^{19}F NMR Study on Pentacyclo[4.3.0.0^{2,3}.0^{3,8}.0^{5,7}]nonanyl and Tetracyclo[3.3.1.0^{2,8}.0^{4,6}]nonanyl Cation

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By comparison of the ^{19}F chemical shift of *p*-fluorophenyl substituted Coates cation **1** with that of triasteryl cation **2**, $\pi\sigma$-participation by the remote cyclopropyl group in ion **1** is shown to be more effective than σ-participation by the adjacent cyclopropyl group in ion **2** in the delocalization of positive charge.

Solvolysis of the parent 9-pentacyclo[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]nonanyl *p*-nitrobenzoate proceeds with an exceptionally large rate (10^{12}) over that of the related 7-norbornyl derivatives. This major rate enhancement was attributed to $\pi\sigma$-participation by the remote cyclopropyl group leading to the formation of a tris(homocyclopropenium) ion intermediate **1**.[1] However, it is well known that the degree of charge delocalization into a neighbouring cyclopropyl group in ion intermediates depends substantially on the geometric arrangement.[2] In view of this fact, the cyclopropyl groups in tetracyclo[3.3.1.0.^{2,8}.0^{4,6}]nonanyl cation **2** (triasteryl cation) may have a different effect on the charge delocalization relative to the substituted Coates cation **1**. We reported previously the results of a ^{19}F NMR study on the *p*-fluorophenyl substituted triasteryl cation **2**, indicating the extreme stability compared to the related cation species in superacidic solution,[3] and the ^{19}F NMR spectral data for ion **2** are given in Fig. 1.

We now wish to report the results of a ^{19}F NMR study on the *p*-fluorophenyl substituted Coates cation **1**. In order to obtain the ^{19}F chemical shift data for ion **1**, we have synthesized the 9-*p*-fluorophenyl pentacyclo[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]nonan-9-ol by our modified route.[4] The ^{1}H and ^{13}C NMR data for the substituted Coates alcohol were consistent with data previously reported by Coates and coworkers, and the alcohol was further identified by MS. ^{19}F NMR spectroscopy has the advantage of greater sensitivity to electron demand of the adjacent cation centre, and comparative insensitivity to magnetic anisotropy of the solvent.[5] When a positive charge is dispersed into an adjacent *p*-fluorophenyl ring, the chemical shift of the fluorine atom on the phenyl ring moves downfield compared with that of the uncharged species. Less efficient charge delocalization in the *p*-fluorophenyl ring should result in greater charge dispersion by the neighbouring substituent. Thus, the chemical shift of the fluorine atom can provide important information on the degree of charge delocalization through neighbouring group participation.

Treatment of the *p*-fluorophenyl substituted Coates alcohol with FSO_3H/SO_2ClF at −90 °C gave a clear, red–brown solution,† the ^{19}F NMR spectrum of ion **1** showed a nonet at

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† Cation **1**: 80 MHz ^{1}H NMR (δ, CD_2Cl_2): 7.76 (dd, 2H, H*o*; $J_{Ho,F}$ 5.2, $J_{Ho,Hm}$ 8.9 Hz), 7.28 (t, 2H, H*m*; $J_{Ho,Hm} = J_{Hm,F} = 8.6$ Hz), 4.58 (m, 2H, H-1 and H-8), 3.46 (m, 2H, H-4 and H-5), 2.26 (m, 4H, H-2, H-3, H-6 and H-7). 20 MHz ^{13}C NMR (δ, CD_2Cl_2): 166.51 (C-13; $J_{C,F}$ 258 Hz), 135.1 (C-11; $J_{C,F}$ 10.1 Hz), 120.1 (C-10; $J_{C,F}$ 3.1 Hz), 117.9 (C-12; $J_{C,F}$ 22.6 Hz), 90.4 (C-9), 39.6 C-4 and C-5), 36.8 (C-1 and C-8), 36.3 (C-2, C-3, C-6 and C-7).

Quenching of ion **1** in an excess of sodium methoxide/methanol and subsequent work up an purification, gave the corresponding 9-methoxy-ether **1**[1] with the following NMR data; ^{1}H NMR (δ, $CDCl_3$): 7.39 (dd, 2H, and H*o*), 7.0 (t, 2H, H*m*), 2.95 (m, 5H, H-1, H-8 and OCH_3), 2.21 (m, 2H, H-2, H-3, H-6 and H-7), 1.60 (m, 2H; H-4 and H-5). ^{13}C NMR (δ, $CDCl_3$); 161.9 (C-13), 137.3 (C-10), 130.3 (C-11), 114.5 (C-12), 52.6 (C-9), 38.2 (C-4 and C-5), 37.1 (C-1 and C-8), 35.3 (C-2, C-6 and C-7).

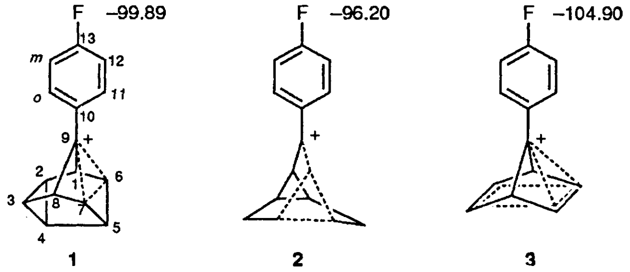

Fig. 1 ^{19}F NMR data, δ relative to CCl_3F.

δ −99.89. Strikingly, the absorption signal of the fluorine atom in ion **1** appeared considerably upfield (3.69) compared to that of ion **2**, while it was shifted downfield (5.04) relative to that of 7-*p*-fluorophenyl norbornadienyl cation (**3**) (Fig. 1). This result may suggest greater charge delocalization into the cyclopropane ring in ion **1** than in ion **2**.

It is clear that πσ-participation by the remote cyclopropyl group in ion **1** is superior to σ-participation by the adjacent cyclopropyl group in ion **2** in the delocalization of positive charge; however, it is inferior to the π-participation by the double bond in ion 3.[6]

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