Phenanthronorbornyl Cation:† A Conformation-locked 1,2-Diarylnorbornyl Cation. Part II.[1] ^{13}C Nuclear Magnetic Resonance Spectroscopy

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A variable temperature study of the ^{13}C n.m.r. spectrum of the title cation (III) has been made, and an upper limit has been estimated for the free energy barrier to narcissistic rearrangement. Spectra of suitable reference compounds are reported and the interpretation of the spectrum of the 1,2-diphenylnorbornyl cation is discussed.

In an earlier paper [1] we presented kinetic evidence for the participation of the 9,10-double bond of phenanthrene in solvolysis reactions of cyclopentaphenanthrenylethyl derivatives (I). A product from the Ag^{I}-catalysed acetolysis of the bromide (I; X = Br) was the hydrocarbon (II), which, on dissolution in fluorosulphuric acid, gave the cation (III). This ion, a supposed intermediate in the solvolysis reactions, was then examined spectroscopically.

There has been a revival of interest recently in 1,2-diarylnorbornyl cations, and the cation (III) represents an unusual example of this class, since in it the aryl groups are constrained in such a manner that both simultaneously present one face to the bridging C-6 carbon atom. Our hope had been that the classical or bridged nature of this cation [(a) or (b), respectively], if not definable by proton n.m.r spectroscopy, might be disclosed by its u.v. spectrum. This was based upon the assumption that an equilibrating ion (IIIa) would have a π-electron system (and electronic spectrum) similar to that of 9-protonated phenanthrene and related cations, whilst the electronic structure (and spectrum) of a non-classical (and more symmetrical) bridged ion (IIIb) should be quite different.

In the event, onset of selective line-broadening in the proton n.m.r. spectrum of (III) at the lowest temperatures attainable (*ca.* —120 °C) was as expected for (IIIa), and this classical equilibrating structure was supported by the similarity between the electronic spectrum of the ion and spectra reported for various related phenanthrenium ions.

Since our original report, attempts to simulate the electronic spectra of both the classical and bridged species have borne out our belief that these would be substantially different, irrespective of the method of calculation. However, simulation of the observed spectrum was not good, and application of the CNDO procedure of Jaffé and del Bene [2,‡] in fact proved inferior to a simple SCF π-electron calculation which adequately reproduced a long-wavelength band at *ca.* 500 nm. This was similar to the results of earlier π-electron calculations [3] on the spectrum of protonated phenanthrene.

In an effort to quantify the barrier height for narcissistic rearrangement of (IIIa), we turned our attention to ^{13}C dynamic n.m.r. spectroscopy, since the large chemical shift difference expected between C-1 and C-2 of the norbornyl cation system might have been sufficient to give coalescence phenomena at temperatures more accessible than was the case with proton n.m.r.

The noise-decoupled spectrum, at —40 °C in fluorosulphuric acid (external Me_4Si standard), is recorded in the Table. Off-resonance decoupling indicated that the low-field peak at δ 153 is due to a carbon atom not bearing hydrogen, and this peak was assigned to C-1 and C-2. At —90 °C (solution diluted with sulphuryl chloride fluoride) selective line broadening was clearly evident,

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† Correctly named as 1,2,3,4,4a,12b-hexahydro-2,4b-methanotriphenylenyl cation.

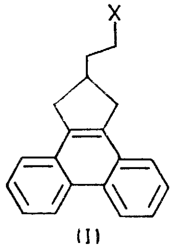
‡ The version of the program used incorporated modifications by Dr. D. R. Roberts (The Open University), whose help we acknowledge.

[1] R. M. Cooper, M. C. Grossel, and M. J. Perkins, *J.C.S. Perkin II*, 1972, 594, is regarded as Part I.

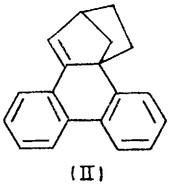
[2] J. Del Bene and H. H. Jaffé, *J. Chem. Phys.*, 1968, **48**, 1807.

[3] G. L. Dallinga, E. L. Mackor, and A. A. Verijn Stuart, *Mol. Phys.*, 1958, **1**, 123.

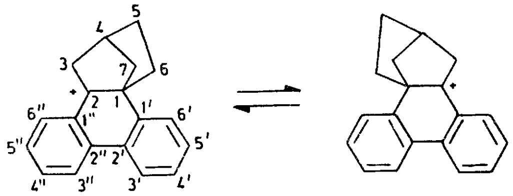
and at −110 °C the line at δ 153 was no longer discernible. However, further temperature reduction to −135 °C did not reveal separate resonances for C-1 and C-2. Although the complete coalescence phenomenon is thus not observable, it is possible to obtain an upper limit for the free energy of activation for the interconversion of the enantiomers of (IIIa). This depends on an estimate of the slow-exchange limit chemical shifts of C-1 and C-2. For this purpose, the trimethylphenanthrenium ion (IV) was selected as an appropriate model. This was generated by the general procedure of Shubin *et al.*,[4a] and at −65 °C quaternary carbon resonances were found at δ 233.1 * and 53.6 corresponding to C-9 and C-10, respectively.



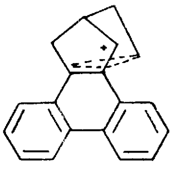
(I)



(II)



(IIIa)

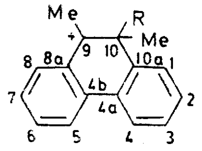


(IIIb)

^{13}C N.m.r. parameters for the cations (III), (IV), (XI), and (XII) in FSO$_3$H–SO$_2$ClF [a]

(III) (−40 °C)	152.9, s, C-1, -2; 138.8, d, C-3′, -3″; 137.2 and 134.3, both s, C-1′, -2′, -1″, -2″; 130.5 and 130.3 ,both d, C-4′, -6′, -4″, -6″; 125.3, d, C-5′, -5″; 44.4 and 44.2, both t, C-3, -6, -7; 37.5, d, C-4; 24.0, t, C-5
(XI) [b]	170.5, s, C-1, -2; 140.5, d, C-*p*′, -*p*″; 136.5, s, C-1′, -1″; 134.1, d, C-*o*′, -*o*″; 130.5, d, C-*m*′, -*m*″; 47.5, t, C-3, -7; 34.3, d, C-4; 32.2, t, C-6; 21.2, t, C-5
(IV) (−85 °C)	233.1, s, C-9; 153.9, s, C-4b; 149.9, s, C-4a; 137.8, s, C-8a or -10a; 134.3, d, C-8; 133.4, s, C-10a or -8a; 131.4, 129.2, and 126.9, all d, C-1, -2, -3, -4, -5, -6, -7; 53.6, s, C-10; 27.6, q, 10-Me$_2$; 25.3, q, 9-Me
(XII) (−53 °C)	237.9, s, C-α; 166.8, s, C-1; 142.5, d, C-3, -5; 138.9 and 136.4, both s, C-4, -1′; 135.4, d, C-4′; 130.6 and 130.1, both d, C-2, -3, -5, -6, -2′, -5′, -6′; 31.3, q, C-β

[a] Chemical shifts in p.p.m. downfield from external Me$_4$Si, splitting pattern on off-resonance decoupling, assignment. [b] Chemical shifts from ref. 15, corrected to Me$_4$Si reference.



(IV) R = Me

(V) R = Ph

Above 0 °C these two resonances had coalesced to a single line at δ 143.4. This is *ca.* 10 p.p.m. upfield from the corresponding peak of the cation (III). It is not a straightforward matter to apportion the contributions of C-1 and C-2 in (III) to this difference. A comparison of the ^{13}C chemical shifts of C-1 and C-2 in norbornane with values for C-2 and C-3 in 2-methylbutane, respectively,[5] predicts a difference in the correct direction for the bridgehead carbon [C-1 in (III)] of *ca.* 8 p.p.m., so that a reasonable estimate of the low-temperature chemical shifts for (III) might be *ca.* 68 p.p.m. for C-1 and *ca.* 238 p.p.m. for C-2. Although these figures are open to question, the difference between the chemical shifts for the two carbons is probably not less than the estimated 170 p.p.m. Taking the coalescence temperature to be −105 °C (probably 15 °C too high), at the resonance frequency employed (22.6 MHz), then allows an upper limit of 6.6 kcal mol^{-1} to be calculated for $\Delta G^{\ddagger}$.

This result confirms our suspicion that alkyl migration in the cation (IIIa) takes place more readily than phenyl migration in the cation (V) [6] ($\Delta G^{\ddagger}$ 9.0 kcal mol^{-1} at −50 °C). These figures may not be directly comparable owing to an appreciable entropy factor in the aryl case arising from the need for a specific orientation of the aryl ring before aryl migration can take place. However the presence of charge-transfer bands in the u.v. spectra of 10-aryl-9,10-dimethylphenanthrenium cations [7] suggests partial bridging in the localised structures of these species, a factor which should lead to a lowering of the barrier for aryl migration. In any case, extrapolation from a comparison between these phenanthrenium ions to a comparison between norbornyl and a dialkylbenzenium ion would be unwise.

Our approximate result does of course depend on a direct application of the Eyring equation. Quite apart from the usual assumptions implicit in this approach, Fong has suggested that the equation will not hold satisfactorily when the magnitude of the activation barrier approaches that of the vibrational quantum of the normal mode which promotes the transition.[8] How closely, in

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* A value of 231.4 at −110 °C (SO$_2$ClF–FSO$_3$H) has recently been reported.[4b]

[4] (*a*) V. G. Shubin, D. V. Korchagina, A. I. Rezvukhin, and V. A. Koptyug, *Doklady Akad. Nauk S.S.S.R.*, 1968, **179**, 119; (*b*) G. I. Borodkin, M. M. Shakirov, V. G. Shubin, and V. A. Koptyug, *J. Org. Chem.* (*U.S.S.R.*) 1974, **10**, 2641.

[5] G. C. Levy and G. L. Nelson, 'Carbon-13 N.M.R. for Organic Chemists,' Interscience, New York, 1972, pp. 40 and 46.

[6] V. G. Shubin, D. V. Korchagina, B. G. Derendjaev, G. I. Borodkin, and V. A. Koptyug, *Zhur. org. Khim.*, 1973, **9**, 1041.

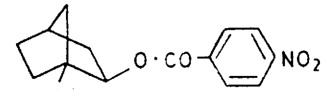
[7] G. I. Borodkin, D. V. Korchagina, B. G. Derendjaev, and V. G. Shubin, *Tetrahedron Letters*, 1973, 539.

[8] F. K. Fong, *J. Amer. Chem. Soc.*, 1974, **96**, 7638.

this context, our cation approximates to norbornyl itself is unclear; it will depend on the motion of the benzene rings to compensate for the shift of the bridging group. On the other hand, in the same discussion by Fong[8] is presented an argument that bridged norbornyl must represent either a *maximum* on the ground state potential surface or a *minimum* on an *excited state surface.*

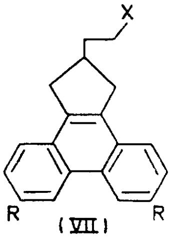
The classical–non-classical controversy involving σ-bridging has recently contracted to include only the parent norbornyl cation, since all substituted systems are now regarded as essentially classical, though evidence has been presented for the onset of σ-delocalisation in 2-aryl-substituted cations when the ' electron-demand ' of the aryl substituent is high.[9]

In addition to Fong's theoretical arguments that norbornyl itself is classical, there has been a review which systematically challenges the evidence favouring a bridged structure,[10] and Brown has presented results which suggest that unsymmetrical norbornyl can be intercepted.[11] On the other hand Traylor has very recently ascribed the enormous rate enhancements (6×10^5) in the solvolysis of the ester (VI) to the enhancement of σ-participation by the $CH_2{\cdot}SnMe_3$ group.[12] Bentley has reinterpreted the solvolysis data for 2-norbornyl derivatives, concluding that *exo*-derivatives are solvolysed more rapidly, and *endo*-derivatives less rapidly, than would be predicted from model systems.[13]

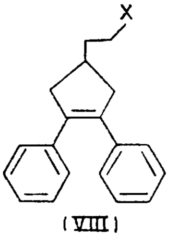


(VI)

Our own work, although fairly remote from norbornyl itself, is nevertheless susceptible to interesting extensions. For example, examination of mono- and symmetrically di-substituted analogues (VII) of (I) could provide evidence on the symmetry of the π-participation. In this context the work of Thornton[14] on the solvolysis of arylcyclopentenylethyl derivatives, *e.g.* (VIII), seems inconclusive, not least because of the interference between the aryl groups in the disubstituted compound, although comparison data show that *cis*- and *trans*-stilbene react at similar rates on bromination.

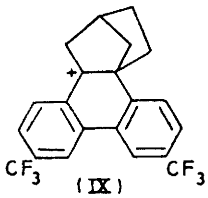


(VII)



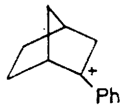
(VIII)

The work of Farnum and Wolf[9] suggests that highly electron-withdrawing aryl substituents can force the onset of σ-delocalisation in the 2-norbornyl cation. Shubin *et al.*[4b] have shown that the presence of two CF_3 substituents at C-3 and C-6 respectively in the phenanthrenium ion (IV) lowers the barrier for methyl migration by *ca.* 4.2 kcal mol^{-1}. Thus the barrier to rearrangement in ions derived from (VII), *e.g.* (IX), might be reduced to the levels discussed by Fong, but, unlike norbornyl, the nature of these ions should be susceptible to elucidation by u.v. spectroscopy, using comparisons with the classical ions of Shubin.

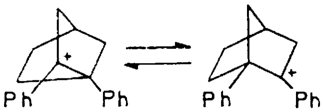


(IX)

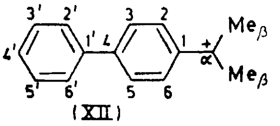
Comparison of the ^{13}C n.m.r. data obtained in this work with those for the 2-phenylnorbornyl (X) and the 1,2-diphenylnorbornyl (XI) cations is interesting. The chemical shift of C-2 in (X) is 257 p.p.m. downfield from external Me_4Si, which is similar to the chemical shift of electron-deficient carbon in several tertiary benzylic systems. The lower values found in (IV), and estimated for (III), may be attributable to charge dispersal over the whole biphenyl system, with the consequence that there is a higher π-electron density at the cation centre than in other tertiary benzylic ions. To test this hypothesis, 4-isopropenylbiphenyl was dissolved in fluorosulphuric acid–dichloromethane at −40 °C, and the ^{13}C n.m.r. spectrum of the resulting cation (XII) was recorded. A peak at 237.9 p.p.m. which remained a singlet on off-resonance decoupling strongly supports the above explanation.



(X)



(XI)



(XII)

The chemical shift of C-1 in (X) is 60 p.p.m., and the difference between this and the value estimated for C-1 in (III) seems consistent with the effect of aryl substitution.

In their ^{13}C n.m.r. study of (XI), Olah and Liang[15] were unable to detect the onset of coalescence phenomena at the lowest temperatures (−135 °C) explored, and

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[9] D. G. Farnum and A. D. Wolf, *J. Amer. Chem. Soc.*, 1974, **96**, 5166.

[10] G. M. Kramer, *Adv. Phys. Org. Chem.*, 1975, **11**, 177.

[11] H. C. Brown and J. H. Kawakami, *J. Amer. Chem. Soc.*, 1975, **97**, 5166.

[12] G. D. Hartman and T. G. Traylor, *J. Amer. Chem. Soc.*, 1975, **97**, 6147.

[13] T. W. Bentley, *Ann. Reports (B)*, 1974, 199.

[14] J. W-T. Wu and E. R. Thornton, *J. Org. Chem.*, 1975, **40**, 1041.

[15] G. A. Olah and G. Liang, *J. Amer. Chem. Soc.*, 1974, **96**, 195.

C-1 and C-2 gave a single resonance at 170.5 p.p.m. This is nearly 20 p.p.m. downfield from the corresponding value for (III). The slow-exchange limit shifts for (XI) were estimated [15] to be 259 for C-2 and 84 p.p.m. for C-1.

The choice of 259 p.p.m. for C-2 is based on the value for (X), and seems curious since the authors assert that (XI) is an atypical benzylic cation in which there is steric inhibition of resonance at C-2 by the phenyl substituent on C-1. The inferred shift at C-1 of 84 p.p.m. is also surprising since it implies an unusually large effect of phenyl substitution. Justification was based on a questionable analogy with the effect of an α-phenyl substituent on the C-1 chemical shift of lithium alkyls. A figure of 68 p.p.m. for C-1 [*cf.* (III)], would require δ_{C-2} to be 271.5 p.p.m., perhaps a more realistic value in view of the apparently poor π-overlap with the phenyl substituent.

Despite this suggested revision of Olah's data on (XI), both ^{1}H and ^{13}C time-averaged chemical shifts are consistent with greater dispersal of positive charge into the aromatic rings in (III) than in (XI), which accords with greater demands on σ-delocalisation in (XI) manifest in the apparently lower $\Delta G^\ddagger$ value for its rearrangement.

One notable difference between the cations (III) and (XI) is the greater stability of solutions of the former, which have a half-life of several hours at room temperature. This is consistent with simultaneous charge delocalisation into both rings of (III), despite its equilibrating classical structure.

^{13}C Spectral data are collected in the Table.

EXPERIMENTAL

Solutions of the cations were prepared according to the procedures outlined in Part I or elsewhere.[6] ^{13}C N.m.r. spectra were recorded on Bruker spectrometers operating at 22.6 MHz, at King's College, London, at P.C.M.U. Harwell, or at Oxford. δ Values are quoted relative to external Me_4Si.

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