EPR Observation of a Radical Cation Salt derived from Hexamethyl(Dewar Benzene) at Room Temperature

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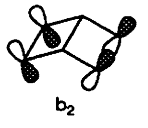
Vapour deposition of hexamethyl(Dewar benzene) or hexamethylprismane onto solid dioxygenyl hexafluoroantimonate at liquid nitrogen temperature followed by warming the sample to room temperature gives rise to 13-line EPR spectra with binomial intensities (g = 2.0025 ± 0.0004; A = 10.7 ± 0.1 G), which are very similar to the spectra previously observed at cryogenic temperatures upon radiolysis of hexamethyl(Dewar benzene).

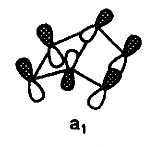
Radical cations derived from strained-ring systems have been the targets of detailed scientific scrutiny[1] by various optical methods as well as chemically induced dynamic nuclear polarization (CIDNP),[2] EPR,[3] ENDOR,[4] and optically detected magnetic resonance (ODMR).[5] The unique bonding in strained-ring systems causes their radical cations to assume unusual structure types and to undergo unusual rearrangements. Among these systems, the radical cation(s) derived from hexamethyl(Dewar benzene) (HMD) has been at the centre of particular interest.[6] While optical methods failed to detect such a species, even as a short-lived intermediate,[6a,b,g] its existence was clearly indicated by CIDNP.[6c] Since CIDNP experiments provide a direct link between a paramagnetic (radical cation) intermediate and the diamagnetic product(s) generated from it, these results provide unambiguous evidence for the HMD$^{\cdot+}$ radical cation.

Ab initio calculations on the parent Dewar benzene radical cation (at the HF/6-31G* level of theory) support two possible minima on this potential energy surface, *i.e.* radical cations of $^2B_2$ and $^2A_1$ symmetry, respectively;[6c] the hexamethyl derivative of the former species clearly is the predominent contributor to the CIDNP effects.[6c] The species of $^2B_2$ symmetry was generated also upon electron-transfer oxidation of hexamethylprismane.[6d] More recently, HMD$^{\cdot+}$ ($^2B_2$) and a neutral radical derived by deprotonation of HMD$^{\cdot+}$ were characterized by EPR[6e,f,h,i] and ODMR.[6j]

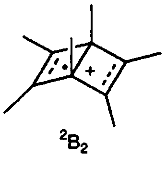
We wish to report a novel method of generating radical cations from hexamethyl(Dewar benzene) and of stabilizing them on the surface of an oxidant; this method allows the observation and characterization of such a radical cation at room temperature. Appropriate salts of the dioxygenyl radical cation, for example, the tetrafluoroborate ($O_2{}^{\cdot+}BF_4{}^-$) or the hexafluoroantimonate ($O_2{}^{\cdot+}SbF_6{}^-$) salts, have been identified as powerful oxidants[7] and as useful reagents for generating radical cation salts.[7b] We have used these salts as oxidants and, simultaneously, as solid supports for the resulting radical cation. When hexamethyl(Dewar benzene) or hexamethylprismane are vacuum-deposited onto solid dioxygenyl hexafluoroantimonate at liquid nitrogen temperature and the sample is warmed slowly to room temperature, a strong EPR spectrum (g = 2.0025 ± 0.0004; A = 10.7 ± 0.1G; FWHH = 3 G) is observed (Fig. 1). The spectrum can be fitted to a 13-line pattern with essentially binomial intensities (the average deviation is 6.8%). The spectrum persists for several hours at room temperature, before decaying to a broad, featureless g = 2 spectrum.



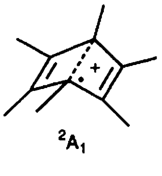
b$_2$



a$_1$



$^2B_2$



$^2A_1$

The generation of radical cation salts is not limited to that derived from HMB; for example, deposition of hexamethylbenzene (HMB) onto $O_2{}^{\cdot+}SbF_6{}^-$ under similar conditions gave rise to a 19-line EPR spectrum (g = 2.00258 ± 0.0003; A = 6.55 ± 0.03 G; FWHH = 3 G); the line intensities of the nine central lines are compatible with the EPR spectrum previously observed upon chemical oxidation of HMB and assigned to the corresponding radical cation (HMB$^{\cdot+}$).[8] Similarly, deposition of pentamethylbenzene (PMB) onto $O_2{}^{\cdot+}SbF_6{}^-$ generated a 13-line EPR spectrum (g = 2.00254 ± 0.0002; A = 10.3 ± 0.03 G; FWHH = 3 G), which appears identical with the spectrum previously assigned to PMB$^{\cdot+}$.[9]

Among these spectra, the 13-line spectrum derived from HMD (Fig. 1) is of particular interest, as it is identical in every respect with spectra previously observed in frozen matrices and ascribed to HMD$^{\cdot+}$ ($^2B_2$).[6e,g,h] To find evidence for the

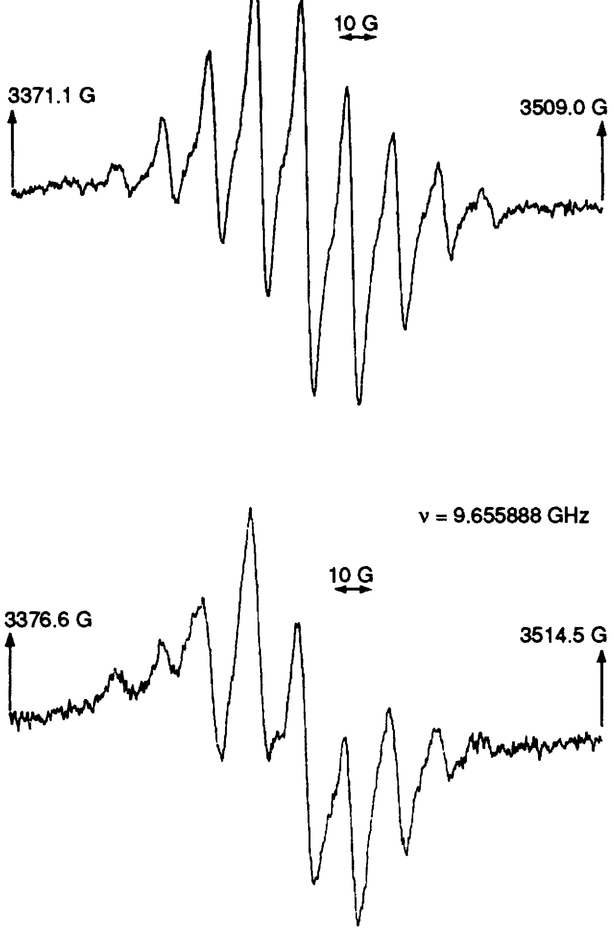


Fig. 1 Room temp. EPR spectrum observed upon vapour deposition of hexamethylprismane (bottom) or hexamethyl(Dewar benzene) (top) onto (solid) dioxygenyl hexafluoroantimonate at liquid nitrogen temperature and allowing the sample to warm to room temp.

same species at room temperature may seem surprising, particularly in view of the documented rapid rearrangement of HMD$^{\cdot+}$ to hexamethylbenzene radical cation (HMB$^{\cdot+}$) in fluid solution.[6a,b,c,g] The persistence of the species at room temperature could be explained as a manifestation of coulombic interactions between the radical cation and the oxidant surface on which it is generated. The crystal structure of the oxidant may play an important role, since the radical cation likely occupies a site in proximity to the oxidant. Although the structure of dioxygenyl hexafluoroantimonate ($O_2^{\cdot+}SbF_6^-$) is not known, it is likely similar to that of oxonium hexafluoroantimonate ($H_3O^+SbF_6^-$), the structure of which has been determined.[10] In the $H_3O^+SbF_6^-$ crystal, the oxonium ion is surrounded by eight SbF_6^- ions in a body-centred cubic structure. A projection of the unit cell along the 111 axis shows an oxonium ion at the centre of a rectangle with the dimensions 515 × 717 pm. The molecular dimensions of the MeC_2-(Me)C_3-C_5(Me)-C_6Me 'base' of HMD$^{\cdot+}$ are estimated at approximately 500 × 580 pm; accordingly, the surface of the $O_2^{+\cdot}SbF_6^-$ unit cell may be suitable for generating and trapping HMD$^{\cdot+}$, as HMD approaches the surface.

We emphasize that the identical appearance of our spectrum (Fig. 1) to those generated by radiolysis at cryogenic temperatures and ascribed to HMD$^{\cdot+}$ does not require the species generated in the two experiments to be identical. The observed hyperfine coupling patterns for these species are characteristic for intermediates whose electron spin is distributed over four equivalent carbons, each of which is substituted with a freely rotating methyl group. Any further assignment goes beyond the mere interpretation of the spectral data and relies, in addition, on secondary information, such as the structure of the precursor, or on chemical intuition. While one of the observed species may indeed by HMD$^{\cdot+}$ ($^2B_2$), the second spectrum may represent a hexamethylbenzene radical cation which is held rigidly in the elongated structure predicted by *ab nitio* calculations as the minimum for the parent $C_6H_6^{\cdot+}$ species[11] and identified by Iwasaki and coworkers in freon matrices at 4 K.[12] The species observed at room temperature shows no similarities to another 'distorted' radical cation, obtained upon radiolysis of HMB at 77 K (A = 11.5 G, 4 Me; A = (−)2.8 G, 2 Me).[13] Considering the vast differences in both temperature and matrix structure this fact is not surprising.

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