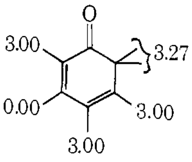
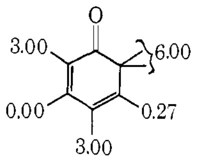
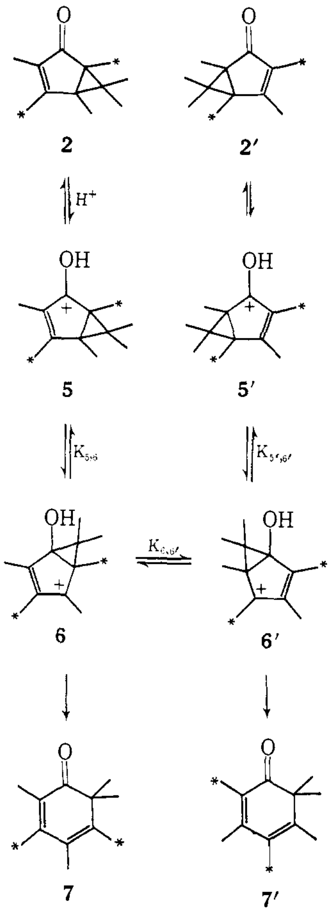


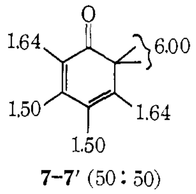
3A



3B

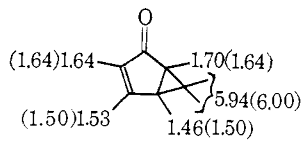
The result is, however, consistent with a mechanism in which **6** and its "enantiomer" **6′** are rapidly equilibrated, and each can collapse by proton loss (to **7** and **7′**). This is shown schematically, with CD_3 groups marked with an asterisk. Rapid equilibration of **6** and **6′** ($K_{6,6'}$) prior to collapse should lead to a 50:50 mixture of **7** and **7′**, with the label distribution shown. This is in rather good agreement with the observed product (**3**-d_6).[6]





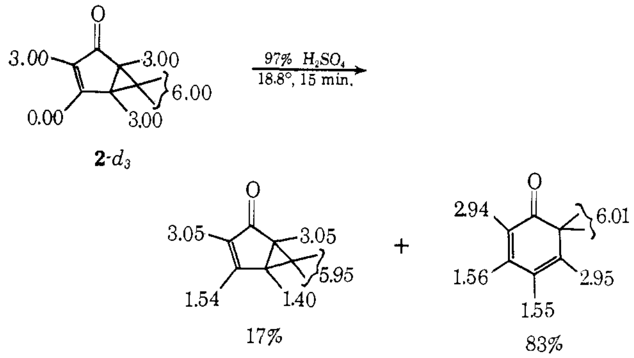
7–**7′** (50 : 50)

To test the possibility that equilibria $K_{5,6}$ and $K_{5',6'}$ might also be rapidly established, and that **2** might be converted to **2′** under the reaction conditions, the following experiment was performed. Compound **2**-d_6 was treated with 97% sulfuric acid at 18.7° for 1 min; after quenching 63% of **2** and 37% of **3** were recovered. The hydrogen distribution in recovered **2** was



The figures in parentheses are the calculated values for complete equilibration of **2** and **2′**.

Consistent with the proposed scheme **2**-d_3 labeled as shown gave the indicated products. This experiment shows that it is specifically the methyls on C-4 and C-5[7] of **2** which equilibrate.



The exceedingly rapid migration of the cyclopropane ring around four of the five sides of the cyclopentane ring is thus clearly established.[8] The precise mechanism by which the carbon bearing the *gem*-dimethyl group migrates around the ring (**5** → **6** → **6′** → **5′**) is being investigated.[10,11]

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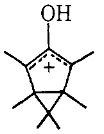
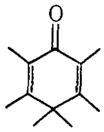
[6] An independent experiment showed that **7**, subjected to the rearrangement conditions, was recovered unchanged; thus *6* → *7* is not reversible.

[7] By implication, the methyls on C-1 and C-3 are the other exchanging pair.

[8] These experiments are inconclusive regarding the fifth side. One might expect ion **8** to collapse to **9**, which is not observed. In stronger sulfuric acid **3** is converted to **9**;[9] the mechanism of this rearrangement



8



9

will be the subject of a separate communication.

[9] H. Hart and D. W. Swatton, *J. Am. Chem. Soc.*, **89**, 1874 (1967); see also V. G. Shybin, V. P. Chzhu, A. I. Rezvukhin, and V. A. Koptyug, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 2056 (1966).

[10] For example, *endo* and *exo* substituents on this carbon may retain their stereochemistry, invert, or become scrambled.

[11] We are indebted to the National Science Foundation for financial support of this work.

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Received June 21, 1967

Quintet Ground States of *m*-Dicarbene and *m*-Dinitrene Compounds

Sir:

We previously reported, as part of another study,[1] that photolysis of 1,3-bis(α-diazobenzyl)benzene (Ia) and 1,3-diazidobenzene (II) at 77°K yielded epr spectra which were much more complex than those observed with triplet states. The spectra were tentatively associated with quintet states of *m*-phenylenebis(phenyl-

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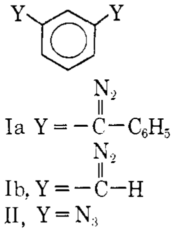
[1] A. M. Trozzolo, R. W. Murray, G. Smolinsky, W. A. Yager, and E. Wasserman, *J. Am. Chem. Soc.*, **85**, 2526 (1963).

methylene) (IIIa) and *m*-phenylenedinitrene (IV), but detailed analyses were not offered.

We now present the results of a combined experimental and theoretical investigation which indicates that we have observed the epr spectra of quintet IIIa, IIIb, and IV. To our knowledge this is the first demonstration of organic quintet states except for the very weakly interacting tetranitroxide radicals.[2] The measurements were carried out at 4°K demonstrating that the quintet is the ground state of the system or at most a few small calories above the ground state.

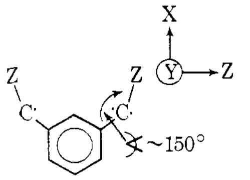
The main features of the epr spectra obtained on irradiation of Ia,b and II[3] were essentially independent of the rigid solvent used. In addition to the triplet absorptions characteristic of the methylenes and nitrenes arising from monodecomposition,[4-6] a number of other features were observed at the X band. From Ia, the additional absorptions occurred within the range of ~500 to ~5400 gauss; from Ib, ~100 to ~6400 gauss; and from II, ~100 to ~8400 gauss.[7]



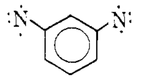
Ia $Y = -\overset{N_2}{\overset{\|}{C}}-C_6H_5$

Ib, $Y = -\overset{N_2}{\overset{\|}{C}}-H$

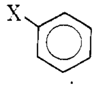
II, $Y = N_3$



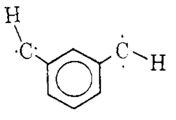
IIIa, $Z = C_6H_5$
IIIb, $Z = H$



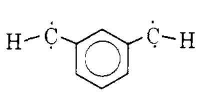
IV



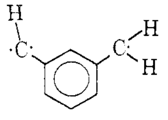
Va, $X = \dot{\underset{\cdot}{C}}-C_6H_5$
Vb, $X = \dot{\underset{\cdot}{C}}-H$
VI, $X = \ddot{\underset{\cdot}{N}}:$



VII



VIII



IX

The Hamiltonian for a quintet state ($S = 2$) in an external magnetic field $\vec{H}$, including the Zeeman and dipolar terms is

$$\mathcal{H} = g\beta\vec{H}\cdot\vec{S} + D\left(S_z^2 - \frac{S(S+1)}{3}\right) + E(S_x^2 - S_y^2)$$

The parameters D and E are mainly determined by the magnetic interaction between the unpaired electrons. Using perturbation theory the energy levels may be determined from $\mathcal{H}$ and a line shape obtained for randomly oriented quintets in a fashion analogous to that used for triplets.[8] The features at the two highest fields are steplike absorptions as found with triplets.[8] To first order, the high-field limit is $H_1 = H_0 + 3D/g\beta$, and the next highest feature is at $H_2 = H_0 + 3(D + 3E)/2g\beta$ with $D > 3E$ and H_0 ~3300 gauss. To determine D and E from the observed values of H_1 and H_2, the exact energy levels of $\mathcal{H}$ are used. We find that for IIIb, $D = 0.0844$, $E = 0.0233$ cm^{-1}. With IIIa and IV, H_2 is not visible and E cannot be obtained directly. Theoretical calculations indicate that a similar D/E ratio may be expected for IIIa,b and IV as this ratio is largely determined by geometry, the two "triplet" methylenes or nitrenes composing the quintet being *meta* on the central ring.[9,10] Given D for IIIa from H_1 and assuming D/E similar to that of IIIb, we find that the absorption used for determining E most probably lies under a line of the monodecomposition triplet. We then assign $D = 0.0701$, $E = 0.020 \pm 0.002$ cm^{-1} for IIIa;[11] for IV, $D = 0.156$, $E = 0.029 \pm 0.006$ cm^{-1}. The uncertainty in E is determined by the width of the overlying triplet absorption. The D and E assignments for the three quintets are also compatible with the low-field spectra. With IIIa the over-all splitting at zero field is comparable to the microwave energy, and a lower limit to absorption at ~500 gauss, as observed, may exist analogous to the $H_{\min}$ transitions in triplet states.[12] No such restriction exists for IIIb and IV.

The parameters D and E are averages of

$$D_{ij}\propto\left\langle\frac{1}{r_{ij}^3} - \frac{3z_{ij}^2}{r_{ij}^5}\right\rangle \text{ and } E_{ij}\propto\left\langle\frac{y_{ij}^2 - x_{ij}^2}{r_{ij}^5}\right\rangle$$

where r_{ij} and its components refer to the distance between two unpaired electrons in the ith and jth orbitals. With four available orbitals and the four unpaired electrons of a quintet there are six such pairs. Then $D = (^1/_6)\Sigma D_{ij}$ and $E = (^1/_6)\Sigma E_{ij}$.[9,10] The largest D_{ij} arises from the interaction of an in-plane electron with the π electron which includes the same divalent carbon or univalent nitrogen. This is just the interaction responsible for the dipolar interactions of the parent triplet state. To convert the observed values of D_t, the D for triplet diphenylmethylene (Va),[4,5] phenylmethylene (Vb),[4] or phenylnitrene (VI),[6] to the appropriate contribution for the quintets, IIIa,b or IV, respectively, we must consider that the z axis in the quintets, as shown in the illustration, is inclined to the z axis of the isolated triplets. If the two bonds to a methylene carbon were colinear, the angle between the triplet and quintet z axis would be 30° and $D_{ij} = (D_t/2)(3\cos^2(30°) - 1) = 5D_t/8$. With two "triplets" in the quintets, and the other interactions taken together as -0.10 cm^{-1},[9] $D = {}^1/_6(^5/_4D_t - 0.10)$ cm^{-1}. The computed values of D for the quintets are then 0.068, 0.091, and 0.178 cm^{-1} for Va,b and VI, respectively. This agreement within 13% between theory and experiment is strong evidence in favor of the assignment of the observed spectra to the quintet systems.

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[2] A. L. Buchachenko, V. A. Golubev, M. B. Neiman, and E. G. Rozantsev, *Dokl. Akad. Nauk SSSR*, **163**, 1416 (1965).

[3] M. O. Forester and H. E. Fierz, *J. Chem. Soc.*, **91**, 1953 (1907); R. W. Murray and A. M. Trozzolo, *J. Org. Chem.*, **29**, 1268 (1964).

[4] E. Wasserman, A. M. Trozzolo, W. A. Yager, and R. W. Murray, *J. Chem. Phys.*, **40**, 2408 (1964).

[5] R. W. Brandon, G. L. Closs, C. E. Davoust, C. A. Hutchison, Jr., B. E. Kohler, and R. Silbey, *ibid.*, **43**, 2006 (1965).

[6] E. Wasserman, G. Smolinsky, and W. A. Yager, *J. Am. Chem. Soc.*, **86**, 3166 (1964).

[7] The lower limit of our magnet was ~100 gauss.

[8] E. Wasserman, L. C. Snyder, and W. A. Yager, *J. Chem. Phys.*, **41**, 1763 (1964).

[9] Unpublished calculations.

[10] J. Higuchi, *J. Chem. Phys.*, **38**, 1237 (1963); **39**, 1847 (1963).

[11] We have received a preprint from Dr. K. Itoh who has measured the parameters of IIIa in a single crystal of benzophenone. At 77°K he finds $D = 0.07131$, $E = 0.01902$ cm^{-1} (K. Itoh, to be published.

[12] J. H. van der Waals and M. S. de Groot, *Mol. Phys.*, **2**, 333 (1959); **3**, 190 (1960).

A simplified form of the relationship discussed in the previous paragraph is that the ratio of D values for the triplet and the corresponding quintets should be approximately constant for a series of *meta* quintets. We find $D_{\mathrm{Va}}/D_{\mathrm{IIIa}} = 5.8$, $D_{\mathrm{Vb}}/D_{\mathrm{IIIb}} = 6.1$, and $D_{\mathrm{VI}}/D_{\mathrm{IV}} = 6.4$.

The theoretical value of the D/E ratio should be ~5 for IV or for IIIa,b if the bonds to the divalent carbon are colinear.[9,10] With IIIb, the one case in which E was determined directly, the ratio is 3.6. A possible explanation for this lower value lies in the potentiality for isomers in the methylenes as these are known to be bent about the divalent carbon atom.[4,13] Simple theoretical arguments[9] indicate that $D/E < 5$, ~ 5, > 5 for IIIb, VII, and VIII, respectively. Thus the absorptions used for the assignment of parameters may arise from the particular isomer IIIb.

The possibility exists that some of the epr lines are due to the quartet states such as IX which could be formally produced from IIIb. Arguments analogous to those used above to relate the parameters of the quintet to those of the corresponding triplet may be used to relate the quartet to those of a triplet and doublet.[9,10] The predicted values for the quartet state should not allow lines at as high or low magnetic fields as we observe experimentally. While quartet states may be present in the observed systems, the assignments we are making are most probably based on quintet resonances.

Acknowledgments. We wish to thank Mr. R. M. R. Cramer for his aid in determining the spectra and Dr. J. Higuchi for interesting discussions.

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[13] A. M. Trozzolo, E. Wasserman, and W. A. Yager, *J. Am. Chem. Soc.*, **87**, 129 (1965).

E. Wasserman, R. W. Murray, W. A. Yager
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Received July 27, 1967

Electrochemical Oxidation of $B_{12}H_{12}^{2-}$ [1]

Sir:

Recent work[2] has shown that the electrochemical oxidation of the $B_{10}H_{10}^{2-}$ ion in acetonitrile parallels the aqueous chemical oxidation,[3-5] and that controlled-potential electrolysis is a useful method of carrying out the oxidative coupling of $B_{10}H_{10}^{2-}$ and its derivatives.[6] Previous attempts to oxidize $B_{12}H_{12}^{2-}$ in aqueous solution have been unsuccessful or have yielded only borates as products.[7,8] We now report the controlled-potential oxidation of $B_{12}H_{12}^{2-}$ in acetonitrile.

Voltammetry of $[(C_2H_5)_4N]_2B_{12}H_{12}$ at a rotating platinum electrode in acetonitrile (0.1 M tetraethylammonium perchlorate as supporting electrolyte) shows an anodic wave with $E_{1/2} = +1.5$ v (*vs.* sce). At a stationary platinum electrode, an anodic peak is observed at +1.5 v, with a shoulder at +1.85 v on a large anodic wave. In a typical run, 30 mmoles of $Na_2B_{12}H_{12}$ in 150 ml of acetonitrile was exhaustively electrolyzed under nitrogen at +1.45 v, using a graphite cloth anode, with no supporting electrolyte. The current was monitored using a strip chart recorder; the value $n = 0.91$ equiv/mole of $Na_2B_{12}H_{12}$ was found. The yellow solution was evaporated to dryness at room temperature, and the residue was dissolved in H_2O. Addition of CsF to the aqueous solution gave white crystals of $Cs_3B_{24}H_{23}\cdot 3H_2O$ (I) which were recrystallized from an acetonitrile–water mixture.

Anal. Calcd for $Cs_3B_{24}H_{23}\cdot 3H_2O$: B, 35.29. Found: B, 35.10. The compound does not melt below 300°.

In a similar experiment, addition of $(C_2H_5)_4NCl$ to the aqueous solution gave the corresponding tetraethylammonium salt of $B_{24}H_{23}^{3-}$.

Anal. Calcd for $[(C_2H_5)_4N]_3B_{24}H_{23}$: C, 42.82; H, 12.42; N, 6.24; B, 38.52. Found: C, 42.93; H, 12.72; N, 6.18; B, 38.66.

Stationary-electrode voltammetry of I in acetonitrile showed only the +1.85-v shoulder found in the voltammetry of $B_{12}H_{12}^{2-}$. The conductivity of I in H_2O gave $\Lambda_m = 462\ \mathrm{ohm}^{-1}\ \mathrm{cm}^{-1}$, typical of a 3:1 electrolyte.

A solution of compound I was passed through a strong acid ion-exchange column, and the liberated acid was neutralized with sodium hydroxide (equivalent weight: calcd, 245.1; found, 246 ± 1). The infrared spectrum of I in KBr showed bands at 2500, 1050, and 940 and multiple bands from 750 to 710 cm^{-1}.

The ^{11}B nmr spectrum of aqueous I at 32.0 Mc consisted of an unsymmetrical doublet at +15.4 ppm relative to external $BF_3\cdot O(C_2H_5)_2$, with $J = 130$ cps. The 100-Mc ^1H spectrum irradiated at 32.0 Mc consisted of two peaks of approximately equal intensities at +3.02 and +3.21 ppm from H_2O. The optimum decoupling frequencies for the two peaks differed by about 30 cps, which implies that the ^{11}B unsymmetrical doublet includes two doublets separated by less than 1 ppm. The low-field ^1H peak was considerably broader under optimum decoupling conditions than was the high-field peak.

The controlled-potential electrolysis of $B_{12}H_{12}^{2-}$ apparently parallels that of $B_{10}H_{10}^{2-}$, a one-electron oxidation followed by a dimerization reaction with the B_{12} cage left intact.

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Received July 31, 1967

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[1] Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the University of Kansas General Research Fund for partial support of this research.

[2] R. L. Middaugh and F. Farha, Jr., *J. Am. Chem. Soc.*, **88**, 4147 (1966).

[3] A. Kaczmarczyk, R. D. Dobrott, and W. N. Lipscomb, *Proc. Natl. Acad. Sci. U. S.*, **48**, 729 (1962).

[4] B. L. Chamberland and E. L. Muetterties, *Inorg. Chem.*, **3**, 1450 (1964).

[5] M. F. Hawthorne, R. L. Pilling, and P. F. Stokeley, *J. Am. Chem. Soc.*, **87**, 1893 (1965).

[6] R. L. Middaugh and A. P. Schmitt, unpublished work.

[7] D. Kaczmarczyk, G. B. Kolski, and W. P. Townsend, *J. Am. Chem. Soc.*, **87**, 1413 (1965).

[8] M. F. Hawthorne, "The Chemistry of Boron and Its Compounds," E. L. Muetterties, Ed., John Wiley and Sons, Inc., New York, N. Y., 1967, Chapter 5.

Steroid Conjugates. III.[1] The Synthesis of a Sulfoglucuronide Derivative of Estriol

Sir:

We wish to describe the first chemical synthesis of estriol 3-sulfate 16-glucuronide (3-sulfooxy-17β-hydroxyestra-1,3,5(10)-trien-16α-yl-β-D-glucopyranosidur-

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[1] Paper II: E. W. Cantrall, M. G. McGrath, and S. Bernstein, *Steroids*, **8**, 967 (1966).