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P-PHENYLENE-BIS(CYCLOHEPTATRIENYLIUM CATION),* A STABLE DICARBONIUM ION

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Along with recent interest in the chemistry of dicarbonium ions(2) there have been attempts to isolate pure crystalline salts of these materials. Successful attempts to isolate such salts(3) have been limited to those of Hart's dicarbonium ion(4) and dicarbonium ions of the bis-azulene and triarylmethyl type.(6,7) Freedman has reported that the crystalline salt originally ascribed(8) to a dicarbonium ion from 3,4-dibromotetraphenylcyclobutene is, in fact, a chloromonocation salt.(9)

We wish to report the synthesis of p-phenylene-bis(cycloheptatrienylium cation), (I), a dicarbonium ion system whose singular stability stems from the presence of the tropylium Hückel aromatic system.(10) The parent hydrocarbon, 1,4-bis(7-cycloheptatrienyl)benzene (1,4-ditropylbenzene), (II), is obtained from the reaction of 1,4-dilithiobenzene

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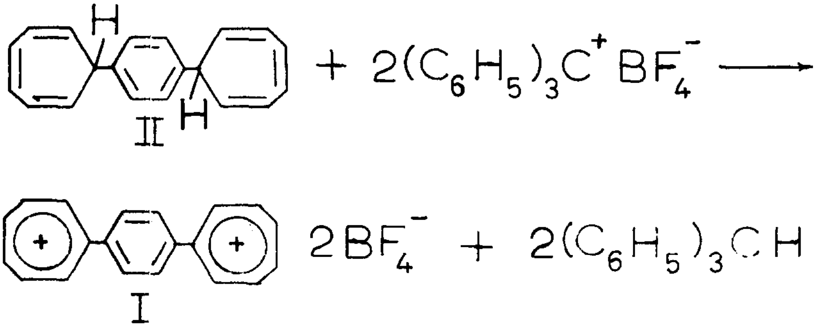
*The absence of a systematic nomenclature for carbonium ions presents a doubly difficult problem in the case of dicarbonium ions. Following the suggestions made by Hart and Fish(1) would lead to p-phenylenecycloheptatrienyl dication as a name for the subject compound. We have chosen the title name as being somewhat more unique, but feel that either is acceptable.

with two moles of tropylium bromide or, in smaller yield, from the thermal or photochemical decomposition(11) of 1,4-bis(α-diazomethyl)benzene(12) in benzene.

When a methylene chloride solution of II is treated with a 50% excess of trityl fluoborate(13) and the solution allowed to stand for 64 hrs., I precipitates in 97% yield.(14) Workup of the methylene chloride solution affords a quantitative yield of triphenylmethane. The rust-red, crystalline difluoborate of I is instantly soluble in cold water.(15) The salt was recrystallized from acetonitrile - carbon tetrachloride to give small needles of difluoborate which did not melt < 350 °C (darkened at ca. 230 °C). (Anal. Calcd. for $C_{20}H_{16}B_2F_8$: C,55.9; H,3.75; F,35.4. Found: C,55.8; H,4.22; F,34.9). The ultraviolet and visible spectrum of I had $\lambda_{max}^{CH_3CN}$ 225 mμ(log ε,4.69), 271(log ε,4.40), 382(log ε,4.45), and 450(sh.). Phenyltropylium fluoborate has a reported(16) ultraviolet - visible spectrum of $\lambda_{max}^{H_2SO_4}$ 227 mμ(log ε,4.38), 272(log ε,3.7), and 387. The infrared spectrum of I (KBr pellet) showed a strong broad band at 8.9 - 9.9 μ which is characteristic of the fluoborate anion.(17)



The n.m.r. spectrum of I in liquid SO_2 consists of just two absorptions (Fig. 1).$^{(18)}$ A broad multiplet at 1.34 is assigned to the tropylium ring protons, while a sharp singlet at 2.37 is assigned to the aromatic protons. The ratio of integrated intensities for tropylium to aromatic protons was 12:4. This spectrum compares favorably with that of phenyltropylium fluoborate reported by Wilt and Piszkiewicz.$^{(16)}$ This latter monosalt has absorptions at 2.17, 2.06 (phenyl) and 0.98 (tropylium) with deuteriomethanol as solvent.

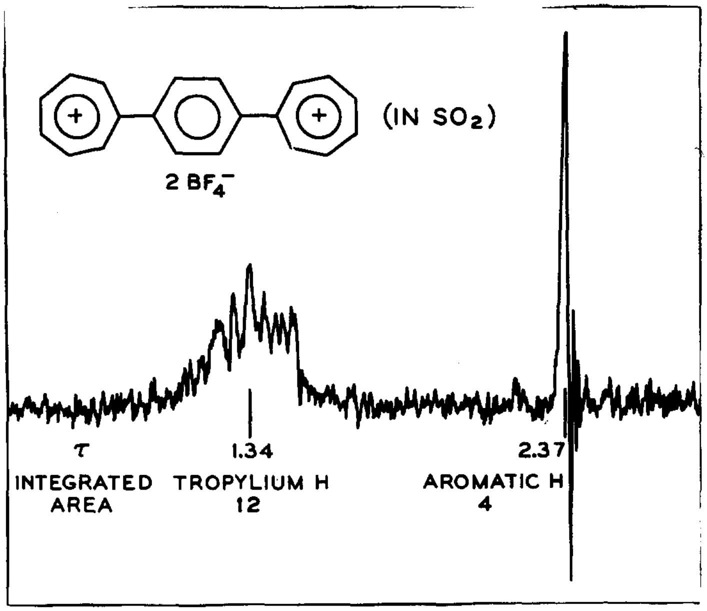


Fig. 1 The n.m.r. spectrum of I in liquid SO_2.

Further evidence for the structure of I was obtained by treating it with excess sodium methoxide in methanol which caused the immediate loss of the red-orange color. Workup of this reaction gave the dimethyl ether of I as a colorless oil.(19) Treatment of a solution of this oil in pentane with anhydrous hydrogen bromide caused the immediate precipitation of the orange-colored dibromide of I. This salt has ultraviolet and visible absorptions at $\lambda_{max}^{CH_3CN}$ 220 mμ,271,382, 450(sh.). (Anal. Calcd. for $C_{20}H_{16}Br_2$: C,57.7; H,3.88; Br, 38.4. Found: C,57.9; H,4.00; Br,37.9.)

Chemical evidence for the structure of the dicarbonium ion is provided by the facile conversion of an aqueous solution of the difluoborate to p-terphenyl (m.p. 205 - 207°C), in quantitative yield, upon treatment with dilute hydrogen peroxide.(16) The reaction is accompanied by evolution of a gas, presumably carbon monoxide.

Additional evidence for the dicarbonium ion structure of I was obtained by measuring its F^{19} n.m.r. spectrum.(9) A liquid SO_2 solution of I showed a singlet(21) at 62.0 p.p.m., relative to external trifluoroacetic acid.(22) Integration of this absorption and comparison with an internal standard indicated the presence of 8.15 ± 0.20 fluorines. The position of the F^{19} absorption in trityl fluoborate, in the same solvent, was found to be 61.9 p.p.m. relative to trifluoroacetic acid. Irradiation of the protons in I, in a double resonance experiment, caused no change in the appearance of the F^{19} absorption indicating the absence of any fluorine-proton coupling. These data are in complete accord with the difluoborate formulation for I.

The structure of the parent hydrocarbon, II, is assigned on the basis of analysis (Anal. Calcd. for $C_{20}H_{18}$: C,93.0; H,7.02. Found: C,92.5; H,7.2), ultraviolet spectrum, and n.m.r. spectrum. The ultraviolet spectrum, λ_{max}^{EtOH} 259 mμ (log ε,3.82), 272(sh.) is in accord with that for the phenylcycloheptatriene (λ_{max} 256 mμ, log ε,3.56) which Doering and Knox(10) have concluded is most likely the 7-phenylcyclohepta-1,3,5-triene isomer. The n.m.r. spectrum of II consists of a singlet at 2.68, a triplet at 3.31, a multiplet at 3.80, a quartet at 4.62, and a triplet at 7.33. These absorptions are assigned to the aromatic, the 1,6,1',6' olefinic, 2,5,2',5' olefinic, 3,4,3',4' olefinic, and methine protons, respectively.(20) The integrated peak area ratios are 4.3:4.1:4.2:4.2:2, respectively.

The unusual stability of the dicarbonium ion reported here reflects further the degree of stabilization provided by Hückel aromatic systems.(10) The difluoborate salt, I, is essentially insoluble in carbon tetrachloride, diethyl ether, and methylene chloride. The solid is nonhygroscopic and is not air or light sensitive.

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(14) When shorter reaction times were used the yield of dication was lower and treatment of the methylene chloride filtrate with ether caused precipitation of the monocarbonium ion of II.

(15) The orange-colored, aqueous solution becomes cloudy upon standing and slowly deposits a white, flocculent precipitate.

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(18) N.M.R. spectra were taken on a Varian Associates Model A-60 N.M.R. Spectrometer. Chemical shift values given are Tau values with tetramethylsilane as external standard.

(19) The reaction of I with sodium methoxide presumably leads to the formation of an isomeric mixture of dimethyl ethers. Details of this reaction will be reported in the full paper.

(20) The comparable olefinic and methylenic absorptions in cycloheptatriene occur at 3.45, 3.88, 4.72, and 7.80, respectively. See N.M.R. Spectra Catalog, Varian Associates, 1962, No. 158.

(21) When this spectrum is run at high concentration the singlet absorption is seen to have a slight indication of splitting which is reproducible with repeated running of the spectrum. This may be due to poorly-resolved F^{19}-B^{11} splitting.

(22) We wish to thank Mr. E. W. Anderson of these laboratories for determining the F^{19} spectra.