

A STABLE TRICARBONIUM ION: 1,3,5-TRIS(CYCLOHEPTATRIENYL)BENZENE CATION

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We wish to report the synthesis of 1,3,5-tris(cycloheptatrienyl)benzene cation(I) a stable tricarbonium ion containing only carbon and hydrogen.¹ Evidence that the tropylium rings in I cannot be regarded as isolated centers of positive charge is provided by a comparison of its nmr spectrum with those of some related compounds. A number of hydrocarbon dicarbonium ions have been prepared as stable salts,³⁻⁶ and evidence has been presented for the existence in solution of the tetraphenylcyclobutenium dication.⁷ Only very recently, however, has there been a report of a hydrocarbon tricarbonium ion.⁸ We have also been interested in the synthesis of a tripositively charged species and here report the formation of I, the tricarbonium ion homolog of the dicarbonium ion described earlier by us.⁶

The hydrocarbon precursor of I, 1,3,5-tris(7-cycloheptatrienyl)benzene (II) is obtained by allowing 1,3,5-tribromobenzene to react with three moles of magnesium in refluxing tetrahydrofuran followed by the addition of three moles of tropylium bromide⁹ to the ice-cold tetrahydrofuran solution. A usual Grignard workup and chromatography of the crude product on neutral alumina gave II in 3% yield along with other cycloheptatriene derivatives.

When a methylene chloride solution of II was added to a 25% excess of triethyl fluoborate¹⁰ and the solution allowed to stand for 16 hours, the trifluoborate salt of I precipitated in 51% yield. The salt was recrystallized from acetonitrile-carbon tetrachloride-ethyl ether to give mustard-yellow crystals which darkened but did not melt <350°. (Anal. Calcd. for C₂₇H₂₁B₃F₁₂: C, 53.5; H, 3.5; B, 5.4; F, 37.6. Found: C, 53.4; H, 3.5; B, 5.3; F, 37.5)

The ultraviolet and visible spectrum of I had $\lambda_{\text{max}}^{\text{CH}_3\text{CN}}$ 225 m μ ($\epsilon = 64,000$), 267 ($\epsilon = 32,000$), 349 ($\epsilon = 21,000$).

Particularly telling evidence for the structure of I is available from application of the unusual oxidation reaction discovered by Vol'pin et al.¹¹ Treatment of the water-soluble trifluoborate of I with dilute, aqueous hydrogen peroxide leads to gas evolution and the formation of 1,3,5-triphenylbenzene (m.p. 173-175°, mixed m.p. 173-175.5°).

The nmr spectrum of I (Fig. 1) consists of just two lines. The broad absorption centered at 1.23¹² is assigned to the tropylium protons. The sharp singlet at 1.86 is assigned to the aromatic protons. The integrated intensities of the peaks varied from 6:1 to 10:1, respectively.¹³

A substantial portion of the interest in multicharged organic species centers around the question of intramolecular interaction of the positive charges. In order to examine this point in the present system we have determined the nmr spectra, under identical conditions, of a series of related tropylium ions and cycloheptatriene hydrocarbons (Table 1). The spectra of the ions, given in Fig. 1 also illustrate the effect of increasing number of positive charges. The tropylium protons of phenyltropylium ion (III) absorb at 1.41 as compared to 1.30 for unsubstituted tropylium ion. This upfield shift of the tropylium protons in III due to delocalization of the positive charge in the aromatic ring is accompanied by the expected downfield shift of the aromatic protons in this ion as compared to its precursor, phenylcycloheptatriene. In the dicarbonium ion, p-phenylene-bis(cycloheptatrienylium cation) (IV), the aromatic protons are also shifted downfield as compared to its parent hydrocarbon. This downfield shift in the aromatic protons of the dicarbonium ion is 0.91 ppm as compared to 0.43 ppm for the aromatic proton shift in III thus demonstrating that there is considerable delocalization of the positive charges in the dicarbonium ion. Concurrently with this charge delocalization, however, the tropylium protons in IV absorb at 1.31, a value much closer to that for the simple tropylium ion.

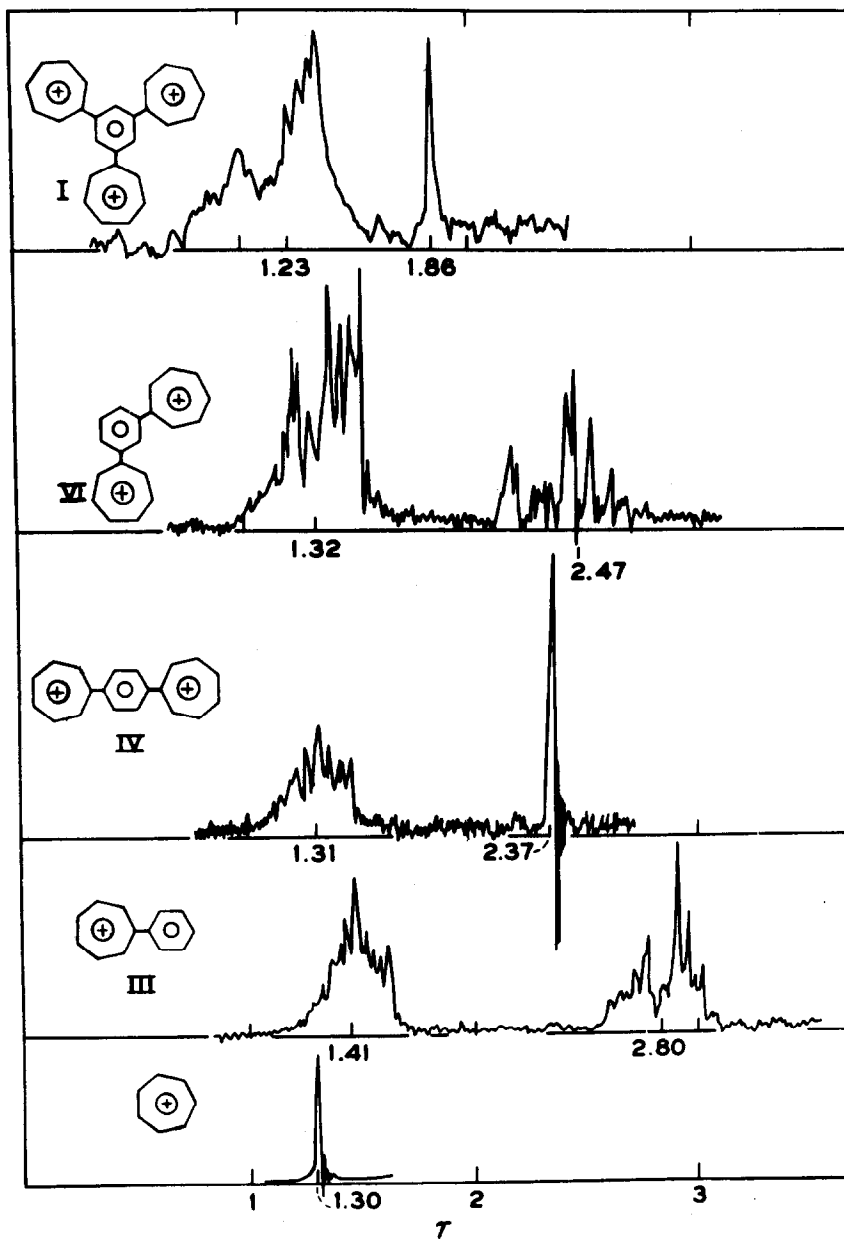


Fig. 1. The nmr spectra of various tropylium ions

Compound Name	Tropylium τ	Aromatic τ	Aromatic $\tau_{\text{hydrocarbon}^+ \text{ion}}$
Tropylium Ion	1.30		
7-Phenylcycloheptatriene	-	3.23	0.43
Phenyltropylium Ion (III)	1.41	2.80	
1-(7-cycloheptatrienyl)-4-cycloheptatrienylium benzene (V)	1.46	2.77	0.51
1,4-Bis(7-cycloheptatrienyl)benzene	-	3.28	0.91
p-Phenylene-bis(cycloheptatrienylium cation) (IV)	1.31	2.37	
1,3-Bis(7-cycloheptatrienyl)benzene	-	3.34	0.87
m-Phenylene-bis(cycloheptatrienylium cation) (VI)	1.32	2.47	
1,3,5-Tris(7-cycloheptatrienyl)benzene (II)	-	3.30	1.44
1,3,5-Tris(cycloheptatrienylium)benzene cation (I)	1.23	1.86	
7-(p-biphenyl)-cycloheptatriene	-	3.11	0.42 ^a
p-Biphenyl-tropylium ion (VII)	1.51	2.69	

^aThis difference calculated using the τ value for the aromatic ring which is directly attached to the tropylium ring.

Table 1. Aromatic and tropylium proton chemical shifts for tropylium and several aryltropylium cations (as the fluoroborates) and their hydrocarbon precursors. The nmr spectra were measured in liquid SO_2 with TMS in chloroform as external standard. All τ values given are for the centers of the appropriate resonance lines.

Thus, while the aromatic protons in IV have felt at least an equivalent effect of the individual tropylium ion substituents as that observed in III, the tropylium proton chemical shift appears to be undisturbed. Furthermore, the tropylium protons in the monocation (V) from this same hydrocarbon absorb at 1.46 while the aromatic protons experience a deshielding of 0.51 ppm. The tropylium proton absorption in the dicarbonium ion, IV, therefore, is not that expected for isolated positive charges, namely a value close that that found in V, but reflects an additional deshielding which we attribute to interaction between the positive charges. A similar effect is seen in the dicarbonium ion, *m*-phenylene-bis(cycloheptatrienylium cation) (VI), when its aromatic and tropylium proton absorptions are compared to those in III and the parent hydrocarbon 1,3-bis(7-cycloheptatrienyl)benzene. Even more conclusive evidence for charge interaction is provided by a similar comparison in the tricarbonium ion, I. Here the tropylium protons are actually shifted to lower field than those in simple tropylium ion. At the same time, a comparison of the aromatic absorption in I and II shows the deshielding effect of the tropylium ion substituents to be more than three times that of the single tropylium substituent in III.

An alternative explanation for the deshielding observed, particularly in I and IV, which is based on the ring current of the tropylium ring, is not considered likely. While it is difficult to construct a model to study this effect it is perhaps pertinent that in the cation (VII) from 7-(*p*-biphenyl)-cycloheptatriene the deshielding effects on the central aromatic ring are comparable to those in III and V and distinctly less than those in IV. Thus if the ring current effects in phenyl and tropylium ion are at all comparable then there must be an additional effect in IV, which we attribute to charge delocalization.

Also, an equation has been developed for estimating the magnitude of the ring current in aromatic ions,¹⁴ as follows:

$$\sigma_1 = 0.63K_b \left(\frac{a_1}{a_b} \right)^2 I_1,$$

where K_b is the shielding constant value given by Johnson and Bovey,¹⁵ a_1 is the radius of the ring in question, a_b is the radius of the benzene ring, I_1 is the ratio of the ring current intensities for the ion and benzene and 0.63 is an empirical constant established by Jonathan, Gordon, and Dailey.¹⁶ Application of this relationship to predict tropylium ring current deshielding effects at the distances involved in the systems discussed leads to deshielding values which are far less than those actually observed.

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