

## Synthesis of 8-Cyano-8-cycloheptatrienylheptafulvenylium Fluoroborate

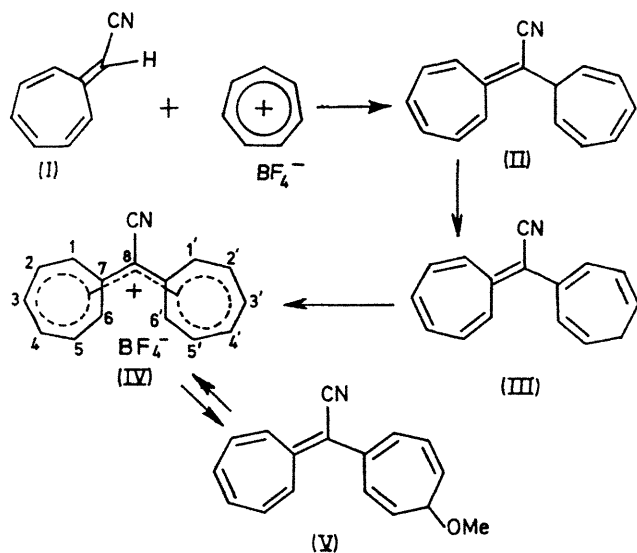
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**Summary** 8-Cyano-8-cycloheptatrienylheptafulvenylium fluoroborate (IV), a stable salt of a new carbonium ion, has been synthesised.

WE report the formation of a salt (IV) of the 8-cyano-8-cycloheptatrienylheptafulvenylium carbonium ion.

Reaction of 8-cyanoheptafulvene (I)<sup>1</sup> with tropylium tetrafluoroborate in the presence of a small excess of triethylamine in methylene chloride at room temperature gave the substituted product, 8-cyano-8-(7-cycloheptatrienyl)heptafulvene (II),<sup>2†</sup> red needles, m.p. 61.5–62°, (84%),  $\nu_{\max}$  (KBr) 3000w, 2200m, 1630w, 1549s, 741s, and 709vs  $\text{cm}^{-1}$ ;  $\lambda_{\max}$  (iso-octane) 239(log $\epsilon$  4.17), 255sh(4.11), 334(4.25), 420sh(2.69), 450sh(2.59), 492sh(2.40) and 535sh nm (2.12);  $\tau$  (CCl<sub>4</sub>, Me<sub>4</sub>Si) 3.04(br. d,  $J$  ca. 10 Hz, 1H), 3.25(t-like, 2H), 3.76(m, 7H), 4.70(ddd,  $J$  9.2, 5.2, and 1.0 Hz, 2H), and 7.80(dt,  $J$  5.2, and 1.0 Hz, 1H). The spectral data are consistent with structure (II).



Hydrogen abstraction from (II) with triphenylmethyl fluoroborate was unsuccessful; (II) was therefore converted into the isomer (III) by heating under reflux with xylene for 2 h. Compound (III) was obtained in 53% yield together with a yellow oil (34%), the structure of which has not yet

been deduced. The compound (III) is a red liquid with spectral data:  $\nu_{\max}$  (liquid film) 3000m, 2190s, 1630m, 1605w, 1545s, 1257m, 807s, 750s, 733s, and 669m  $\text{cm}^{-1}$ ;  $\lambda_{\max}$  (iso-octane) 217sh (log $\epsilon$  4.24), 280sh(3.80), and 364 nm (4.22);  $\tau$  (CCl<sub>4</sub>, Me<sub>4</sub>Si), 6.9(m, 2H), 6.3(m, 7H), 5.5(m, 2H), and 2.35(t,  $J$  6.6 Hz, 2H).

When triphenylmethyl fluoroborate was added to a solution of (III) in methylene chloride a dark blue colour was immediately obtained; the addition of dry ether then gave dark blue crystals of 8-cyano-8-cycloheptatrienylheptafulvenylium fluoroborate (IV),<sup>†</sup> m.p. 159.5–160.5°, (69%). Compound (IV) is stable in air at room temperature; it is readily soluble in acetonitrile, and in 0.01N-HCl, slightly soluble in methylene chloride, and insoluble in ether. The spectral data of (IV) are:  $\nu_{\max}$  (KBr) 2200m, 1603m, 1470s, 1368s, 1238s, 1060s, 826s, and 768s  $\text{cm}^{-1}$ ;  $\lambda_{\max}$  (0.1N-HCl) 216(log $\epsilon$  4.56), 270(3.95), 300(3.53), and 592 nm (4.41);  $\tau$  (MeCN, CH<sub>2</sub>Cl<sub>2</sub> as a secondary standard) 1.70 (m,  $\omega_{\frac{1}{2}}$  16 Hz), and 2.20(m,  $\omega_{\frac{1}{2}}$  10 Hz) in a ratio of 1:2 of integral area,  $\tau$  (CF<sub>3</sub>CO<sub>2</sub>H, CH<sub>2</sub>Cl<sub>2</sub> as standard) 1.33(m) and 1.90(m) in the ratio 1:2. The visible absorption at 592 nm is intense, suggesting full conjugation. The n.m.r. spectra show only two kinds of protons, indicating the equivalence of the two seven-membered rings. The signals at  $\tau$  1.70 can be assigned to the four *ortho*-protons (1-, 6-, 1'- and 6'-H) and at  $\tau$  2.20 to *meta*- and *para*-protons (2~5-H, and 2'~5'-H), the former probably being deshielded by the cyano and the cycloheptatrienyl groups. These results indicate that the positive charge is not localized in any part of the molecule. The chemical shift of the ring protons ( $\tau$  2.20) is  $\tau$  1.3 higher than that of tropylium fluoroborate ( $\tau$  0.91 in MeCN), which is consistent with a decrease of positive charge on each carbon atom from ca. 1/7 to 1/15.

The observed  $\text{p}K_{\text{R}}$  value for (IV) in 23% aqueous EtOH,  $3.44 \pm 0.05$ ,<sup>‡</sup> lies in between values for the tropylium ion (4.7)<sup>2</sup> and the triphenylcyclopropenium ion (2.8),<sup>3</sup> and confirms the stability of (IV).

The dilute methanolic solution of (IV) is orange but it turns dark blue on the addition of a small amount of mineral acid. Addition of a weak base yields quantitatively a mixture of isomeric methyl ethers ( $\lambda_{\max}$  368 nm) the n.m.r. spectrum of which suggests the predominance of compound (V). The n.m.r. spectrum of the mixture in trifluoroacetic acid is identical with that of (IV) in the same solvent, indicating a reversible interchange.

In view of the negative stabilization effect of the cyano-group on carbonium ions, a higher electronic stability of the parent cation of (IV) might have been expected.

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<sup>†</sup> Satisfactory elemental analyses have been obtained.

<sup>‡</sup> This was measured spectroscopically.

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<sup>3</sup> R. Breslow and H. Chang, *J. Amer. Chem. Soc.*, 1961, **83**, 2367.