

The Electron Spin Resonance Spectra of Dialkyl- and Diaryl-diacetylene Radical Cations

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When dialkyl- and diaryl-diacetylenes are photolysed in trifluoroacetic acid containing mercury(II) trifluoroacetate, the e.s.r. spectra of the corresponding radical cations can be observed.

No electron spin resonance spectra of monomeric acetylene radical cations have hitherto been observed in fluid solution. One-electron oxidation of dialkylacetylenes gives tetra-alkylcyclobutadiene radical cations by dimerisation (equation 1),¹ or hexa-alkylbutadiene radical cations by rearrangement (equation 2),² and, under the same conditions, diarylacetyl-

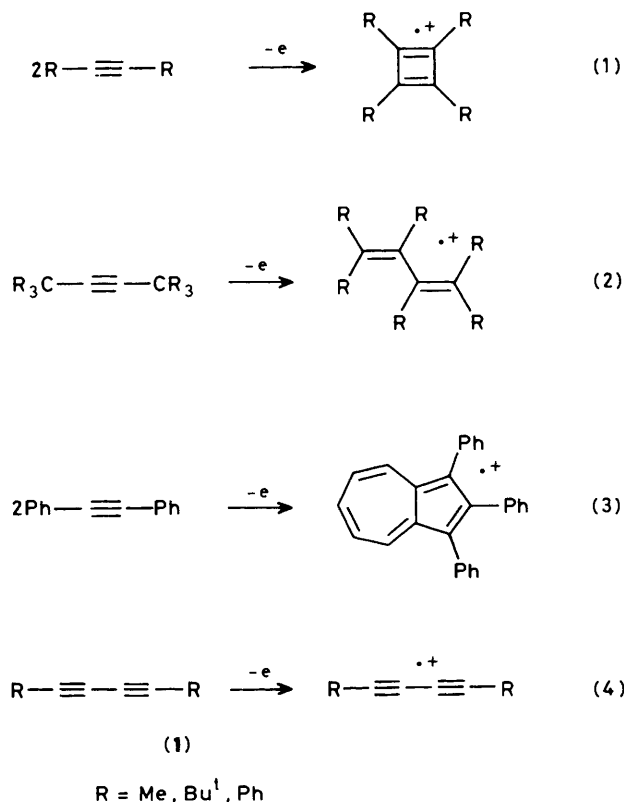
enes give the triarylazulene radical cations in a process involving both dimerization and rearrangement (equation 3).³ We report now the observation of the e.s.r. spectra of monomeric dialkyl- and diaryl-diacetylene radical cations⁴ (equation 4). Details of the spectra are given in Table 1.

Hexa-2,4-diyne (**1**, R = Me) (*ca.* 10 mg) in trifluoroacetic

Table 1. E.s.r. spectra of dialkyl- and diaryl-diacetylene radical cations and anions.

Compound	Radical cation ^a			Radical anion		
	T/K	a(H)/G ^b	g	T/K	a(H)/G	g
MeC≡C-C≡CMe	263	8.00(6H)	1.9997			
Bu ^t C≡C-C≡CBu ^t	263	0.61(18H)	1.9998		<0.1	1.9830 ^c
PhC≡C-C≡CPh	263	2.34(4H <i>ortho</i>) 0.70(4H <i>meta</i>) 3.20(2H <i>para</i>)	2.0013	203	2.47(4H <i>ortho</i>) 0.67(4H <i>meta</i>) 3.96(2H <i>para</i>)	2.0022 ^d

^a In CF₃CO₂H. ^b 1 G = 10⁻⁴ T. ^c In tetrahydrofuran, counterion Na⁺ or K⁺. ΔH_{pp} 0.25 G.⁵ ^d In (MeOCH₂)₂: counterion Na⁺ or K⁺.^{5,6}



acid (1 cm³) containing mercury(II) trifluoroacetate (100 mg) at 8°C was photolysed in the e.s.r. cavity with light from a high-pressure mercury arc filtered through Pyrex glass, whence a septet spectrum which we assign to the radical cation (1^{•+}, R = Me) was observed. 2,2,7,7-Tetramethylocta-3,5-diyne (1, R = Bu^t) similarly gave rise to a spectrum (see Figure 1) assigned to the radical cation (1^{•+}, R = Bu^t), which could be simulated using the hyperfine coupling constants as given in Table 1, though the spectrum now was strongest when unfiltered light was used. Pyrex-filtered light was also used for generating the spectrum of the diphenylbutadiyne radical cation (1^{•+}, R = Ph). Some of the lines showed some reproducible distortion which appears to be associated with the presence of satellites due to ¹⁹⁹Hg hyperfine coupling, but a good simulation of the rest of the spectrum can be obtained using the coupling constants which are given in Table 1. Also included in Table 1 are data on related radical anions (1^{•-}, R = Bu^t,⁵ and R = Ph^{6,7}) which have been observed previously.

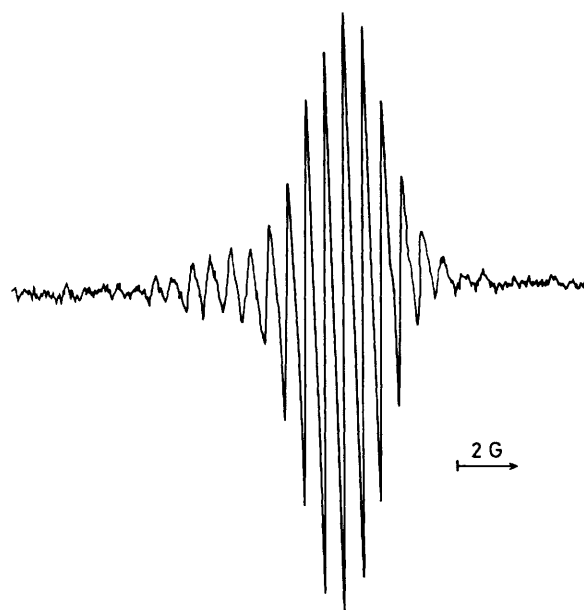


Figure 1. E.s.r. spectrum of the radical cation Bu^tC≡C-C≡CBu^t•⁺ in CF₃CO₂H at 297 K. The signals at low field are due to the presence of an impurity, perhaps Bu^tC≡C-C≡CH.

The spectra of these new radical cations raise three particular points of interest. First, the *g*-values are all low, lower than for free spin, but similar to those which have been observed in the corresponding radical anions (1^{•-}, R = Bu^t or Ph; see Table 1). In the radical anions, this has been ascribed to spin-orbit coupling between the nearly degenerate 2*p_x* and 2*p_y* orbitals of the diyne system,⁷ and a similar effect may be operating in the radical cations.

Secondly, in (1^{•+}, R = Ph), the hyperfine coupling constants are smaller than in (1^{•-}, R = Ph). Normally the hyperfine couplings in a radical cation are larger than those in the corresponding radical anion, and this is usually ascribed to the contraction of the orbitals under the influence of the positive charge.⁸ The only other exception to this general rule that we are aware of relates to a rather poor spectrum of the quaterphenyl radical cation,⁹ where it was suggested that the anomaly arose from differences in the dihedral angles between the aromatic ring in the radical anion and cation. A similar difference in dihedral angles may be present in (1^{•+}) and (1^{•-}, R = Ph).¹⁰

Thirdly, the spectrum of (1^{•+}, R = Ph) is gradually replaced by a more complex spectrum which we have not yet been able

to analyse in detail. We do not know yet whether this represents the formation of a cyclobutadiene (*cf.* equation 1), an azulene (*cf.* equation 3), or some other product.

The di-*t*-alkyldiacetylenes used in this work were synthesized by a new method which is analogous to an established route to di-*t*-alkylacetylenes.¹¹ An example of our procedure is as follows.

Aluminium trichloride (0.125 g) was added over 15 min to a stirred solution of bistrimethylsilylbutadiyne (Aldrich Chemical Co. Ltd.) (2.0 g) and *t*-butyl chloride (1.91 g) in dichloromethane under nitrogen at -78°C . The mixture was stirred at this temperature for 2 h, the progress of the reaction being monitored by ^1H n.m.r. spectroscopy of aliquots which were worked up in the same way as the bulk of the solution, as follows. The mixture was allowed to warm to room temperature, when the solvent was removed and the residue extracted into pentane yielding crude 2,2,7,7-tetramethylocta-3,5-diyne (68%). After purification by chromatography on silica gel, the product was identical with authentic material.¹²

We thank the S.E.R.C. for support, and University College London for the award of a Franz Sondheimer bursary to P. S. G.

Received, 13th May 1986; Com. 638

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