197. *Unstable Intermediates. Part XXVII.* Cations of Hexamethylbenzene and Durene.*

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Exposure of solutions of hexamethylbenzene in sulphuric acid to 3650 Å light results in the formation of a radical whose electron spin resonance spectrum has all the features expected for the corresponding radical cation. Attempts to prepare other benzene cations by this procedure were not successful, but a spectrum thought to be that of the cation of durene was obtained from irradiated solutions of the hydrocarbon in oleum.

Although a very wide range of monocyclic hydrocarbon radical anions, including that of benzene, have been prepared and studied, the only cation so far reported is that of the hexamethylbenzene.[1] These results are now presented and discussed fully, together with results for a radical thought to be the cation of durene.

Use of ultraviolet light for preparative purposes has been exploited considerably in the

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* Part XXVI, *J.*, 1965, 378.

[1] Hulme and Symons, *Proc. Chem. Soc.*, 1963, 241.

field of radical anions,[2] but does not seem to have been used in the preparation of cations.

Our attempts to prepare hexamethylbenzene cations by chemical oxidation in sulphuric acid,[3] although fruitful in that high concentrations of a radical species (I) resulted, failed to give radicals whose spectra were in accord with expectation. The nature of radical (I) will be the subject of a further communication.

EXPERIMENTAL AND RESULTS

Materials.—Hexamethylbenzene and durene had m. p. 165 and 79° respectively after recrystallisation from glacial acetic acid. Alkylbenzene impurities were not detected by nuclear magnetic resonance (n.m.r.) or vapour phase chromatography (v.p.c.) methods. AnalaR sulphuric acid (98%) was used without purification: dilute oleums were prepared by suitable admixture with 65% oleum. No spin resonance absorption was detected on illumination of the solvents alone.

Preparation of Solutions.—Finely powdered solutes were vigorously shaken with sulphuric acid for a few minutes, and excess of solid was then quickly removed in order to minimise side reactions. Solutions in oleum when prepared from those in sulphuric acid in order to avoid extensive charring.

Ultraviolet Photolyses.—Solutions were irradiated in a Varian general purpose cavity in silica cells, with light from a medium pressure mercury lamp focused by a silica lens.

Electron Spin Resonance Measurements.—A Varian spectrometer operating at about 9489 Mc./sec. was used with 100 kc./sec. modulation. Superheterodyne detection was available but the lines were never narrow enough to warrant its use. Magnetic fields were measured by proton resonance.

Hexamethylbenzene.—Freshly prepared solutions in sulphuric acid gave no electron spin resonance spectrum. On exposure to ultraviolet light the spectrum shown in Fig. 1 developed to a steady intensity after a few seconds. The spectrum consists of a single, odd-numbered set of equally spaced lines separated by 6·45 ± 0·05 gauss. Only 13 lines have been positively identified, their relative intensities being as shown in Table 1.

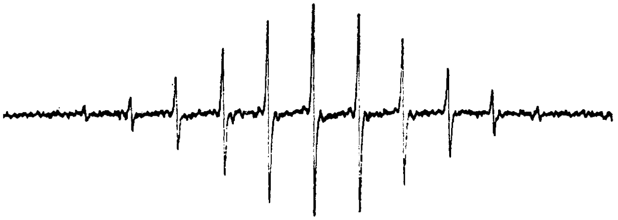

FIG. 1. First derivative of the electron spin resonance spectrum assigned to the hexamethylbenzene cation formed by exposure of a dilute solution of hexamethylbenzene in 98% sulphuric acid to ultraviolet light.

TABLE 1.

Comparison of relative intensities of various lines in the spectrum assigned to hexamethylbenzene cations with those calculated for spectra having 15, 17, 19, or 21 lines of binomial distribution of intensities.

a. Relative intensities for the central groups of 13 lines. Line (0) is the central component.

No. of lines	(0)	1	2	3	4	5	6
15	245	214·5	143	71·5	26	6·5	1
17	107	95·3	66·7	36·4	15·2	4·66	1
19	59·7	53·6	39	22·7	10·5	3·75	1
31	38·1	34·7	26·0	16·0	8·0	3·2	1
Experimental	56	50	38	22	10·2	3·5	1

b. Relative intensities for the central group of 9 lines.

No. of lines	(0)	1	2	4	4
15	9·4	8·25	5·5	2·75	1
17	7·1	6·3	4·4	2·4	1
19	5·7	5·1	3·7	2·17	1
21	4·76	4·33	3·25	2·0	1
Experimental	5·7	5·0	3·7	2·15	1

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[2] Ayscough and Wilson, *J.*, 1963, 5412; Ayscough, Sargent, and Wilson, *J.*, 1963, 5418.

[3] Hulme and Symons, unpublished results.

All attempts to reduce the line-width between points of maximum slope below about 0·25 gauss, by adjustment of temperature, microwave power, and modulation amplitude failed, although the instrument was capable of resolving lines having widths in the region of 0·03 gauss. We were unable to alter the widths of individual lines even at maximum microwave power, under which conditions the spectra of cations such as that of 9,10-dimethylanthracene [4] are markedly broadened.

At high gain, satellite lines probably due to radicals containing one ^{13}C atom were detected (Fig. 2). Two sets could be detected, the larger splitting being 2·27 gauss and the smaller in the region of 1 gauss. The latter hyperfine splitting constant is very approximate since the lines appear only as shoulders on the sides of the main lines.

A g-factor of 2·00267 ± 0·0001 was calculated for the radical from simultaneous measurements of the D.C. field and microwave frequency.

In the absence of ultraviolet light the signal decayed very rapidly, by what was roughly established to be a second-order process. Concentrated solutions of hexamethylbenzene gave, on prolonged photolysis, a second radical having a spectrum identical with that of the duroquinone cation,[5] with a g-factor of 2·00336 ± 0·0001. In contrast with the spectrum assigned to the hexamethylbenzene cation, this spectrum was markedly broadened on increasing the microwave power.

Durene.—Pale yellow solutions in 98% sulphuric acid did not give rise to a detectable electron resonance spectrum. Exposure to ultraviolet light gave the duroquinone cation in high yield.

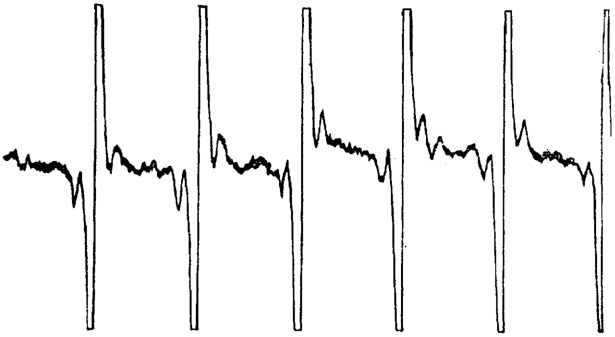

FIG. 2. The spectrum assigned to hexamethylbenzene cations at high gain, showing satellite lines assigned to radicals containing ^{13}C.

In dilute oleums, photolysis gave no radicals, but for more concentrated oleums (>30%) photolysis gave a spectrum consisting of a single odd-numbered set of lines having a hyperfine splitting of 11·0 ± 0·2 gauss. Only eleven lines were detected with certainty, but the intensities of these lines compared well with expectation for a spectrum of thirteen lines having a binomial distribution of intensities (Table 2). As with the spectrum attributed to the hexamethylbenzene cation, the lines are quite broad, and could not be resolved into further components under any conditions. A definite decrease in intensity was observed at high levels of microwave power, but the effect was less marked than that for the anthracene cation. The spectrum of this radical, shown in Fig. 3, shows, in addition, features due to the duroquinone cation, saturated and broadened because of the high microwave power used. The difference in g-values

TABLE 2.

Relative intensities of the central lines of the spectrum assigned to durene cations compared with calculated intensities for a spectrum of 13 lines having a binomial distribution of intensities.

No. of lines	(0)	1	2	3	4
13	14·3	11·9	7·2	3·4	1
Experimental	14·0	12·0	7·5	3·4	1

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[4] Brivati, Hulme, and Symons, *Proc. Chem. Soc.*, 1961, 384.
[5] Bolton and Carrington, *Proc. Chem. Soc.*, 1961, 385.

of these radicals is most marked, as is the overall span of the spectrum. The *g*-value for the new radical was 2·0027 ± 0·0001. We were not able to distinguish satellite spectra from radicals containing ^{13}C because of interference from the spectrum of durosemiquinone cations.

FIG. 3. The spectrum assigned to durene cations, formed by exposure of a dilute solution of durene in oleum to ultraviolet light.

DISCUSSION

Evidence for the Hexamethylbenzene Cation.—Our identification is based upon the following factors: (i) The spectrum is remarkably simple, showing only one proton hyperfine coupling constant. (ii) Only thirteen of the expected nineteen lines were detected, but the relative intensities totally eliminate either fourteen or sixteen equivalent protons, and fit better with eighteen protons than with twenty (Table 1). (iii) Only two different types of carbon atom could be seen from ^{13}C hyperfine satellite lines, and the intensities for the outermost pairs of lines are correct for molecules having six equivalent carbon atoms, one being ^{13}C. (iv) The line-width could not be reduced below 0·25 gauss despite every precaution to avoid extraneous broadening effects. Furthermore, with the maximum microwave power available the lines did not broaden. There results are qualitatively similar to those for the anion of benzene,[6] and the cation and anion of coronene [7,8] which, like the hexamethylbenzene cation, have orbitally degenerate ground states. This behaviour can be understood in terms of a combination of dynamic Jahn–Teller distortion and spin–orbital coupling.[9,10]

(v) The proton hyperfine coupling of 6·45 gauss is quite reasonable for the cation of hexamethylbenzene. Hyperfine coupling constants to β-protons for various cations, anions, and neutral radicals are compared in Fig. 5. The derivation of the *Q* values for these radicals is explained in a later section of this Paper.

The *g*-factor of 2·00267 is close to those obtained for other hydrocarbon cations and differs substantially from those generally found for oxidised species such as protonated semiquinones.

All these factors are in good accord with expectation for the hexamethylbenzene cation and it is hard to formulate any alternative radical which should have such properties.

Evidence for the Durene Cation.—Our reasoning is similar to that given above: (i) The spectrum is again simple, with just one proton hyperfine splitting. Only eleven lines were detected, but their relative intensities are close to those expected for thirteen lines having binomial distribution of intensities (Table 2). The cation of durene should have twelve equivalent protons coupling strongly with the unpaired electron, provided the degeneracy of the symmetric and antisymmetric orbitals (Fig. 4) is sufficiently lifted by the asymmetry of the ion, in such a manner that the antisymmetric level is uppermost. Since, by hyperconjugation, methyl groups can help to fill the " hole " in the π-system, we would expect the antisymmetric level to be half-filled and to have a node passing through the two ring

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[6] de Boer and Weissman, *J. Amer. Chem. Soc.*, 1958, **80**, 4549.

[7] Bolton and Carrington, *Mol. Phys.*, 1961, **4**, 271.

[8] Townsend and Weissman, *J. Chem. Phys.*, 1960, **32**, 309.

[9] McConnell, *J. Chem. Phys.*, 1961, **34**, 13.

[10] McConnell and McLachlan, *J. Chem. Phys.*, 1961, **34**, 1.

protons. Provided the orbital splitting is sufficiently large, hyperfine coupling to these two protons would not be detected. (ii) Little can be deduced from the line-widths since these are expected to contain any residual triplet splitting from the ring protons. Furthermore, there are clear indications of second-order splitting on some lines.[11] The lines do show signs of saturation at high microwave power levels, but they are more difficult to saturate than are those for radicals having no low-lying excited states.

The very small value for the hyperfine splitting for the ring protons is unexpected. It has been suggested by a Referee that this may be the result of a fortuitous cancellation of two effects, one giving rise to a small negative spin density, and the other a small positive spin density. The former would result from configuration interaction with excited states, whist the latter could be the result of a vibronic coupling. (iii) The hyperfine coupling constant of 11·0 gauss is qualitatively in accord with expectation. If, however, the Q-value for hexamethylbenzene is used, and the coupling constant modified to take account of the increased spin densities on the four ring carbons, a predicted coupling constant of 9·67 gauss is derived, which is markedly smaller than the experimental result. This increase in the effective Q-value is of the same form as that found for comparable cations and anions,[12,13] and is discussed in a later section. (iv) Again, the g-value is that expected for a simple cation of an aromatic hydrocarbon and is clearly different from that for oxidised species. This is illustrated in Fig. 3 where the spectrum of the corresponding diprotonated semiquinone can be seen superimposed on that of the durene cation.

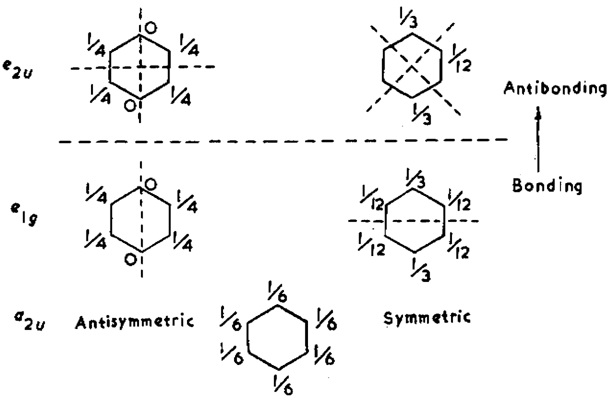

FIG. 4. Spin densities associated with bonding and antibonding π-orbitals for hexamethylbenzene and durene.

Photolyses.—Perhaps the simplest explanation of the extreme facility of the reactions under consideration is that the species photolysed is the protonated hydrocarbon, $\mathrm{ArH^+}$. This will be strongly stabilised by solvent molecules oriented in a manner comparable with that expected to satisfy the radical-cation which would result by loss of a hydrogen atom from the photo-excited carbonium ion:

$$\mathrm{ArH^{+}{}_{solv}} + h\nu \text{ — } \mathrm{Ar^{\dot{+}}{}_{solv}} + \mathrm{H}\cdot \qquad (1)$$

The life-time of these radical-ions is short so the stationary concentration is low. This may explain why no radicals can be detected from durene in 100% sulphuric acid, since the concentration of protonated ions is relatively small. However, it may also be that the solvent participates more directly in the " removal " of the hydrogen atom, and that oleum is more effective than sulphuric acid. We recall that hydrogen atoms are relatively

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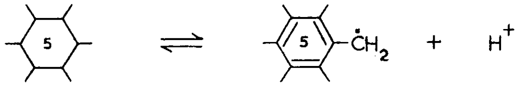
[11] de Boer and Mackor, *Mol. Phys.*, 1962, **5**, 493.

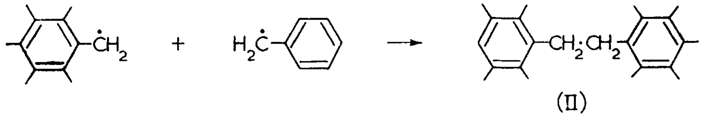
[12] Bolton, Carrington, and McLachlan, *Mol. Phys.*, 1962, **5**, 31.

[13] de Boer and Mackor, *Mol. Phys.*, 1962, **5**, 493; *Proc. Chem. Soc.*, 1963, 23.

stable in solid sulphuric acid[14] and this may be due to a weak chemical bonding which should also be effective in the fluid medium.[15]

No attempt has been made to isolate the final products of photolysis but it has been verified that the dimer of hexamethylbenzene (II) does not react thermally to give radicals in the media used. Thus the simplest reaction would be





(II)

If the first step is a rapid equilibrium then the decay should be of the second order. This is approximately the case for hexamethylbenzene cations.

The Effect of Charge-density on Hyperconjugation.—Although Q-values for a wide range of radicals and radical ions, defined by

$$a_{\alpha\text{H (i)}} = Q_\alpha \rho_{\alpha\text{c (i)}}$$

are reasonably constant, this is not the case when hyperfine couplings to β-hydrogen atoms ($a_{\beta\text{H(i)}}$) are considered. Thus for example, if the value of 26·9 gauss for ethyl radicals were used for Q_β, then values of 4·5 and 6·7 gauss are expected for hexamethylbenzene and durene cations: alternatively, if one allows for electron-delocalisation on to methyl[16] and hence uses a Q-value of about 30, then values of 5 and 7·5 gauss are estimated for the aromatic cations.

Theories of hyperconjugation require that the degree of electron delocalisation in the ground state should increase with increase in formal positive charge on the trigonal carbon atom. The present results illustrate this in a rather direct fashion, since both charge-densities and Q_β-values are derived without the use of approximations. Our approach has been to calculate values of Q_β from the experimental hyperfine coupling constants, by assuming initially that ρ_c was equal to 1·0, 0·167, and 0·25 for ethyl radicals, hexamethyl benzene, and durene cations, but allowing for delocalisation on to methyl according to the method outlined previously.[16] Results are plotted against the formal positive charge densities of 0, 0·167, and 0·25 in Fig. 5, and suggest an approximately linear dependence of delocalisation upon charge density.

Results calculated for other hydrocarbon radicals are included in Fig. 5, both for cations and anions, but there is more uncertainty regarding the values used. One can assume generality for this correlation and hence estimate values for hyperfine coupling constants when charge densities are known. This may be a help in interpreting spectra of unknown radicals.

^{13}C *Hyperfine Coupling.*—It is remarkable that the larger of the two coupling constants for ^{13}C hyperfine interaction in the hexamethylbenzene cation (2·27 gauss) is almost identical with that for ^{13}C in the benzene anion.[17] It is tempting therefore to assign this to the ring carbon atoms and the smaller coupling to the methyl carbons. However, if

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[14] Livingston, Zeldes, and Taylor, *Discuss. Faraday Soc.*, 1955, **19**, 166.
[15] Atkins, Keen, Symons, and Wardale, *J.*, 1963, 5594.
[16] Symons, *Tetrahedron*, 1962, **18**, 333.
[17] Tuttle and Weissman, *J. Amer. Chem. Soc.*, 1958, **80**, 5342.

there is to be a genuine reduction in spin-density on the ring carbons as a result of hyperconjugation, and if there are no major compensating effects, then the coupling constants should be decreased to about 1·84 gauss. This value lies about midway between the two experimental values and it will thus be necessary to label the ion specifically with ^{13}C before a reliable assignment can be made. We defer further discussion pending results with labelled ions.

g-Factors.—The results for the two cations under consideration are of interest in connection with the theory of *g*-factors for radicals with nearly degenerate levels.[9] In these examples there seems to be little if any change from values for cations with non-degenerate ground-states.

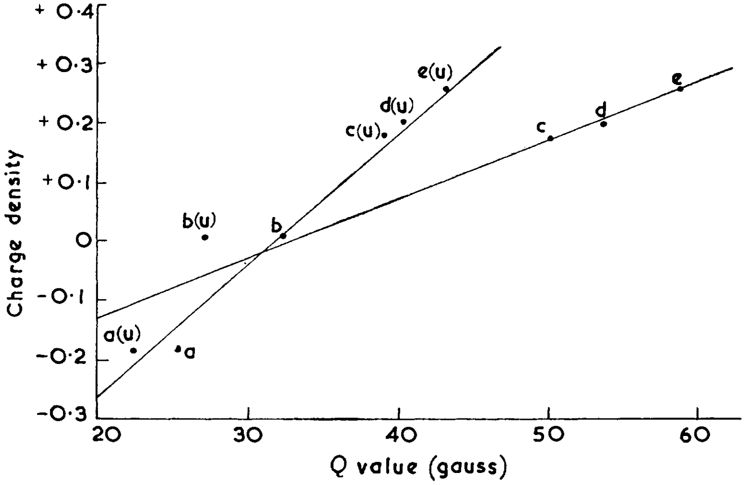

FIG. 5. Trends in *Q*-values for β-protons with charge-density. Points marked (*u*) are for *Q*-values uncorrected for delocalisation on to methyl. *Q*-Values for the radical anion and cation of 9,10-dimethylanthracene are somewhat arbitrarily assigned, on the basis of measured distributions in unmethylated radicals.

a, 9,10-Dimethylanthracene anion; *b*, ethyl radical; *c*, hexamethylbenzene cation; *d*, 9-methylanthracene cation; *e*, durene cation.

Results for radicals derived from a variety of other methyl substituted benzenes in sulphuric acid and oleum which are less readily interpreted will be described in a later communication.

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