The ESR Spectra of 2- and 6-Methoxyazulene Anion Radicals

Yusaku IKEGAMI and Shuichi SETO

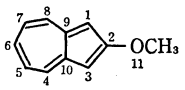
Chemical Research Institute of Non-Aqueous Solutions, Tohoku University, Katahira-2-chome, Sendai

(Received December 21, 1970)

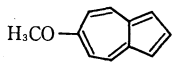
The electron spin resonance spectra of 2- and 6-methoxyazulene anion radicals have been examined. The radicals were generated from neutral species either by electrolytic reduction in *N,N*-dimethylformamide or by the reduction with alkali metals in ethereal solvents. The experimental splitting constants are explained satisfactorily in terms of the calculated spin densities by McLachlan's procedure.

The electron spin resonance (ESR) spectrum of azulene anion radical was first reported by Bernal *et al.*[1] The calculations of the π-electron spin density ρ_i for the anion radical were used with the experimental splitting constants a_i to make a comparison with the predicted bond angle variation of the parameters Q^{H}_{CH} in the McConnell relation, $a_i=Q^{H}_{CH}\rho_i$.[2] Among the relatively few studies on the anion radicals of azulene derivatives, a recent result on 2,2'-biazulenyl[3] has shown that the observed splitting constants are related to the calculated spin densities by rather larger Q^{H}_{CH} values (23—28 gauss) than that suggested by Bernal *et al.* Reddoch[4] has found the anomalous effects of temperature and concentration on the splitting constants for azulene anion radical. This is of interest in connection with the fact that azulene is a non-alternant hydrocarbon. Since only a few ESR works on azulene derivatives have been reported, more systematical studies are desired for elucidation of ESR spectroscopic properties of azulenes.

The present authors attempted to prepare the anion radicals of azulene derivatives. Two methoxy derivatives, 2- and 6-methoxyazulenes, were first chosen because the presence of the substituent at 2- or 6-position does not lower the structural symmetry of azulene, and also the affinity of methoxy substituent with ethereal solvents might favor the generation of relatively stable anion radicals. The ESR spectra of the radicals will be reported in this paper.



I



II

Experimental

Both of the materials, 2-methoxyazulene, mp 82—83°C[5], and 6-methoxyazulene, mp 112—113°C[6], were recrystallized from methanol and finally purified by sublimation in a vacuum. All solvents were degassed by at least five freezing-pumping cycles after being purified. 1,2-Dimethoxyethane (DME) and tetrahydrofuran (THF) were each preserved as solutions of sodium anthracenide in a flask connected with a high vacuum apparatus. *N,N*-Dimethylformamide (DMF) was distilled on to a molecular sieve (4A, small pellet) which had been flame dried in a vacuum. The solvent was moved usually by distillation into the reaction vessels connected with the sample tube for measurement.

The technique employed in the electrolytic generation of free radical is similar to that used by Hirayama.[7] A cell with platinum electrodes was designed so that electrolysis could be performed within the cavity for the preparation of radicals unstable at room temperature. Tetra-*n*-propylammonium perchlorate was used as the supporting electrolyte for the electrolysis in DMF. The alkali metal reduction was performed by the usual method, using lithium, sodium, and potassium metals as the reducing agents.

The ESR spectra were measured with a Hitachi X-band ESR spectrometer, Model MPU-3B or Model 771, using a field modulation of 100 kHz. Analysis of the spectra was confirmed by simulation for which a JEOL spectrum computer, JRA-5, was used.[8] Numerical calculations were carried out on the NEAC 2230 at the Computer Centre, Tohoku University.

Results and Discussion

2-Methoxyazulene Anion Radical. *a) Generation and Spectrum of the Radical*: Treatment of 2-methoxyazulene (I) solution with an alkali metal in degassed DME or THF at −5°C usually resulted in an immediate disappearance of its pink color. This is similar to the case of formation of azulene anion radical in which a deep

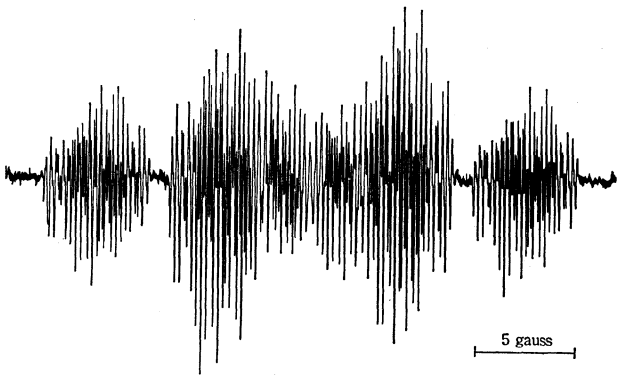


Fig. 1. ESR spectrum of the anion radical generated by the reduction of 2-methoxyazulene with sodium metal in THF (g=2.0032).

1) I. Bernal, P. H. Rieger, and G. K. Fraenkel, *J. Chem. Phys.*, **37**, 1489 (1962).

2) H. M. McConnell, *ibid.*, **24**, 632, 764 (1956); H. M. McConnell and H. H. Dearman, *ibid.*, **28**, 51 (1958); H. M. McConnell and D. S. Chesnut, *ibid.*, **28**, 107 (1958).

3) Y. Ikegami and S. Seto, *Mol. Phys.*, **16**, 101 (1969); This Bulletin, **43**, 2409 (1970).

4) A. H. Reddoch, *J. Chem. Phys.*, **41**, 444 (1964).

5) T. Nozoe, S. Seto, and S. Matsumura, This Bulletin, **35**, 1990 (1962).

6) K. Takase, T. Asao, Y. Takagi, and T. Nozoe, *Chem. Commun.*, **1968**, 368.

7) M. Hirayama, This Bulletin, **40**, 1822 (1967).

8) The authors express their thanks to the computer staff of JEOL, Co. Ltd.

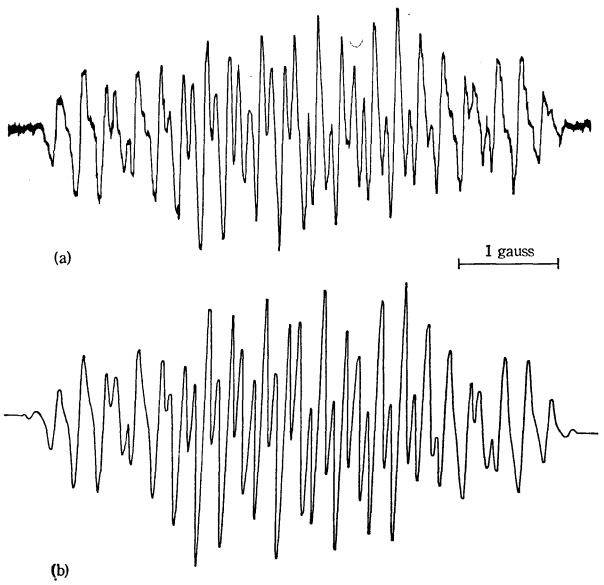


Fig. 2. (a) Enlarged spectrum for the lower 6 gauss of Fig. 1. (b) Simulated spectrum of the above ($\Delta H_{1/2}$=90 milligauss).

purple-blue color of the neutral species changed into a pale greenish yellow.[1] The colorless solution exhibited a strong ESR signal. Although the anion radical is stable for a long period at room temperature, careful procedure was required to obtain it, since a crystalline product was formed at times if the solution was kept in contact with the metal for a long period at room temperature.

Na—THF: The spectrum of the anion radical generated by the reduction of I with sodium metal in THF is shown in Fig. 1. Complicated hyperfine structure of the spectrum suggests the presence of splittings due to the coupling of the radical with a sodium cation. It is easy to read the two splitting constants, 8.598 and 6.133 gauss, from the spectrum, one of which represents the coupling with one hydrogen atom and the other that with two equivalent hydrogen atoms. The enlarged spectrum shown in Fig. 2a for the lower 6 gauss of Fig. 1 is analyzed with three splitting constants, 1.252 (2H), 0.237 (5H) and 0.567 gauss (1Na). A combination of these three constants with eight nuclear spins afforded the simulated spectrum shown in Fig. 2b, confirming the analysis.

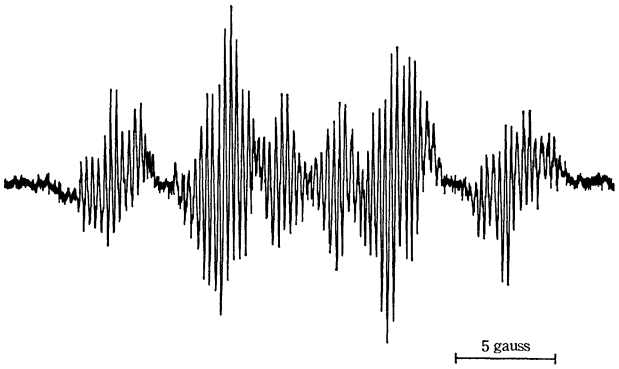


Fig. 3. ESR spectrum of the anion radical generated by the reduction of 2-methoxyazulene with sodium metal in DME (g=2.0030).

Na—DME: Figure 3 shows the spectrum of the anion radical formed by the reduction of I with sodium metal in DME. Hyperfine structure of the spectrum can be interpreted assuming that there are metal splittings with the coupling constant comparable to the least constant in the anion radical. Four splitting constants listed in Table 1 and rather large line-width ($\Delta H_{1/2}$, *ca.* 0.27 gauss) permit analysis of the hyperfine structure.

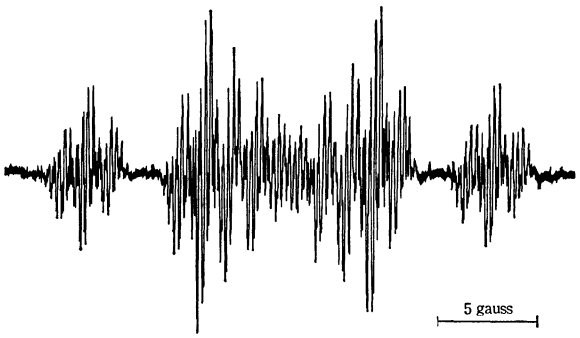


Fig. 4. ESR spectrum of the anion radical generated by the reduction of 2-methoxyazulene with potassium metal in THF (g=2.0017).

K—THF: Generation of the radical with potassium metal in THF afforded the spectrum shown in Fig. 4. It is easy to read three splitting constants, 8.359 (1H), 5.862 (2H) and 1.149 gauss (2H), from the spectrum. Final splittings are explained as those consisting of seven bands of relative intensities 1:4:7:8:7:4:1, each splits into three lines (a_i, *ca.* 0.1 gauss). Relative intensities of the seven bands should be due to the fact that the two constants for potassium metal and methoxy protons are close to each other.

K—DME, Li—THF and Li—DME: Hyperfine structures of the ESR spectra of the radical generated by these systems are simpler than those of Figs. 1 and 3, and the analysis of each spectrum revealed that the metal splitting constant is comparable to that of the least constant for the radical. The hyperfine lines are comparatively broad because of the large line-width close to the least splitting constant. The observed constants are included in Table 1.

Electrochemical Reduction: Electrolytic reduction of I in DMF at *ca.* 1.9V produced the anion radical, which exhibited the ESR spectrum shown in Fig. 5. Hy-

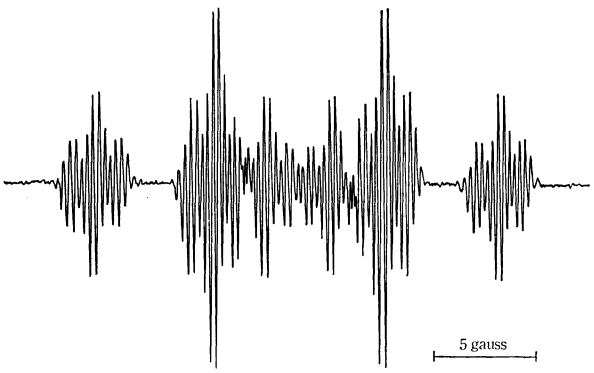


Fig. 5. ESR spectrum of 2-methoxyazulene anion radical generated by the electrolytic reduction in DMF (g=2.0038).

Table 1. Observed hyperfine splitting constants (a_i) for 2-methoxyazulene anion radical

Position	Electrolysis in DMF	a_i, gauss					
		K—THF	Na—DME	K—DME	Li—DME	Na—THF	Li—THF
1, 3 (2H)	0.26	0.1	0.29	0.24		0.23_7	0.23
4, 8 (2H)	5.804	5.862	5.670	5.96	6.02	6.133	6.21
5, 7 (2H)	1.097	1.149	1.163	1.17	1.21	1.252	1.31
6 (1H)	8.326	8.359	8.529	8.55	8.62	8.598	8.76
OCH_3(3H)	0.26	0.27	0.29	0.24	0.27	0.23_7	0.23
Metal		0.27	0.29	0.24	0.27	0.56_7	0.23

perfine structure of the spectrum can be readily analyzed with four splitting constants included in Table 1. The analysis was confirmed by spectral simulation.

The observed constants are summarized in Table 1. Assignments for the constants were given according to the type of splitting and by comparing them with the calculated spin densities.

b) Calculation of Spin Density. Calculations of unpaired spin densities (ρ_i) for the anion radical were carried out by employing the Hückel MO theory and the approximate configuration interaction treatment proposed by McLachlan.[9] The Coulomb and resonance integral parameters for C–OCH_3 group were chosen from the values suggested by Streitwieser.[10] The results are given in Table 2. As generally known for many aromatic anion radicals[9] including some azulene anion radicals,[1,3] the McLachlan's procedure gave much more satisfactory results than the Hückel MO calculations. The application of some other parameters for the 9,10-bond ($\beta_{9,10}$:1β) and the C–OCH_3 group (β_{C-O}: $0.6—1.0\beta$, α_O: $\alpha+0.5—2.0\beta$) did not alter the assignments for the observed constants shown in Table 2. The Q^H_{CH} values obtained by the McConnell relation are also shown in the table.

6-Methoxyazulene Anion Radical. a) Generation and Spectrum of the Radical: The anion radical of 6-methoxyazulene (II) is not so stable as that of 2-isomer. The solution of II in degassed DME or THF reacted readily with an alkali metal at room temperature losing its pink color, but no ESR signal has been observed.

Table 2. Calculated spin densities(ρ_i) for 2-methoxyazulene anion radical[a]

Position	ρ_i		$\lvert Q^H_{CH}\rvert$[b]
	Hückel	McLachlan	
1, 3	0.0009	−0.0161	16.2
2	0.1066	0.1048	
4, 8	0.2039	0.3032	19.1
5, 7	0.0125	−0.0753	14.6
6	0.2514	0.3819	21.8
9, 10	0.0980	0.0434	
11(OCH_3)	0.0114	0.0030	

a) Parameters for the calculation: $\alpha_{11}=\alpha+2\beta$, $\beta_{2,11}=0.8\beta$, $\beta_{9,10}=0.9\beta$ and $\lambda=1.2$.

b) Q^H_{CH} values in the relation of $a_i = Q^H_{CH}\rho_i$, in which the observed a_i in an electrolytic reduction and the McLachlan spin densities were used.

9) A.D. McLachlan, *Mol. Phys.*, **3**, 233 (1960).

10) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley & Sons, New York (1962), p. 120.

The anion radical was identified when the pink solution came into contact with an alkali metal at −78°C and was measured at a temperature lower than −20°C. The radical generated with sodium metal in DME exhibited the ESR spectrum shown in Fig. 6, which was measured at −100°C. Three splitting constants, 6.63 (2H), 3.67 (1H) and 1.53 gauss (2H), are obtained from the hyperfine structure of the spectrum. The signal intensity decreases with increasing temperature and disappears completely at −10°C. Other systems, Li—THF, Na—THF and K—THF, also showed the ESR signals, each of which consists of broad hyperfine lines.

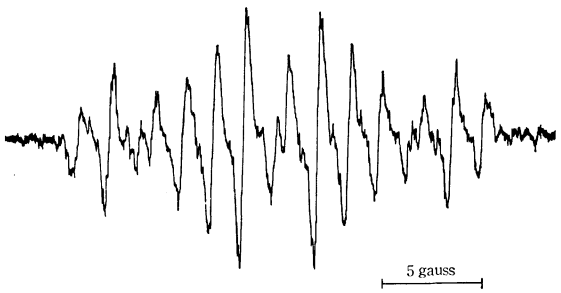


Fig. 6. ESR spectrum of the anion radical generated by the reduction of 6-methoxyazulene with sodium metal in THF, measured at −100°C.

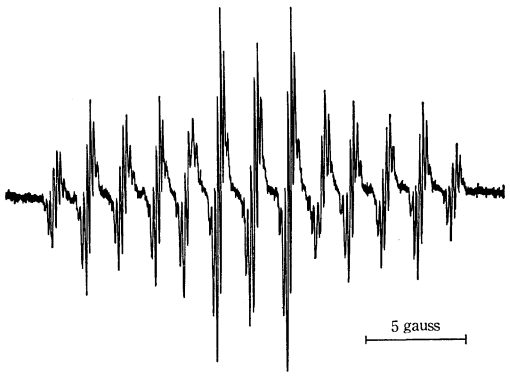


Fig. 7. ESR spectrum of 6-methoxyazulene anion radical generated by the electrolytic reduction in DMF at room temperature (g=2.0029).

In contrast to the above, electrolytic reduction of II produced the stable radical at room temperature. Electrolysis of the solution of II in DMF at *ca.* 1.9V resulted in a pale brown solution which exhibited an ESR spectrum shown in Fig. 7. No decay of the intensity of the spectrum is observed during the course of a few hours. Hyperfine structure of the spectrum is analyzed with four splitting constants listed in Table

3 and the assignments for the constants are reasonably made by comparing them with the calculated spin densities.

TABLE 3. OBSERVED HYPERFINE SPLITTING CONSTANTS (a_i) AND CALCULATED SPIN DENSITIES (ρ_i) FOR 6-METHOXYAZULENE ANION RADICAL

Position	a_i, gauss		ρ_i[a]		$\lvert Q^H_{CH}\rvert$[b]
	Na-DME	Electrolysis in DME	Hückel	McLachlan	
1, 3(2H)		0.16	0.0061	−0.0206	7.8
2 (1H)	3.67	3.542	0.1034	0.1113	31.8
4, 8(2H)	6.63	6.659	0.2216	0.3085	21.6
5, 7(2H)	1.53	1.701	0.0032	−0.0890	19.1
6			0.2480	0.3509	
9, 10			0.0806	0.0582	
OCH_3(3H)		0.16	0.0257	0.0236	

a) Parameters for the calculation: $\alpha_{11}=\alpha+2\beta$, $\beta_{6,11}=0.8\beta$, $\beta_{9,10}=0.9\beta$ and $\lambda=1.2$.
b) See footnote b in Table 2.

b) Calculation of Spin Density. Calculations of unpaired spin densities for the anion radical were carried out in a similar way as those for 2-isomer. The results are listed in Table 3 together with the Q^H_{CH} values obtained by the McConnell relation.

Discussion. Both 2- and 6-methoxyazulenes produced the stable anion radicals through their electrolytic reductions in DMF. The formation of radicals is consistent with the suggestion by polarographic study on azulene, which showed the first reversible reduction potential ($E_{1/2}$) at −1.10 V in DMF.[11] In the generation of 2-methoxyazulene anion radical by alkali metal reduction, the radical was identified as a rather unstable form sometimes producing solid precipitates. The instability might be due to the further reduction of the radical with alkali metal leading to the decomposition of 2-methoxyazulene structure in ethereal solvent. The solution did not reproduce the pink color of neutral species by exposure to air, while it is known that the complex of guaiazulene with sodium in ethereal solvent shows the immediate reappearance of the original blue color by exposure to air.[12]

The spectra of 2-methoxyazulene anion radical generated by the reduction with alkali metals all showed the coupling with the cation, indicating that the radical species exist mostly as ion pairs. For the radical solutions of Na—DME (Fig. 3), Li—DME and Li—THF systems, co-existence of the ion pairs and the solvent-separated ion pairs might be assumed to explain the asymmetric feature of the splittings observed within the outer 6 gauss of their spectra.

In Table 1, the splitting constants at 4(8)-, 5(7)- and 6-positions are smallest for a case of the generation of the radical by electrolytic reduction, and each of the constants increases for the reductions with alkali metals roughly in the order K—THF, Na—DME, K—DME, Li—DME, Na—THF and Li—THF systems. This is similar to the observation by Reddoch,[13] who pointed out the empirical correlation for proton coupling constants of azulene anion radical in various solvents with various cations. The variation of the constants can be ascribed to the electrostatic perturbation of the cation as stated by him.

The Q^H_{CH} values in Tables 2 and 3, which are given for the free radical in DMF, are reasonable if the variation of the value with bond angle in an aromatic ring is assumed as estimated by Bernal *et al.*[1] The value for each position is close to that at the same position for azulene anion radical.[1] However, the values on the carbon atoms in the seven-membered ring are clearly smaller than those for 2,2′-biazulenyl anion which is a very stable radical with deep blue color.[3]

We wish to express our appreciation to Profs. T. Toda and T. Asao for the supply of materials. We are also grateful to Prof. T. Isobe and Dr. H. Yokoi for their helpful discussions.

11) P. H. Given and M. E. Poever, *Coll. Czech. Chem. Comm.*, **25**, 3195 (1960).
12) J. Melville, *J. Amer. Chem. Soc.*, **55**, 3288 (1933); K. S. Birrell, *ibid.*, **57**, 893 (1935).
13) A. H. Reddoch, *J. Chem. Phys.*, **43**, 225 (1965).