Radical Cations of Alkylazulenes: An EPR and ENDOR Study

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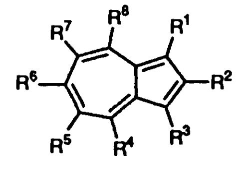
Azulene (**1**) and its alkyl derivatives **2**–**15** were oxidized in a UV-irradiated stationary system by mercury(II) trifluoroacetate in dichloromethane. These derivatives are: 4,6,8-trimethyl- (**2**), 1,4,6,8-tetramethyl- (**3**), 6-*tert*-butyl-1,4,8-trimethyl- (**4**), 2,4,6,8-tetramethyl- (**5**), 1,3-dimethyl- (**6**), 1,3-di-*tert*-butyl- (**7**), 1,3,5-tri-*tert*-butyl- (**8**), 1,3,6-trimethyl- (**9**), 6-*tert*-butyl-1,3-dimethyl- (**10**), 1,3,5,7-tetramethyl- (**11**), 1,3,4,6,8-pentamethyl- (**12**), 1,3,4,8-tetramethyl-6-propyl- (**13**), 6-*tert*-butyl-1,3,4,8-tetramethyl-(**14**) and 1,2,3,4,6,8-hexamethyl-azulene (**15**). Only radical cations substituted in both reactive positions C-1 and -3 (**6**$^{\cdot+}$–**15**$^{\cdot+}$) were sufficiently persistent to be characterized by their hyperfine data with the use of EPR spectroscopy. Those bearing *tert*-butyl substituents at C-1 and -3 (**7**$^{\cdot+}$ and **8**$^{\cdot+}$) or having three alkyl groups at the seven-membered ring in addition to the 1,3-dimethyl substituents (**12**$^{\cdot+}$–**15**$^{\cdot+}$) were also amenable to ENDOR and TRIPLE resonance studies. In contrast, the radical cations with none (**1**$^{\cdot+}$, **2**$^{\cdot+}$ and **5**$^{\cdot+}$) or only one methyl group in the positions C-1 and -3 (**3**$^{\cdot+}$ and **4**$^{\cdot+}$) rapidly reacted to yield follow-up products. For **1**$^{\cdot+}$–**4**$^{\cdot+}$, these products were identified by EPR and ENDOR spectroscopy as the radical cations of correspondingly substituted 1,1′-biazulenyls (**1a**–**4a**). A mechanism is proposed for the formation of the primary (**6**$^{\cdot+}$–**15**$^{\cdot+}$) and the secondary radical cations (**1a**$^{\cdot+}$–**4a**$^{\cdot+}$). The failure to detect the radical cation of biazulenyl **5a**$^{\cdot+}$, starting from **5**, must be due to instability of **5a**$^{\cdot+}$ in which two pairs of methyl substituents sterically interact. The high reactivity of the azulene radical cations in the positions C-1 and -3 is consistent with the unusually high π-spin populations $\rho_{1,3}$ at these centres, as manifested by the largest by far coupling constants $|a_{H1,3}|$ of the α- and methyl β-protons.

Azulene and its substituted derivatives are easily reduced, both by electrolysis and with alkali metals, and the relatively persistent radical anions thus formed have widely been studied by EPR and (in part) ENDOR spectroscopy.[1–6] In contrast, the corresponding radical cations cannot readily be generated from their neutral precursors by conventional methods such as electrolysis and oxidation with a Brønsted or a Lewis acid, although these methods have successfully been applied to other non-alternant hydrocarbons.[3,7] For nearly 20 years, the azulene radical cations studied by EPR spectroscopy had been restricted to those of the parent hydrocarbon and its 4,6,8-trimethyl derivative; they were obtained by oxidation of the neutral compounds with cobalt(III) acetate in trifluoroacetic acid, using a flow system.[8] More recently, EPR and ENDOR spectra could be observed for the radical cation of four azulene derivatives in a UV-irradiated stationary system which consisted of a precursor in trifluoroacetic acid or in dichloromethane containing tris(2,4-dibromophenyl)ammoniumyl antimonyhexachloride.[5] It is noteworthy that these radical cations had a fully substituted five-membered ring and that, at least, one of the substituents was an aryl group.

Here, we report on EPR and ENDOR spectra of radical cations generated from azulene (**1**) and its polyalkyl derivatives **2**–**15** with an oxidizing agent in a UV-irradiated stationary system.



	R¹	R²	R³	R⁴	R⁵	R⁶	R⁷	R⁸
1	H	H	H	H	H	H	H	H
2	H	H	H	Me	H	Me	H	Me
3	Me	H	H	Me	H	Me	H	Me
4	Me	H	H	Me	H	Bu^t	H	Me
5	H	Me	H	Me	H	Me	H	Me
6	Me	H	Me	H	H	H	H	H
7	Bu^t	H	Bu^t	H	H	H	H	H
8	Bu^t	H	Bu^t	H	Bu^t	H	H	H
9	Me	H	Me	H	H	Me	H	H
10	Me	H	Me	H	H	Bu^t	H	H
11	Me	H	Me	H	Me	H	Me	H
12	Me	H	Me	Me	H	Me	H	Me
13	Me	H	Me	Me	H	Pr	H	Me
14	Me	H	Me	Me	H	Bu^t	H	Me
15	Me	Me	Me	Me	H	Me	H	Me

Results

When mercury(II) trifluoroacetate was added to solutions of **1**–**15** in dichloromethane at *ca.* 250 K, their colour changed from blue to yellow. No EPR signals could be detected at this stage. Only upon intense UV-irradiation by Xe/Hg lamp, the solutions exhibited strong EPR spectra of radical cations. Modifications of this procedure, such as replacement of the trifluoroacetate by acetate or use of trifluoroacetic acid instead of its mercury salt, proved less successful. The EPR and ENDOR spectra were taken between 250 and 298 K. Lowering of the temperature below this range led, in general, to a marked decrease in the intensity of the spectra.

The compounds **1**–**15** can be divided into three classes, *A*, *B* and *C*, according to the decreasing persistence of their radical cations. These classes comprise azulenes with the following alkyl substitutions:

(*A*) 1,3-di-*tert*-butyl (**7**), 1,3,5-tri-*tert*-butyl (**8**), 1,3,4,6,8-

Table 1 Proton-coupling constants, a_{H_μ} in mT,[a] for the azulene radical cations **1**$^{\cdot+}$, **2**$^{\cdot+}$ and **6**$^{\cdot+}$–**15**$^{\cdot+}$

	μ				
	1,3	2	4,8	5,7	6
1$^{\cdot+b}$	−1.065 (2 α-H)	+0.152 (1 α-H)	+0.038 (2 α-H)	−0.415 (2 α-H)	+0.112 (1 α-H)
2$^{\cdot+c}$	−1.150 (2 α-H)	+0.150 (1 α-H)	−0.077 (6 β-H)	−0.438 (2 α-H)	−0.100 (3 β-H)
6$^{\cdot+}$	+1.161 (6 β-H)	+0.128 (1 α-H)	+0.070 (2 α-H)	−0.444 (2 α-H)	+0.108 (1 α-H)
7$^{\cdot+}$	+0.046 (18 γ-H)	+0.120 (1 α-H)	+0.070 (2 α-H)	−0.426 (2 α-H)	+0.101 (1 α-H)
8$^{\cdot+}$	+0.044 (18 γ-H)	+0.113 (1 α-H)	+0.044 (2 α-H)	−0.393 (1 α-H) +0.017 (9 γ-H)	+0.113 (1 α-H)
9$^{\cdot+}$	+1.171 (6 β-H)	+0.110 (1 α-H)	+0.068 (2 α-H)	−0.423 (2 α-H)	−0.110 (3 β-H)
10$^{\cdot+}$	+1.173 (6 β-H)	+0.110 (1 α-H)	+0.066 (2 α-H)	−0.417 (2 α-H)	<0.010 (9 γ-H)
11$^{\cdot+}$	+1.170 (6 β-H)	+0.123 (1 α-H)	+0.022 (2 α-H)	+0.485 (6 β-H)	+0.103 (1 α-H)
12$^{\cdot+}$	+1.126 (6 β-H)	+0.109 (1 α-H)	−0.074 (6 β-H)	−0.430 (2 α-H)	−0.109 (3 β-H)
13$^{\cdot+}$	+1.124 (6 β-H)	+0.117 (1 α-H)	−0.070 (6 β-H)	−0.427 (2 α-H)	−0.070 (2 β-H) +0.020 (2 γ-H)
14$^{\cdot+}$	+1.127 (6 β-H)	+0.118 (1 α-H)	−0.069 (6 β-H)	−0.424 (2 α-H)	<0.010 (9 γ-H)
15$^{\cdot+}$	+1.124 (6 β-H)	−0.151 (3 β-H)	−0.074 (6 β-H)	−0.424 (2 α-H)	−0.109 (3 β-H)

[a] Experimental error: ±0.001 mT for $a_{\mathrm{H}2}$, $a_{\mathrm{H}4,8}$ and $a_{\mathrm{H}6}$; ±0.002 mT for $a_{\mathrm{H}5,7}$; ±0.005 mT for $a_{\mathrm{H}1,3}$. [b] From ref. 8. [c] By fitting program[9] applied to the EPR spectrum in ref. 8.

pentamethyl (**12**), 1,3,4,8-tetramethyl-6-propyl (**13**), 6-*tert*-butyl-1,3,4,8-tetramethyl (**14**) and 1,2,3,4,6,8-hexamethyl (**15**); (*B*) 1,3-dimethyl (**6**), 1,3,6-trimethyl (**9**), 6-*tert*-butyl-1,3-dimethyl (**10**) and 1,3,5,7-tetramethyl (**11**); (*C*) none (**1**), 4,6,8-trimethyl (**2**), 1,4,6,8-tetramethyl (**3**), 6-*tert*-butyl-1,4,8-trimethyl (**4**) and 2,4,6,8-tetramethyl (**5**).

The radical cations **7**$^{\cdot+}$, **8**$^{\cdot+}$ and **12**$^{\cdot+}$–**15**$^{\cdot+}$ (class *A*) as well as **6**$^{\cdot+}$ and **9**$^{\cdot+}$–**11**$^{\cdot+}$ (class *B*), were sufficiently long-lived to be studied by EPR spectroscopy. Those of the class *A* were also amenable to the ENDOR and TRIPLE-resonance techniques, as they persisted for 20–40 min at 273–283 K after the UV irradiation was stopped.†

The EPR and ENDOR spectra of **15**$^{\cdot+}$ (class *A*) and the EPR spectrum of **10**$^{\cdot+}$ (class *B*) are shown in Figs. 1 and 2 as examples. Table 1 lists the hyperfine data for **6**$^{\cdot+}$–**15**$^{\cdot+}$ (g = 2.0027 ± 0.0001), refined by the application of a fitting program[9] to the EPR spectra. The corresponding values for **1**$^{\cdot+}$ and **2**$^{\cdot+}$, determined in a flow system,[8] are also given for comparison. The assignments of the coupling constants a_{H_μ} to the ring α-protons and the alkyl β-protons‡ in the positions μ of azulene follow the experimentally[5,8] and theoretically[10] well established sequence: $|a_{\mathrm{H}1,3}| > |a_{\mathrm{H}5,7}| > |a_{\mathrm{H}2}| > |a_{\mathrm{H}6}| > |a_{\mathrm{H}4,8}|$. The signs of a_{H_μ} are those required by theory; they have been confirmed by general-TRIPLE-resonance experiments carried out on the ENDOR signals of **7**$^{\cdot+}$, **8**$^{\cdot+}$ and **12**$^{\cdot+}$–**15**$^{\cdot+}$,[11] assuming that the coupling constants $a_{\mathrm{H}1,3}$ and $a_{\mathrm{H}5,7}$ with the largest absolute values are negative for the α- and positive for the β-protons.

The radical cations **1**$^{\cdot+}$–**5**$^{\cdot+}$ (class *C*) were too short-lived for EPR studies, as they rapidly reacted to yield secondary products. For **1**$^{\cdot+}$–**4**$^{\cdot+}$, *i.e.* with the exception of **5**$^{\cdot+}$, these products were identified by their EPR and ENDOR spectra as the relatively persistent radical cations of the correspondingly substituted 1,1′-biazulenyls **1a**–**4a**. In the case of **5**$^{\cdot+}$, no EPR spectrum attributable to **5a**$^{\cdot+}$ could be observed.

The biazulenyl structure of **1a**$^{\cdot+}$–**4a**$^{\cdot+}$ was corroborated by the finding that direct oxidation of **1a** leads to the same spectra as those obtained from **1**. In Fig. 3, the EPR and ENDOR spectra of **3a**$^{\cdot+}$, generated from **3**, are reproduced as an example, while Table 2 gives the proton-hyperfine data of **1a**$^{\cdot+}$–**4a**$^{\cdot+}$ (g = 2.0027 ± 0.0001). The assignments and the absolute signs of the coupling constants a_{H_μ} rely on the values calculated by the McLachlan procedure;[12] the relative signs are in accord with the TRIPLE-resonance spectra.

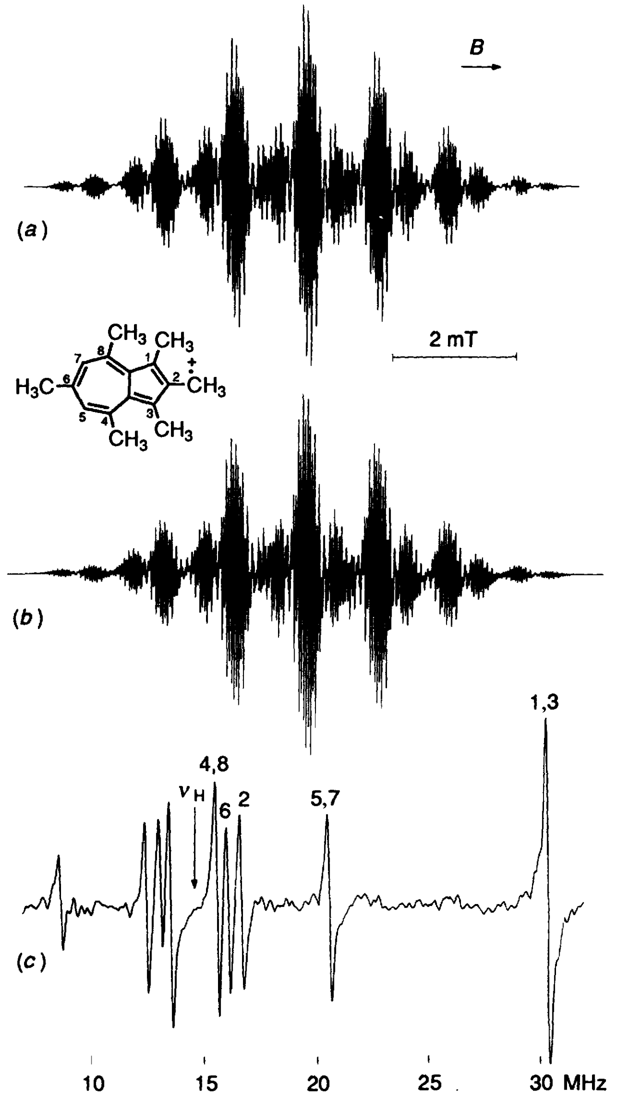


Fig. 1 (*a*) EPR spectrum of **15**$^{\cdot+}$; solvent CH_2Cl_2, counterion $CF_3CO_2^-$, temperature 253 K. (*b*) Simulation using the coupling constants in Table 1; line-shape Lorentzian, line-width 0.030 mT. (*c*) Proton-ENDOR spectrum taken under the same conditions.

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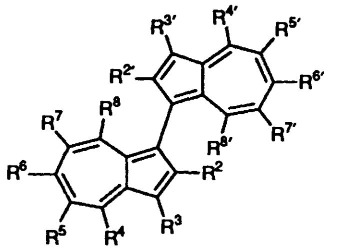
† Our equipment does not allow the use of the ENDOR technique while the sample is irradiated.

‡ In EPR spectroscopy, protons separated from a π-centre by 0,1,2, . . . sp^3-hybridized carbon atoms are denoted α,β,γ, . . .

Table 2 Proton-coupling constants, a_{H_μ} in mT,[a] for the 1,1'-biazulenyl radical cations **1a**$^{\bullet+}$–**4a**$^{\bullet+}$

	μ				
	2,2'	3,3'	4,4',8,8'	5,5',7,7'	6,6'
1a$^{\bullet+}$	−0.069 (2 α-H)	−0.246 (2 α-H)	+0.069 (4 α-H)	−0.305 (4 α-H)	+0.095 (2 α-H)
2a$^{\bullet+}$	−0.068 (2 α-H)	−0.262 (2 α-H)	−0.068 (12 β-H)	−0.298 (4 α-H)	−0.068 (6 β-H)
3a$^{\bullet+}$	−0.051 (2 α-H)	+0.236 (6 β-H)	−0.076 (12 β-H)	−0.313 (2 α-H) −0.291 (2 α-H)	−0.076 (6 β-H)
4a$^{\bullet+}$	−0.050 (2 α-H)	+0.242 (6 β-H)	−0.075 (6 β-H) −0.068 (6 β-H)	−0.308 (2 α-H) −0.292 (2 α-H)	< 0.010 (18 γ-H)

[a] Experimental error: ±0.01 mT in $|a_{H_\mu}|$ < 0.1 mT; ±0.02 in $|a_{H_\mu}|$ > 0.1 mT



	$R^{2,2'}$	$R^{3,3'}$	$R^{4,4'}$	$R^{5,5'}$	$R^{6,6'}$	$R^{7,7'}$	$R^{8,8'}$
1a	H	H	H	H	H	H	H
2a	H	H	Me	H	Me	H	Me
3a	H	Me	Me	H	Me	H	Me
4a	H	Me	Me	H	Bu^t	H	Me
5a	Me	H	Me	H	Me	H	Me

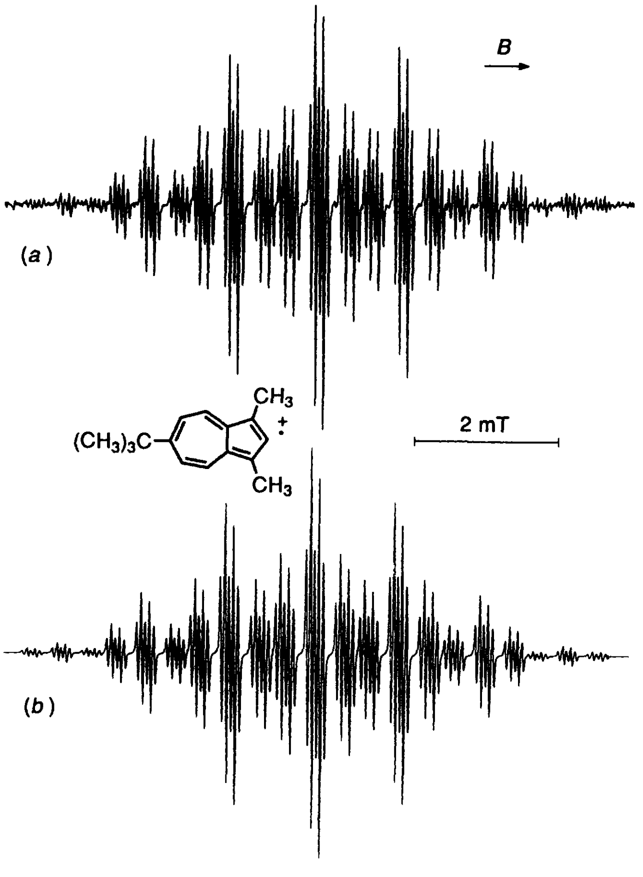


Fig. 2 (*a*) EPR spectrum of **10**$^{\bullet+}$; solvent CH_2Cl_2, counterion $CF_3CO_2^-$, temperature 273 K. (*b*) Simulation using the coupling constants in Table 1; line-shape Lorentzian, line-width 0.015 mT.

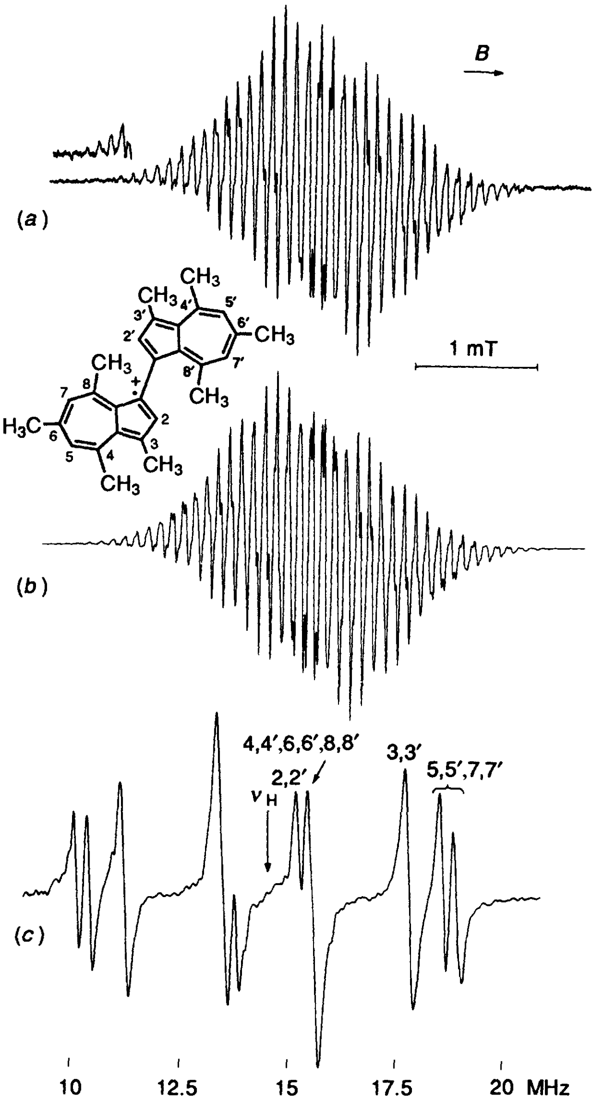


Fig. 3 (*a*) EPR spectrum of **3a**$^{\bullet+}$; solvent CH_2Cl_2, counterion $CF_3CO_2^-$, temperature 263 K. (*b*) Simulation using the coupling constants in Table 2; line-shape Lorentzian, line-width 0.030 mT. (*c*) Proton-ENDOR spectrum taken under the same conditions.

Discussion

Spin Distribution.—The HOMO and the LUMO of azulene (**1**) are a paradigm for the frontier orbitals of a non-alternant hydrocarbon which lack the pairing properties exhibited by such orbitals of alternant hydrocarbons.[13] As illustrated by the orbital diagrams in Fig. 4, the LUMO ψ_6 exhibits large $|c_{6\mu}|$ values of the LCAO coefficients at the even- and small ones at the odd-numbered centres μ. Consequently, the π-spin popu-

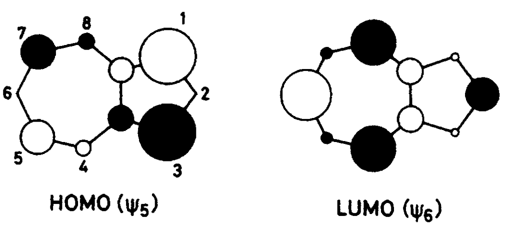
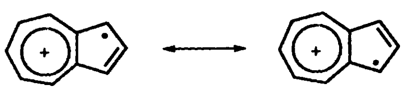


Fig. 4 Orbital diagrams of the HOMO and the LUMO of azulene (**1**)

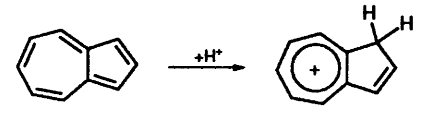
lations ρ_μ in the radical anion **1**$^{\cdot-}$ are high and positive at the former ($\mu = 2, 4, 6$ and 8), but low and negative at the latter ($\mu = 1, 3, 5$ and 7). The clear-cut distinction between the two sets of centres μ is shared by the HOMO ψ_5 and the radical cation **1**$^{\cdot+}$; the situation is, however, diametrically opposed. The $|c_{5\mu}|$ values in ψ_5 are zero or small at the even- and large at odd-numbered centres μ (Fig. 4), so that **1**$^{\cdot+}$ has high and positive π-spin populations at the latter ($\mu = 1, 3, 5$ and 7), but low and negative at the former ($\mu = 2, 4, 6$ and 8). The proportionality factors converting ρ_μ into the coupling constants a_{H_μ} have similar magnitude for an α-proton at the centre μ and the three β-protons in a freely rotating methyl substituent which replaces this α-proton. However, on passing from ρ_μ to a_{H_μ}, the sign is changed for the α- but retained for the β-protons.[14] Thus, the coupling contants a_{H_μ} for **1**$^{\cdot+}$, **2**$^{\cdot+}$ and **6**$^{\cdot+}$–**15**$^{\cdot+}$ fall into four distinct groups: For α-protons, they are large and negative at $\mu = 1, 3, 5$ and 7 but small and positive at $\mu = 2, 4, 6$ and 8, whereas for the β-protons, they are large and positive at $\mu = 1, 3, 5$ and 7 but small and negative at $\mu = 2, 4, 6$ and 8.

The prominent feature of the π-spin distribution in **1**$^{\cdot+}$ is the occurrence of extremely high π-spin populations ρ_μ at the centres C-1 and 3 ($\rho_1 = \rho_3 \approx 0.4$) which, therefore, represent by far the most reactive positions. Accordingly, the two mesomeric formulae significantly contribute to the structure of **1**$^{\cdot+}$. The proton-hyperfine data in Table 1 testify that this structure is not markedly altered by alkyl substitutions. General rules for the effect of such substitutions on the π-spin distribution in the azulene radical cations, like those formulated in the study of corresponding radical anions,[6] cannot readily be derived. This is because the data for the radical cations unsubstituted in both 1 and 3 positions are scarce and because the coupling constants a_{H_μ} of the β-protons cannot simply be taken as a measure of the π-spin populations ρ_μ at the substituted centres μ. These values depend not only on ρ_μ but also on the charge populations q_μ at the centres μ in question; hyperconjugation implies that such a dependence is much more pronounced for the positively charged centres in the radical cations than for the negatively charged ones in the radical anions.[14,15]



Interestingly, both the MO models and the experimental hyperfine data in Table 2 point out that the general pattern of the π-spin distribution with the high positive ρ_μ values at the odd-numbered centres ($\mu = 3, 3', 5, 5'$ and $7, 7'$) is on the whole preserved on passing from the radical cations of azulenes to those of 1,1′-biazulenyls.

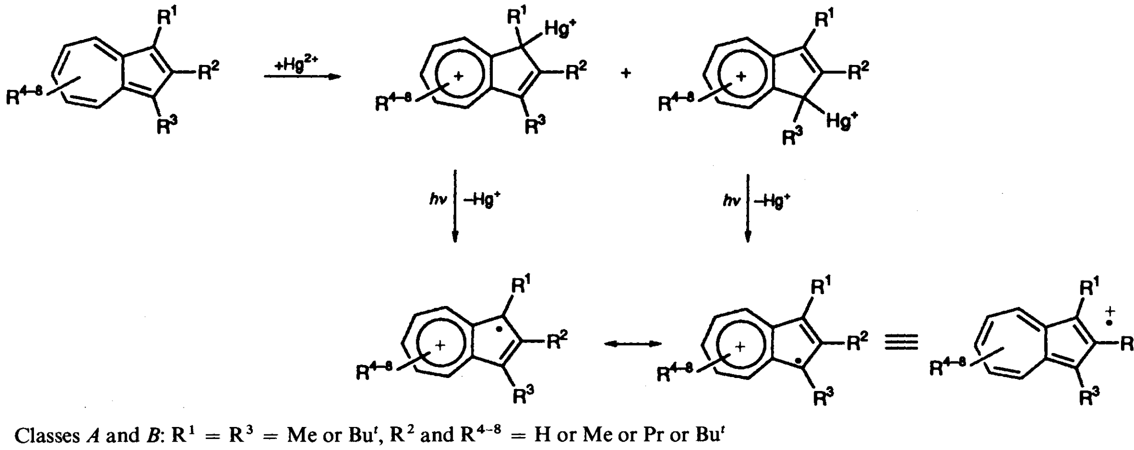
Formation of Radical Cations.—The change of colour from blue to yellow observed for the solutions of **1**–**15** in dichloromethane upon treatment with mercury(II) trifluoroacetate should be due to addition of Hg^{2+} ion at the position 1 or 3 (Schemes 1 and 2). The adducts have the structure of a Hg^+-substituted vinyltropylium ion, because their electronic spectra resemble that of the conjugate acid of azulene.[16]



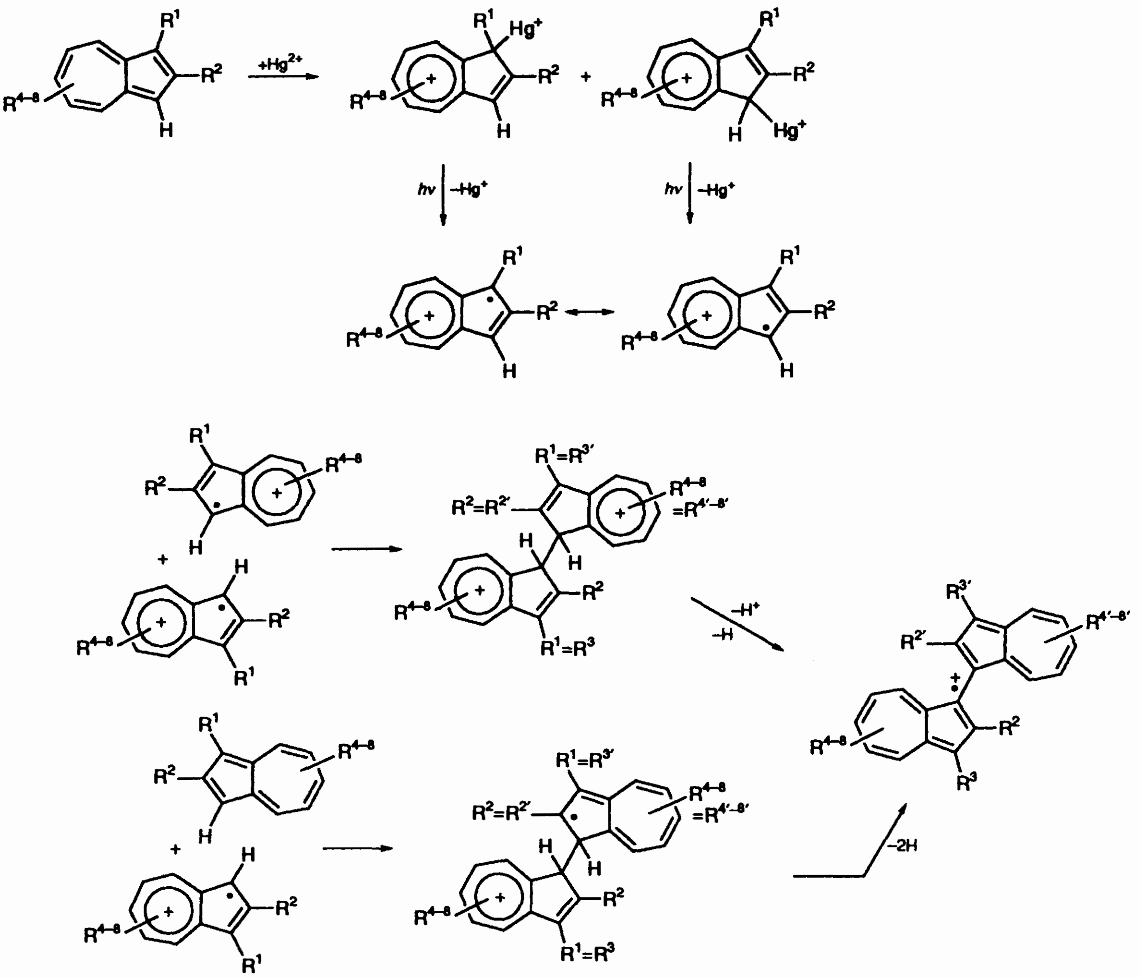
Considering the marked propensity of azulenes to electrophilic substitution in the positions C-1 and 3, this structure of an adduct should be preferred to a charge transfer complex such as that described for hexamethylbenzene and mercury(II) trifluoroacetate.[17]

UV-irradiation led to loss of the Hg^+ ion and to formation of the azulene radical cations. Their persistence proved to depend on the position, the number and the nature of the alkyl substituents, most relevant being the presence of such groups in the reactive positions C-1 and 3. Only the azulene radical cations bearing alkyl substituents in both positions (Classes *A* and *B*; Scheme 1) were persistent enough to be characterized by their hyperfine data (Table 1), whereby the persistence of **7**$^{\cdot+}$, **8**$^{\cdot+}$ and **12**$^{\cdot+}$–**15**$^{\cdot+}$ (Class *A*) was markedly higher than that of **6**$^{\cdot+}$ and **9**$^{\cdot+}$–**11**$^{\cdot+}$ (Class *B*). The minimum condition for the primary radical cation to yield a readily observable EPR spectrum was the 1,3-dimethyl substitution; it is met in **6**$^{\cdot+}$. An additional alkyl group in the 6-position of **9**$^{\cdot+}$ and **10**$^{\cdot+}$ or in the positions C-5 and 7 of **11**$^{\cdot+}$ did not significantly enhance the persistence of these radical cations relative to **6**$^{\cdot+}$. However, a considerably longer life-time resulted from replacement of the methyl groups in the positions C-1 and 3 by the bulky *tert*-butyl substituents, as is the case in **7**$^{\cdot+}$ and **8**$^{\cdot+}$. A similar effect was achieved in **12**$^{\cdot+}$–**15**$^{\cdot+}$ by introduction of three further alkyl substituents in the positions C-4, -6 and -8 in addition to the methyl groups in C-1 and -3.

In contrast, the radical cations **1**$^{\cdot+}$–**5**$^{\cdot+}$ having both or one of



Scheme 1 Classes *A* and *B*: $\text{R}^1 = \text{R}^3$ = Me or Bu^t, R^2 and R^{4-8} = H or Me or Pr or Bu^t



Scheme 2 Class *C*: R^1 = H or Me, R^2 and R^{4-8} = H or Me or Bu^t

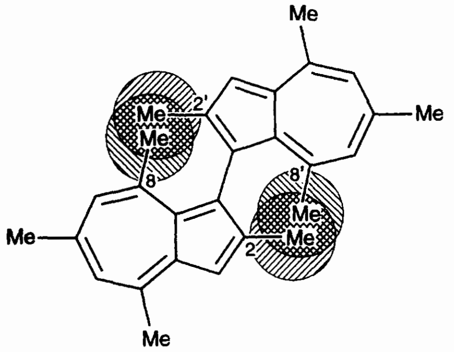


Fig. 5 Steric interaction of the methyl substituents in the C-2,8′- and 2′,8 positions of **5a**$^{\bullet+}$

the reactive positions C-1 and 3 unprotected by alkyl groups were too short-lived to be characterized by their hyperfine data (Class *C*), as they rapidly decayed to form secondary products. In the case of **1**$^{\bullet+}$–**4**$^{\bullet+}$, the presence of the radical cations of correspondingly substituted 1,1′-biazulenyls **1a**–**4a** was revealed by EPR and ENDOR spectroscopy (Table 2).

The formation of **1a**$^{\bullet+}$–**4a**$^{\bullet+}$ could proceed *via* dimerization of **1**$^{\bullet+}$–**4**$^{\bullet+}$ to the dications of 1,1′-dihydro-1,1′-biazulenyls and/or *via* attack of **1**$^{\bullet+}$–**4**$^{\bullet+}$ on their neutral precursors **1**–**4** (still present in the solutions) to yield the radical cations of these dimers. Rapid conversion to the fully conjugated **1a**$^{\bullet+}$–**4a**$^{\bullet+}$ must formally occur by loss of a hydrogen atom and a proton from the dications of the dihydrobiazulenyls or by elimination of two hydrogen atoms from the corresponding radical cations (Scheme 2). The failure to observe the spectra **5a**$^{\bullet+}$, starting from **5**, is certainly due to an overcrowding by the methyl groups in the positions C-2 and 8′ as well as in 2′ and 8 (Fig. 5). The steric congestion hindered **5a**$^{\bullet+}$ from adopting the energetically preferred planar geometry and made this radical cation, if formed at all, too short-lived to be detected by EPR spectroscopy.

It is noteworthy that spectra of π-dimers $\mathbf{1}_2^{\bullet+}$–$\mathbf{5}_2^{\bullet+}$ which might be formed by association of **1**$^{\bullet+}$–**5**$^{\bullet+}$ with their neutral precursors **1**–**5**, were in no case observed. Such relatively persistent dimers which have frequently been encountered with benzenoid hydrocarbons,[17,18] could be suggested as intermediates in the conversion of **1**$^{\bullet+}$–**4**$^{\bullet+}$ into the radical cations of the covalently bonded dihydrobiazulenyls.

Experimental

Azulene (**1**) was a commercial product of EGA, Chemie. The alkyl derivatives **2**–**6** and **9**–**15** were recently prepared[19] (for **2** see also ref. 20). The *tert*-butyl-substituted azulenes **7** (m.p. 94.8–96.2 °C; see also ref. 21) and **8** (m.p. 136.6–137.5 °C) were obtained on treating **1** with *tert*-butyl alcohol in diethyl ether containing tetrafluoroboric acid (in analogy to the procedure in ref. 22). 1,1-Biazulenyl (**1a**)[23] was a generous gift from Professor Kahei Takase, Tohoku University, Sendai, Japan. Mercury(II) trifluoroacetate was purchased from Aldrich. The azulenes, **1**–**15**, and the mercury salt were used in a ratio 1 : 1 and in a concentration of 10^{-4}–10^{-3} mol dm^{-3}. The Xe/Hg lamp for UV irradiation was a 1000 W apparatus of PTI, Hamburg. EPR spectra were taken on Varian-E3- and E9-instruments, while a Bruker-ESP-300 system served for ENDOR and TRIPLE-resonance studies.

Acknowledgements

This work was supported by the Swiss National Science Foundation.

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Paper 4/05264A
Received 30*th August* 1994
Accepted 25*th October* 1994