These preliminary results suggest that the reaction chemistry of **1** can be viewed as the disproprotionation of two Rh(II) centers into the Rh(III) fragment Cp^*RhCl_2 and the Rh(I) fragment Cp^*Rh. This latter species looks particularly interesting in view of the highly reactive nature of the Cp^*ML (M = Rh and Ir, L = PMe_3 or CO) fragments.[17] Further chemistry with these complexes and the utilization of **1** as a source of Cp^*Rh are under investigation and will be the subjects of a forthcoming full paper.

Acknowledgment. The support of this work by the Division of Chemical Sciences, Office of Basic Energy Sciences, Office of Energy Research, U.S. Department of Energy (DE-FG02-88ER13880), ARCO Chemical, and Johnson Matthey (a loan of $RhCl_3$) is gratefully acknowledged. The National Science Foundation provided a portion of the funds for the purchase of the X-ray (CHE-7820347) and NMR (PCM-8115599) equipment.

Supplementary Material Available: ORTEP diagrams of the second molecule of **1** (twofold site) and the minor orientation of **4** and tables of positional and thermal parameters for **1** and **4** (4 pages). Ordering information is given on any current masthead page.

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$^2B_2$: The Ground State of the Hexamethyl(Dewar benzene) Radical Cation. Time-Resolved Fluorescence Detected Magnetic Resonance[†]

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The hexamethyl(Dewar benzene) radical cation ($HMDB^{\bullet+}$) has attracted considerable interest as an assumed intermediate in the photosensitized conversion of HMDB to hexamethylbenzene (HMB).[1,2] Recently, the electronic structure of $HMDB^{\bullet+}$ has been studied extensively, but the assignment of its ground state is still in doubt. The two highest molecular orbitals of HMDB are the b_2 and a_1 orbitals.[2,3] In the $^2B_2$ state of $HMDB^{\bullet+}$, spin density is confined in the bonds between the two pairs of olefinic carbons, while in the $^2A_1$ state of $HMDB^{\bullet+}$, spin density is localized in the bond between the two transannular carbons. Ab initio calculations by Roth et al.[2] predict that $^2B_2$ is the ground state and is 8 kcal/mol more stable than the $^2A_1$ state. But a MINDO/3 calculation by Bews and Glidewell[4] predicts that $^2A_1$ has the minimum-energy geometry. In a CIDNP study of photoreactions of HMDB with excited (triplet) electron acceptors, Roth et al.[2] presented indirect evidence for the formation of both $^2B_2$ and $^2A_1$ states generated by competing pathways, and the ground state was not assigned experimentally. More recently, Rhodes[5] reported EPR studies of $HMDB^{\bullet+}$ in freon matrices. He observed $HMDB^{\bullet+}$ in the $^2B_2$ state in $CFCl_3$ and in the $^2A_1$ state in $CF_2ClCFCl_2$ and suggested that the ground state of $HMDB^{\bullet+}$ is $^2A_1$. We have studied $HMDB^{\bullet+}$ in freon matrices but failed to confirm the $^2A_1$ $HMDB^{\bullet+}$ in $CF_2ClCFCl_2$.[6] Recently, other workers have also reexamined this system.[7] In view of the strong interactions of solid freon matrices that can change the electronic state of the solute radical cations,[5,8] it is useful to examine $HMDB^{\bullet+}$ in nonpolar solvents. Here, we report our study of $HMDB^{\bullet+}$ in liquid alkanes by time-resolved fluorescence detected magnetic resonance (FDMR).[9] We conclude that the ground state of $HMDB^{\bullet+}$ is $^2B_2$ rather than $^2A_1$.

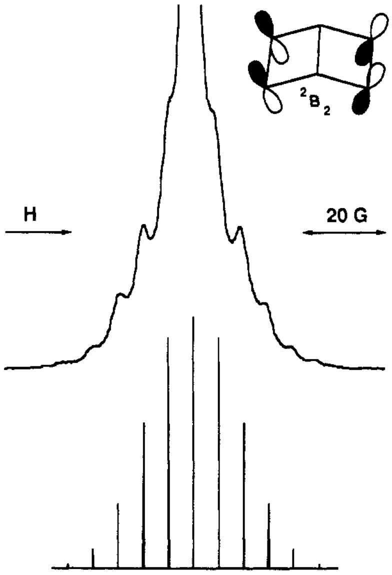

Figure 1. FDMR spectrum observed at 205 K in cyclopentane containing 10^{-2} M hexamethyl(Dewar benzene) and 10^{-4} M perdeuterated anthracene.

$HMDB^{\bullet+}$ was produced in a solution of 10^{-2} M HMDB and 10^{-4} M perdeuterated anthracene (A) in cyclopentane by using pulsed electron beam irradiation. Our observations were carried out at temperatures between 205 and 245 K. Electron beam pulses with a width of 12 ns were generated by a 3-MeV electron Van de Graaff accelerator at a repetition rate of 720 pulses/s. The ionizing radiation creates singlet-phased radical ion pairs in cyclopentane (RH) consisting of a cyclopentane radical cation and an electron (eq 1). Most of the ion pairs recombine geminately in a few picoseconds (eq 2). A few percent of the cyclopentane (gas-phase ionization potential (IP) = 10.5 eV)[10] cations are scavenged by transferring positive charge to HMDB (IP = 7.8 eV)[3] solute to form $HMDB^{\bullet+}$ (eq 3), while some of the electrons are converted to the scintillator radical anion ($A^{\bullet-}$) (eq 4). The resulting radical ion pairs consisting of $HMDB^{\bullet+}$ and $A^{\bullet-}$ are still spin-correlated. Upon recombination, an excited singlet state ($^1A^*$) is generated (eq 5), resulting in fluorescence (A*) which is detected.

$$RH \xrightarrow{e^-} RH^{\bullet+} + e^- \quad (1)$$

$$RH^{\bullet+} + e^- \rightarrow RH^* \quad (2)$$

$$RH^{\bullet+} + HMDB \rightarrow RH + HMDB^{\bullet+} \quad (3)$$

$$e^- + A \rightarrow A^{\bullet-} \quad (4)$$

$$HMDB^{\bullet+} + A^{\bullet-} \rightarrow HMDB + {}^1A^* \quad (5)$$

[†] Work performed under the auspices of the Office of Basic Energy Science, Division of Chemical Science, US-DOE, under contract number W-31-109-ENG-38.

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The time-resolved EPR spectrum, shown in Figure 1, of radical ion pairs of HMDB$^{\bullet+}$ and A$^{\bullet-}$ which recombine to give ^{1}A* was obtained by measuring the fluorescence intensity as a function of the applied magnetic field. The resonant decrease in the intensity of fluorescence is induced by the application of a single 100-ns microwave pulse immediately following the electron beam pulse. The fluorescence signal was integrated by a boxcar detector over a 100-ns time window beginning immediately after the microwave pulse. The details of the time-resolved FDMR spectroscopy method have been described elsewhere.[9]

The FDMR spectrum consists of an intense central line (offscale) due to the unresolved EPR lines of scintillator ions superimposed on a wider, multiplet spectrum. As indicated by the stick spectrum, the multiplet shows 11 lines out of a binomial 13-line pattern with a single spacing of 9.2 G, which is due to the interaction from 12 protons of four olefinic methyl groups. The spectrum is assigned to HMDB$^{\bullet+}$ in the $^2B_2$ state and is inconsistent with HMDB$^{\bullet+}$ in the $^2A_1$ state, which should give rise to a septet EPR spectrum with the major hyperfine coupling to only six protons of the two bridgehead methyl groups.

The FDMR spectrum differs from that of HMB$^{\bullet+}$, to which HMDB may rearrange upon electron removal. FDMR spectra[11] of HMB$^{\bullet+}$ obtained between 205 and 298 K in cyclopentane containing 10^{-3} M HMB show a coupling constant of 6.7 G in agreement with the published value.[5b,12]

In order to probe the longevity of HMDB$^{\bullet+}$, a study was carried out by delaying application of the microwave pulse with respect to the electron beam pulse. The intensity of the FDMR spectrum decreased with increasing time delay from 0 to 1000 ns. But even after 1000 ns, the multiplet due to HMDB$^{\bullet+}$ could be clearly recognized, indicating that $^2B_2$ HMDB$^{\bullet+}$ can persist for a microsecond or longer (before recombining with A$^{\bullet-}$) under our experimental conditions. In the time frame of our observations, no FDMR features that can be assigned to HMDB$^{\bullet+}$ in the $^2A_1$ state were observed, and no evidence of the HMB$^{\bullet+}$ spectrum could be seen.

HMDB$^{\bullet+}$ was also studied in *n*-pentane solvent. Similar results were obtained. Rhodes[5] proposed that the $^2A_1$ state he observed in the less rigid $CF_2ClCFCl_2$ matrix be assigned to the ground state, while the $^2B_2$ state observed in $CFCl_3$ is due to the more tightly packed matrix that prevents the HMDB$^{\bullet+}$ from relaxing via stretching of the transannular bond to form the $^2A_1$ state. Our result disagrees with this proposal, and very recent work refutes the Rhodes[5] assignment of the $^2A_1$ state.[7] Additionally, an EPR study of the bicyclo[1.1.0]butane radical cation in $CFCl_3$ has demonstrated that stretching of the transannular bond of the cation is not hindered in the rigid $CFCl_3$ matrix.[13]

Our FDMR results indicate that the lifetime of HMDB$^{\bullet+}$ in nonpolar alkane solvents is significantly longer than the reported value of less than 15 ns in a study of isomerization of HMDB to HMB catalyzed by excited electron acceptors in polar solvents.[1c] A recent optical study[14] of HMDB$^{\bullet+}$ pulse radiolytically generated in 3-methylpentane containing 1-butyl chloride as an electron scavenger gives rate constants of 1.71 s^{-1} and 0.015 s^{-1} for the valence isomerization of HMDB$^{\bullet+}$ at 93 and 77 K, respectively, which also points to longer lifetimes of HMDB$^{\bullet+}$.

The relative longevity of the HMDB radical cation obtained in our study suggests that we are observing a ground-state species, which is the $^2B_2$ state.

We have found no evidence of HMDB$^{\bullet+}$ in the $^2A_1$ state, even though one expects charge transfer from the solvent radical cation to populate both states of the HMDB radical cation since the energy difference between them is expected to be small.[2,3] If both states of HMDB$^{\bullet+}$ are produced and the $^2A_1$ state quickly rearranges to HMB$^{\bullet+}$, we would expect to see the HMB$^{\bullet+}$ FDMR spectrum, which was not the case. As we have mentioned above, the HMB$^{\bullet+}$ FDMR spectrum was easily observed when HMB was the solute in cyclopentane. We conclude that there is a fast conversion of the $^2A_1$ into the $^2B_2$ state and the reverse is not thermally accessible. Such an interconversion is state symmetry forbidden,[15] but is not without precedent.[16]

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Registry No. HMDB, 7641-77-2; HMDB$^{\bullet+}$, 85293-78-3.

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Structure of the Paramagnetic Species Formed upon γ-Irradiation of Hexamethyl(Dewar benzene) in a $CF_2ClCFCl_2$ Matrix. An ESR and ENDOR Study[1]

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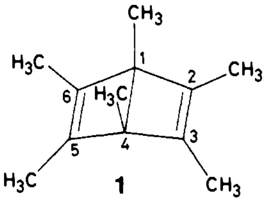
Two recent communications[2,3] reported on the ESR studies of the radical cation generated from hexamethyl(Dewar benzene) (hexamethylbicyclo[2.2.0]hexa-2,5-diene, **1**) by γ-rays in $CFCl_3$ and $CF_2ClCFCl_2$ matrices at 77 K. With $CFCl_3$ as the matrix,[2]



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the ESR spectrum obtained consisted of a multiplet spaced by 0.95 mT, which was assigned to the 12 equivalent protons of the four outer methyl groups in the 2,3,5,6-positions of the primary radical cation **1**$^{\bullet+}$. Annealing of the sample led to rearrangement of **1**$^{\bullet+}$ into the radical cation of hexamethylbenzene (**2**).[2] When $CF_2ClCFCl_2$ was used as the matrix,[2] the ESR spectrum, also taken at 77 K, differed completely from that observed for **1**$^{\bullet+}$ in $CFCl_3$. This spectrum was regarded as a septet spaced by 1.4 mT, stemming from six equivalent protons of the two inner methyl groups in the 1,4-positions of **1**$^{\bullet+}$.[3] On annealing, some features seemingly due to **2**$^{\bullet+}$ became apparent. The author[3] claims that the different ESR spectra observed at 77 K with $CFCl_3$ and $CF_2ClCFCl_2$ arise from *different electronic states of the same radical cation*, and he tentatively suggests that this difference is caused by an effect of the matrix on the relaxing framework of **1**$^{\bullet+}$.

We have performed ESR studies on γ-irradiated **1** in $CFCl_3$, CF_3CCl_3, and $CF_2ClCFCl_2$ matrices. The results reported previously[2] with $CFCl_3$ were confirmed, and an ESR spectrum similar to that observed with this matrix at 77 K was obtained with

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