E.S.R. Evidence for a Low-temperature Distortion in the Hexamethylbenzene Radical Cation

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The e.s.r. spectrum of the radical cation of hexamethylbenzene at 77 K shows that the degeneracy of the ψ_A and ψ_S orbitals is lifted, since four strongly coupled methyl groups (11.5 G) and two weakly coupled methyl groups [(–)2.8 G] are observed; at 130 K, all six methyl groups become equivalent as a result of dynamic averaging of the hyperfine couplings.

Substituted benzene radical cations have been studied extensively by e.s.r. spectroscopy, both in the liquid phase,[1—5] and, more recently, in Freon matrices,[6—10] and the results interpreted mainly in terms of the electronic influences of the substituents. The cation of benzene itself has been studied in a frozen sulphuric acid matrix[11] and on a silica surface,[12] and shows six equivalent protons. In a definitive study, Iwasaki *et al.*[13] observed e.s.r. spectra of the benzene cation at low temperatures in Freon matrices and found that, at 4 K, a static distortion of the structure occurred which lifted the degeneracy of the ψ_A and ψ_S orbitals, the unpaired electron occupying the ψ_S level.

We recently became interested in the hexamethylbenzene radical cation ($HMB^{+\cdot}$) following our observation[14,15] by e.s.r. spectroscopy of the 'Dewar' isomer cation ($HMD^{+\cdot}$) and its thermal rearrangement to the more thermodynamically stable isomer ($HMB^{+\cdot}$). This was confirmed by the identity of the spectrum obtained on annealing to 150 K with that from $HMB^{+\cdot}$ cations obtained from an authentic sample of HMB at the same temperature, which showed all six methyl groups to be equivalent. On recooling the sample to 77 K, the spectrum changed markedly, and we originally suggested that this might be due to diminished resolution resulting from the loss of free rotation of the methyl groups at low temperature. However, we have pursued this problem further, and conclude that the low temperature spectral change is, in fact, due to structural distortion of the cation.

The spectrum recorded from HMB at 77 K, following γ-irradiation as a dilute solution in $CFCl_3$, is shown in Figure 1. We feel that the most reasonable analysis of this spectrum is in terms of coupling of the unpaired electron to the protons of four equivalent methyl groups [A(H) 11.5 G; G = 10^{-4} T] and two equivalent methyl groups [A(H) 2.8 G]; in which case, the SOMO is the ψ_A orbital (I). Interestingly, this is opposite to the ψ_S SOMO which is selected in the distorted form of the unsubstituted benzene cation.[13]

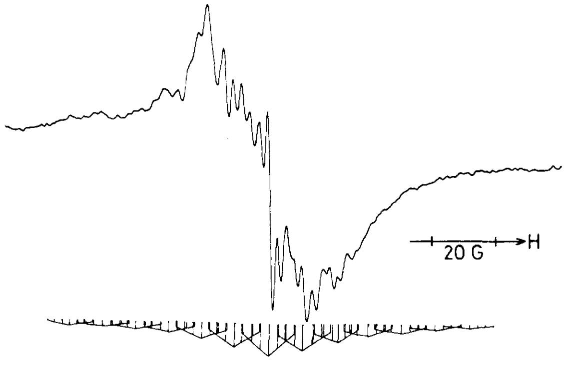
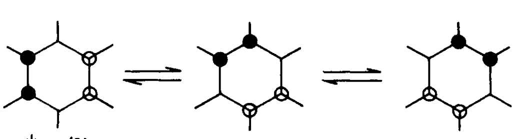


Figure 1. E.s.r. spectrum of hexamethylbenzene radical cations ($HMB^{+\cdot}$) recorded at 77 K.



ψ_A (I)

We consider that the sign of the 2.8 G coupling is probably negative, since it is often found that small couplings observed experimentally to nuclei which are located at nodal regions predicted by simple M.O. theory are due to negative spin densities: a good example of this is the pyrene radical anion,[15] in which couplings are observed to protons bonded to carbon atoms in the nodal plane of the SOMO predicted by Hückel theory. A more detailed calculation, which included excited configurations, predicted negative spin densities at these positions;[16] this is confirmed by an n.m.r. study of solid potassium pyrenide.[17]

On annealing the sample containing hexamethylbenzene cations to 130 K, the spectrum in Figure 2 was observed. This shows that all six methyl groups have become equivalent, as was observed in the liquid phase at room temperature,[1] and we interpret this change in terms of a dynamic averaging taking place between three equivalent structures (I). From our 77 K data, we predict that such averaging would lead to a coupling constant of $(2 \times 11.5 - 2.8)/3 = 6.7$ G, which agrees with that observed (6.7 G) at 130 K. This supports our assignment of the low temperature spectrum and the negative sign of the smaller coupling; other potential analyses agree poorly with the high temperature data when averaged in this way. On recooling to 77 K, the spectrum is essentially restored to that observed initially, as expected if our interpretation is correct, although we note some loss of resolution following annealing.

Iwasaki *et al.*[13] suggested that the lifting of the ψ_A/ψ_S degeneracy in the $C_6H_6^{+\cdot}$ cation might be explained by matrix perturbations, but that a driving force for distortion must be provided by Jahn–Teller instability. In the present case,

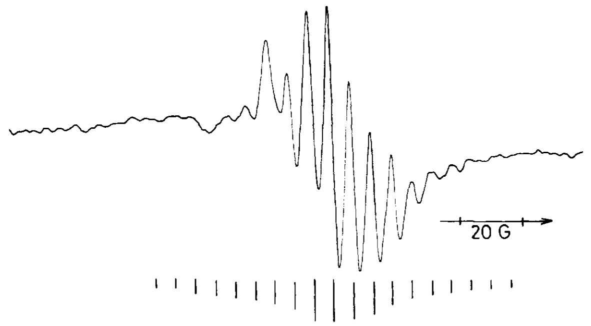


Figure 2. E.s.r. spectrum of hexamethylbenzene radical cations ($HMB^{+\cdot}$) recorded at 130 K.

environmental effects could also be invoked to explain the degeneracy breaking; however, since the SOMO in the $C_6Me_6^{+\bullet}$ cation is ψ_A rather than ψ_S, as in the $C_6H_6^{+\bullet}$ cation, we suggest that the nature of any ring distortion resulting from Jahn–Teller instability must be different in the two cations. We are presently carrying out M.O. calculations on this matter.

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