

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

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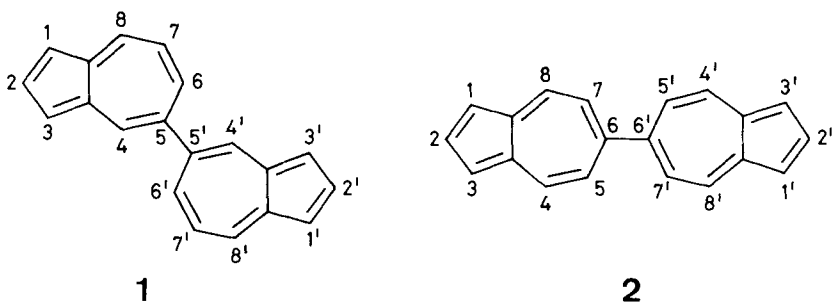
Summary

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**-d₄ and **2**-d₄). The reduction processes of **1** and **2** leading to these radical anions (**1**[•] and **2**[•]) and the dianions (**1**²⁻ and **2**²⁻) have been investigated by polarography and cyclic voltammetry. The half-wave reduction potential of **1** and the π -spin distribution in **1**[•] are consistent with the model of two weakly interacting azulene π -systems, whereas the analogous findings for **2** and **2**[•] 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 **1**[•] and **2**[•]. These studies also include the



1,1',3,3'-tetradeuteriated derivatives $1-d_4^\ominus$ and $2-d_4^\ominus$. In the case of $2^\ominus$ and $2-d_4^\ominus$, 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 $1^\ominus$, $2^\ominus$ and $3^\ominus$. Further reduction of $1^\ominus$ and $2^\ominus$ at $E_{1/2}^{(2)}$ leads to the dianions $1^\ominus$ and $2^\ominus$. 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 ($1 + e^\ominus \rightarrow 1^\ominus$)	-1.19 ($2 + e^\ominus \rightarrow 2^\ominus$)	-1.63 ($3 + e^\ominus \rightarrow 3^\ominus$)
$E_{1/2}^{(2)}$	-1.77 ($1^\ominus + e^\ominus \rightarrow 1^\ominus$)	-1.39 ($2^\ominus + e^\ominus \rightarrow 2^\ominus$)	

^{a)} Relative experimental error: ± 0.01 V.

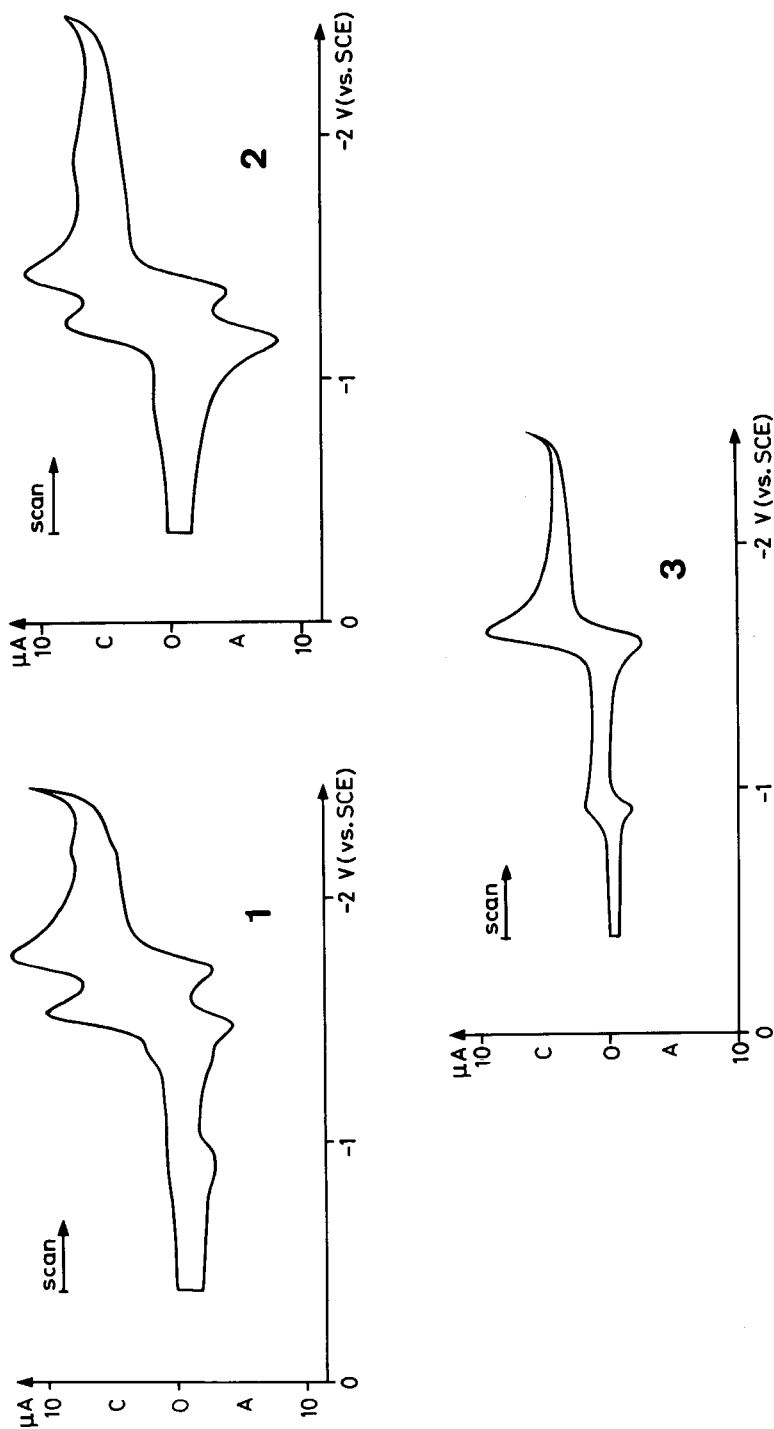


Fig. 1. Cyclic voltammograms of 5,5'- and 6,6'-biazulenyl (1 and 2) and of azulene (3). Solvent DMF, counter-ion Et_4N^+ , temperature 298 K. The curves are photographic reproductions of records taken on an oscilloscope. C = cathodic, A = anodic current.

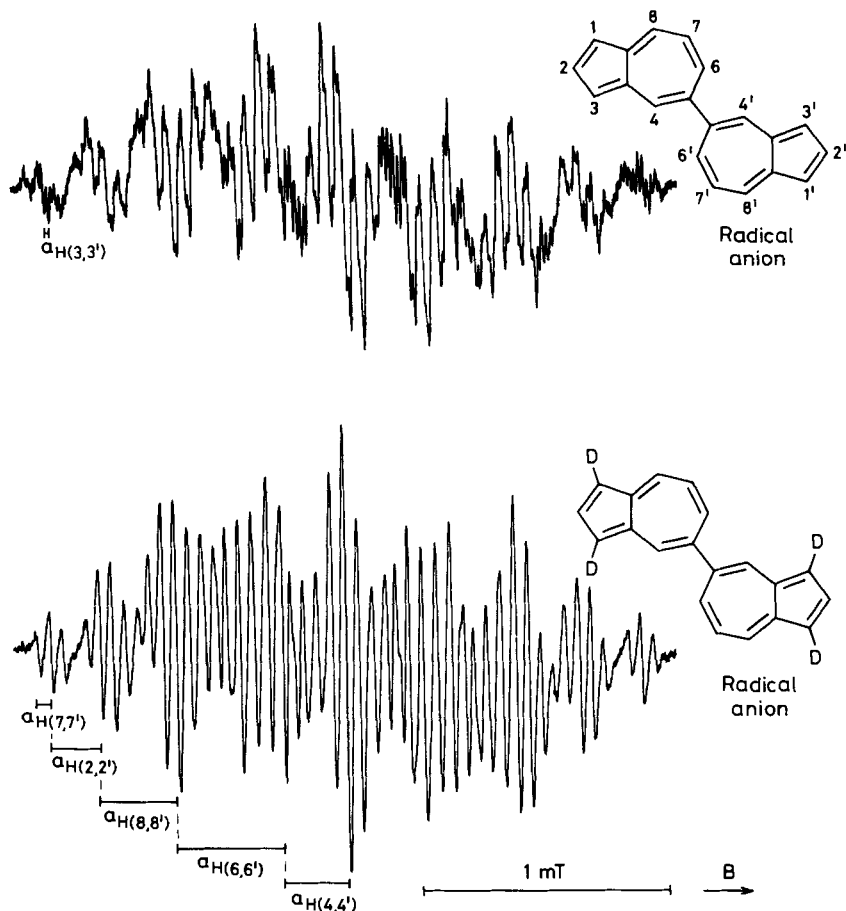


Fig. 2. ESR. spectra of the radical anions of 5,5'-biazulenyl (1) (top) and its 1,1',3,3'-tetradeuterio-derivative (1-d₄; isotopic purity ca. 90 percent) (bottom). Solvent DME, counter-ion K⁺, temperature 183 K

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 scanings. 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 $E_{1/2}^{(1)}$ ($1 + e^- \rightarrow 1^{\ominus}$). The following-up reactions must thus be preceded by the uptake of a second electron ($1^{\ominus} + e^- \rightarrow 1^{\ominus\ominus}$).

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 **1**^{•−} and **2**^{•−} differ greatly in their stabilities. Whereas the half-lifetime of **1**^{•−} is about 10 min at 213 K, the concentration of **2**^{•−}

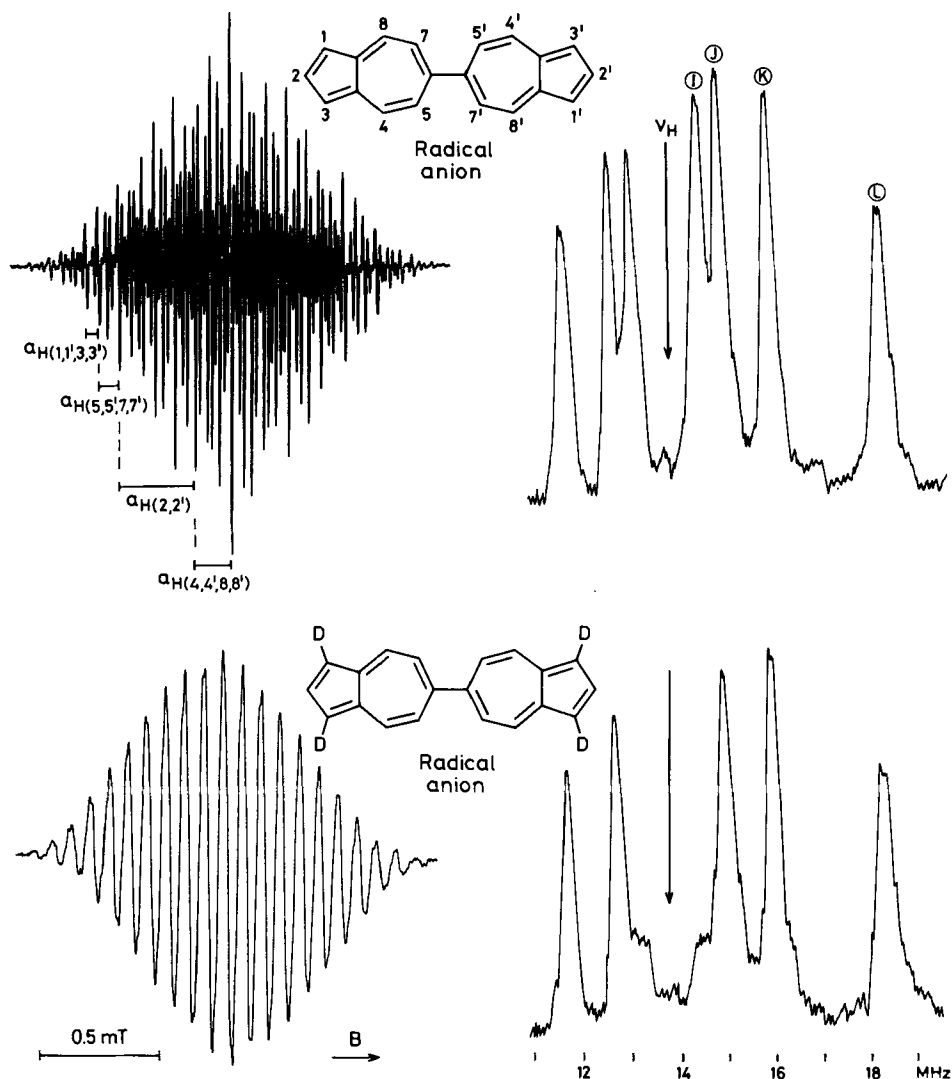


Fig. 3. ESR. and ENDOR. spectra of the radical anions of 6,6'-biazulenyl (2) (top) and its 1,1',3,3'-tetra-deuterio-derivative (2-d₄; isotopic purity ca. 80 percent) (bottom). Solvent DME, counter-ion K⁺, temperature 183 K. The ENDOR. signals were assigned to the protons in the following positions: ①: 1,1',3,3'; ②: 5,5',7,7'; ③: 4,4',8,8' and ④: 2,2'. Note the shrinking of the signal ④ on passing from 2[•] to 2-d₄[•]. 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[•] and its 1,1',3,3'-tetra-deuterio-derivative (1-d₄[•]), taken in DME at 183 K (counter-ion: K⁺). 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)
$\mu = 1, 1'$	($\pm$)0.005	(+)0.050		$\mu = 1$	(+)0.027	[(+)0.01]
$\mu = 2, 2'$	(-)0.209	(-)0.314		$\mu = 2$	(-)0.398	[(-)0.20]
$\mu = 3, 3'$	(+)0.015	(+)0.050		$\mu = 3$	(+)0.027	[(+)0.01]
$\mu = 4, 4'$	(-)0.259	(-)0.151		$\mu = 4$	(-)0.613	[(-)0.31]
$\mu = 5, 5'$	-	(-)0.082		$\mu = 5$	(+)0.121	[(+)0.06]
$\mu = 6, 6'$	(-)0.438	-		$\mu = 6$	(-)0.873	[(-)0.44]
$\mu = 7, 7'$	(+)0.054	(-)0.082		$\mu = 7$	(+)0.121	[(+)0.06]
$\mu = 8, 8'$	(-)0.315	(-)0.151		$\mu = 8$	(-)0.613	[(-)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 $Et_4N^\oplus$, 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 ($2\text{-}d_4^\ominus$). 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 $Et_4N^\oplus$), 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 deuteration 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 deuteration 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 $1^\ominus$ and the halved values $a_{H(\mu)}$ of the protons in $3^\ominus$. 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 $1^\ominus$ 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 $1^\ominus$ and $3^\ominus$ (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 $1^\ominus$. These inequalities served to distinguish between the coupling constants of the pairs of protons at these centres (the pertinent positions are equivalent in $3^\ominus$).

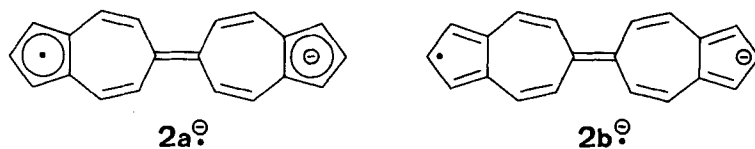
Discussion. – The 5,5'- and 6,6'-biazulenyls (**1** and **2**) differ considerably in the melting points (**1**: 106° [3], **2**: 315° [4]) and in their solubilities (**1** is almost as readily soluble as azulene, but **2** is only sparingly soluble in organic solvents). These properties indicate that **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 $1^\ominus$ and $2^\ominus$. 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 $1^\ominus$ 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 $2^\ominus$. 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 $1^{\ominus\ominus}$ and $2^{\ominus\ominus}$ 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 **1**^{•−} and in **3**^{•−}. The model therefore presupposes a strong resemblance between the hyperfine data for **1**^{•−} and the halved values $a_{H(\mu)}$ of the protons at the analogous positions μ in **3**^{•−}. 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 **2**^{•−} is conveniently pictured by formulae like **2a**^{•−}, in which a five-membered ring carries the unpaired spin or the negative charge. Such formulae must have an appreciable weight in **2**^{•−}, whereas the analogous formulae for **1**^{•−} are highly unfavourable.



An important mesomeric contribution to **2a**^{•−} is the formula **2b**^{•−}, 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 **2**^{•−} 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 **3**^{•−} ($|a_{H(2)}| < |a_{H(4,8)}|$).

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

A final comment concerns the kinetic stability (persistence) of **1**^{•−} and **2**^{•−}. Experimental evidence (see results) indicates that **2**^{•−} is not only thermodynamically more stable than **1**^{•−} (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 **1**^{2−} rather than the radical anion **1**^{•−}, two steps may be envisaged in the observed decay of the ESR. signal of **1**^{•−}:

- (1) $2 \text{ 1}^{\bullet-} \rightarrow \text{1} + \text{1}^{2-}$ (disproportionation),
- (2) $\text{1}^{\bullet-} \rightarrow \text{products}$.

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**-d₄ and **2**-d₄) were prepared from the corresponding hydrocarbons by repeated isotope exchange in 85 percent D₃PO₄ (Merck, Darmstadt). The estimated purity was 90 (**1**-d₄) and 80 percent (**2**-d₄).

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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