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ESR Spectra of Anion Radicals of 8,8-Dicyanoheptafulvene and Its 4,5-Benzo Derivative

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The hyperfine splitting constants for the 8,8-dicyanoheptafulvene anion radical generated electrolytically at low temperature indicate that the unpaired spin belongs to an a_2 orbital of the group C_{2v}. Its 4,5-benzo derivative gives a stable anion radical by reduction with alkali metals. The odd electron belongs to a b_2 orbital.

8,8-Dicyanoheptafulvene (=2,4,6-cycloheptatrien-1-ylidenepropanedinitrile),1) which is one of the most stable derivatives of heptafulvene, is not reduced with alkali metals. Electrochemical generation of the anion radical to measure the ESR spectrum at room temperature has also been unsuccessful because of its instability. We have then carried out an electrolytical generation at low temperature. The result will be reported together with results on the anion radical of its 4,5-benzo derivative prepared by reduction with alkali metals.

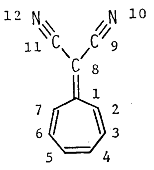
Results and Discussion

Electrolytic generation of 8,8-dicyanoheptafulvene in degassed butyronitrile was carried out within the cavity of an ESR spectrometer, using a cell modified slightly from Allendoerfer *et al.*2) and Ohya-Nishiguchi.3) Tetrabutylammonium perchlorate was used as the supporting electrolyte. The reduction at −100 °C gave the ESR spectrum shown in Fig. 1. A similar spectrum was obtained by an electrolysis in a mixed solvent of acetonitrile and 1,2-dimethoxyethane (DME) (1 : 9) at −80 °C using tetrapropylammonium perchlorate as the supporting electrolyte. Three splitting constants (Table 1) obtained correspond closely to those of the tropone anion radical (0.858, 0.01, and 0.505 mT).4)

Similarity of the hyperfine structure to that of the tropone anion radical substantiates that the unpaired spin belongs to an a_2 orbital, in which the spin localizes in the seven-membered ring. Therefore, as has been discussed for the C_{2v} tropone structure,4) the Hückel MO calculation would show zero spin densities at all atoms in the $C=C(CN)_2$ moiety. The McLachlan spin densities calculated by employing the parameters proposed by Streitwieser are shown in Table 1, demonstrating a good agreement between the experimental and calculated spin densities. Calculations were also carried out by introducing the bond alternation parameter k ($=\beta_s/\beta_d$, the ratio of resonance integral parameters for the C–C and C=C bonds in the seven-membered ring) in order to represent the aromaticity of 8,8-dicyanoheptafulvene. However, the reduction of k-parameter to 0.9 replaced the unpaired spin orbital by the b_2 orbital, with which the observed splitting constants cannot be rationalized. Although such a replacement of the orbitals is avoidable if one adopts other resonance and Coulomb integral parameters for the $C=C(CN)_2$ group, the calculations by the use of some possible parameters show poorer agreements than that seen in Table 1. It is thus concluded that the k-parameter must be close to 1, which means the complete delocalization of π-electrons in the 8,8-dicyanoheptafulvene anion radical, while a considerable bond alternation in the conjugated seven-membered ring has been observed for the neutral species in solid state.5)

TABLE 1. SPLITTING CONSTANTS (a_i) AND SPIN DENSITIES (ρ_i) FOR THE 8,8-DICYANOHEPTAFULVENE ANION RADICAL

Position	a_i/mT	ρ_i	
		Exptl[a]	Calcd[b]
10, 12			−0.0173
9, 11			−0.0091
8			−0.0098
1			−0.0677
2, 7	0.88	0.37	0.3774
3, 6	0.02	0.01	−0.0111
4, 5	0.50	0.21	0.1989



a) With the relation, $a_i = Q^{H}_{CH}\rho_i$, in which $|Q^{H}_{CH}| = 2.37$ mT was adopted. b) Calculated by the McLachlan procedure. Parameters for the calculation: $\alpha_N = \alpha + 0.5\beta$. Resonance integrals for the C–C and C–N bonds are all 1β.

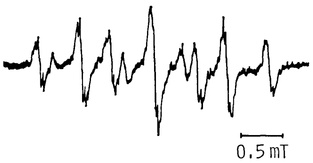


Fig. 1. ESR spectrum of the 8,8-dicyanoheptafulvene anion radical generated by the electrolysis in butyronitrile at −100 °C.

In contrast to the instability of the above, the anion radical of the 4,5-benzo derivative (=7*H*-benzocyclohepten-7-ylidenepropanedinitrile)6) was produced in a stable form by reduction with an alkali metal at room temperature. The ESR spectra are shown in Fig. 2 for the two solutions prepared by reducing the neutral species with sodium metal in DME and with potas-

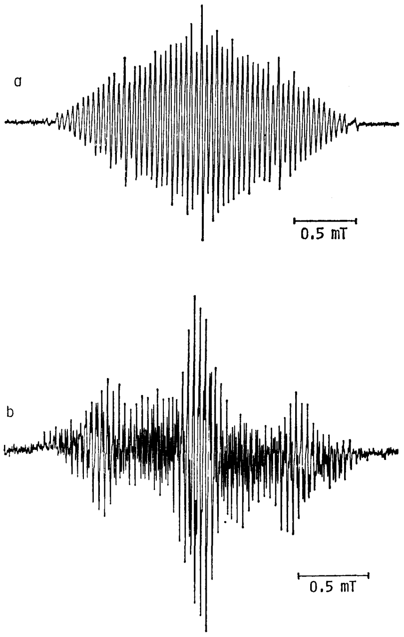
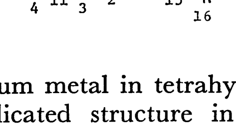


Fig. 2. ESR spectra of the 8,8-dicyano-4,5-benzoheptafulvene anion radical generated by the reduction (a) with Na in DME and (b) with K in THF at room temperature.

Table 2. Splitting constants (a_i) and spin densities (ρ_i) for the 8,8-dicyano-4,5-benzoheptafulvene anion radical[a)]

Position	a_i/mT Na-DME	Na-THF	K-THF	ρ_i Exptl (Na-DME)	Calcd
14, 16	0.087	0.085	0.081		0.0379
13, 15					0.0279
12					−0.0079
1					0.2454
2, 9	0.166	0.168	0.151	0.070	−0.0784
3, 8	0.626	0.630	0.616	0.264	0.2718
10, 11					0.0100
4, 7	0.249	0.251	0.256	0.105	0.0947
5, 6	0.125	0.126	0.108	0.053	0.0372
M+	b)	b)	0.040		



a) See footnotes in Table 1.
b) Not observed.

sium metal in tetrahydrofuran (THF). A much complicated structure in the latter spectrum is caused by an appearance of the splittings due to the potassium ion. Analysis of the hyperfine structures afforded the splitting constants summarized in Table 2 together with those for the Na–THF system. The assignments for the constants were tentatively given according to the type of splitting and by comparing them with the calculated spin densities. As seen from Table 2, the agreement between the calculated and experimental spin densities is satisfactory. An introduction of k-parameter to the seven-membered ring does not lead to the replacement of unpaired spin orbital (b_2 species) by another one, in distinction from the case of 8,8-dicyanoheptafulvene. However, the reduction of the k-value to less than 0.8 makes the agreement between the experimental and calculated spin densities worse. Thus, no information of the bond alternation in the seven-membered ring was obtained.

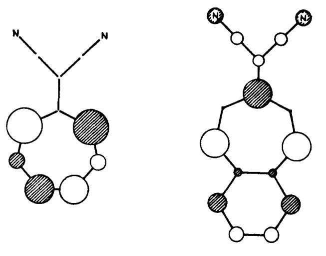


Fig. 3. Illustration of the unpaired-spin distributions for two anion radicals.

The contrast in stability between the above two anion radicals is properly ascribed to the difference in their π-electron systems. The difference can be illustrated with Fig. 3 as an idiomatic expression for the unpaired spin orbitals. In this figure, the radii of the circles are proportional to the absolute value of the LCAO-coefficient in the Hückel MO calculations and blank and shadowed circles refer to relative signs of these coefficients. A noteworthy difference between the unpaired-spin distributions in their dicyanoheptafulvene moieties might be related to the contrast in their stabilities.

Experimental

8,8-Dicyanoheptafulvene, mp 199—200 °C,[1)] and the 4,5-benzo derivative, mp 267 °C,[6)] were prepared by the authentic methods and recrystallized from methanol and a mixture of benzene–cyclohexane, respectively. Solvent butyronitrile (guaranteed reagent) was treated with potassium permanganate and sodium carbonate[7)] and distilled under a nitrogen pressure of 2×10^3 Pa. The middle fraction was degassed and distilled again under a high vacuum to be stored over previously dried molecular sieves 4A in a storage vessel. Other solvents were purified by the procedures reported previously.[8)]

ESR spectra were measured with a Varian E-109E EPR spectrometer. An electrolysis cell for ESR measurements was constructed by modifying slightly from those reported earlier.[2,3)] In this cell, a helical electrode wound with a 0.5 mm diameter silver wire and a straight platinum wire of 0.5 mm diameter are supported in a quartz tube (3.2 mm in inner diameter) connected to a Pyrex tube through a graded seal. The upper Pyrex part, holding two leading wires sealed, has no glass joints and is connected to a branch tube, which can be joined to a vacuum line in order to prepare solutions under vacuum. Spectral simulations were carried out with a JEOL JEC-5 minicomputer.

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