areas consistent with an end-on, upright orientation. The six compounds **10–15** showed no evidence of monolayer formation. These shorter compounds have only four or five fused rings and only nominal hydrophilic character (in the case of **15**, no hydrophilicity). They are included to indicate the relationship between structure- and monolayer-forming ability,[5] and their behavior stands in contrast to that of the other compounds studied. The compounds which do form stable monolayers possess extensive ring systems which enhance film-forming capacity through cohesive interaction of the aromatic moieties. End-on packing maximizes interaction between the molecular surfaces and minimizes contact of the hydrophobic molecular surfaces with the water surface.

The present results indicate that the extended, rigid systems described here may be of considerable value in the construction of a variety of functional multilayer systems formed by the Langmuir–Blodgett transfer technique. Quinones are essential elements of any biomimetic model based on the photosynthetic reaction center as well as for other electron transfer model systems and electrochemical studies. Additionally, these very long, stiff molecules of accurately known length possessing extended π-bonded systems provide unusual possibilities for optical and electronic properties in monolayer assemblies.

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An ESR Investigation of the Structure and Rearrangement of the Hexamethyl(Dewar benzene) Radical Cation

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Despite the much greater thermodynamic stability of hexamethylbenzene (HMB) over its strained "Dewar" isomer (HMD), the thermal conversion of HMD to HMB proceeds with an activation energy of 37 kcal/mol;[1,2] this has been partly ascribed to the orbital symmetry forbidden nature of the process.[3] In contrast, photosensitized conversion of HMD to HMB is well-known.[4]

The mechanism proposed for this reaction involves the transfer of an electron from HMD to the photosensitizer with the formation of HMD$\bullet^+$. radical cations.[2] Since this mechanism requires a very facile rearrangement of HMD$\bullet^+$ to HMB$\bullet^+$, it has been questioned whether HMD$\bullet^+$ can be an energy minimum. A laser-flash spectroscopic study has recently shown the presence of only the HMB$\bullet^+$ cation, indicating that the lifetime of the HMD$\bullet^+$ cation must be less than 15 ns.[5]

In order to study the structure and stability of this elusive HMD$\bullet^+$ cation, we used the now well established method of exposing dilute frozen solutions of substrates in freon solvents to ionizing radiation.[6,7] This technique often gives well-resolved ESR spectra of the corresponding substrate radical cations, following what is essentially a single electron oxidation by $CFCl_3\bullet^+$ cations, and is applicable to substrates with ionization potentials of <11.8 eV.

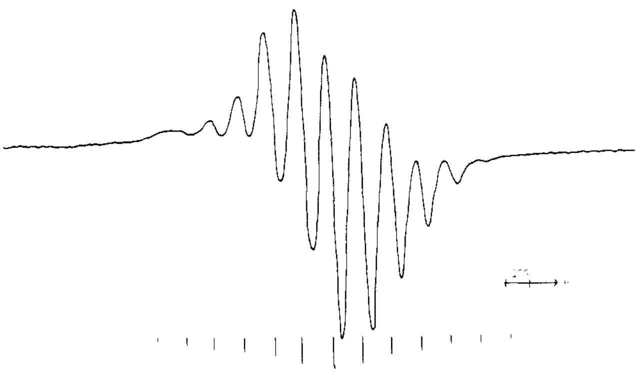


Figure 1. ESR spectrum of hexamethyl(Dewar benzene) radical cations $(HMD)\bullet^+$ in a $CFCl_3$ matrix at 77 K.

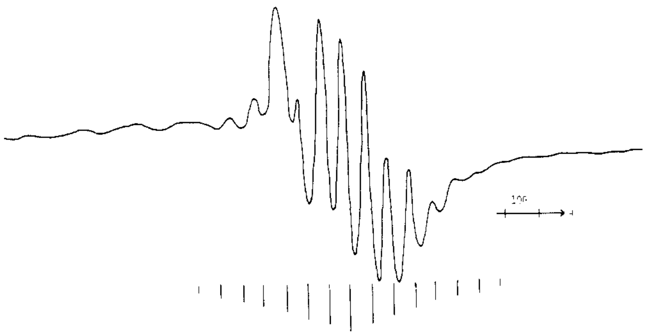
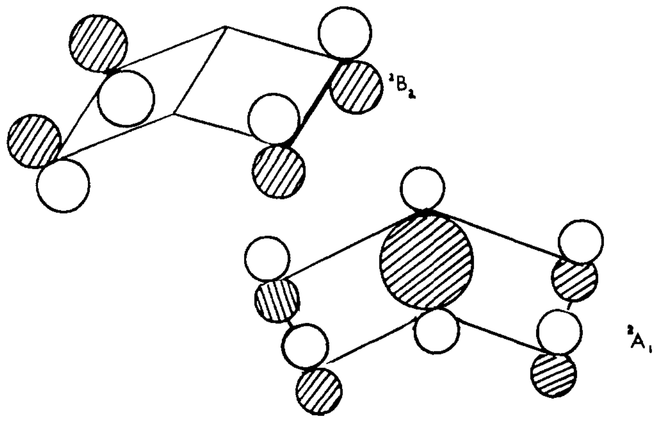


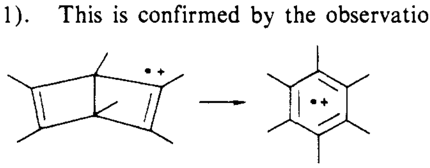
Figure 2. ESR spectrum recorded at 150 K, showing features assigned to hexamethylbenzene radical cations $(HMB)\bullet^+$ formed by ring opening of HMD$\bullet^+$ cations.

Chart I



The spectrum obtained from HMD is shown in Figure 1. This comprises a set of 13 lines with nearly binomial intensities and a single splitting of 9.5 G, indicating hyperfine coupling to four equivalent methyl groups. This must be due to the HMD$^+$ radical cation, which is *stable* in the $CFCl_3$ matrix.

On annealing the sample to ca. 150 K, the spectrum suddenly changed to that shown in Figure 2. We interpret this in terms of a rearrangement of the HMD$\bullet^+$ cation to its more stable isomer, HMB$\bullet^+$ (eq 1). This is confirmed by the observation of an



(1)

identical spectrum from an authentic sample of HMB. The coupling of 6.7 G is virtually identical with that previously observed for HMB$\bullet^+$ cations in a sulfuric acid solution.[8] On recooling either sample containing HMB$\bullet^+$ cations to 77 K, the spectrum

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reduced to a poorly resolved singlet, but with a very similar overall width to that observed at the higher temperature. This is consistent with the freezing-out of the rotational motions of the methyl groups in this sterically hindered radical, giving a broad range of conformations, and consequently a spread of hyperfine couplings, hence the low resolution.

The ESR spectrum of the HMD•$^+$ cation indicates that the SOMO is essentially the $^2B_2$ orbital of the parent Dewar benzene molecule.[9] This was also the conclusion drawn from the nature of the polarizations observed in a photo-CIDNP study of HMD with excited (triplet) electron acceptors.[10] However, polarization of the protons on the bridge-head methyl groups was also observed, which leads these workers to conclude that the most likely explanation for this was the simultaneous formation of a second cation ($^2A_1$) via. a competing pathway, with its spin density confined mainly to the transannular bond.

The idea of competing pathways was borne out by the results obtained with different electron acceptors, which caused variations in the relative polarizations of the olefinic and bridge-head methyl groups. This is reasonable since calculations on the parent Dewar benzene molecule indicate that the $^2B_2$ and $^2A_1$ orbitals are of very similar energy. Our results, however, show only the presence of the $^2B_2$ cation.

It is of interest to consider why the $CFCl_3$ matrix is so successful in stabilizing the obviously highly unstable HMD•$^+$ cation. We feel that the most reasonable explanation is that the $CFCl_3$ molecules pack tightly and rigidly around the substrate molecule so that when it is ionized to its radical cation, although there is a large driving potential for rearrangment to the HMB•$^+$ cation, the molecular framework cannot relax to achieve the necessary planar arrangement. On annealing, softening of the rigid matrix allows the rearrangement to occur. A similar effect was proposed previously to account for changes in the optical spectra of radical cations on annealing the solid matrix in which they were isolated.[11]

Acknowledgment. I thank Prof. Symons for access to ESR facilities.

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Surface Photochemistry: Products Retained on Pt(111) during Photolysis of Adsorbed CH_3Br

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The photochemistry of molecules at the gas-solid interface has been successfully investigated in a number of laboratories,[1-11] but very little work has shown photochemistry on *clean metal* surfaces. Previous work from this research group[12] showed that the photolysis of methyl halides (CH_3Br, CH_3Cl) adsorbed on Pt(111) lead to a detectable amount of methane (290 K), but no other hydrocarbons, in TPD. For CH_3Br, Br desorbed as atoms between 720 and 950 K. Significantly, these two methyl halides show no thermal chemistry on Pt(111).

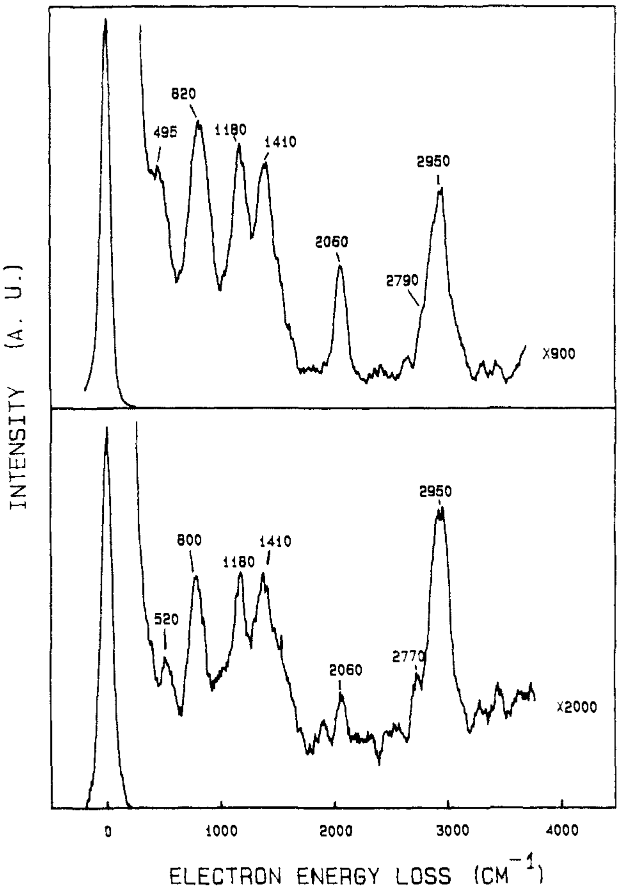

Figure 1. Specular (upper panel) and off-specular (lower panel) HREELS taken after irradiation for 90 min of a submonolayer of $CH_3Br/Pt(111)$ and flashing briefly to 220 K to remove remaining molecular CH_3Br.

The results suggest that, as in the gas phase, CH_3X (X = Br, Cl) absorbs UV light and forms an electronically excited state that is repulsive and, with significant probability, cleaves the C-X bond even though other relaxation paths exist.[14]

In this communication we identify, using vibrational spectroscopy, the adsorbed species formed during UV irradiation of CH_3Br on Pt(111). By comparison with measurements on CH_3I, which thermally decomposes to CH_3(a) and I(a),[15] we identify adsorbed methyl as the hydrocarbon fragment formed and retained during the photolysis.

A detailed description of the ultra-high-vacuum (UHV) system has been given elsewhere.[16] The Pt(111) surface was cleaned by Ar$^+$ ion sputtering, oxidation, and high-temperature annealing until no impurities were detected in Auger electron spectroscopy. With the sample at 100 K, purified CH_3Br was dosed through a 3 mm i.d. tube positioned 6 mm from the sample. A CH_3Br coverage slightly less than a monolayer was produced by warming multilayer $CH_3Br/Pt(111)$ to 135 K, which desorbs the multilayer

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