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224. The Radical Anions of 5,5′- and 6,6′-Biazulenyl

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Summary

ESR. and, in part, ENDOR. studies are reported on the radical anions of 5,5′- and 6,6′-biazulenyl (**1** and **2**, resp.), as well as on their 1,1′,3,3′-tetradeuterio-derivatives (**1**-d_4 and **2**-d_4). The reduction processes of **1** and **2** leading to these radical anions ($\mathbf{1}^{\dot{\ominus}}$ and $\mathbf{2}^{\dot{\ominus}}$) and the dianions ($\mathbf{1}^{\ominus}$ and $\mathbf{2}^{\ominus}$) have been investigated by polarography and cyclic voltammetry. The half-wave reduction potential of **1** and the π-spin distribution in $\mathbf{1}^{\dot{\ominus}}$ are consistent with the model of two weakly interacting azulene π-systems, whereas the analogous findings for **2** and $\mathbf{2}^{\dot{\ominus}}$ point to a strong interaction between two such systems. This difference can be traced to the distinct inequality $|c_{65}| \ll |c_{66}|$ in the LCAO coefficients $c_{6\mu}$ at the centres $\mu = 5$ and 6 for the LUMO ψ_6 of azulene.

Introduction. - The lowest unoccupied orbital (LUMO) ψ_6 of azulene is characterized by large absolute values of the LCAO coefficients $c_{6\mu}$ at the even-numbered centres ($\mu = 2$, 4, 6 and 8) and small values at the odd-numbered ones ($\mu = 1$, 3, 5 and 7). Since the LUMO of a symmetric μ,μ'-biazulenyl, formed by linking the equivalent positions of two azulene moieties, can be considered as a bonding combination of two LUMO's of azulene, its energy and shape depend crucially on whether μ (and μ') is even or odd. This dependence should manifest itself in strongly differing properties of the corresponding radical anions such as their ease of formation and their π-spin distribution.

Some years ago, the radical anion of 2,2′-biazulenyl was found to be relatively stable and to exhibit a well defined ESR. hyperfine pattern [1], whereas the 1,1′-counterpart had a low stability and the ESR. spectrum ascribed to it [1] stems probably from a secondary paramagnetic species [2].

Another pair of μ,μ'-biazulenyls, in which μ is odd and even, are the 5,5′- and 6,6′-compounds (**1** [3] and **2** [4], resp.). The present paper begins with the polarography and cyclic voltammetry of **1** and **2**. Subsequently, it describes the ESR. spectra of the resulting radical anions $\mathbf{1}^{\dot{\ominus}}$ and $\mathbf{2}^{\dot{\ominus}}$. These studies also include the

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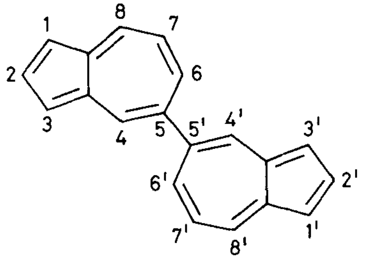

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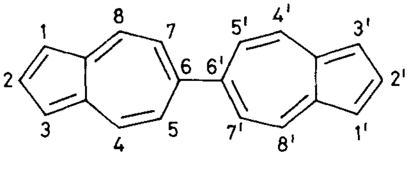

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1,1',3,3'-tetradeuteriated derivatives $\mathbf{1}$-d$_4^{\underset{\cdot}{\ominus}}$ and $\mathbf{2}$-d$_4^{\underset{\cdot}{\ominus}}$. In the case of $\mathbf{2}^{\underset{\cdot}{\ominus}}$ and $\mathbf{2}$-d$_4^{\underset{\cdot}{\ominus}}$, they are complemented by the use of the ENDOR. technique.

Results. - *Polarography and cyclic voltammetry.* The 5,5'- and 6,6'-biazulenyls (**1** and **2**), as well as the reference compound azulene (**3**), were reduced polarographically in DMF with tetraethylammonium bromide (0.1 M) and Ag/AgCl as the supporting electrolyte and the reference electrode, respectively. In the potential range less negative than -2 V, either **1** and **2** yield two half-waves at $E_{1/2}^{(1)}$ and $E_{1/2}^{(2)}$, while only one, at $E_{1/2}^{(1)}$, is observed for **3** [5]. *Table 1* gives the reduction potentials, $E_{1/2}^{(1)}$ and $E_{1/2}^{(2)}$, along with the electron transfer processes occurring at them. Each of the half-waves is attributed to the uptake of one electron, so that at $E_{1/2}^{(1)}$ the neutral molecules **1**, **2** and **3** are converted to the radical anions $\mathbf{1}^{\underset{\cdot}{\ominus}}$, $\mathbf{2}^{\underset{\cdot}{\ominus}}$ and $\mathbf{3}^{\underset{\cdot}{\ominus}}$. Further reduction of $\mathbf{1}^{\underset{\cdot}{\ominus}}$ and $\mathbf{2}^{\underset{\cdot}{\ominus}}$ at $E_{1/2}^{(2)}$ leads to the dianions $\mathbf{1}^{⊜}$ and $\mathbf{2}^{⊜}$. This interpretation is fully supported by cyclic voltammetry of the three compounds.

Figure 1 displays the cyclic voltammogrammes of **1**, **2** and **3**, which were performed in DMF with tetraethylammonium fluoroborate (0.1 M) as the supporting electrolyte. Mercury coated platinum disc and Ag/AgCl served as the working and reference electrode, respectively. The two half-waves for **1** and **2**, and the one of **3** appear at potentials which, in the limits of experimental error, agree with the polarographic data $E_{1/2}^{(1)}$ and $E_{1/2}^{(2)}$ in *Table 1.* It is evident that all of these waves can be considered as reversible.

Cyclic voltammetry also provides information about the following-up reactions, in which respect the behaviour of **2** is different from that of **1** and **3**. Whereas for **2** no additional re-oxidation half-waves are observed, the presence of such anodic

Table 1. *Polarographic half-wave reduction potentials,* $E_{1/2}$ *in Volts, for 5,5'- and 6,6'-biazulenyl (***1** *and* **2**, *respectively) and azulene* (**3**). All values[a]) are standardized to the SCE scale by taking the $E_{1/2}^{(1)}$ value of **3** as reference [5]

	1	**2**	**3**
$E_{1/2}^{(1)}$	-1.50 $(\mathbf{1}+e^{\ominus}\rightarrow\mathbf{1}^{\underset{\cdot}{\ominus}})$	-1.19 $(\mathbf{2}+e^{\ominus}\rightarrow\mathbf{2}^{\underset{\cdot}{\ominus}})$	-1.63 $(\mathbf{3}+e^{\ominus}\rightarrow\mathbf{3}^{\underset{\cdot}{\ominus}})$
$E_{1/2}^{(2)}$	-1.77 $(\mathbf{1}^{\underset{\cdot}{\ominus}}+e^{\ominus}\rightarrow\mathbf{1}^{⊜})$	-1.39 $(\mathbf{2}^{\underset{\cdot}{\ominus}}+e^{\ominus}\rightarrow\mathbf{2}^{⊜})$	

[a]) Relative experimental error: ± 0.01 V.

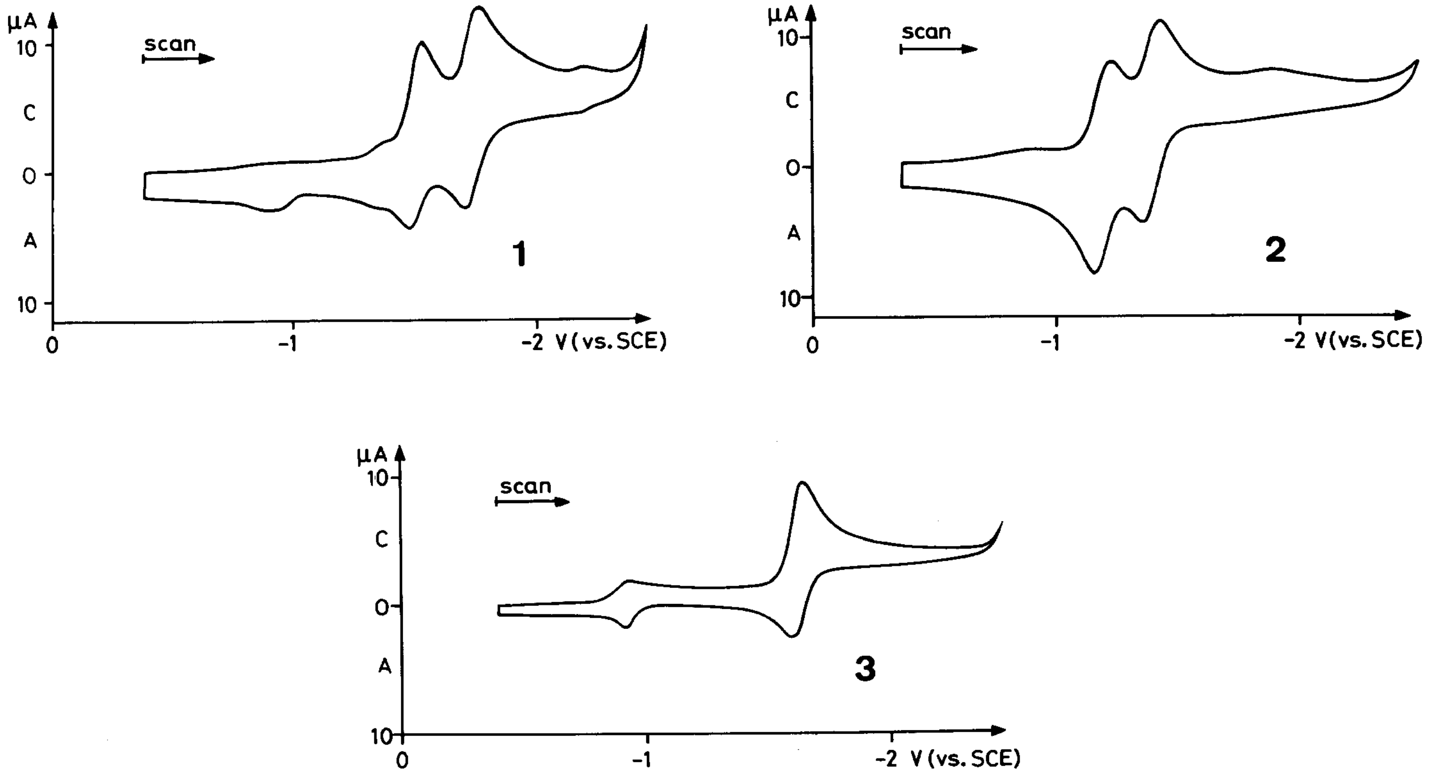


Fig. 1. *Cyclic voltammogrammes of 5,5'- and 6,6'-biazulenyl* (**1** *and* **2**) *and of azulene* (**3**). Solvent DMF, counter-ion $Et_4N^{\oplus}$, temperature 298 K. The curves are photographic reproductions of records taken on an oscilloscope. C = cathodic, A = anodic current.

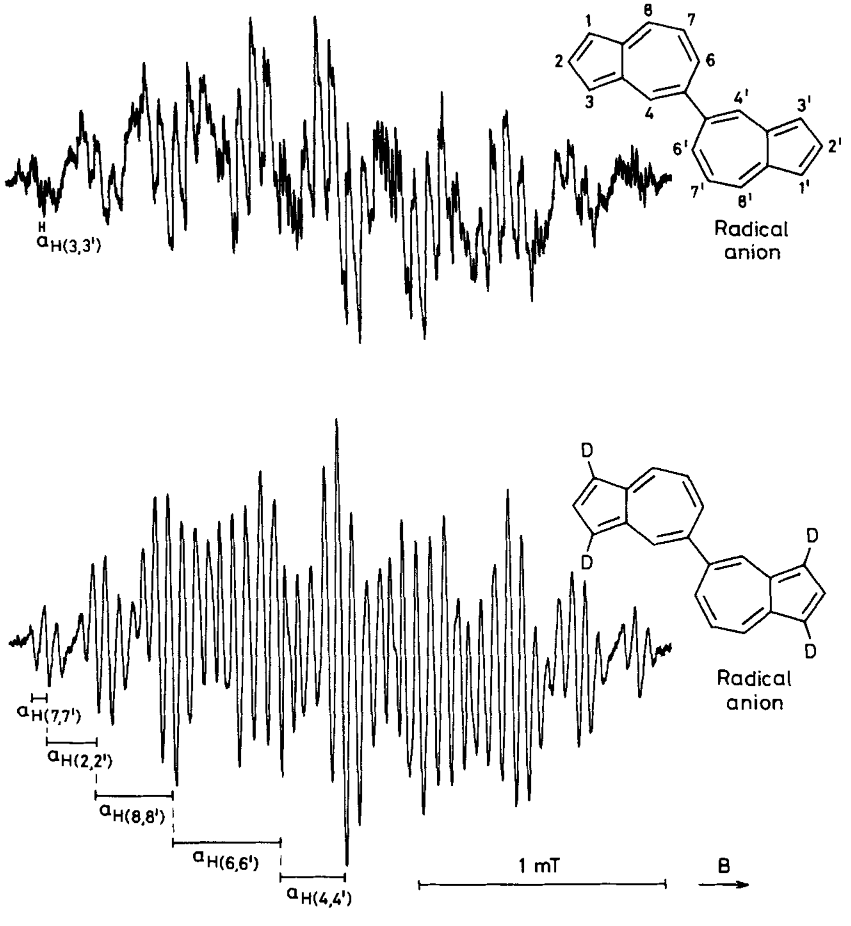


Fig. 2. *ESR. spectra of the radical anions of 5,5'-biazulenyl* (**1**) (top) *and its 1,1',3,3'-tetradeuterio-derivative* (**1**-d_4; isotopic purity *ca.* 90 percent) (bottom). Solvent DME, counter-ion $K^{\oplus}$, temperature 183 K

waves is revealed by new peaks in the voltammogrammes of **1** and **3** *(Fig. 1)*. These peaks have their cathodic equivalents, as confirmed by subsequent scannings. In the case of **1**, it was found that the new peaks do not show up when the voltage scan is reversed after the appearance of the first half-wave at $E_{1/2}{}^{(1)}$ ($\mathbf{1} + e^{\ominus} \rightarrow \mathbf{1}^{\ominus}$). The following-up reactions must thus be preceded by the uptake of a second electron ($\mathbf{1}^{\ominus} + e^{\ominus} \rightarrow \mathbf{1}^{\ominus}$).

ESR. and ENDOR. spectra. The radical anions of 5,5'- and 6,6'-biazulenyl were prepared from the respective neutral compounds (**1**) and (**2**) by reaction with potassium in 1,2-dimethoxyethane (DME) and by electrolytic reduction in *N,N'*-dimethylformamide (DMF) with tetraethylammonium perchlorate (0.1 M) as the supporting salt. The radical anions $\mathbf{1}^{\ominus}$ and $\mathbf{2}^{\ominus}$ differ greatly in their stabilities. Whereas the half-lifetime of $\mathbf{1}^{\ominus}$ is about 10 min at 213 K, the concentration of $\mathbf{2}^{\ominus}$

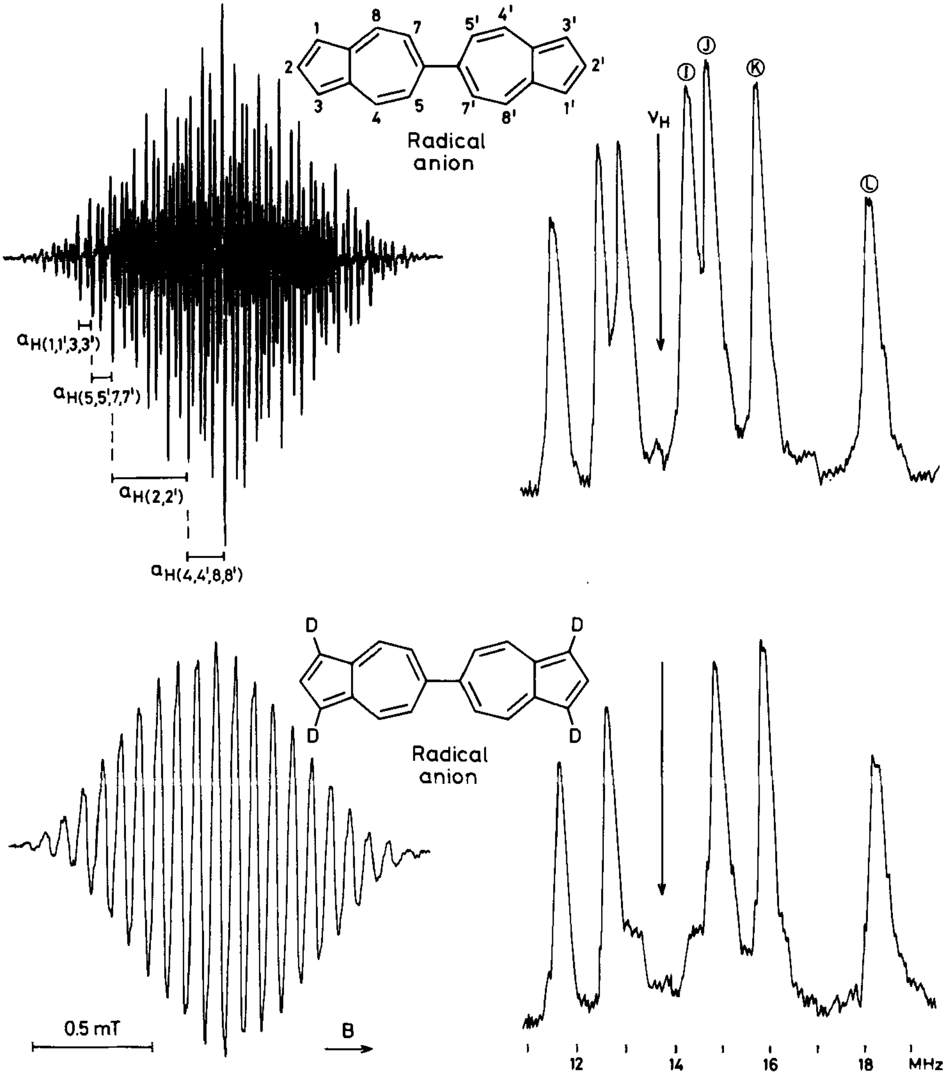


Fig. 3. *ESR. and ENDOR. spectra of the radical anions of 6,6'-biazulenyl* (**2**) (top) *and its 1,1',3,3'-tetradeuterio-derivative* (**2**-d$_4$; isotopic purity *ca.* 80 percent) (bottom). Solvent DME, counter-ion K$^\oplus$, temperature 183 K. The ENDOR. signals were assigned to the protons in the following positions: Ⓘ: 1,1';3,3'; Ⓙ: 5,5',7,7'; Ⓚ: 4,4',8,8' and Ⓛ: 2,2'. Note the shrinking of the signal Ⓘ on passing from **2**$^\ominus$ to **2**-d$_4^\ominus$. ν_H = frequency of the free proton.

does not appreciably decrease when a solution of this radical anion is allowed to stand for several days at room temperature.

Figure 2 shows the ESR. spectra of **1**$^\ominus$ and its 1,1',3,3'-tetradeuterio-derivative (**1**-d$_4^\ominus$), taken in DME at 183 K (counter-ion: K$^\oplus$). The low stability of these radical anions prevented an efficient use of the complementary ENDOR. technique.

Table 2. *Proton coupling constants, $a_{H(\mu)}$ in mT*a), *and g factors for the radical anions of 5,5′- and 6,6′-biazulenyl (***1** *and* **2**, *respectively) and azulene* (**3**)b)

	1$^{\ominus}$	**2**$^{\ominus}$		**3**$^{\ominus}$		
				c)	d)	e)
μ=1,1′	(±)0.005	(+)0.050	μ=1	(+)0.027	(+)0.027	[(+)0.01]
μ=2,2′	(−)0.209	(−)0.314	μ=2	(−)0.398	(−)0.398	[(−)0.20]
μ=3,3′	(+)0.015	(+)0.050	μ=3	(+)0.027	(+)0.027	[(+)0.01]
μ=4,4′	(−)0.259	(−)0.151	μ=4	(−)0.613	(−)0.632	[(−)0.31]
μ=5,5′	-	(−)0.082	μ=5	(+)0.121	(+)0.131	[(+)0.06]
μ=6,6′	(−)0.438	-	μ=6	(−)0.873	(−)0.894	[(−)0.44]
μ=7,7′	(+)0.054	(−)0.082	μ=7	(+)0.121	(+)0.131	[(+)0.06]
μ=8,8′	(−)0.315	(−)0.151	μ=8	(−)0.613	(−)0.632	[(−)0.31]
g	2.0026	2.0026	g	2.0027		

a) The signs of the coupling constants are those suggested by MO calculations.

b) Experimental error: ±0.001 mT in values $|a_{H(\mu)}| < 0.1$ mT, 0.002 mT in $|a_{H(\mu)}| > 0.1$ mT, and ±0.0001 in g.

c) Solvent DME, counter-ion K$^{\oplus}$, temperature 183 K.

d) Solvent DMF, counter-ion Et$_4$N$^{\oplus}$, temperature 213 K.

e) Average half-values.

On the other hand, both ESR. and ENDOR. spectra could be obtained for **2**$^{\ominus}$ and its 1,1′,3,3′-tetradeuterio-derivative (**2**-d$_4$$^{\ominus}$). They have been reproduced in *Figure 3;* the conditions are the same as for the ESR. spectra of *Figure 2. Table 2* lists the coupling constants $a_{H(\mu)}$ for **1**$^{\ominus}$ and **2**$^{\ominus}$, along with the corresponding data for the radical anion of azulene (**3**). Since the values $a_{H(\mu)}$ for **1**$^{\ominus}$ and **2**$^{\ominus}$ do not depend markedly on the solvent (DME or DMF), the counter-ion (K$^{\oplus}$ or Et$_4$N$^{\oplus}$), or the temperature (**1**$^{\ominus}$: 183-213 K; **2**$^{\ominus}$: 183-293 K), only one entry has been introduced for each radical anion in *Table 2*. The assignment of these values is justified by the procedure described below.

In general, unless the assignment of coupling constants $a_{H(\mu)}$ to protons at carbon π-centres μ can be derived from experiment, it is based on π-spin populations ρ_μ calculated for the centres μ by means of a MO model [6]. However, in the case of **3**$^{\ominus}$ and even more in that of **1**$^{\ominus}$ and **2**$^{\ominus}$, the values ρ_μ computed by the HMO-*McLachlan* [7] or the INDO method [8] correlate only poorly with the observed data $a_{H(\mu)}$ and could merely be used for the assignment of these data in a qualitative way. For **2**$^{\ominus}$, such a use was restricted to the relationship $|\rho_{4,4',8,8'}| > |\rho_{5,5',7,7'}|$ indicated by HMO-*McLachlan* calculations; it allowed one to distinguish between the coupling constants of the four-proton sets at these centres. The remaining values $a_{H(\mu)}$ for **2**$^{\ominus}$ could be unequivocally assigned from experimental evidence, owing to deuteriation in the 1,1′,3,3′-positions and to the unique multiplicity of the protons at the centres 2 and 2′.

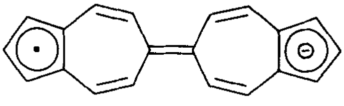
The situation was less favourable for **1**$^{\ominus}$, in which all protons are pairwise equivalent. The only experimental evidence, provided by deuteriation in the 1,1′- and 3,3′-positions, bore out the expectation that the two smallest coupling constants belong to the two pairs of protons in these positions. Nevertheless, a reliable assignment of the bulk of the hyperfine data for **1**$^{\ominus}$ was possible by means of the following argument. Comparison of these data with those of **3**$^{\ominus}$ reveals the existence of a striking resemblance between the coupling constants for **1**$^{\dot{\ominus}}$ and the halved values $a_{H(\mu)}$ of the protons in **3**$^{\dot{\ominus}}$. As it will be shown in the discussion, one has good reasons to assume that this close correspondence reflects an almost identical pattern of π-spin distributions. Therefore, the coupling constants for **1**$^{\dot{\ominus}}$ were assigned in such a way that the protons, of which the values $a_{H(\mu)}$ exhibit the afore-mentioned similarity, occupy analogous positions μ in **1**$^{\dot{\ominus}}$ and **3**$^{\dot{\ominus}}$ *(Table 2)*. The assignment was completed with the use of relationships $|\rho_{8,8'}| > |\rho_{4,4'}|$ and $|\rho_{3,3'}| > |\rho_{1,1'}|$, required by HMO-*McLachlan* calculations on **1**$^{\dot{\ominus}}$. These inequalities served to distinguish between the coupling constants of the pairs of protons at these centres (the pertinent positions are equivalent in **3**$^{\dot{\ominus}}$).

Discussion. - The 5,5'- and 6,6'-biazulenyls (**1** and **2**) differ considerably in the melting points (**1**: 106° [3], **2**: 315° [4]) and in their solubilities (**1** is almost as readily soluble as azulene, but **2** is only sparingly soluble in organic solvents). These properties indicate that **2** must have a considerably higher lattice energy than **1**, and it is tempting to suggest that the two azulene moieties are coplanar in the crystals of **2**, whereas they are not in those of **1**. The verification is left to X-ray structural analyses which so far have not been carried out. With respect to the conformation of **1** and **2** in solution, one would, nevertheless, anticipate that both biazulenyls should exhibit a comparable trend to twist about the bond linking the azulene moieties. This is because either bond should be an essential single one (HMO bond orders: $p_{55'} = 0.394$ in **1** and $p_{66'} = 0.391$ in **2**), and the considerable steric hindrance by the H-atoms in adjacent positions will affect the planarity of **1** and **2** to roughly the same extent.

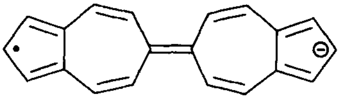
Substantially larger structural differences than for the neutral biazulenyls **1** and **2** are expected for the corresponding radical anions **1**$^{\dot{\ominus}}$ and **2**$^{\dot{\ominus}}$. It has been pointed out in the introduction that these differences can be considered as a consequence of linking the two azulene moieties in positions which are odd- (5) and even-numbered (6), respectively. More strictly speaking, the energies and the shape of the LUMO's of **1** and **2** are largely determined by the distinct inequality $|c_{65}| \ll |c_{66}|$ which holds for the LCAO coefficients $c_{6\mu}$ at the pertinent carbon π-centres μ and the LUMO ψ_6 of azulene (**3**) (HMO: $|c_{65}| = 0.102$ and $|c_{66}| = 0.511$). Because of this inequality, one predicts that two weakly interacting azulene π-systems would be an adequate model for discussing the 'one-electron properties' of **1**$^{\dot{\ominus}}$ such as the ease of formation and π-spin distribution. By contrast, this model is expected to fail for the interpretation of the analogous properties of **2**$^{\dot{\ominus}}$. In fact, the first half-wave reduction potential $E_{1/2}{}^{(1)}$ of **1**, which is a measure of the LUMO energy and the ease of formation of the radical anion, lies rather closely to the value $E_{1/2}{}^{(1)}$ of **3**, whereas the corresponding potential of **2** is considerably less negative *(Table 1)* (HMO energies of the LUMO's: $\alpha - 0.379\,\beta$ for **1**, $\alpha - 0.162\,\beta$ for **2** and $\alpha - 0.400\,\beta$ for **3**). The finding that reduction of either **1** and **2** gives rise to a second half-wave at a potential $E_{1/2}{}^{(2)}$, which is only by *ca.* 0.2 V more negative than $E_{1/2}{}^{(1)}$, is readily understood. Since, in the same range, only one half-wave appears upon reduction of **3**, the occurrence of two such waves for **1** and **2** must arise from the presence of two azulene moieties. Due to this structural feature, the formation of the dianions **1**$^{\ominus}$ and **2**$^{\ominus}$ is facilitated. It is noteworthy that the potential $E_{1/2}{}^{(1)}$ of **3** coincides with the average value of the potentials $E_{1/2}{}^{(1)}$ and $E_{1/2}{}^{(2)}$, at which the first and the second electron subsequently enter the LUMO of **1**.

The model of two weakly interacting azulene moieties also implies that the shape of the LUMO in each of these moieties of **1** should mimic the corresponding orbital of **3**. Since the shape of a LUMO is, in general, faithfully reproduced by the π-spin distribution in the radical anion [6], such a statement must equally apply to π-spin populations ρ_μ at the carbon centres μ in an azulene moiety of $\mathbf{1}^{\overset{\ominus}{\cdot}}$ and in $\mathbf{3}^{\overset{\ominus}{\cdot}}$. The model therefore presupposes a strong resemblance between the hyperfine data for $\mathbf{1}^{\overset{\ominus}{\cdot}}$ and the halved values $a_{H(\mu)}$ of the protons at the analogous positions μ in $\mathbf{3}^{\overset{\ominus}{\cdot}}$. Such a resemblance was, in fact, found by experiment, and served for the assignment of these data (see results).

In contrast to **1**, a substantial interaction between the azulene π-systems in **2** should markedly alter the shape of the LUMO in each of these systems relative to the corresponding orbital of **3**. The concomitant redistribution of the π-spin population among the centres μ in $\mathbf{2}^{\overset{\ominus}{\cdot}}$ is conveniently pictured by formulae like $\mathbf{2a}^{\overset{\ominus}{\cdot}}$, in which a five-membered ring carries the unpaired spin or the negative charge. Such formulae must have an appreciable weight in $\mathbf{2}^{\overset{\ominus}{\cdot}}$, whereas the analogous formulae for $\mathbf{1}^{\overset{\ominus}{\cdot}}$ are highly unfavourable.



$\mathbf{2a}^{\overset{\ominus}{\cdot}}$



$\mathbf{2b}^{\overset{\ominus}{\cdot}}$

An important mesomeric contribution to $\mathbf{2a}^{\overset{\ominus}{\cdot}}$ is the formula $\mathbf{2b}^{\overset{\ominus}{\cdot}}$, according to which a considerable portion of π-spin population should accumulate at the centres 2 and (by equivalence) 2'. In fact, a prominent feature of the hyperfine pattern of $\mathbf{2}^{\overset{\ominus}{\cdot}}$ is the large value $|a_{H(2,2')}|$ which exceeds by far the next largest one, $|a_{H(4,4',8,8')}|$, while the opposite is true for $\mathbf{3}^{\overset{\ominus}{\cdot}}$ ($|a_{H(2)}| < |a_{H(4,8)}|$).

The weight of the formulae like $\mathbf{2a}^{\overset{\ominus}{\cdot}}$ suggests that the linkage C(6)–C(6') between the azulene moieties acquires a substantial double bond character on passing from **2** to $\mathbf{2}^{\overset{\ominus}{\cdot}}$. On the other hand, the insignificance of analogous formulae for $\mathbf{1}^{\overset{\ominus}{\cdot}}$ indicates that the corresponding bond C(5)–C(5') remains an essential single one when **1** is converted to $\mathbf{1}^{\overset{\ominus}{\cdot}}$ (HMO: $p_{55'} = 0.401$ in $\mathbf{1}^{\overset{\ominus}{\cdot}}$ and $p_{66'} = 0.492$ in $\mathbf{2}^{\overset{\ominus}{\cdot}}$). It can therefore be expected that the trend to twist about the bond linking the azulene fragments will be considerably less in $\mathbf{2}^{\overset{\ominus}{\cdot}}$ than in $\mathbf{1}^{\overset{\ominus}{\cdot}}$.

A final comment concerns the kinetic stability (persistence) of $\mathbf{1}^{\overset{\ominus}{\cdot}}$ and $\mathbf{2}^{\overset{\ominus}{\cdot}}$. Experimental evidence (see results) indicates that $\mathbf{2}^{\overset{\ominus}{\cdot}}$ is not only thermodynamically more stable than $\mathbf{1}^{\overset{\ominus}{\cdot}}$ (as shown by the half-wave reduction potentials of **1** and **2**), but that it is also more persistent. Since according to cyclic voltammetry, the following-up reactions of **1** involve the dianion $\mathbf{1}^{\ominus\ominus}$ rather than the radical anion $\mathbf{1}^{\overset{\ominus}{\cdot}}$, two steps may be envisaged in the observed decay of the ESR. signal of $\mathbf{1}^{\overset{\ominus}{\cdot}}$:

(1) $2\,\mathbf{1}^{\overset{\ominus}{\cdot}} \rightarrow \mathbf{1} + \mathbf{1}^{\ominus\ominus}$ (disproportionation),

(2) $\mathbf{1}^{\ominus\ominus} \rightarrow$ products.

Experimental Part. - The syntheses of 5,5'- and 6,6'-biazulenyl (**1** and **2**, respectively) have been described elsewhere (**1** [3]; **2** [4]). Their 1,1',3,3'-tetradeuterio-derivatives (**1**-d_4 and **2**-d_4) were prepared from the corresponding hydrocarbons by repeated isotope exchange in 85 percent D_3PO_4 (*Merck*, Darmstadt). The estimated purity was 90 (**1**-d_4) and 80 percent (**2**-d_4).

The polarograph was a E-310-universal modular instrument of *Bruker*, while the equipment for cyclic voltammetry included a potentiostat/galvanostat model 173 and a current-to-voltage converter model 174, both of *Princeton Applied Research* (PAR). The spectral apparatus consisted of a *Varian* ENDOR-1700-system attached to a *Varian*-ESR-E9-spectrometer.

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