Electron Spin Resonance Spectra of Radical Cations derived from Stilbenes and Phenanthrenes

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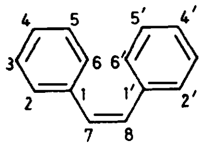
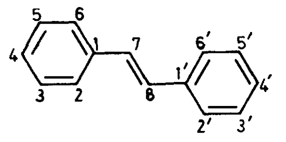
The same e.s.r. spectrum is observed when either *cis*- or *trans*-stilbene is photolysed in a solution of mercury(II) trifluoroacetate in trifluoroacetic acid. This spectrum is ascribed to the near-planar *trans* radical cation in which rotation about the Ph–C bonds is fast on the e.s.r. time scale, with *a*(2H olefinic) and *a*(2H *para*) 4.53, *a*(4H *ortho*) 2.78, *a*(4H *meta*) 0.715 G. In contrast, the *trans* radical anion shows restriction of rotation about the Ph–C bonds. The spectra of the radical cations derived from *trans*-4,4'-dimethyl- and *trans*-4,4'-di-t-butyl-stilbene are compatible with this interpretation. These stilbene radical cations do not cyclise to phenanthrenes: solutions of phenanthrene and dimethylphenanthrene under the same conditions show the different spectra of the corresponding phenanthrene radical cations. A satisfactory simulation of the spectrum of the former compound can be obtained with the hyperfine coupling constants *a*[H(1,8)] 2.94, *a*[H(2,7)] 1.34, *a*[H(3,6)] 2.94, *a*[H(4,5)] 1.34, *a*[H(9,10)] 4.91 G.

Experimental methods for generating radical anions in solution for e.s.r. studies[1] are better developed than those for radical cations,[2] and there are many simple and important hydrocarbons for which the radical anions but not the radical cations have been observed. Yet in two senses the cations are more important than the anions. First, the SOMO of the radical cation correlates with the HOMO of the parent and e.s.r. spectroscopy provides the best way of investigating its π-electron distribution.[3] Second, many radical cations react with their progenitors, and have an important potential in organic synthesis.[4]

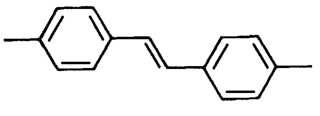
This is the current situation with the *cis*- and *trans*-stilbenes (I) and (II) and phenanthrene (V). In 1965, Lewis and Singer showed that the e.s.r. spectra of a number of π-conjugated hydrocarbons could be observed when the compounds were treated with $SbCl_5$ in dichloromethane.[5] However, under these conditions *trans*-stilbene gave only a weak, broad, and unresolved spectrum. Yet, at that time the e.s.r. spectrum of the radical anion of *trans*-stilbene had already been observed, and has been repeatedly investigated since.[6–10] Similarly the e.s.r. spectrum of the phenanthrene radical cation ($V^{+\bullet}$) is not reported in the literature,[2] although again the spectrum of the corresponding radical anion is well known.[11]



(I)



(II)



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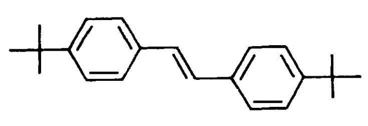

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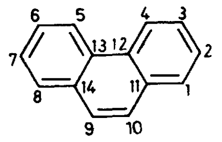

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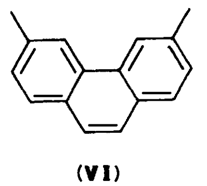


(VI)

We report here a study of the e.s.r. spectra of the radical cations derived from *cis*- and *trans*-stilbene (I) and (II), *trans*-4,4'-dimethyl- and *trans*-4,4'-di-t-butyl-stilbene (III) and (IV), phenanthrene (V), and 3,6-dimethylphenanthrene (VI).

Results

A solution of *cis*- or *trans*-stilbene in trifluoroacetic acid containing mercury(II) trifluoroacetate (Kochi's reagent)[12] was irradiated in a silica tube in the e.s.r. cavity with light from a 500 W high-pressure mercury arc at 266—288 K. The spectrum obtained from the *trans*-isomer is shown in Figure 1. The *cis*-isomer gave the same spectrum though of lower intensity. With 4,4'-dimethyl- and 4,4'-di-t-butyl-stilbene, the most intense spectra were obtained when the u.v. light was filtered through Pyrex glass. For both these compounds the lines were relatively broad (ΔH_{pp} *ca.* 0.5 and 1 G respectively), but could not be resolved further when the spectra were recorded at a higher derivative.

The radical cations from phenanthrene and 3,6-dimethylphenanthrene were generated in the same way using unfiltered u.v. light; examples of the spectra are shown in Figures 2 and 3. The phenanthrene samples sometimes showed the subsequent development of a second spectrum, which we believe to be due to mercuriation of the molecule.

Details of the spectra are given in Tables 1 and 2.

Discussion

Stilbenes.—Although resolved e.s.r. spectra of the stilbene radical cations have not been observed previously, the electronic absorption spectra of both the radical cations and anions have been studied in rigid matrices by Suzuki and his co-workers. The radical cation of *trans*-stilbene was generated by γ-irradiation of a frozen solution in s-butyl chloride or in a Freon mixture at 77 K, and it was concluded that ($II^{+\bullet}$) in solid or liquid solution has an approximately *trans*-coplanar structure similar to that of (II) itself, or of ($II^{-\bullet}$) or (II^{2-}).[13]

Table 1. E.s.r. hyperfine coupling constants (a/G) and g values of stilbene and substituted stilbene radical ions

	a(H *ortho*)	a(H *meta*)	a(H *para*)	a(H olefinic)	g
trans-Stilbene radical cation (**II**$^{+\bullet}$)					
Observed[a]	2.78	0.715	4.53	4.53	2.0026
Calc. (H/M)[b,c]	−2.00	−0.16	−2.61	−5.11	
Calc. (H/M/M)[c–e]	−2.53	0.85	−3.50	−5.61	
trans-Stilbene radical anion (**II**$^{-\bullet}$)					
Observed[f]	3.03 1.94	0.83 0.30	4.00	4.51	2.0027
Calc. (H/M)[b,g]	−1.69	−0.14	−2.20	−4.32	
Calc. (H/M/M)[d,e,g]	−2.14	0.72	−2.97	−4.73	
trans-4,4′-Dimethylstilbene radical cation (**III**$^{+\bullet}$)					
Observed[a]	2.25	0.44	6.20 (2Me)	4.00	2.0027
trans-4,4′-Di-t-butylstilbene radical cation (**IV**$^{+\bullet}$)					
Observed[a]	2.25	0.70		4.50	2.0025

[a] In trifluoroacetic acid at 266 K. [b] Hückel–McConnell. [c] $Q = -26.6$ G. [d] Hückel–McConnell–McLachlan. [e] $\lambda = 1.2$. [f] In dimethoxyethane at 173—373 K, counterion K$^+$.[8] [g] $Q = -22.5$ G.

Table 2. E.s.r. hyperfine coupling constants (a/G) and g values of phenanthrene and 3,6-dimethylphenanthrene radical ions

	a[H(1,8)]	a[H(2,7)]	a[H(3,6)]	a[H(4,5)]	a[H(9,10)]	g
Phenanthrene radical cation (**V**$^{+\bullet}$)						
Observed[a]	2.94	1.34	2.94	1.34	4.91	2.0024
Calc. (H/M)[b]	3.09	0.05	2.63	1.44	4.56	
Calc. (H/M/M)[b]	4.26	1.17	3.35	1.01	5.57	
Phenanthrene radical anion (**V**$^{-\bullet}$)						
Observed[c]	3.56	0.30	2.88	0.70	4.28	2.0027
Calc. (H/M)[b]	2.16	0.05	2.23	1.21	3.88	
Calc. (H/M/M)[b]	3.60	0.99	2.84	0.86	4.46	
3,6-Dimethylphenanthrene radical cation (**VI**$^{+\bullet}$)						
Observed[a]	3.32	1.11	6.18[d]	0.81	4.54	2.0025
Calc. (H/M)[b]	2.61	0.05	3.62	1.21	3.88	
Calc. (H/M/M)[b]	3.60	0.99	4.62	0.86	4.46	

[a] In trifluoroacetic acid at 266 K. [b] See notes to Table 1. [c] In MeCN or DMF at 298 K, counterion Pr$_4$N$^+$.[11] [d] a(2Me).

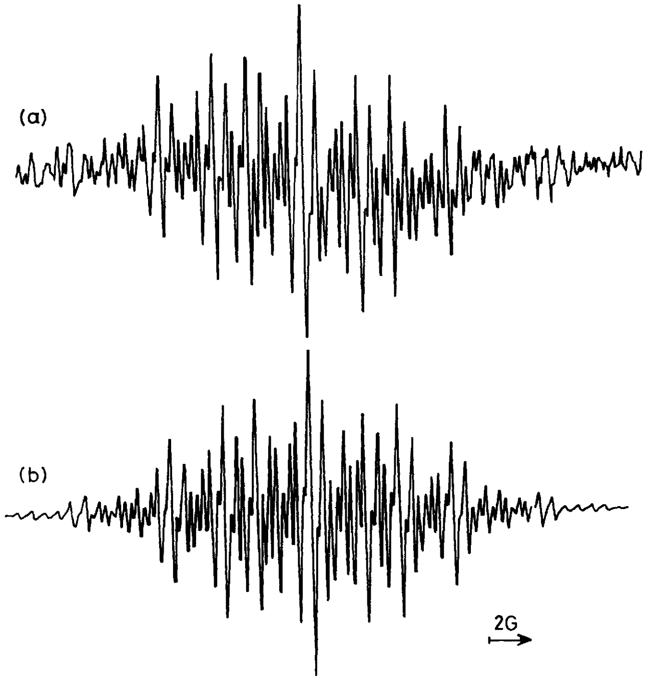


Figure 1. (a) Observed, and (b) simulated e.s.r. spectrum of the radical cation of *trans*-stilbene in trifluoroacetic at 265 K

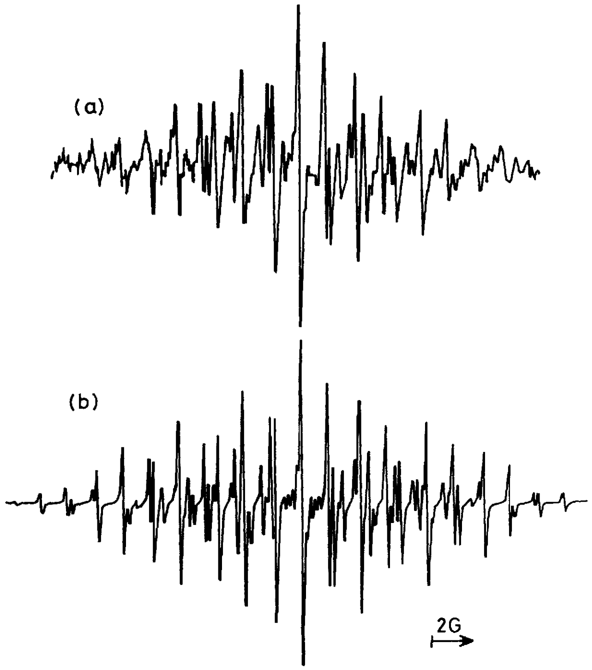


Figure 2. (a) Observed, and (b) simulated e.s.r. spectrum of the radica cation of phenanthrene in trifluoroacetic acid at 265 K

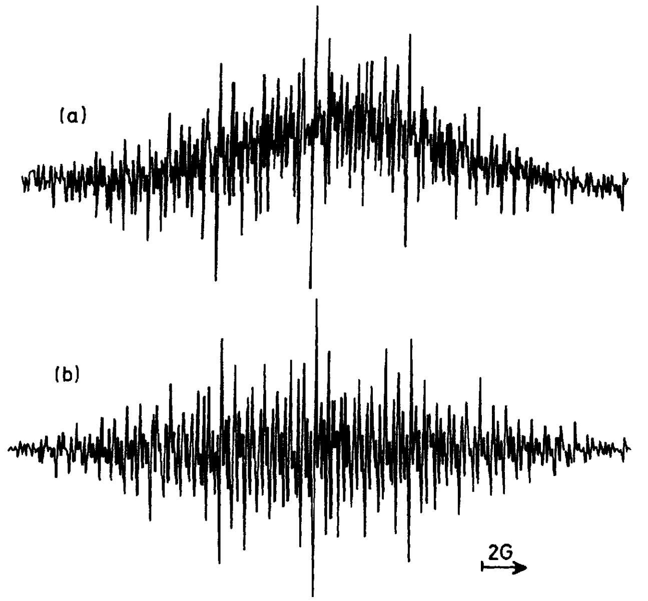
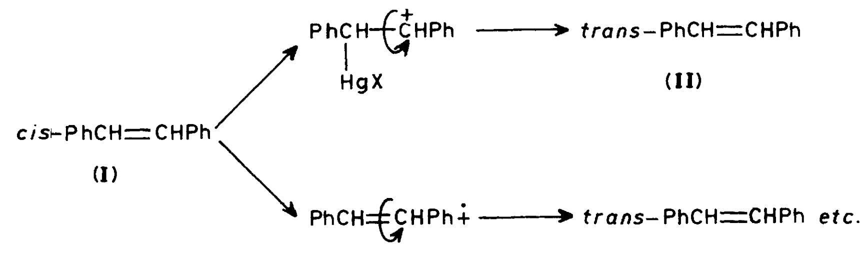


Figure 3. (a) Observed, and (b) simulated e.s.r. spectrum of the radical cation of 3,6-dimethylphenanthrene in trifluoroacetic acid at 265 K

Similar experiments with *cis*-stilbene gave ($\mathbf{I}^{+\bullet}$) with a geometry which appeared to be similar to that of (**I**) itself [and ($\mathbf{I}^{-\bullet}$)], with dihedral angles of *ca.* 0° about the central C(7)–C(8) bond, and *ca.* 30° about the bonds C(7)–C(1) and C(8)–C(1′) to the phenyl groups. This structure persisted on limited warming, but on illumination with visible light, ($\mathbf{I}^{+\bullet}$) rearranged to ($\mathbf{II}^{+\bullet}$) [and ($\mathbf{I}^{-\bullet}$) to ($\mathbf{II}^{-\bullet}$)].[14]

The first notable feature of our experiments is that we obtain the same e.s.r. spectrum (Figure 1 and Table 1) and hence presumably the same radical cation, whether we start with *cis*-stilbene (**I**) or *trans*-stilbene (**II**). As Suzuki has shown that distinct radical cations are derived from (**I**) and (**II**) under his conditions and that ($\mathbf{I}^{+\bullet}$) rearranges to ($\mathbf{II}^{+\bullet}$) on photolysis,[13,14] we assign the spectrum which we observe from either (**I**) or (**II**) to the *trans*-radical cation ($\mathbf{II}^{+\bullet}$).



It is not clear whether under our conditions this rearrangement involves a simple cation, or a radical cation, derived from stilbene, although there is evidence that the latter reaction can occur under suitable conditions. ^{1}H N.m.r. spectroscopy shows that (**I**) does not rearrange during 1 h in trifluoroacetic acid at room temperature, but if mercury(II) trifluoroacetate is present a 60% yield of (**II**) is formed in 15 min, and the rearrangement is complete overnight. Under these non-photolytic conditions, no e.s.r. spectrum can be observed.

Reasonable mechanisms can be envisaged which involve either a carbenium ion or, in a chain reaction, a radical cation.

If only the latter process were involved we might expect to see some indication of the spectrum of ($\mathbf{I}^{+\bullet}$) during the early stages of photolysis of (**I**). A spectrum recorded within 5 min of mixing (**I**) with Kochi's reagent appears similar to the ultimate spectrum which we ascribe to ($\mathbf{II}^{+\bullet}$), though the lines are relatively broad. Even if the signals of ($\mathbf{I}^{+\bullet}$) could conclusively be shown to be absent however, this would not prove that ($\mathbf{I}^{+\bullet}$) was not being formed because ($\mathbf{I}^{+\bullet}$) can rearrange to ($\mathbf{II}^{+\bullet}$).

Suzuki's evidence for the photolytic isomerisation of ($\mathbf{I}^{+\bullet}$) to ($\mathbf{II}^{+\bullet}$) is quoted above.

The thermal isomerisation of ($\mathbf{I}^{+\bullet}$) to ($\mathbf{II}^{+\bullet}$) by a radical-cation chain mechanism has also been reported. Thus treatment of *cis*- or *trans*-stilbene with $Mn(OCOCH_3)_3$, $Co(OCOCH_3)_3$, or $Tl(OCOCF_3)_3$ in acetic acid gave a mixture of *meso*- and (±)-hydrobenzoins with a composition which was independent of the stereochemistry of the starting material, and it was concluded that the mechanism involved isomerisation in an intermediate stilbene radical cation.[15]

Similarly F. D. Lewis and his co-workers showed that the quenching of singlet-excited 9,10-dicyanoanthracene (DCA) by (**I**) or (**II**) leads to a steady-state mixture consisting of 98.8% (**II**) and 1.2% (**I**), and they ascribe this to a chain process in which the *cis*-stilbene radical cation ($\mathbf{I}^{+\bullet}$) rearranges thermally to the *trans*-isomer [equations (1)—(3)].[16]

$$^1\mathrm{DCA}^* + (\mathbf{I}) \longrightarrow \mathrm{DCA}^{-\bullet} + (\mathbf{I}^{+\bullet}) \qquad (1)$$

$$(\mathbf{I}^{+\bullet}) \longrightarrow (\mathbf{II}^{+\bullet}) \qquad (2)$$

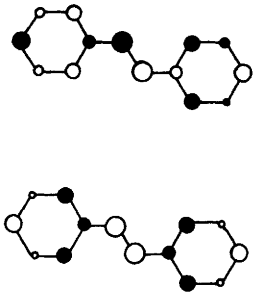
$$(\mathbf{II}^{+\bullet}) + (\mathbf{I}) \longrightarrow (\mathbf{II}) + (\mathbf{I}^{+\bullet}) \qquad (3)$$

Lewis *et al.* concluded that the activation energy for the isomerisation ($\mathbf{I}^{+\bullet}$) ⟶ ($\mathbf{II}^{+\bullet}$) is appreciably lower than that for (**I**) ⟶ (**II**) ($46 + 4$ kJ mol^{-1}).[17] This would be consonant with the fact that the unpaired electron is being removed from an orbital which is bonding between the olefinic carbon atoms (see Scheme 1).

As stilbene is an alternant hydrocarbon the pairing principle applies, and the bond orders will be same in the stilbene radical cations and anions. The radical anion would therefore be expected also to rearrange readily, and Gerson has shown that ($\mathbf{I}^{-\bullet}$) does rearrange to ($\mathbf{II}^{-\bullet}$) with a half-life of 20 min at −80 °C.[18]

The second interesting feature of our spectra is the fact that only one hyperfine coupling constant is observed in ($\mathbf{II}^{+\bullet}$) for the *ortho*-hydrogen atoms [H(2,6,2′,6′)] and one for the *meta*-hydrogen atoms [H(3,5,3′,5′)]. In contrast, the e.s.r. spectrum of ($\mathbf{II}^{-\bullet}$) up to 373 K shows hyperfine coupling from two non-equivalent pairs of *ortho* and *meta*-hydrogen atoms. This implies that rotation about the C–Ph bonds in ($\mathbf{II}^{-\bullet}$) is slow on the e.s.r. time scale whilst it is apparently fast in ($\mathbf{II}^{+\bullet}$). The radical ions of tetraphenylethene show a similar anomaly with apparent free rotation about the C–Ph bonds in the radical cation but not in the radical anion,[19] and it seems unlikely that the greater simplicity of the spectra of the radical cations is the result of accidental degeneracy of the hyperfine couplings.

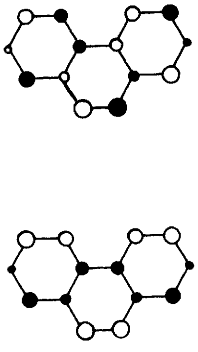
The bond orders between the alkene moiety and the phenyl groups in the anion and cation pairs should be the same



$$\Psi_8 = -0{\cdot}217(\phi_1 - \phi_{1'}) + 0{\cdot}274(\phi_2 + \phi_6 - \phi_{2'} - \phi_{6'}) + 0{\cdot}079(\phi_3 + \phi_5 - \phi_{3'} - \phi_{5'}) - 0{\cdot}314(\phi_4 - \phi_{4'}) - 0{\cdot}438(\phi_7 - \phi_8)$$

$$\Psi_7 = 0{\cdot}217(\phi_1 - \phi_{1'}) + 0{\cdot}274(\phi_2 + \phi_6 + \phi_{2'} + \phi_{6'}) - 0{\cdot}079(\phi_3 + \phi_5 + \phi_{3'} + \phi_{5'}) - 0{\cdot}314(\phi_4 - \phi_{4'}) - 0{\cdot}438(\phi_7 + \phi_8)$$

Scheme 1.



$$\Psi_8 = 0{\cdot}340(\phi_1 - \phi_8) - 0{\cdot}042(\phi_2 - \phi_7) - 0{\cdot}315(\phi_3 - \phi_6) + 0{\cdot}233(\phi_4 - \phi_5) + 0{\cdot}415(\phi_9 - \phi_{10}) - 0{\cdot}164(\phi_{11} + \phi_{14}) + 0{\cdot}174(\phi_{12} - \phi_{13})$$

$$\Psi_7 = 0{\cdot}340(\phi_1 - \phi_8) + 0{\cdot}042(\phi_2 + \phi_7) - 0{\cdot}315(\phi_3 + \phi_6) - 0{\cdot}233(\phi_4 + \phi_5) - 0{\cdot}415(\phi_9 + \phi_{10}) + 0{\cdot}164(\phi_{11} + \phi_{14}) + 0{\cdot}174(\phi_{12} + \phi_{13})$$

Scheme 2.

(Scheme 1), and we speculate that the apparent greater rigidity in the radical anions may result from a specific interaction with the alkali-metal counter cation. We intend to look for further examples of this phenomenon.

The third interesting feature of the spectrum concerns the values of the ^1H hyperfine coupling constants.

Table 1 compares the observed values of *a*(H) for (**II**$^{-\bullet}$) and (**II**$^{+\bullet}$) with the values calculated on a simple Hückel–McConnell model (see Scheme 1), and with those obtained by McLachlan's modification of this treatment which takes account of spin correlation. We have used the same *Q* values as we did in discussion of the biphenyl radical cation,[20] namely -22.5 G (taken from $C_6H_6^{-\bullet}$) for (**II**$^{-\bullet}$), and -26.6 G (taken from $C_6H_6^{+\bullet}$) for (**II**$^{+\bullet}$). On the basis of the pairing principle, these elementary models suggest that the hyperfine coupling constants in (**II**$^{-\bullet}$) and (**II**$^{+\bullet}$) should differ only by the ratio of the *Q* values for the two species.

The correlation between the observed hyperfine coupling constants of (**II**$^{-\bullet}$) and (**II**$^{+\bullet}$), and between the observed and calculated values in the two species, is rather poor. One notable feature is that in (**II**$^{+\bullet}$) the observed coupling constants relating to the olefinic protons [H(7,8)] and to the *para* protons in the phenyl groups [H(4,4′)] are accidentally equivalent.

The cause of this disparity is not obvious. One contributory factor may be the different interactions which may occur with the solvents [CF_3CO_2H for (**II**$^{+\bullet}$) and dimethoxyethane for (**II**$^{-\bullet}$)] and particularly the counterions [$CF_3CO_2^-$, $(CF_3CO_2)_3Hg^-$, or $(CF_3CO_2)_3Hg_2^-$ for (**II**$^{+\bullet}$) and Na^+ or K^+ for (**II**$^{-\bullet}$)]. A second is the possibility of intramolecular strain and subsequent distortion from planarity. For example, Atherton investigated the effect of steric hindrance between the olefinic protons and the ring protons in (**I**$^{-\bullet}$) by varying the Coulomb integral of the Ph–C bond.[8] His results suggest that the hyperfine coupling constants to the olefinic protons and the *para* protons should become equal when the Coulomb integral of the Ph–C bond is taken to be $\alpha - 0.30\ \beta$.

In an attempt to probe further our interpretation of the spectrum of the stilbene radical cation, the radical cations were also generated from 4,4′-dimethyl- and 4,4′-di-t-butyl-stilbene. The lack of detail in the broad-lined spectra makes it difficult to arrive at convincing unique interpretations of the spectra, but the hyperfine coupling constants corresponding to the best analysis which could be obtained are shown in Table 1.

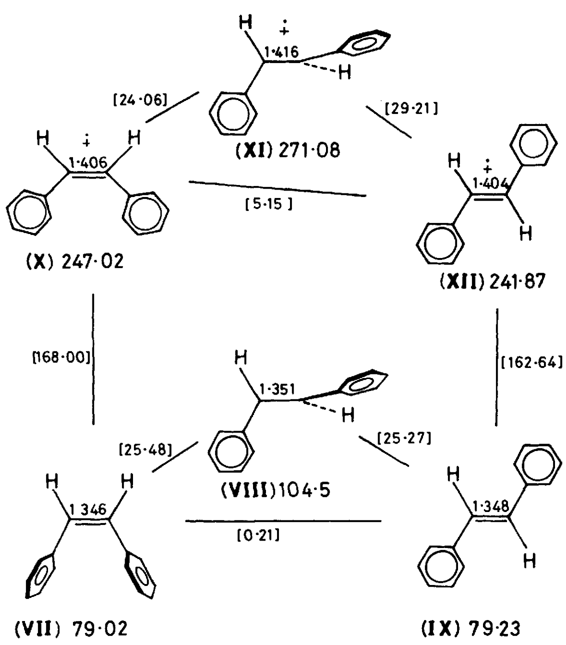
These values are consistent with those obtained for (**II**$^{+\bullet}$) from stilbene itself. It will be noted that again for both compounds only one hyperfine coupling is obtained for the *ortho* protons, and only one for the *meta* protons, supporting the view that this equality results from free rotation about the Ph–C bond rather than from an accidental degeneracy. In the methyl-substituted compound, the hyperfine coupling to the methyl protons now appears to be greater than that to the olefinic protons, as would be expected if our analysis of the spectrum of (**II**$^{+\bullet}$) is correct.

The stilbene molecule and its radical cation were also examined by semi-empirical UMNDO and UMINDO/3 calculations, and the results from the latter are shown in Scheme 3.

The neutral stilbene molecule serves as a calibrant for these calculations.

The optimised structure of neutral *cis*-stilbene (**VII**) has a near-planar central olefinic section, with the phenyl groups approximately orthogonal to this plane, although this structure with a heat of formation of 79.0 kcal mol^{-1} is only 0.3 kcal mol^{-1} more stable than the wholly planar structure. The most stable form of *trans*-stilbene (**IX**) is planar, and with a heat of formation of 79.2 kcal mol^{-1} it is calculated to be 0.2 kcal mol^{-1} less stable than the *cis* form. The orthogonal structure (**VIII**) is found to be *ca.* 25.4 kcal mol^{-1} less stable than the planar *cis* or *trans* structures.

Haselbach *et al.* have published the results of MINDO/3 calculations carried out on *trans*-stilbene with the constraints of local D_{6h} symmetry in the benzene rings, and overall C_2 symmetry.[21] They obtained a minimum-energy conformation, ΔH_f° 79.5 kcal mol^{-1}, in which the aromatic rings were twisted by 90° out of the plane of the olefinic moiety, and they comment that the MINDO/3 program is poor for processes involving



Scheme 3. UMINDO/3 Structures and enthalpies of formation of stilbenes and stilbene radical cations. Values of ΔH_f°/kcal mol^{-1} are given after the compound number, and differences in ΔH_f° are in square brackets on the connecting tielines. The length of the central bond is shown in Å

small barriers of rotation around essentially single bonds in π systems.

The experimental evidence is that in the vapour state electron diffraction shows that in *cis*-stilbene the benzene rings are twisted by 43° with respect to the plane of the alkene moiety,[22] though the electronic spectrum suggests that this angle reduces to 29° in heptane solution.[14] In the crystal, the *trans*-stilbene is planar,[23] and it is probably planar or nearly so in solution,[13] though an electron diffraction study indicates that in the vapour state the phenyl dihedral angle may be 30°.[24] The *trans* form is found to be 2.3 ± 0.3 kcal mol^{-1} more stable than the *cis* form,[25] and the activation energy for inversion is found to be 46 ± 2 kcal mol^{-1}.[17]

The fully optimised radical cation (**X**) derived from *cis*-stilbene is calculated to have a heat of formation ΔH_f° of 247.0 kcal mol^{-1}. It is twisted by 23° about the olefinic bond, and the two benzene rings subtend dihedral angles of 11.3 and 12.0°, respectively, with this bond. The *trans* form (**XII**) (ΔH_f° 241.9 kcal mol^{-1}) is 5.2 kcal mol^{-1} more stable than the *cis* form and is near-planar. The orthogonal structure (**XI**) has ΔH_f° 271.1 kcal mol^{-1}, and as in the neutral species (**VIII**), the benzene rings are coplanar with the central carbon–carbon bond.

An INDO calculation using the UMINDO/3 geometry derived for the stilbene radical cation (**XII**) gives the hyperfine coupling constants *a*(H *ortho*) −3.75 and −3.84, *a*(H *meta*) 2.15 and 2.18, *a*(H *para*) −4.89, and *a*(H olefinic) −4.18 G, to be compared with the experimental values given in Table 1.

Phenanthrenes.—The benzene radical cation reacts with benzene to give the biphenyl radical cation.[20] Lewis found that no significant amount of phenanthrene was formed when stilbene was irradiated in the presence of dicyanoanthracene in the absence or presence of oxygen,[16] but Bendig *et al.* showed that irradiation in the presence of electron acceptors such as tetracyanoethylene, and of oxygen, did lead to the formation of phenanthrene.[26] To exclude the possibility that some of the spectra which we have ascribed to stilbenes were in fact derived from phenanthrenes, we have therefore briefly investigated the spectra of the phenanthrene (**V**) and 3,6-dimethylphenanthrene (**VI**) radical cations.

The spectrum of ($V^{+\cdot}$) is shown in Figure 2(a), and the simulation which is obtained using the hyperfine coupling constants listed in Table 2 is shown in Figure 2(b). This spectrum is clearly different from that [Figure 1(a)] derived from *cis*- or *trans*-stilbene, establishing that the spectrum derived from the stilbenes does not relate to phenanthrene.

The spectrum [Figure 3(a)] which we have obtained from 3,6-dimethylphenanthrene (**VI**) can be satisfactorily simulated [Figure 3(b)] using the hyperfine coupling constants listed in Table 2. Again, the spectrum is different from that of the corresponding stilbene, confirming that the cyclisation of ($\mathbf{III}^{+\cdot}$) to ($\mathbf{VI}^{+\cdot}$) does not take place under our reaction conditions.

Table 2 also includes values of the coupling constants calculated on the basis of the Hückel–McConnell and Hückel–McConnell–McLachlan models using the coefficients shown in Scheme 2, and also data on the known phenanthrene anion for comparison.

Experimental

4,4′-Dimethylstilbene was prepared by the Wittig reaction between 4-methylbenzylidenetriphenylphosphorane and 4-methylbenzaldehyde,[27] m.p. 177—178 °C; δ($CDCl_3$) 2.2 (6 H, s, 2Me) and 7.2 (10 H, m, ArH and olefinic).

4,4′-Di-t-butylstilbene was obtained accidentally during the attempted synthesis of bis-(4-t-butylphenyl)acetylene. The reaction of 1-dibromomethyl-4-t-butylbenzene with copper in toluene at 90—100 °C gave 1,2-dibromo-1,2-bis-(4-t-butylphenyl)ethane [28] (Found: C, 58.15; H, 6.2; Br, 35.3. Calc. for $C_{22}H_{28}Br_2$: C, 58.4; H, 6.2; Br, 35.4%). When this was heated with KOH in dioxane for 24 h,[28] the stilbene was isolated, m.p. 175—176 °C (lit.,[28] 179—180 °C); δ($CDCl_3$) 1.28 (18 H, s, Bu^t), 6.80 (2 H, s, olefinic), and 7.13 (8 H, s, ArH); *m/z* 292 (91.8%), and 27.7 (100).

3,6-Dimethylphenanthrene was prepared by the photolytic isomerisation of *trans*-4,4′-dimethylstilbene to the *cis* isomer which was then photolytically oxidised with oxygen in the presence of iodine to give the phenanthrene which was purified by column chromatography and recrystallised from ethanol,[27] m.p. 136—137 °C; δ($CDCl_3$) 2.6 (6 H, s, 2Me), 7.6 (6 H, m), and 8.3 (2 H, br s).

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