Articles

^{13}C-^{1}H Coupling Constant as a Criterion for the Presence of π Bridging in Substituted 9-Benzonorbornenyl Cation

Gweon-Young Ryu and Jung-Hyu Shin*

Department of Chemistry, Seoul National University, Seoul 151-742. Received July 30, 1992

The discrete structure of substituted 9-benzonorbornenyl cation 3a and 3c was studied using the empirical ΔJ equation which was developed by Kelly and coworker[5]. The ΔJ values of substituted 9-benzonorbornenyl cations were obtained from *p*-methyl-6,7-dimethyl benzonorbornen-9-yl (3a) and 9-methyl 6,7-dimethyl benzonorbornen-9-yl (3c) cations under stable ion conditions, and were compared with those of the corresponding ketone analog; these cations were generated by dissolving the corresponding carbinols in superacid at -120°C and the nmr spectra taken at -60°C $\sim$$-90$°C. The Δ$J$ values are 8.7 Hz for the bridgehead carbons in cation 3c and 3.1 Hz for cation 3b. The ΔJ values at $C_{5,8}$ in fused benzene ring are 14.3 Hz. for cation 3c and 8.7 Hz for cation 3a. The excellent correlation of the ΔJ values with ^{19}F chemical shifts of *p*-fluorophenyl 6,7-dimethylbenzonorbornenyl cation (3b) indicate that ΔJ value is a reliable probe to charge density at adjacent cationic carbon and These NMR parameters These NMR parameters strongly support that the symmetrically π-bridged nonclassical structure (type 2) of substituted 9-benzonorbornenyl cations in stable ion conditions.

Introduction

The acetolysis rate of *anti*-7-norbornenyl brosylate was, due to the anchimeric effect of the double bond, 10^{11} times faster than that of saturated 7-norbornyl brosylate[1]. Even the fused benzene ring in *anti*-9-benzonorbornenyl brosylate facilitates the ionization in acetic acid/sodium acetate by a factor of 10^5 relative to 7-norbornyl brosylate. A priori one can discuss an unsymmetrical transition state (type 1) and a symmetrical transition state (type 2) for the solvolysis of *anti*-9-benzonorbornenyl brosylate.
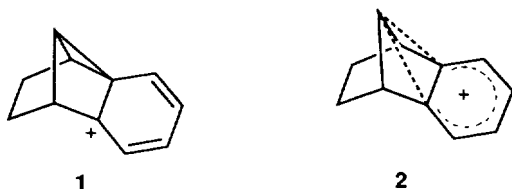
Barlett and Giddings[2] discuss in their communication a symmetrical transition state. This is supported by solvolysis studies of 9-benzo-norbornenyl brosylate with various substituted on the fused benzene ring by Tanida and coworker[3]. The substituent effects in *anti*-9-benzonorbornenyl derivatives[4] were cooperative rather than additive on the solvolysis rate. The introduction of a methoxy substituent in the C-6 position increases the rate by a factor of 53.7, whereas two methoxy substituents in the symmetrical C-6 and C-7 positions increase the rate by a factor of 3000, which is approximately the square of the value for the single substituent. The substituent effects on the rates of solvolysis is very large, far larger than what can be accounted for in terms of a simple inductive effect. According to the solvolytic studies, Tanida has suggested that intermediate in the solvolysis of *anti*-9-benzonorbornenyl brosylate is a symmetrically π-

bridged nonclassical struture (type 2). Unfortunately, the solvolytic data only provide partial information about the exact structure of the involved intermediate. Thus the question remains as to the discrete structure of the incipient cations produced by departure of the leaving group in 9-benzonorbornenyl derivatives; namely is it a equilibrating asymmetrical structure 1, or a symmetrical structure 2.

We now wish to report our investigation of the structure for substituted benzonorbornen-9-yl cations using one-bond ^{13}C-^{1}H coupling constants ($^{1}J_{CH}$). These cations were generated from 9-*p*-methylphenyl-6,7-dimethyl benzonorbornen-9-ol 9-*p*-fluoro-phenyl-6,7-dimethyl benzonorbornen-9-ol, and 9-methyl-6,7-dimethyl benzonorbornen-9-ol in FSO_3H/SO_2ClF soultion.

Results and Discussion

From a systematic investigation of the factors influencing one-bond ^{13}C-^{1}H coupling constant ($^{1}J_{CH}$) in cations, Kelly and coworker[5] developed an empirical ΔJ equation, in which the $^{1}J_{CH}$ values in the cation were compared with those of an appropriate model neutral compounds (ketone), and this equation was applied to get conformational information of acyclic trialkyl, dialkylaryl, and bicyclic cations. Recently, he has demonstrated that the ΔJ criterion can be used to provide convincing evidence for the symmetrically σ-bridged nonclassical structure of the tricyclo [3.2.1.1^{2,4}] oct-8-yl cation (5) in super acidic media[6].

To apply the ΔJ equation, the $^{1}J_{CH}$ values in the substituted 9-benzonorbornen-9-yl cations were compared with those of the corresponding ketone analog. Cations 3a, 3b and 3c were prepared by reaction of the corresponding alcohols with fluorosulfonic acid in SO_2ClF solution at -120 and -65°C, respectively, and ^{13}C spectra of the cations were recorded between -90 and -100°C. The one-bond ^{13}C-^{1}H coupling

constants for these cations were obtained by 2D *J*-resolved gated decoupling experiments.

The ΔJ values at $C_{5,8}$, based on the value for 6,7-dimethyl-benzonorbornen-9-one (154.5 Hz), are 14.3 Hz for cation **3c** and 8.7 Hz for cation **3a**.

3   **3a**   **3c**
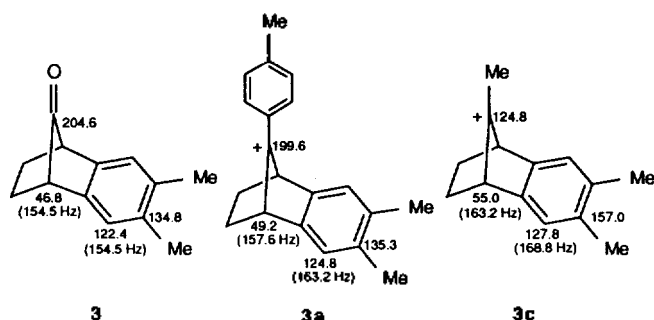
The use of aryl substituents to vary the charge density at the attached cationic carbon is well documented in both solvolytic[7] and nmr studies[8] under stable ion conditions. Thus it would be expected that the positive charge in case of cation **3c** is much more delocalized into the fused benzene ring than that of cation **3a**.

The 7-norbornenyl system is known reference to provide an interesting example in which the discrete structure of the substituted 9-benzonorbornenyl cation can be determined by using the ΔJ value. Although there is still some debate as to the exact nature of the intermediate generated during the solvolyses of 7-*anti*-norbornenyl derivatives, there is a large body of data[9] that supports the symmetrically π-bridged structure **4** particularly in superacid[11].

4   **5**   **6**

R = *p*-Fluorophenyl : a

Methyl   : b
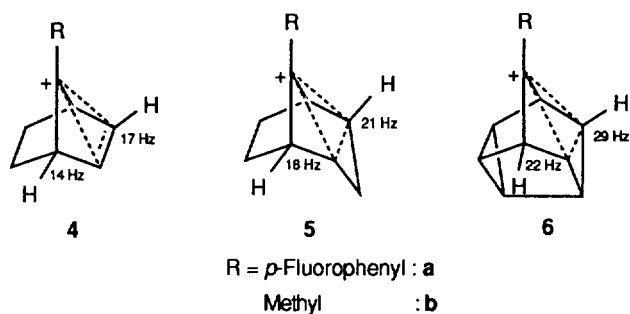
Measurements of the coupling constants for the ketone, together with those for the cation **4b** recorded by Olah and coworkers[10], provided the ΔJ values of 17 Hz for the bridging carbons ($C_{2,3}$) and 14 Hz for the bridgehead carbons ($C_{1,4}$). For equilibrating classical structures formed by a C_7-C_1→C_7-C_2 bond migration the ΔJ value at C_1 should be substantially larger as those observed in staatic bicyclic ssystems, *e.g.*, 2-methyl bicyclo[2.2.1] hept-2-yl (22 Hz)[5]. Smaller ΔJ values for 7-methyl norbornen-7-yl cation thus support the π-bridged structure **4**. It should be pointed out that the symmetrical ethano-bridged trishomocyclopropenium cation **5b** and **6b** yields exceptionally high ΔJ values at bridgehead carbons ($C_{1,5}$). Kelly[6] has suggested that the high values observed for ion **5** reflect the greater strain involved in the formation of the πσ-bridge of the trishomocyclopropenium cation.

In a similar view point, the equilibrating classical structure

1 is expected to have the ΔJ values of *ca.* 22 Hz for the bridgehead carbons ($C_{1,4}$) in 9-benzonorbornenyl cations. However, the ΔJ values at $C_{5,8}$ (14.3 Hz) and the bridgehead $C_{1,4}$ carbons (8.7 Hz) are reduced from those for ion **4b**, as expected from the available solvolyses data[5,8] and our previous 19F-NMR study[11]. Since 19F-NMR spectroscopy is very sensitive toward changes in electron density the 19F chemical shifts of the *p*-fluoro substituent of the cations is a good measure for the extent of charge delocalization from C-9 into the benzene ring. The 19F chemical shift of 7-*p*-fluorophenyl-norborneny-7-yl cation (**4a**) (δ-95) appeared at high field than that of 9-*p*-fluoro-phenylbenzonorbornenyl-9-yl cation **4b** (δ-62.3), in which the fused benzene ring in 9-benzonorbornenyl cations is vastly inferior to the double bond in 7-norbornenyl cation in assisting ionization of the cation precursors. The 19F-NMR spectrum[12] of the Coates cation **6a** showed a nonet at δ-99.89, and the absorption signal of the fluorine atom in Coates cation was shifted considerably upfields (4.89) relative to that of 7-norbornenyl cation **4a**. This result may suggest greater charge delocalization into the remote cyclopropane ring in cation **6a** than cation **4a**.

Furthermore, the observed 19F chemical shifts of these cation show a good correlation with the ΔJ values for the bridging carbons in cation **4b**, **6b** and the fused benzene ring in cation **3b**.

As mentioned previously, ΔJ values for the bridgehead carbons ($C_{1,4}$) increase from 3.1 Hz for cation **3a** to 8.7 Hz for cation **3c**. The substitution at the cationic carbon by aryl groups should be result in smaller ΔJ value due to diminution of delocalization of charge into remote benzene ring. However, it is surprising that the ΔJ values for the bridgehead carbons ($C_{1,4}$) for benzonorbornenyl cation systems yielded a significantly smaller ΔJ values compared with that of the 7-methyl norbornen-7-yl cation **4b**. To help resolve this question, the nmr studies on the 7-methyl norbornan-7-yl cation, 5,8-dimethyl benzonorbornen-9-yl cation and 2-methyl benzonorbornen-2-yl cation in super acid media, and MO calculations are currently under investigation.

The 13C chemical shifts for cation **3a** and **3c** are given over, and only three resonance signals appeared for six carbons in fused benzene ring. The assignments for C_{10}, C_5, and C_6 were made on the basis of analogy with a large number of substituted 9-arylbenzonorbornenyl cations (the data available in our own work) in which C_6 is always at lower field that C_{10}. In the fully coupled spectrum of cation **3c**, for example, one resonance signal appears at 127.8 ppm. This resonance signal was due to the C_5 and C_8 carbons; these are the only carbon atoms with an attached proton in the fused benzene ring of ion **3c**. The resonance at 124.8 ppm was then assigned to C_9, since the signal pattern of cationic carbon usually shows a broad low intensity singlet. The observation of these three signals in downfield (aromatic region) provided a very strong implication for the high degree of symmetry in the 6,7-dimethyl-benzonorbornen-9-yl cations.

The excellent correlation of the ΔJ values with 19F chemical shifts of cation **3b-6b** indicates that ΔJ value is a reliable probe to charge density at adjacent cationic carbon and strongly suggests that the substituted 9-benzonorbornenyl cations are the symmetrically π-bridged nonclassical structure (type 2) in stable ion conditions.

Experimental Section

NMR Spectra

The proton and carbon NMR spectra were obtained on a Varian VXR-200 or a Bruker AC-80 spectrometer. Spectra of neutral compounds were recorded at room temperature in $CDCl_3$ solution and chemical shifts were reported in ppm relative to tetramethylsilane. Spectra of the cations were recorded at $-90°C$ or $-100°C$ using 10 mm tubes containing a trace of CD_2Cl_2 for field stabilization. ^{13}C chemical shifts are reported in ppm relative to CD_2Cl_2 (internal reference). The coupled spectra were obtained using the gated decoupling 2D J-resolved technique, using 32767 data points, spectra widths of 5000 Hz and between 2000 transients. Coupling constansts (± 0.1 Hz) were measured by cursor in monitor on instrument. Assignment of carbon spectra were assisted by DEPT experiment.

Preparation of Cations

The cations were prepared from the corresponding alcohols in FSO_3H/SO_2ClF at -120 and $-60°C$ under nitrogen atmosphere using a specially designed cation generation apparatus.

Synthesis

6,7-Dimethylbenzonorbornen-9-one (6). Ketone **6** was prepared according to the modified literature procedure starting from p-toluidine[3b]: ^{1}H-NMR ($CDCl_3$) δ 1.32 (q, 2H), 2.17 (m, 2H), 2.26 (s, 6H), 3.25 (t, 2H), 7.07 (s, 2H); ^{13}C-NMR ($CDCl_3$) δ 19.63 (CH_3), 46.88 ($C_{2,4}$), 22.61 ($C_{2,3}$), 122.46 ($C_{5,8}$), 134.84 ($C_{6,7}$), 204.64 (C_9), 138.09 ($C_{10,11}$); IR (KBr disk): 3301, 2922, 2943, 1772, 1474, 1456, 893, 879.

9-p-methylphenyl-6,7-dimethylbenzonorbornen-9-ol (7). The ketone **6** (365 mg) was added in p-methylphenyl-magnesium bromide in anhydrous diethyl ether at room temperature, and the mixture was heated under reflux for 1 h, hydrolysis, and extracted with ether. The solvent were dried over anhydrous magnesium sulfate and the filtrate was evaporate *in vacuo* to give crude alcohol **7**. The alcohol was purified by silica gel column using CH_2Cl_2 as the eluant to give 365 mg (69%) of **7** as white solid: mp. 153.5-155.6°C ; ^{1}H-NMR ($CDCl_3$) δ 1.25 (m, 2H), 1.80 (s, 1H), 2.00 (s, 3H), 2.40 (m, 2H), 3.35 (t, 2H), 6.80 (s, 2H), 6.90 (d, 2H), 7.20 (d, 2H); ^{13}C-NMR ($CDCl_3$) δ 19.85 (CH_3), 50.49 ($C_{1,4}$), 26.24 ($C_{2,3}$), 122.48 ($C_{5,8}$), 135.34 ($C_{6,7}$), 9200 (C_9), 143.29 ($C_{10,11}$), 139.70 (C_{ip}), 128.65 (C_o), 127.49 (C_m), 138.50 (C_p); IR (KBr disk) 3567, 3436, 2970, 2943, 1612, 1516, 1477, 1448, 1382, '1294, 1112, 1042, 936, 870, 843.

9-p-Fluorophenyl-6,7-dimethylbenzonorbornen-9-ol (8). This alcohol **8** was prepared from the reaction of ketone **6** (300 mg) with p-fluorophenylmagnesium bromide in anhydrous diethyl ether. Similarly, alcohol **8** was purified by silica gel column using CH_2Cl_2 as the eluant: to give 154 mg (78%) of **8** as white solid: mp. 114.7-116.6°C ; ^{1}H-NMR ($CDCl_3$) δ 1.29 (m, 2H), 1.88 (s, 1H), 2.13 (s, 6H), 2.40 (m,

2H),-3.42 (t, 2H), 6.80 (s, 2H), 6.86 (m, 2H), 7.28 (dd, 2H); ^{13}C-NMR ($CDCl_3$) δ 19.83 (CH_3), 50.89 ($C_{1,4}$), 26.36 ($C_{2,3}$) 122.67 ($C_{5,8}$), 133.92 ($C_{6,7}$), 91,79 (C_9), 143.13 ($C_{10,11}$), 138.59 (C_{ip}), 129.49 (C_o), 114.79 (C_m), 161.66 (C_p); IR (KBr disk) 3391, 2968, 2955, 1636, 1508, 1477, 1232, 1159, 1117, 837.

9-Methyl-6,7-dimethylbenzonorbornen-9-ol (9). This alcohol **9** was prepared also from reaction of ketone **6** (180 mg) with methyl magnesium iodide in anhydrous ether. The alcohol **9** was purified by silica gel column using CH_2Cl_2 as eluant to give 154 mg (78%) of **9** as aolid: mp. 123.3-124 °C ; ^{1}H-NMR ($CDCl_3$) δ 1.14 (q, 2H), 1.06 (s, 3H), 1.85 (s, 1H), 2.25 (m, 2H), 2.20 (s, 6H), 2.81 (t, 2H), 6.90 (s, 2H); ^{13}C-NMR ($CDCl_3$) δ 20.84 (CH_3), 19.71 (9-CH_3) 52.02 ($C_{1,4}$), 25.94 ($C_{2,3}$), 122.77 ($C_{5,8}$), 133.28 ($C_{6,7}$), 89.00 (C_9), 144.19 ($C_{10,11}$); IR (KBr disk) 3352, 2805, 1482, 1459, 1376, 1300, 1278, 1171, 881, 802.

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