The time-resolved EPR spectrum, shown in Figure 1, of radical ion pairs of HMDB$^{\bullet+}$ and $A^{\bullet-}$ which recombine to give $^1A^*$ 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 (off-scale) 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]

Acknowledgment. We thank R. H. Lowers for the operation of the Van de Graaff accelerator and other technical support. We thank Professor F. Williams for communicating the results of his study[7a] with us.

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

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(11) Qin, X.-Z.; Werst, D. W.; Trifunac, A. D. Unpublished results.

(12) Hulme, R.; Symons, M. C. R. *J. Chem. Soc.* **1965**, 1120.

(13) Gerson, F.; Qin, X.-Z.; Ess, C.; Kloster-Jensen, E. *J. Am. Chem. Soc.* **1989**, *111*, 6456.

(14) Gebicki, J.; Marcinek, A.; Mayer, J. *J. Am. Chem. Soc.* **1989**, *111*, 3098.

(15) Goldstein, M. J.; Leight, R. S. *J. Am. Chem. Soc.* **1977**, *99*, 8112.

(16) (a) Haselbach, E.; Bally, T.; Lanyiova, Z.; Baertschi, P. *Helv. Chim. Acta* **1979**, *62*, 583. (b) Raghavachari, K.; Haddon, R. C.; Roth, H. D. *J. Am. Chem. Soc.* **1983**, *105*, 3110. (c) Gebicki, J. L.; Gebicki, J.; Mayer, J. *Radiat. Phys. Chem.* **1987**, *30*, 165.

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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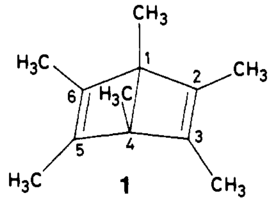
Received September 27, 1989

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]



1

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 $\mathbf{1}^{\bullet+}$. Annealing of the sample led to rearrangement of $\mathbf{1}^{\bullet+}$ 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 $\mathbf{1}^{\bullet+}$ 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 $\mathbf{1}^{\bullet+}$.[3] On annealing, some features seemingly due to $\mathbf{2}^{\bullet+}$ 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 $\mathbf{1}^{\bullet+}$.

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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(1) Applications of ENDOR Spectroscopy to Radical Cations in Freon Matrices. 8. Part 7: Aebischer, J.-N.; Bally, T.; Roth, K.; Haselbach, E.; Gerson, F.; Qin, X.-Z. *J. Am. Chem. Soc.* **1989**, *111*, 7909. Part 6: Gerson, F.; de Meijere, A.; Qin, X.-Z. *J. Chem. Soc., Chem. Commun.* **1989**, 1077.

(2) Rhodes, C. J. *J. Am. Chem. Soc.* **1988**, *110*, 4446.

(3) Rhodes, C. J. *J. Am. Chem. Soc.* **1988**, *110*, 8567.

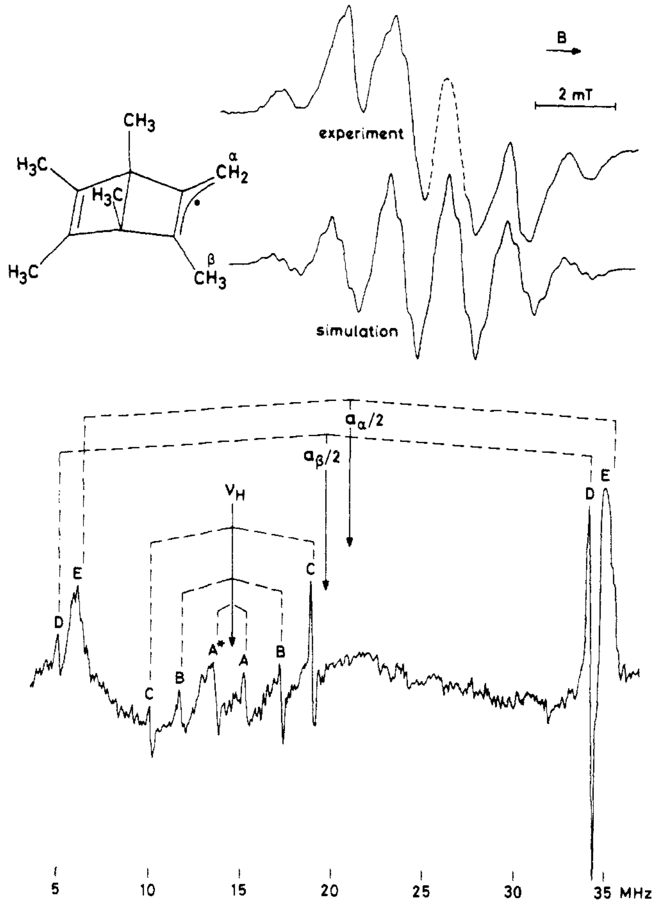
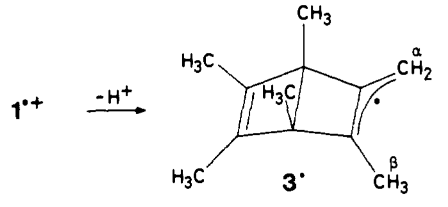


Figure 1. Top: ESR spectrum of **3**$^\bullet$ in a $CF_2ClCFCl_2$ matrix at 115 K ($g = 2.0026 \pm 0.0002$). The dashed curve was obtained by deducing an absorption from the γ-irradiated quartz tube. The simulation made use of the coupling constants, in mT: 1.50 (2 H), 1.405 (3 H), 0.315 (3 H), 0.197 (3 H), and 0.056 (3 H); line shape Gaussian; line width 0.2 mT. Bottom: corresponding proton ENDOR spectrum. The low-frequency A signal, marked by an asterisk, overlaps with a ^{19}F ENDOR absorption from the matrix.

CF_3CCl_3 at the same temperature. It can reasonably be assigned to the primary radical cation **1**$^{\bullet+}$. Conversion of **1**$^{\bullet+}$ into **2**$^{\bullet+}$ was also detected at elevated temperatures, this rearrangement occurring less readily in a CF_3CCl_3 than in a $CFCl_3$ matrix.

However, with $CF_2ClCFCl_2$ as the matrix, our analysis and interpretation of the ESR spectrum are at variance with those given previously.[3] The multiplet with an average spacing of 1.44 mT is clearly *a five-proton sextet and not a six-proton septet*, as revealed by the ESR spectrum in Figure 1. (The broad, weak signal at low field in Figure 1 of ref 3 does not belong to this multiplet, but stems from an unknown impurity.) As the five protons giving rise to the major hyperfine splitting of 1.4–1.5 mT must be located in one CH_3 and one CH_2 group, the obvious structure of the paramagnetic species in question is the neutral cycloallyl radical **3**$^\bullet$, which has been formed from **1**$^{\bullet+}$ by the loss of a proton.



The structure **3**$^\bullet$ has been corroborated by the corresponding ENDOR spectrum also displayed in Figure 1. The two outer pairs of ENDOR signals (D and E), centered at $a_\beta/2 = 19.68$ and $a_\alpha/2 = 21.01$ MHz, are separated by twice the free proton frequency, $\nu_H = 14.56$ MHz.[4] In a unit of magnetic field (B), the two coupling constants amount to $a_\beta = 1.405 \pm 0.005$ and $a_\alpha = 1.50 \pm 0.10$ mT. The smaller value (1.405 mT), associated with the narrow signals D, arises from the three equivalent β-protons in the freely rotating methyl substituent of the allyl π-system, whereas the larger one (1.50 mT), represented by the broad signals E, is appropriate for the two nonequivalent α-protons of the allyl methylene group. These assignments are fully compatible with the hyperfine data for structurally related allyl radicals.[5] The broadening of the E signals is attributed to the hyperfine anisotropy of the α-protons and to the unresolved difference in the coupling constants for the endo and exo positions. The three inner pairs of ENDOR signals (A, B, and C), centered at $\nu_H = 14.56$ MHz, are separated by the coupling constants of 1.58, 5.52, and 8.84 MHz or, in a unit of the magnetic field, by 0.056 ± 0.002, 0.197 ± 0.002, and 0.315 ± 0.002 mT. They belong to the protons of three methyl substituents further removed from the allyl π-system of **3**$^\bullet$; the coupling constant of the protons in one methyl group evidently fails to be observed or the associated ENDOR signals coincide with A or B or C. Assignments of the three values to methyl substituents in individual positions are difficult.[6] Nevertheless, their nonequivalence accords with the low symmetry (C_1) of **3**$^\bullet$.

Additional evidence favoring the structure of a neutral allyl radical is the persistence, unusual for radical cations in freon matrices. Thus, the ESR spectrum of **3**$^\bullet$ could still be observed at 150 K, well above the softening point of $CF_2ClCFCl_2$.

As stated in a paper by Williams et al.,[9] conversion of **1**$^{\bullet+}$ to **3**$^\bullet$ in the $CFCl_2CF_2Cl$ matrix occurs when the concentration of **1** exceeds ca. 1 mol %. This finding indicates that the reaction is bimolecular, i.e., the neutral **1** acts as the proton acceptor. Such ion–molecule reactions have often been observed in the relatively mobile $CF_2ClCFCl_2$ matrix.[10]

Acknowledgment. This work was supported by the Swiss National Science Foundation. We are obliged to Prof. E. Haselbach, Université de Fribourg, for the permission to use his ^{60}Co source of γ-rays and to the Bruker Analytische Messtechnik GmbH, Karlsruhe (FRG), for taking the ENDOR spectrum above 35 MHz. Our thanks are also due to Prof. F. Williams, University of Tennessee, Knoxville, TN, for a preprint of his paper.

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[4] See, e.g.; Kurreck, H.; Kirste, B.; Lubitz, W. *Electron Nuclear Double Resonance of Radicals in Solution*; VCH Publishers: New York, 1988; Chapter 2.

[5] Landolt-Börnstein, *Magnetic Properties of Free Radicals*; Fischer, H., Hellwege, K.-H., Eds.; Springer-Verlag: Berlin, 1977; Volume II/9b.

[6] Calculations by AM1[7] and INDO[8] (based on AM1 optimized geometry) were not very helpful in this respect.

[7] Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902.

[8] Pople, J. A.; Beveridge, D. L. *Approximate Molecular Orbital Theory*; McGraw-Hill: New York, 1970.

[9] Williams, F.; Guo, Q.-X.; Nelsen, S. F. *J. Am. Chem. Soc.*, third of three papers in this issue.

[10] See ref 9 for the pertinent literature.

Reinvestigation of the Hexamethyl(Dewar benzene) Radical Cation in Freon Matrices

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Received October 16, 1989

Rhodes recently reported[1,2] that the *electronic state* of the hexamethyl(Dewar benzene) (HMDB) radical cation generated