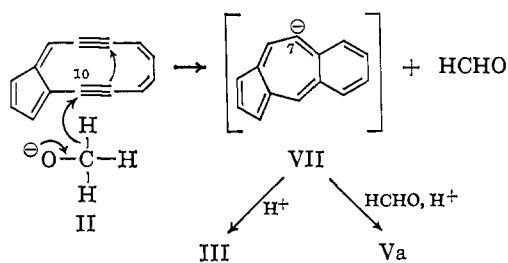


(acetic anhydride, pyridine, 16 hr at room temperature) gave the acetate Vb, mp 94.5–95.5°. The nmr spectrum (60 Mcps, CCl<sub>4</sub> solution) of Vb showed a singlet at  $\tau$  1.73 (1 H, assigned to H-4), a complex multiplet at 2.03–2.92 (8 H, remaining ring protons), a singlet at 4.54 (2 H, methylene protons), and a singlet at 7.96 (3 H, methyl protons).

Catalytic hydrogenation of Va in ethanol over 5% palladium–calcium carbonate (10 hr) led to the octahydro derivative VI (presumably a stereoisomeric mixture) as a colorless liquid. The ultraviolet spectrum [ $\lambda_{\text{max}}^{\text{pentane}}$  258, 263, and 271 m $\mu$  ( $\epsilon$  270, 300, and 260)] was characteristic of an *o*-disubstituted benzene.<sup>5</sup> The mass spectrum gave the expected molecular ion (23%) at  $m/e$  216 (C<sub>15</sub>H<sub>20</sub>O). The base peak was at  $m/e$  185 (C<sub>14</sub>H<sub>17</sub><sup>+</sup>), due to  $\beta$  cleavage between C-7 and C-15. There appeared also a strong peak (60%) at  $m/e$  117 (C<sub>9</sub>H<sub>9</sub><sup>+</sup>) which must be derived by  $\beta$  cleavage, as indicated in formula VI, with associated loss of the hydroxyl group.<sup>6</sup> These fragments show the hydroxymethyl group to be attached either to C-4 or C-7. The C-4 position is excluded by the nmr spectrum, leading to the 7-hydroxymethyl formulation.

Treatment of the bicyclic hydrocarbon II<sup>1</sup> under the above-described vigorous alkaline conditions led to the same three 5,6-benzazulenes III, IV (a or b), and Va, in comparable yields. The hydrocarbon II is therefore presumably an intermediate in the conversion of I to these benzazulenes.

The transformation of II to 5,6-benzazulene (III) with base involves the addition of two atoms of hydrogen. This reaction may proceed by hydride ion transfer from methoxide, ring closure to VII, and protonation, formaldehyde being formed. The 7-hydroxymethyl-5,6-benzazulene (Va) is presumably formed by a similar mechanism, the anion VII reacting with the formaldehyde prior to protonation.<sup>7,8</sup> The finding



that the hydroxymethyl group in Va is situated at a position  $\alpha$  to the six-membered ring provides additional support for the structure (II) assigned to the green

(5) See W. R. Moore, E. Marcus, S. E. Fenton, and R. T. Arnold, *Tetrahedron*, **5**, 179 (1959).

(6) See H. M. Grubb and S. Meyerson in "Mass Spectroscopy of Organic Ions," F. W. McLafferty, Ed., Academic Press Inc., New York, N. Y., 1963, Chapter 10.

(7) A related mechanism has been proposed by J. W. Cornforth, R. H. Cornforth, and R. Robinson (*J. Chem. Soc.*, 680, 682 (1942)) for the nuclear alkylation of indoles and phenols with sodium alkoxides, although a temperature of ca. 220° was required.

(8) It could be shown that the 7-hydroxymethyl-5,6-benzazulene (Va) was not the product of a secondary reaction of 5,6-benzazulene (III), since no Va was formed when III was treated under the basic reaction conditions in the presence of 5% aqueous formaldehyde. Moreover, reaction of III with formaldehyde is expected to occur at C-1 or C-3 (see W. Keller-Schierlein and E. Heilbronner in "Non-benzenoid Aromatic Compounds," D. Ginsburg, Ed., Interscience Publishers, Inc., New York, N. Y., 1959, Chapter VI). In practice, Vilsmeier formylation of III and subsequent lithium aluminum hydride reduction led to two hydroxymethyl derivatives, presumably the 1 and 3 isomers, which differed from Va.

bicyclic hydrocarbon.<sup>1</sup> Moreover, the fact that the hydroxymethyl group is introduced at C-7 indicates that the C-10 position in II is the most electrophilic center.

The methoxy-5,6-benzazulene IVa or IVb can arise from II by normal nucleophilic attack by methoxide ion, again followed by ring closure and protonation. This consideration leads us to assign the 4 or the 7 position to the methoxyl group in this substance. Since the C-10 position in II appears to be the most electrophilic center, it is probable that the methoxyl group in IV is at C-4 (IVa). The 4-methoxy structure IVa is also favored by the fact that the lowest-field, one-proton nmr band appears as a multiplet, suggesting the absence of H-4 (H-4 appears as a low-field singlet in III and Vb). However, the possibility cannot be definitely excluded that the methoxy compound possesses the 7-methoxy structure IVb, and that introduction of the 7-methoxy group into 5,6-benzazulene (III) alters the charge densities in such a way as to cause the H<sup>4</sup> singlet to appear at higher field (becoming part of the eight-proton multiplet).<sup>9</sup>

**Acknowledgment.** We are indebted to Dr. D. H. Williams (Cambridge) as well as to Professors R. Breslow and G. Stork (New York) for valuable discussions. We also thank the Royal Society for financial support.

(9) Catalytic hydrogenation of the methoxybenzazulene over a palladium–calcium carbonate catalyst and examination of the product by nmr and mass spectroscopy provided no significant structural information.

(10) Taken from a Ph.D. thesis submitted by J. Mayer to the Weizmann Institute of Science, Sept. 1965.

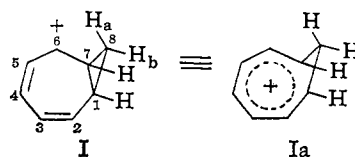
Joseph Mayer,<sup>10</sup> Franz Sondheimer  
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Received November 29, 1965

## The Protonation of Cyclooctatetraene

Sir:

We have previously reported that protonation of cyclooctatetraene leads to the formation of the stable homotropylum cation (I); the hexachloroantimonate salt of I has been isolated as a yellow crystalline solid following addition of HSbCl<sub>6</sub> to cyclooctatetraene, and the same cation is quantitatively formed upon dissolution of cyclooctatetraene in concentrated H<sub>2</sub>SO<sub>4</sub>.<sup>1</sup>



The cation I, the structure of which is the subject of the following paper, displays absorptions in the nmr spectrum at  $\tau$  1.4, 3.4, 4.8, and 10.6 (areas 5:2:1:1) attributed to the protons on carbons 2–6, 1 and 7, H<sub>b</sub>, and H<sub>a</sub>, respectively. The large difference in chemical shift between the two protons H<sub>a</sub> and H<sub>b</sub> is attributed to

(1) J. L. von Rosenberg, J. E. Mahler, and R. Pettit, *J. Am. Chem. Soc.*, **84**, 2842 (1962).

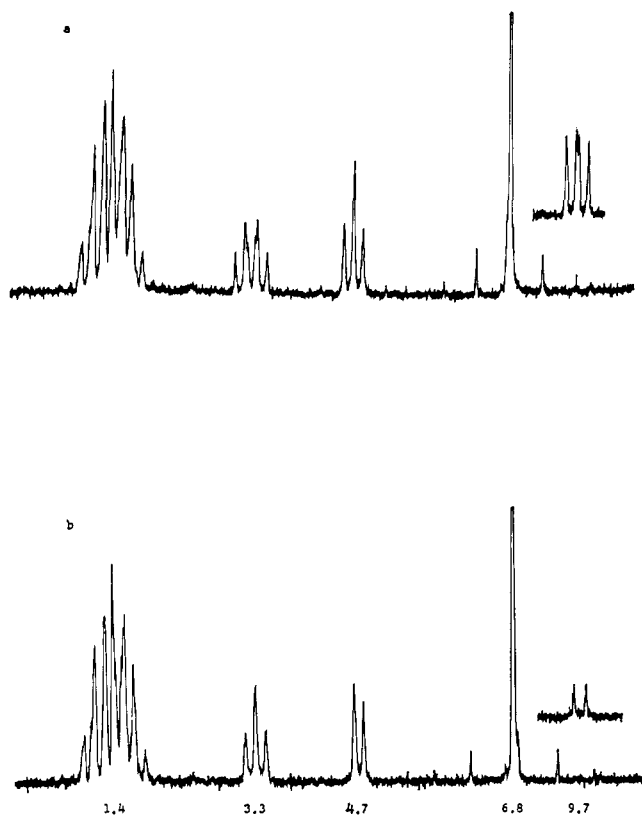


Figure 1. The nmr spectrum of methylcyclooctatetraene in (a)  $\text{H}_2\text{SO}_4$ , (b)  $\text{D}_2\text{SO}_4$ . Chemical shifts are given in  $\tau$  units.

the existence of a ring current in the molecule, as is implied in structure Ia.

The purpose of the present note is to present evidence which suggests a more detailed understanding of the protonation process of cyclooctatetraene leading to the formation of the homotropylium cation.

The spectrum of cyclooctatetraene in  $\text{D}_2\text{SO}_4$ <sup>1</sup> displays absorptions of the same chemical shift as that in  $\text{H}_2\text{SO}_4$ , but the areas now occur in the ratio 5:2:0.5:0.5. It can be concluded that the protonation of cyclooctatetraene is irreversible under these conditions. On this basis it is readily seen that there should exist six isomeric monosubstituted homotropylium cations. However, the addition of a proton to methylcyclooctatetraene by concentrated  $\text{H}_2\text{SO}_4$  is now found to give only one such isomer. The nmr spectrum of methylcyclooctatetraene<sup>2</sup> in concentrated  $\text{H}_2\text{SO}_4$  is given in Figure 1a.<sup>3</sup>

Excluding the absorption due to the methyl group at  $\tau$  6.8 (singlet, area 3), the values of the chemical shifts of the ring protons are very similar to those displayed by the parent cation (*vide supra*); however, the areas of the absorptions are 5:1:1:1 in the methyl derivative compared to 5:2:1:1 in the parent system. The spectrum indicates that within the limits of the measurement the protonation of methylcyclooctatetraene has occurred to give exclusively the 1-methyl derivative II; no evidence is seen for the formation of any of the other five isomers possible.

The nmr spectrum of methylcyclooctatetraene in  $\text{D}_2\text{SO}_4$  is further revealing. The spectrum (Figure 1b) dis-

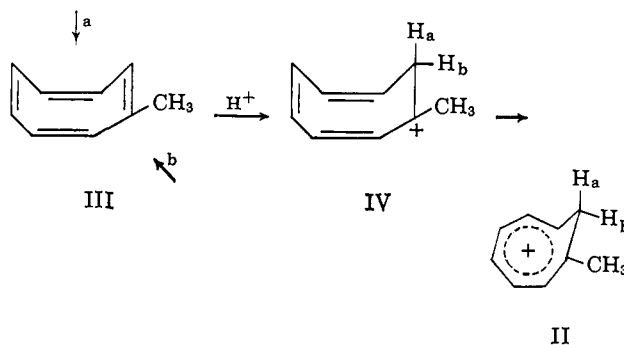
(2) Prepared through reaction of cyclooctatetraenyllithium with methyl iodide.

(3) The coupling constants are  $J_{a,b} = 8.0$  cps,  $J_{a,7} = 10.0$  cps, and  $J_{b,7} = 7.5$  cps; these closely parallel those of the parent system which are 6.7, 9.9, and 7.6 cps, respectively (J. L. von Rosenberg, J. C. Davis, J. E. Mahler, and R. Pettit, unpublished work).

plays absorptions of the same chemical shift; however, the areas of the ring protons occur in the ratio 5:1:0.75:0.25 (the methyl group remains area 3 at  $\tau$  6.8). The ratio of the latter two absorptions indicates that there is a preference for the proton which is added to occupy the *endo* position ( $\text{H}_a$ ) rather than the *exo* position ( $\text{H}_b$ ) in the methylhomotropylium cation.

Protonation of phenylcyclooctatetraene<sup>4</sup> by  $\text{H}_2\text{SO}_4$  appears to be similar to that of methylcyclooctatetraene, though the spectra are less readily interpreted owing to the coincidence of several absorptions. In  $\text{H}_2\text{SO}_4$  the absorptions occur at  $\tau$  1.36 (broad multiplet, area 10), 3.80 (broad multiplet, area 2), and 9.13 (apparent triplet, area 1). These are assigned to the five phenyl plus the five  $\text{H}_2$ - $\text{H}_6$  protons, the  $\text{H}_7$  and  $\text{H}_8$  protons, and the  $\text{H}_a$  proton, respectively. Again, the 1-phenyl isomer appears to be the only derivative formed; also, when taken in  $\text{D}_2\text{SO}_4$ , the areas of the absorptions again indicate a strong preference for the incoming proton to occupy the *endo* position in the final cation.<sup>5</sup>

The above results can be rationalized on the basis of the protonation occurring in the manner indicated.



The addition of the proton to methylcyclooctatetraene occurs with the latter existing in the tub conformation III and proceeds to form the classical carbonium ion IV; the cation IV then undergoes an irreversible low energy conformational change with concomitant development of the 1:7 interaction to give the methylhomotropylium cation II. The rate-determining step in the over-all protonation is the formation of the ion IV.<sup>6</sup> Since the carbonium ion IV is the most stable of the nine such classical ions possible following addition of a proton to III, it is this factor then which is responsible for the formation of the particular methylhomotropylium which is produced.

The carbonium ion III can arise from two different reaction paths depending upon whether the incoming proton approaches along the direction a or b. The predominant formation of the isomer possessing deuterium in place of  $\text{H}_a$  when methylcyclooctatetraene is dissolved in  $\text{D}_2\text{SO}_4$  suggests that path a is the preferred direction of addition in this case; this would seem reasonable on the basis that early in the addition simultaneous interaction of the proton with the electron clouds of two of the opposing double bonds is possible in this case.

(4) Phenylcyclooctatetraene was prepared in the manner described by A. C. Cope and M. R. Kinter, *J. Am. Chem. Soc.*, **73**, 3424 (1951).

(5) The simplification of the spectrum in  $\text{D}_2\text{SO}_4$  supports the structure in which the phenyl group occupies the  $\text{C}_1$  position rather than the *exo*  $\text{C}_8$  position.

(6) It is of course possible that the cation IV resembles the transition state rather than exists as a stable intermediate.

**Acknowledgment.** We thank the administrators of the Petroleum Research Fund and the Robert A. Welch Foundation for financial assistance. We also thank Badische Anilin und Soda Fabrik for a gift of cyclooctatetraene.

(7) NASA Trainee, 1965-1966.

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## The Electronic Structure of the Homotropylium Cation

Sir:

There exists an interesting problem concerning the electronic structure of the homotropylium cation (I).<sup>1</sup> The nmr spectrum of the cation displays absorptions at  $\tau$  1.4, 3.4, 4.8, and 10.6 (areas 5:2:1:1) which can be assigned to the five protons on C<sub>2</sub>-C<sub>6</sub>, the two equivalent protons H<sub>1</sub> and H<sub>7</sub>, and the protons H<sub>b</sub> and H<sub>a</sub>,

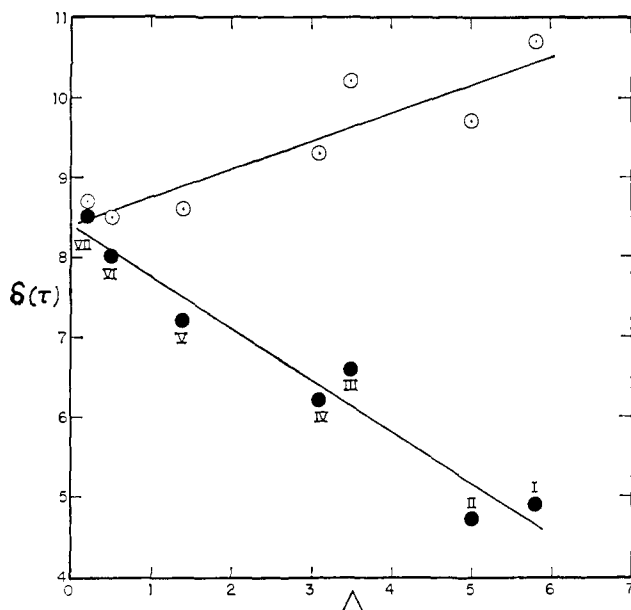
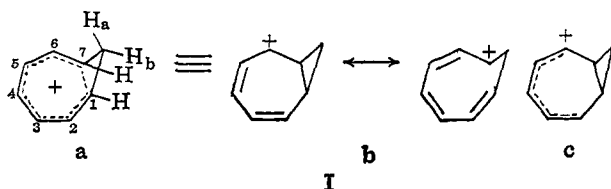


Figure 1. Plot of  $\delta$  vs.  $\Delta$  for the systems related to the homotropylium cation. The roman numerals refer to the compounds indicated in the text. The open circles refer to the proton H<sub>a</sub> while the full circles refer to H<sub>b</sub>.  $\delta$  is given in  $\tau$  units while  $\Delta$  is in parts per million.

respectively. Primarily on the basis of the extraordinarily large difference in chemical shift (5.8 ppm) between the two protons H<sub>a</sub> and H<sub>b</sub> which, as far as we are aware, is the biggest separation in chemical shift ever



reported for two protons attached to the same carbon atom, we have suggested that there exists a ring current in the molecule. H<sub>a</sub> which is over the ring is shielded,

(1) J. L. von Rosenberg, J. E. Mahler, and R. Pettit, *J. Am. Chem. Soc.*, **84**, 2842 (1962).

while H<sub>b</sub>, which is more nearly in the plane of the ring is deshielded. The system is thus presumed to have the nonclassical homotropylium structure I which can be represented either in molecular orbital terms as a  $\sigma$ , what is equivalent, in valence bond terms as a resonance hybrid, e.g., b.

Deno on the other hand has stated that the properties of the cation are in accord with structure Ic and implies that nothing more than the normal stabilization of a cation by a cyclopropane ring is operative.<sup>2</sup> However, for the following three reasons there would seem to be no scientific basis for this statement. (a) The chemical shifts of the four protons in the "cyclopropyl" ring in homotropylium differ by 7.2 ppm whereas those in the several "normal" cyclopropylcarbonium ions studied by Deno and co-workers when they differ at all do so at most by 0.6 ppm.<sup>3</sup> (b) In homotropylium the coupling constant  $J_{b,1}$  is 7.6 cps, whereas  $J_{1,7}$  is close to 0.0 cps, at most 1.5 cps.<sup>4</sup> (c) We have been unable to isolate bicyclo[5.1.0]octane derivatives upon reaction of the homotropylium cation with such nucleophiles as LiAlH<sub>4</sub> or sodium acetate. There is therefore no evidence that the cation possesses a conventional cyclopropyl ring as is implied in Ic, and we consider that the nonclassical formulation remains the best description of the system.

A large part of the support for the homoaromatic formulation rests on the assumption that the origin of the large difference in chemical shift between protons H<sub>a</sub> and H<sub>b</sub> is the presence of a significant ring current in the system. We now wish to present evidence for the validity of this explanation.

Johnson and Bovey<sup>5</sup> have deduced that in a constant applied magnetic field the chemical shift ( $\delta'$ ) of a proton due to the presence of a ring current in the molecule is related in the manner

$$\delta' \propto I \times f(xyz) \quad (1)$$

where  $I$  is the magnitude of the ring current and  $f(xyz)$  is a function of the coordinates of the position of the proton relative to the ring.

If we now consider a series of related structures in which the geometry of the carbon skeleton remains fixed and in which two protons H<sub>a</sub> and H<sub>b</sub> experience different shielding due to the presence of a ring current in the system, then it follows from eq 1 that for differing values of the size of the ring current there should exist a linear relationship between  $\delta$ , the chemical shift of one proton, and  $\Delta$ , the difference in chemical shift between the two protons. In the present case of the C<sub>8</sub>H<sub>9</sub><sup>+</sup> cation the further upfield is proton H<sub>a</sub>, or downfield is proton H<sub>b</sub>, then proportionately larger should be the separation between H<sub>a</sub> and H<sub>b</sub>. In Figure 1 we have plotted the position of H<sub>a</sub> and H<sub>b</sub> ( $\delta$ ) vs. the chemical shift separation of H<sub>a</sub> and H<sub>b</sub> ( $\Delta$ ) for homotropylium and six other systems which would be expected to have a closely related carbon skeleton. The systems plotted are homotropylium (I),<sup>1</sup> methylhomotropylium (II),<sup>6</sup> the C<sub>8</sub>H<sub>9</sub><sup>+</sup>Mo(CO)<sub>3</sub> cation (III),<sup>7</sup> 2-hydroxyhomotro-

(2) N. C. Deno, *Progr. Phys. Org. Chem.*, **2**, 157 (1964).

(3) N. C. Deno, H. G. Richey, Jr., J. S. Liu, D. N. Lincoln, and J. O. Turner, *J. Am. Chem. Soc.*, **87**, 4533 (1965).

(4) J. L. von Rosenberg, J. E. Mahler, J. C. Davis, and R. Pettit, unpublished observations. The coupling between the equivalent protons H<sub>1</sub> and H<sub>7</sub> was obtained from calculation of the theoretical spectrum.

(5) C. E. Johnson and F. A. Bovey, *J. Chem. Phys.*, **29**, 1012 (1958).

(6) C. E. Keller and R. Pettit, *J. Am. Chem. Soc.*, **88**, 604 (1966).

(7) S. Winstein, H. D. Kaesz, C. G. Kreiter, and E. C. Friedrich, *ibid.*, **87**, 3267 (1965).