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An Electron Spin Resonance Study of 1,1′- and 2,2′-Biazulenyl Anion Radicals

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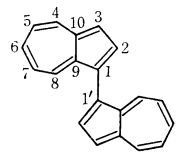
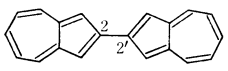
The electron spin resonance (ESR) spectra of the anion radicals of 1,1′- and 2,2′-biazulenyls have been examined. The ESR spectrum of the latter shows that the unpaired spin is distributed equally between both azulene rings of the molecule. Theoretical calculation of the spin densities by the McLachlan procedure gave satisfactory agreement with the experimentally estimated densities. The ESR spectrum of the anion radical of 1,1′-biazulenyl, which could only be generated by an electrolytic technique, is explained by the fact that the spin exchange between the two halves of the molecule is slow. However, the ESR spectrum of the anion radical of the 3,3′-dicarbethoxy derivative of 1,1′-isomer showed rapid spin exchange through 1,1′-bond.

Recent success in the synthesis of 1,1′- (I) and 2,2′-biazulenyls (II) by Morita and Takase[1] revealed that there is a wide difference in the physical properties of the two isomers. Difference of their absorption spectra, for example, is distinct at around 400 mμ region: the absorption maximum of I is at 382 mμ ($\varepsilon=13200$) while II has two peaks at 406 (25600) and 432 mμ (45300) in dimethoxyethane (DME). A similar tendency for the positions of the absorption maxima is noted in the spectra of 3,3′- and 2,2′-biguaiazulenyls which have been reported by Hagen, Heilbronner and Straub.[2] It is presumed that a conformational problem between two planar azulene rings of biazulenyls might be closely related to the essential features of their electronic spectra.



I



II

Several investigators[3] have studied the electron spin resonance (ESR) spectra of the anion radicals

1) T. Morita and K. Takase presented at the 20th Annual Meeting of the Chemical Society of Japan in Tokyo, 1967.

2) R. Hagen, E. Heilbronner and P. A. Straub, *Helv. Chim. Acta*, **51**, 45 (1968).

3) P. H. Rieger and G. K. Fraenkel, *J. Chem. Phys.*, **37**, 2795 (1962); **39**, 609 (1963); K. Ishizu, This Bulletin, **37**, 1093 (1964); M. Hirayama, *ibid.*, **40**, 2530 (1967).

formed by the reduction of biphenyl derivatives and have discussed the planarity of the two aromatic rings. ESR studies of azulene anion radical, a particularly interesting compound as a non-alternant hydrocarbon, have been made by some investigators,[4-6] and the π-electron densities estimated theoretically and experimentally have been discussed in detail.[4] It should be possible to obtain considerable information on the spin density contribution in the biazulenyls, as well as their molecular structures, by ESR study of their anion radicals. The ESR spectra and the calculated spin densities for the biazulenyl anion radicals are reported in this paper.

Experimental

The materials, 1,1′-biazulenyl, mp 104°C, 2,2′-biazulenyl, mp 200°C, and 3,3′-dicarbethoxy-1,1′-biazulenyl, mp 212°C, were purified by recrystallization. All solvents were degassed by at least five freezing-pumping cycles after being purified. 1,2-Dimethoxyethane (DME) and tetrahydrofuran (THF) were preserved in each flask, connected with a high vacuum apparatus as solutions of sodium anthracenide. *N,N*-Dimethylformamide (DMF) was distilled on to a molecular sieve (4A, small pellet) which had been flame dried in a vacuum. The solvents were distilled into the reaction vessels connected with the sample tube for measurement.

Reduction with alkali metal was performed by the usual method using lithium, sodium and potassium metals as reducing agents. The technique employed in the electrolytic generation of free radicals is similar to that used by Hirayama.[7] Electrolytic reduction was performed using DMF as a solvent and tetra-*n*-propylammonium perchlorate as the supporting electrolyte.

The ESR spectra were measured at room temperature with a Hitachi X-band ESR spectrometer, Model MPU-3B, using a field modulation of 100 kcps. Analysis of the spectra was confirmed by simulation for which a JEOL spectrum computer, JRA-5, was used.*1 Numerical calculation was carried out on the NEAC 2230 at the Computation Center, Tohoku University.

The absorption spectra were measured in the degassed solvent at room temperature by using a Cary Model 14 spectrophotometer.

Results and Discussion

2,2′-Biazulenyl Anion Radical. Treatment of 2,2′-biazulenyl (II) with lithium, sodium or potassium metal in degassed DME or THF caused an immediate change in color to deep blue. The

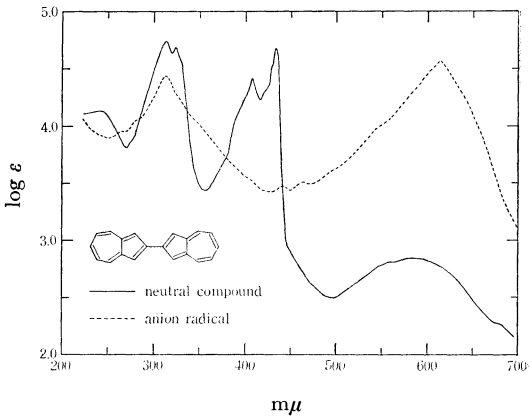


Fig. 1. Absorption spectra of 2,2′-biazulenyl (II) and its anion radical generated by the reduction of II with lithium metal in degassed DME.

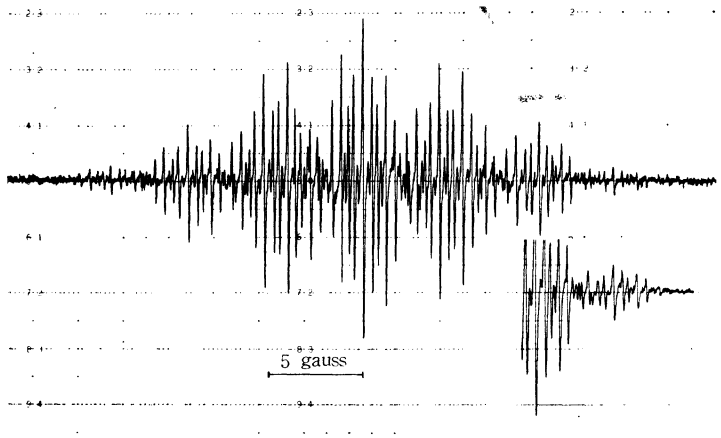


Fig. 2. ESR spectrum of 2,2′-biazulenyl anion radical generated by the reduction of II with lithium metal in DME.

4) I. Bernal, P. H. Rieger and G. K. Fraenkel, *J. Chem. Phys.*, **37**, 1489 (1962).
5) A. H. Reddoch, *ibid.*, **41**, 444 (1964).
6) A. H. Reddoch, *ibid.*, **43**, 225 (1965).
7) M. Hirayama, This Bulletin, **40**, 1822 (1967).

*1 The authors express their thanks to the computer staff of Japan Electron Optics Laboratory, Co., Ltd.

Table 1. Observed hyperfine splitting constants (a_i^H) for 2,2′-biazulenyl anion radical

Ring position (Number of H)	a_i^H, gauss						
	Metal reduction						Electrolysis in DMF
	Li-DME	Li-THF	Na-DME	Na-THF	K-DME	K-THF	
1,3,1′,3′ (4H)	0.475	0.477	0.492	0.478	0.481	0.496	0.494
4,8,4′,8′ (4H)	4.037	4.026	4.097	4.041	4.051	4.051	4.111
5,7,5′,7′ (4H)	1.200	1.227	1.239	1.219	1.233	1.239	1.248
6, 6′ (2H)	5.259	5.261	5.345	5.256	5.274	5.286	5.355
Total extent	33.4	33.4	34.0	33.5	33.6	33.7	34.1

colored solution is quite stable for a long period and shows a strong ESR signal. The absorption spectrum of the solution generated by the treatment of II with a lithium metal for a few days at room temperature is shown in Fig. 1, and compared with the spectrum of the neutral compound. Further treatment of the colored solution with the metal for a a week resulted in a loss of both the blue color and the ESR signal. This might be due to the formation of the diamagnetic dianion of II by the further reduction of the anion radical.

The ESR spectrum of the blue solution in Fig. 2 was measured at room temperature. Similar spectra were obtained by the reduction of II with sodium or potassium metal in DME or THF and by the electrolytic reduction of II in DMF using tetra-*n*-propylammonium perchlorate as the supporting electrolyte. Hyperfine structure of the spectrum was analyzed with four splitting constants (a_i^H), as expected for the symmetrical structure of II. It is thus recognized that the unpaired electron in the anion radical is distributed equally between both azulene rings. No metal coupling has been observed in all the spectra. The line widths for the spectra are between 75 and 140 milligauss. The observed splitting constants and their assignments are given in Table 1. The assignments were made reasonably by comparison with the calculated spin densities.

Calculations of unpaired spin densities (ρ_i) for the anion radical were carried out by employing both the Hückel LCAO molecular orbital theory and the approximate configuration interaction treatment proposed by McLachlan.[8] The resonance integral parameters (β_{ij}) for the 2,2′- and 9,10- (9′,10′-) bonds were varied over the following ranges:

$$0.6\beta \leqq \beta_{2,2'} \leqq 1.2\beta,$$

$$0.9\beta \leqq \beta_{9,10} = \beta_{9',10'} \leqq 1.0\beta.$$

All other bond length variations were neglected and the λ parameter in the McLachlan procedure was fixed at the value, $\lambda = 1.2\beta$, in our calculation. The $|Q_{CH}^H|$ values obtained by the relation, $a_i^H = Q_{CH}^H \cdot \rho_i$, using the observed splitting constants and the calculated spin densities, are compared with the resonance integral parameters. As easily expected from the fact that the total extent of the spectrum, 33.4—34.1 gauss, suggests the presence of negative spin densities, the McLachlan procedure showed better values than by Hückel molecular orbital calculation.

Variations of the $|Q_{CH}^H|$ values versus the parameter, $\beta_{2,2'}$, are shown in Figs. 3a and 3b for the cases in which $\beta_{9,10}$ are 0.9β and 1.0β. We see that the parameter $\beta_{2,2'}$ mostly affects the Q_{CH}^H values at the 1- and 3-(1′- and 3′-)positions. As far as the above parameters are concerned, each of the McLachlan spin densities at the positions from 4 through 8 (also

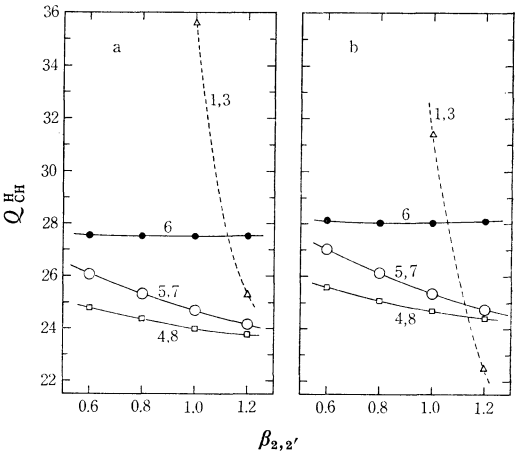


Fig. 3. Q_{CH}^H values in the relation, a_i^H(obsvd.) = $Q_{CH}^H \rho_i$ (calcd.), as a function of the resonance integral parameter for the 2,2′-bond ($\beta_{2,2'}$) of 2,2′-biazulenyl anion radical.
a: $\beta_{9,10} = 1.0\beta$, b: $\beta_{9,10} = 0.9\beta$.

4′ through 8′) in the seven membered rings differs by less than 12%. Assuming the tendency of the variation of Q_{CH}^H with bond angle in the azulene anion radical, estimated by Bernal *et al.*[4] a good agreement with the experimental splitting constants is recognized by the McLachlan method when both the parameters, $\beta_{9,10}$ and $\beta_{2,2'}$, were close to 1.0β. Using 0.9β[4] as the $\beta_{9,10}$, a good result was also obtained when $\beta_{2,2'}$ was close to 1.0β; the re-

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

TABLE 2. CALCULATED SPIN DENSITIES (ρ_i) FOR 2,2′-BIAZULENYL ANION RADICAL

Position	$\beta_{9,10}$[a] $=0.9\beta$			$\beta_{9,10}$[a] $=1.0\beta$		
	ρ_i		$\lvert Q^H_{CH}\rvert$[b]	ρ_i		$\lvert Q^H_{CH}\rvert$[b]
	Hückel	McLachlan		Hückel	McLachlan	
1, 3,1′, 3′	0.01899	0.01553	31	0.01749	0.01366	36
2, 2′	0.04368	0.03519		0.04087	0.03139	
4, 8,4′, 8′	0.11491	0.16545	25	0.11793	0.16987	24
5, 7,5′, 7′	0.00324	−0.04853	26	0.00309	−0.04977	25
6, 6′	0.12755	0.18996	28	0.12999	0.19356	28
9,10,9′,10′	0.02724	0.00497		0.02606	0.00376	

a) The resonance integral parameters for 9,10- and 9′,10′-bonds. All other bond length variations were neglected.

b) $\lvert Q^H_{CH}\rvert$ value in the relation of $a^H_i = Q^H_{CH}\rho_i$, in which the average a^H_i observed and the McLachlan spin density were used.

sults are listed in Table 2. Thus, the π-electrons of the two halves in II conjugate freely through the central 2,2′-bond, and it is clear that the two azulene rings are co-planar in the anion radical. Bernal *et al.*[4] estimated theoretically the Q^H_{CH} value for a regular seven-membered aromatic ring to be −15.2 gauss. However, the $\lvert Q^H_{CH}\rvert$ value does not seem to be far from 23—28 gauss as seen from Table 2. Similar values are also seen for the cases of 2-methoxyazulene anion radical,[9] tropone anion radical,[10] cycloheptatrienyl radical[11] and cycloheptatrienyl dianion radical.[12]

1,1′-Biazulenyl Anion Radical. The anion radical of 1,1′-biazulenyl (I) is not so stable as that of its 2,2′-isomer. For example, the solution of I in degassed DME or 2-methyltetrahydrofuran reacted readily with an alkali metal losing its green color. However, no ESR signals were observed during the course of reaction at room temperature. Electrolysis of the green solution of I in DMF at *ca.* 2.3 V, however, resulted in a pale greenish yellow solution which exhibited a stable ESR spectrum of the anion radical. The spectrum is shown in Fig. 4. No decay of the intensity of the spectrum was observed during the course of a few hours.

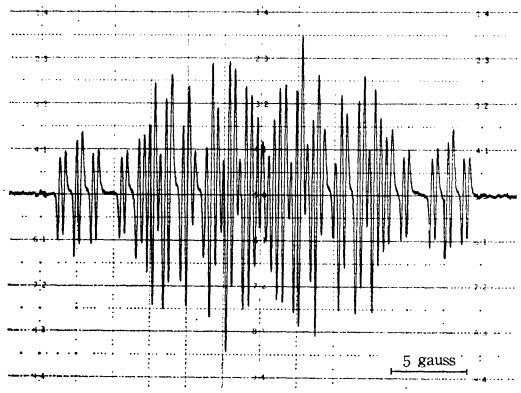


Fig. 4. ESR spectrum of 1,1′-biazulenyl anion radical generated by the electrolytic reduction in DMF.

Interesting facts seen from the spectrum are that it does not have a central strong line and that the hyperfine structure consists of five splitting constants, listed in Table 3, each of which is close to that of the azulene anion radical.[4-6] Thus, the spectrum resembles that of the azulene anion radical except that the smallest splitting is shown by doublets of relative intensities 1 : 1 as in Fig. 4. The simplest explanation of the spectrum is that spin exchange between the two halves of the molecule is slow, and the hyperfine structure originates from the seven protons on one half of the molecule. The assignment for the splitting constants is made by comparison with that for the azulene anion radical,[4] as indicated in Table 3. It might be necessary to see if the rate of intramolecular electron transfer of the anion of I can be increased by measuring its spectrum at elevated temperatures. However, measurement has not been successful because of the instability of the anion radical.

The slow spin exchange in the anion of I is analogous to the situation existing in the anion radical of

TABLE 3. OBSERVED HYPERFINE SPLITTING CONSTANTS (a^H_i) FOR 1,1′-BIAZULENYL ANION RADICAL COMPARED WITH THOSE FOR AZULENE ANION RADICAL[4]

Ring position (Number of H)		a^H_i, gauss	a^H_i for azulene anion radical
3	(1H)	0.361	0.274 (2H)
2	(1H)	4.091	3.948
4, 8	(2H)	5.903	6.219
5, 7	(2H)	1.120	1.338
6	(1H)	8.640	8.829

9) Y. Ikegami, unpublished result.

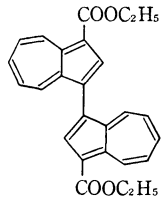
10) Y. Ikegami and S. Seto, This Bulletin, **41**, 2225 (1968).

11) A. Carrington and I. C. P. Smith, *Mol. Phys.*, **7**, 99 (1963).

12) N. L. Bauld and M. S. Brown, *J. Amer. Chem. Soc.*, **87**, 4390 (1965).

bis(*p*-nitrophenyl)ether.[13] In the anion radical of I, the localization of the unpaired electron should be attributed to the inability of the π-electrons in both azulene rings to overlap at the position of the 1,1′-bond. Moreover, the equivalence of both protons at 4- and 8-positions (and also 5- and 7-positions), shown by their splitting constants, indicates that the electronical interaction through the 1,1′-bond between the five-membered rings is small. The steric repulsion between ring protons at 2- and 8′- (2′- and 8-)positions probably makes it impossible for the two azulene rings to be co-planar. This difficulty might also be assisted by the electronical repulsion between the five-membered rings which are usually known to be negatively charged in azulene structure.[14] Such a slow spin exchange was not observed in the ESR spectrum of 1,1′-binaphthyl anion radical, prepared by the reduction of 1,1′-binaphthyl with sodium metal in DME, in which at least 135 hyperfine splitting lines with a central strong line were observed within the total extent of 22 gauss of the spectrum.[15]

The Anion Radical of 3,3′-Dicarbethoxy-1,1′-biazulenyl. In contrast to the case of I, the dicarbethoxy derivative (III) of I exhibits rapid spin exchange through 1,1′-bond.



III

The anion radical of III generated by reduction with sodium metal in DME showed an ESR spectrum which is analyzed with four hyperfine splitting constants. The spectrum and the splitting constants are shown in Fig. 5 and Table 4, respectively. Each of the constants represents coupling with two equivalent protons giving triplets of relative intensities 1 : 2 : 1. A similar spectrum was obtained by the electrochemical reduction of III in DMF. The splitting constants are included in Table 4. Measurement of the spectrum at −50°C did not show any signs of slow spin exchange as in the spectrum of the anion radical of compound I.

Total extent of the spectrum (14.3 gauss) in Fig. 5 suggests that a considerable amount of spin density might be expected to be on the two carbethoxy groups in the molecule. However, an explanation of this suggestion by the calculation of the McLachlan spin densities, using some parameters related to the carbethoxy group[7,16] and resonance integral parameters for the 1,1′-bond, can not be given yet, although the two splitting constants, 2.923 and 0.640 gauss, could be easily assigned to the protons at 6- and 2- (6′- and 2′-)positions, respectively. ESR measurements of the anion radicals of other carbethoxy derivatives of azulene may provide some information on the effect of the substituents in the anion of III. However, our experiments for the cases of 1-carbethoxyazulene[17] and 1,3-dicarbethoxyazulene[18] did not show any ESR signals by standard techniques. Further attempts are being made.

Table 4. Observed hyperfine splitting constants (a_i^H) for the anion radical of 3,3′-dicarbethoxy-1,1′-biazulenyl

Reducing method	a_i^H*, gauss				Total extent
Na in DME	2.923	1.906	1.663	0.640	14.3
Electrolysis in DMF	2.882	1.845	1.691	0.737	14.3

* Each represents coupling with two equivalent protons.

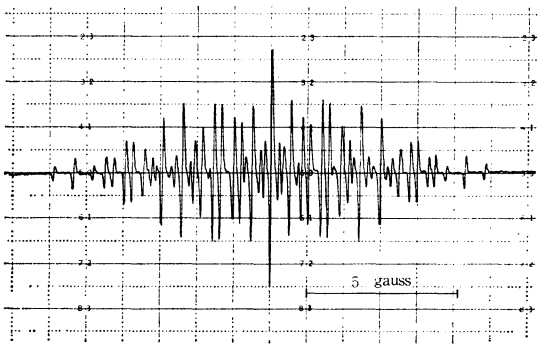


Fig. 5. ESR spectrum of the anion radical of 3,3′-dicarbethoxy-1,1′-biazulenyl (III) generated by the reduction with sodium metal in DME.

The authors wish to express their appreciation to Professor K. Takase and Mr. T. Morita for their donation of materials. We are also grateful to Professor T. Isobe, Dr. M. Hirayama and Dr. H. Yokoi for their helpful discussions.

13) J. E. Harriman and A. H. Maki, *J. Chem. Phys.*, **39**, 778 (1963).
14) A. Julg, *Compt. Rend.*, **239**, 1498 (1954); *J. Chem. Phys.*, **52**, 377 (1955); A. G. Anderson, Jr., and B. M. Steckler, *J. Amer. Chem. Soc.*, **81**, 4941 (1959).
15) Y. Ikegami, unpublished result.
16) M. Hirayama and T. Isobe, This Bulletin, **41**, 1502 (1968).
17) W. Treibs, H.-J. Neupert and J. Hiebsch, *Chem. Ber.*, **92**, 1216 (1959).
18) T. Nozoe, S. Seto, S. Matsumura and T. Asano, *Proc. Japan Acad.*, **32**, 339 (1956).