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Cyclohepta[*ℓ*]phenanthrenylium Ions.
Intramolecular Cyclization of 2-Biphenylylcycloheptatrienes

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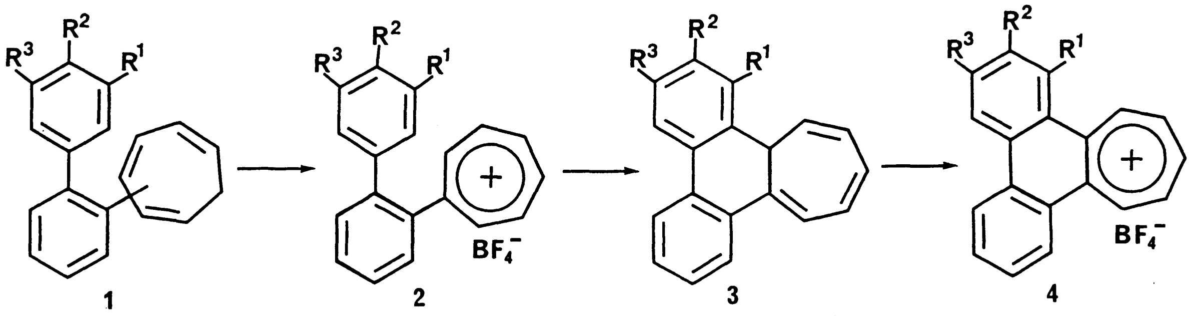
The intramolecular Friedel-Crafts type reaction of 3'-methoxy- and 3',5'-dimethoxy-2-biphenylylcycloheptatrienes allowed to construct the corresponding cyclohepta[*ℓ*]phenanthrenylium ions in reasonable yields. Some physical properties (UV, ^{1}H-NMR, and pK_{R^+}) of these new cations were also described.

A decade ago we reported the synthesis of a series of 2-biphenylyltropylium tetrafluoroborates (**2a-d**) by hydride abstraction from the corresponding 2-biphenylylcycloheptatrienes (**1a-d**).1) Although intramolecular ring closure between the tropylium ring and the proximate benzene ring in these products was expected, such reactions did not occur when the substituents were R=H (**2a**), 4'-CH_3 (**2b**), 4'-OCH_3 (**2c**), 4'-*t*-C_4H_9 (**2d**), and 3',5'-$(CH_3)_2$ (**2e**). However, 3',5'-dimethoxy-2-biphenylylcycloheptatriene (**1f**) was treated with an equimolar amount of triphenylmethyl (trityl) tetrafluoroborate in acetonitrile for 0.5 h followed by addition of dry ether to give 1,3-dimethoxycyclohepta[*ℓ*]phenanthrenylium tetrafluoroborate (**4f**)2) in 8% yield instead of the uncyclized 3',5'-dimethoxy-2-biphenylyltropylium salt (**2f**). When four equivalents of the trityl salt was employed the yield of **4f** reached up to 68%. In a typical experiment, to a stirred solution of trityl tetrafluoroborate (2.93 g, 8.88 mmol) in acetonitrile(10 mL) was added a solution of **1f** (675 mg, 2.22 mmol) in acetonitrile (5 mL) at room temperature. After stirring for 0.5 h, dry ether (100 mL) was added to the

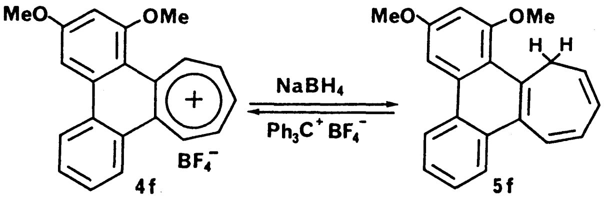


1a, 2a; $R^1 = R^2 = R^3 = H$
1b, 2b, $R^1 = R^3 = H$, $R^2 = CH_3$
1c, 2c; $R^1 = R^3 = H$, $R^2 = OCH_3$
1d, 2d; $R^1 = R^3 = H$, $R^2 = t\text{-}C_4H_9$
1e, 2e; $R^2 = H$, $R^1 = R^3 = CH_3$
1f, 2f, 3f, 4f; $R^2 = H$, $R^1 = R^3 = OCH_3$
1g, 2g, 3g, 4g; $R^1 = R^2 = H$, $R^3 = OCH_3$

reaction mixture. The resulting precipitates were collected by filtration and washed with dry ether to afford **4f** (590 mg, 68.3%) as a red powder, mp >300 °C,[3] Anal. Found: C,64.97; H, 4.36%. Calcd for $C_{21}H_{17}O_2BF_4$: C,64.98; H,4.41%.

Unlike **1f**, on treatment with an equimolar amount of trityl tetrafluoroborate under the same reaction conditions, 3'-methoxy-2-biphenylylcycloheptatriene (**1g**) was simply converted into the uncyclized tropylium ion salt (**2g**).[4] However, when the reaction was carried out with four equivalents of the trityl salt for 12 h the cyclized tropylium ion salt (**4g**)[5] was obtained as a red powder, mp >300 °C in 62 % yield without isolation of **2g**. These results suggest that a mechanism to account for the formation of **4f** and **4g** from **1f** and **1g**, respectively, would be that intramolecular Friedel-Crafts type cyclization reaction of the initially formed 2-biphenylyltropylium salts (**2f** and **2g**) happens to give the intermediates, **3f** and **3g**, which can be converted to the final products by further hydride abstraction. Although the tropylium ion is known to react as an electrophile with electron-rich aromatic compounds such as phenols[6] and azulenes,[7] the intramolecular version of this Friedel-Crafts type reaction is, to our knowledge, the first example.

The structures of **4f** and **4g**, which provided first example of this ring system, were confirmed on the basis of their spectroscopic properties and elemental analyses together with chemical reactions. Thus, on reduction with sodium borohydride in acetonitrile **4f** was reduced to the corresponding cycloheptatriene derivative (**5f**)[8] (pale yellow



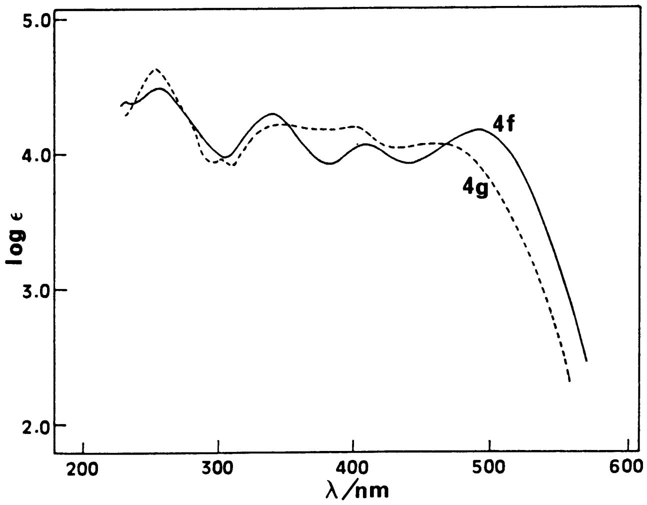
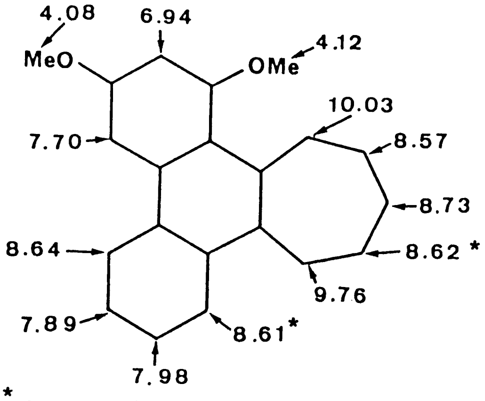


Fig. 1. UV-Vis spectra of **4f**(———) and **4g**(··········) in CH_2Cl_2.



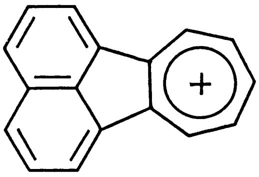
*These assignments are tentative due to the severe peak overlapping.

Fig. 2. ^{1}H-NMR data of **4f** (δ values; in CD_3CN, 500 MHz).

prisms, mp 122 °C) in 67% yield from which the original tropylium ion salt **4f** could be regenerated by treatment with trityl tetrafluoroborate in 73% yield.

As illustrated in Fig. 1 the electronic spectra of **4f** and **4g** exhibit long wavelength absorptions at 490 and 460 nm, respectively, suggesting charge delocalization in these molecules to some extent. Furthermore, this is also borne out by the shielded ^{1}H-NMR resonances at δ=8.57-8.73 for the tropylium ring protons (expect H-9 and H-13) of **4f** compared with that of the tropylium ion itself (δ=9.2)[9] along with the deshielded methoxy resonances at δ=4.12 and 4.08.[10]

These spectroscopic properties of **4f** and **4g** are suggestive of the greater thermodynamic stabilities of both cations than that of tropylium ion. However, the pK_R+ values of **4f** and **4g** measured by standard spectrophotometric method are 3.1 and 1.9, respectively, revealing that both cations are less stable than tropylium ion itself ($pK_R+=4.75$).[11] It is well-known that aromatic ring annelation leads to decreased stabilization in the tropylium ring.[12] This is also the case for cyclohepta[*l*]phenanthrenylium ion. In this connection, it recall us to the earlier finding that cyclohept[*a*]acenaphthenium ion **(6)** enjoys abnormally high thermodynamic stability ($pK_R{}^+= 8.7$).[13]



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References

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2) A parent carbon skeleton of this ring system, 8b*H*-cyclohepta[*ℓ*]phenanthrene, has been reported: H. Dürr, K-H. Pauly, and K. Fisher, Chem. Ber., 116, 2855 (1983).

3) **4f**: UV/VIS λ_{max}(log ε) (in CH_2Cl_2) 490(4.16), 407(4.06), 340(4.29), 257(4.49), (in CH_3CN) 476(4.15), 399(4.07), 333(4.31), 256(4.50); IR(KBr) ν cm^{-1} 1602, 1350, 1295, 1246, 1206, 1090-1005, 760.

4) **2g**: UV/VIS λ_{max}(log ε) (in CH_2Cl_2) 368(3.85), 420(shoulder); IR(KBr) ν cm^{-1} 1600, 1474, 1120-1040, 760; ^{1}H-NMR(60 MHz, in CD_3CN) δ 8.90-8.80(m, $C_7H_6^+$), 7.62-6.50(m, Ar), 3.62(s, OMe).

5) **4g**: UV/VIS λ_{max}(log ε)(in CH_2Cl_2) 460(4.10), 400(4.23), 345(4.25), 255(4.62), (in CH_3CN) 444(4.01), 375(4.07), 335(4.31), 252(4.58); IR(KBr) ν cm^{-1} 1614, 1434, 1374, 1240, 1130-1050, 752; ^{1}H-NMR(400 MHz, in CD_3CN) δ 9.89(d, J=10.8 Hz, H-9), 9.76(d, J=10.4 Hz, H-13), 8.88-8.83(m, H-11), 8.74-8.68(m, H-10,12), 8.66(d, J=8.4 Hz, H-8), 8.59(d, J=9.3 Hz, H-1), 8.57-8.55(m, H-5), 7.96-7.92 (m, H-6), 7.87(d, J=2.6 Hz, H-4), 7.85-7.81(m, H-7), 7.37(dd, J=9.3, 2.6 Hz, H-2), 4.07(s, OCH_3); Anal. Found: C,67.11; H,4.20%. Calcd for $C_{20}H_{15}OBF_4$: C,67.07; H,4.22%.

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7) K. Hafner, A. Stephan, and C. Bernhard, Justus Liebigs Ann. Chem., 650, 42 (1961); T. Nozoe, T. Toda, T. Asao, and A. Yamanouchi, Bull. Chem. Soc. Jpn., 41, 2935 (1968).

8) The structure of **5f** was elucidated unequivocally by the elemental analyses [Anal. Found: C,83.34; H,6.11%. Calcd for $C_{21}H_{18}O_2$: C,83.42; H,6.00%], and 400 MHz ^{1}H-NMR spectrum [(in $CDCl_3$) δ 8.54(d, J=8.1 Hz, H-5), 8.47(d, J=11.9, H-9), 8.34(d, J=8.2 Hz, H-8), 7.68(d, J=2.2 Hz, H-4), 7.60(dt, J=8.2, 7.2 Hz, H-7), 7.54(dt, J=8.1, 7.2 Hz, H-6), 6.76(dd, J=11.9, 4.6 Hz, H-10), 6.72(d, J=2.2 Hz, H-2), 6.23(dd, J=4.6, 9.0 Hz, H-11), 6.00-5.94(m, H-12), 3.98(s, OMe), 3.94(s, OMe), 3.26(broad, s, H-13)].

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