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The ESR Spectrum of 2-Dimethylaminoazulene Anion Radical

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ESR studies of the anion radicals of biazulenyls[1] and methoxyazulenes[2] were reported in previous papers. A similar study has been carried out on the anion radical of 2-dimethylaminoazulene obtained in a relatively stable form.

Experimental

2-Dimethylaminoazulene, mp 99°C,[3] was purified by recrystallization. The solvent *N*,*N*-dimethylformamide (DMF) and acetonitrile (AN) were distilled onto Molecular Sieve after being purified and degassed. Electrolytic reduction was carried out using DMF and AN as the solvent and tetra-*n*-propylammonium perchlorate as a supporting electrolyte.

The ESR spectra were measured at room temperature with a Hitachi X-band ESR spectrometer, Model 771. A JEOL spectrum computer, JEC-5, was used for spectral simulation.

Results and Discussion

The anion radical of 2-dimethylaminoazulene was prepared by the electrolytic technique which was found useful for the generation of radical ions, particularly of azulene anion radicals.[1,2,4] The electrochemical reduction of the compound in degassed AN gives the ESR spectrum shown in Fig. 1. A similar spectrum was also presented by the electrolysis in DMF.

Hyperfine structure of the spectrum was analyzed with six splitting constants listed in Table 1. The analysis was confirmed by a spectral simulation with the constants and a half-width of 200 milligauss. The assignments for the constants were given according to the type of splitting and by a comparison of the constants with the calculated spin densities.

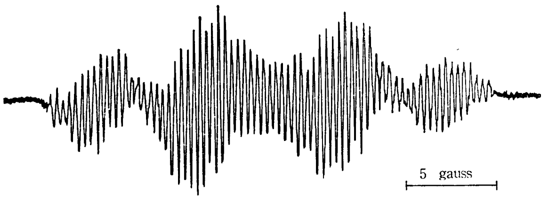
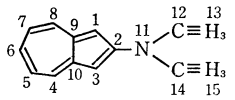


Fig. 1. ESR spectrum of 2-dimethylaminoazulene anion radical generated by the electrolytic reduction in acetonitrile (g=2.0017).

Table 1. Splitting constants (a_i) and spin densities for 2-dimethylaminoazulene anion radical

Position	a_i, gauss		Calcd spin density[a)] ρ_i		$\lvert Q_{\mathrm{CH}}^{\mathrm{H}}\rvert$[b)]
	in AN	in DMF	Hückel	McLachlan	
1,3	0.1	0.1	0.0000	−0.0402	2.5
2			0.1033	0.1060	
4,8	5.62	5.58	0.1937	0.2794	20.0
5,7	1.40	1.40	0.0132	−0.0670	20.9
6	8.01	7.94	0.2435	0.3653	21.8
9,10			0.1020	0.0946	
11 (N)	1.05	1.02	0.0310	−0.0032	
12,14	0.35	0.35	0.0000	−0.0006	
13,15			0.0022	−0.0003	

a) The following parameters were used for the calculation:



$\alpha_{11}=\alpha+1\beta$, $\alpha_{13}=\alpha_{15}=\alpha-0.5\beta$, $\beta_{9,10}=0.9\beta$, $\beta_{2,11}=\beta_{11,12}=\beta_{11,14}=0.8\beta$, $\beta_{12,13}=\beta_{14,15}=3\beta$, and $\lambda=1.2$.
All other bond length variations were neglected.

b) $\lvert Q_{\mathrm{CH}}^{\mathrm{H}}\rvert$ value in the relation of $a_i=Q_{\mathrm{CH}}^{\mathrm{H}}\rho_i$, in which the average a_i observed and the McLachlan spin density were used.

Calculations of unpaired spin densities (ρ_i) for the anion radical were carried out by means of the Hückel MO theory and the approximate configuration interaction treatment proposed by McLachlan.[5] The Coulomb and resonance integral parameters for the dimethylamino group were chosen by referring to a conjugation model for the methyl group.[6] The values are given in the footnote of Table 1. The calculated spin densities are shown in the table. The McLachlan procedure gives a much more satisfactory result than the Hückel MO calculation. The $Q_{\mathrm{CH}}^{\mathrm{H}}$ values obtained by the McConnell relation are reasonable for the seven-membered ring and close to those for azulene anion radicals.[2,4] The low $Q_{\mathrm{CH}}^{\mathrm{H}}$ value for the 1- and 3-positions arises mainly from the inaccuracies of both the spin density and the splitting constant for these positions. The splitting constant is less than the halfwidth of a spectral line. Such a calculation might be applied for the analogous anion radicals.

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