, and cyclic voltammetry. We have observed mono-, di-, tri-, and tetracations by cyclic voltammetry and have indicated that the trication is particularly interesting because it is a ground-state quartet as predicted from topological considerations.8) In the present paper, we report the electron spin resonance (ESR) of the quartet state of TDAB.

TDAB was synthesized from 1,3,5-tribromobenzene and diphenylamine using the Ullmann reaction and was purified by three times of recrystallization from toluene.7) The triradical of TDAB was easily prepared in an ESR sample tube under nitrogen by oxidation of TDAB with trifluoroacetic anhydride in tetrabutylammonium tetrafluoroborate-CH_2Cl_2 solution as shown in Scheme 1. The cationic triradical is orange in color and is stable under vacuum or purified nitrogen at room temperature. A JEOL FEX1G ESR spectrometer was employed, which was operated at a microwave frequency of 9.3 GHz and a field modulation of 100 kHz. The magnetic field was calibrated using a Mn^{2+}/MgO solid solution.



Scheme 1.

Figure 1 shows the ESR spectrum of a solution of the triradical of TDAB in CH_2Cl_2 glass at 123 K. The spectrum consists of several $\Delta m_S = \pm 1$ signals being very similar to those of a triradical of 1,3,5-tris((di-(biphenyl-4-yl)chloromethyl))benzene.9) The ESR *g*-value of the triradical was determined to be 2.002. Since the same spectrum was obtained under various oxidation conditions, it was found that the monoradical is absent in the sample oxidized with trifluoroacetic anhydride. This interesting behavior shows that the cationic triradical is extremely stable in the presence of counter anions such as BF_4^- and so on. The zero-field-splitting parameter D was determined to be 13.1 G (1G = 10^{-4} T) from the difference of H_{z1} and H_{z2}. This value is about one-third of the value observed by Brickmann and Kothe.9) This is an indication of the difference in the spin density distribution between the carbon- and the nitrogen-centered radical species.

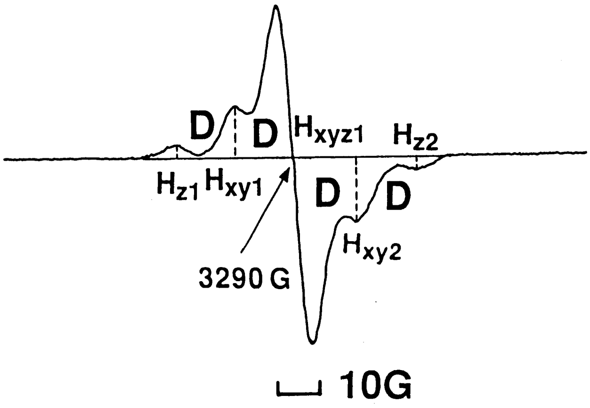


Fig. 1. ESR spectrum of the triradical of TDAB in CH_2Cl_2 glass at 123 K. H_{z1}, H_{xy1}, H_{xyz1}, H_{xy2}, and H_{z2} are the axial resonance fields (see Ref. 9). D is a zero-field-splitting parameter.

Since the temperature-dependence of the signal intensity is complex and the solvent effect on the spin state is unknown, at present we cannot conclude that the quartet state is a ground state. Moreover, the stoichiometry of the charge-transfer complex is not clear. Therefore, it is necessary to examine the spin state of the solid of the TDAB with BF_4^-, ClO_4^-, PF_6^-, and so on.

As shown in Fig. 2, hyperfine splitting probably due to the nitrogen nuclei is observed in the solution spectrum. The solution ESR spectrum is strongly dependent on temperature. This hyperfine splitting disappeared and the spectrum typical of quartet states appeared as the solution was frozen around 183 K. The quartet spectrum was obtained by the electro-chemical oxidation method under the condition that the trication is observed in cyclic voltammetry.7) The intensity was observed to increase with an increase in electro-chemical oxidation time and applied voltage. Even after one week at room temperature under nitrogen atmosphere, the radical species were observed to be alive.

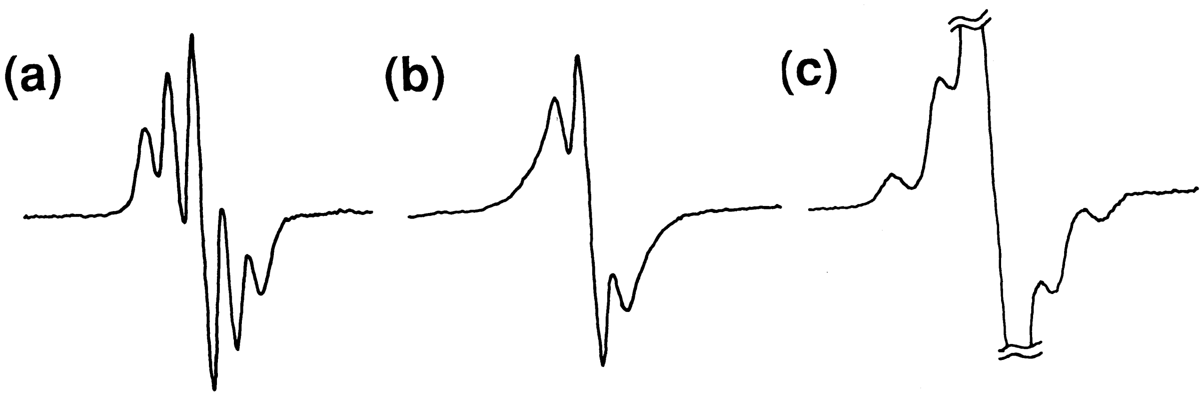


Fig. 2. ESR spectra of the TDAB solution in CH_2Cl_2 at (a) 243, (b) 213, and (c) 183 K measured under the same condition.

In conclusion we have observed the stable quartet state of TDAB. Although organic molecules with ground-state multiplet such as carbenes10) and nitrenes11) have been prepared so far, these types of species are alive only at low temperatures. On the other hand, the cationic triradical of TDAB is observed to be very stable even at room temperature. The stability of this radical is probably originated from the heteroatomic nature with π-conjugation as we know that a DPPH radical is a stable radical. Moreover, examining the role of counter anions is also very important for the understanding of the great stability of this cationic triradical. We are now preparing a single crystal of this triradical by the electro-chemical crystallization technique.12) Further detailed study on the magnetic properties is now undertaken and will be reported in due course.

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