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^1H and ^{13}C Nuclear Magnetic Resonance Spectroscopic Study of 6,6-Disubstituted Fulvenium Ions[1]

George A. Olah,* G. K. Surya Prakash, and Gao Liang

Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106

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A series of 6,6-disubstituted fulvenes including 6-cyclopropyl-6-methylfulvene (5), 6-cyclopropyl-6-phenylfulvene (6), 6,6-(2-norbornylidene)fulvene (7), and 6,6-admantylidenefulvene (8) were prepared by the condensation of cyclopentadiene with the corresponding ketones. Precursor fulvenes were protonated to give the corresponding fulvenium ions under superacidic conditions at low temperatures. Protonation takes place exclusively at the C_2 position of the fulvene ring in accord with the calculated electron density distributions. The effects of substituent at C_6 on charge distributions in the studied fulvenium ions are discussed with regard to their respective ^1H and ^{13}C NMR data.

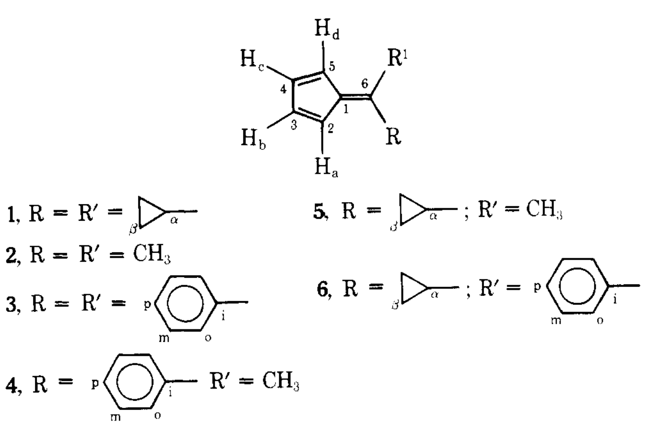
Fulvenes are highly colored compounds with considerable chemical reactivity, isomeric with benzenes, but with properties intermediate between those of aromatic and olefinic systems. Synthesis and properties of fulvenes have been reviewed.[2] For theoretical studies, fulvenes have been of great interest because they represent relatively simple nonalternate hydrocarbons which are readily adaptable to quantum mechanical treatment by either simple valence bond or molecular orbital methods. Thus, for example, the rather large dipole moments found for many 6,6-disubstituted fulvenes have been accounted for by several refinements of HMO type calculations of the parent fulvene.[3-5] Recently more sophisticated calculations were reported on fulvalene ions.[6] These calculations agree on the point that the dipole moment of the fulvenes is a direct consequence of their electronic structure and the moment is directed with its negative pole toward the ring.

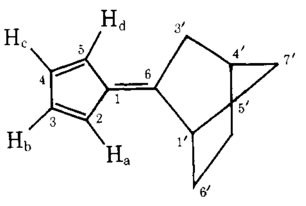
Fulvenes undergo a variety of reactions,[2d] but relatively little is known about their electrophilic reactions.[2c] Such reactions, however, are reported on heptafulvenes.[7] In continuation of our studies on the carbocationic intermediates of electrophilic reactions and particularly on the nature of substituent effects adjacent to carbocationic centers, we wish to report the study, based on ^1H and ^{13}C NMR spectroscopic data, of the carbocations obtained upon protonation of 6,6-disubstituted fulvenes in superacidic media.

Results

6,6-Dicyclopropylfulvene (**1**), 6,6-dimethylfulvene (**2**), 6,6-diphenylfulvene (**3**), and 6-methyl-6-phenylfulvene (**4**) were prepared by reported methods.[8] 6-Cyclopropyl-6-methylfulvene (**5**), 6-cyclopropyl-6-phenylfulvene (**6**), 6,6-(2-norbornylidene)fulvene (**7**), and 6,6-adamantylidenefulvene (**8**) were prepared by the condensation of cyclopentadiene with the corresponding ketones in the presence of sodium ethoxide in ethanol.

Protonation of studied fulvenes was carried out in FSO_3H/SO_2ClF or SO_2F_2 at −78 or −120 °C (using an ethanol/liquid nitrogen bath), respectively. Precursors **2**, **5**, and **7** gave only polymeric materials with all-acid systems such as HF/SbF_5, FSO_3H/SbF_5, and HF/BF_3. Precursors **1**, **3**, **4**, **6**, and **8** gave clean solutions of the resulting ions and the ^1H NMR spectrum of the ion obtained from **1** is shown in Figure 1 together with the ^{13}C NMR spectrum of the precursor **7**. The ^1H and ^{13}C NMR spectra of the ion generated from precursor **8** as representative are shown in Figure 2. The ^1H NMR shifts of the ions obtained are tabulated in Table I. The ^{13}C NMR data of the ions as well as their precursors along with the assignments are listed in Tables II and III, respectively.





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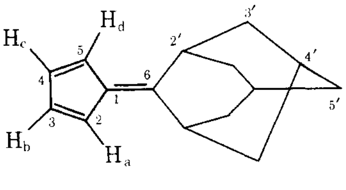

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Discussion

The bonding nature of fulvenes can be qualitatively described in terms of the mesomeric covalent structure **9** and the

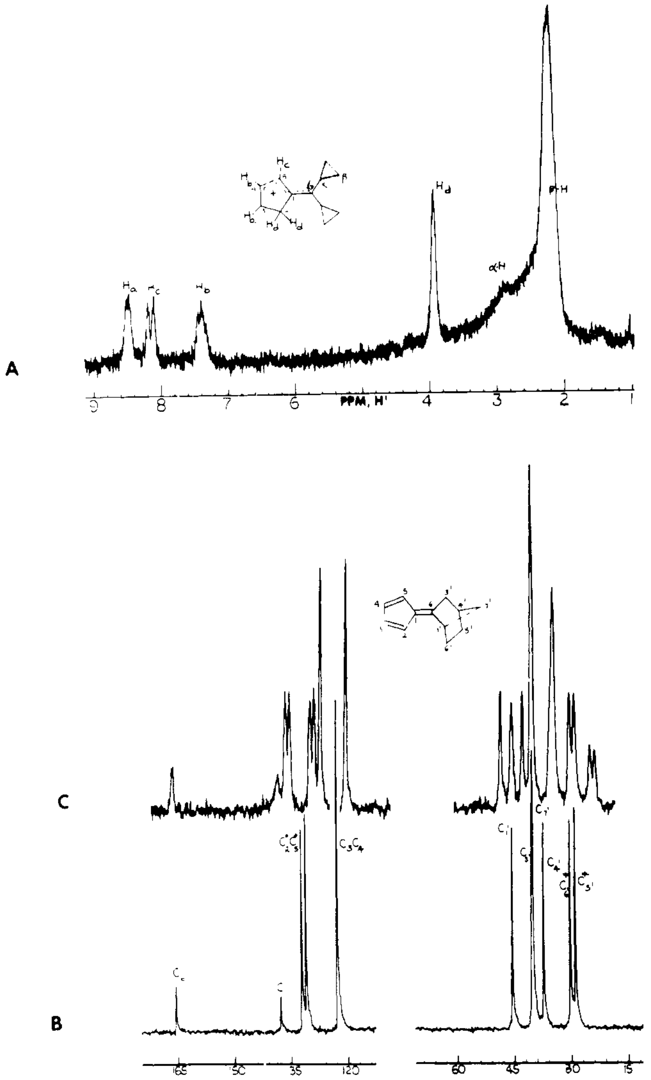


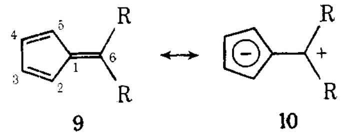
Figure 1. (A) ^1H NMR spectrum of ion **16** in FSO_3H/SO_2F_2 at −70 °C. (B, C) ^{13}C NMR spectrum of precursor **7** in $CDCl_3$ at 37 °C: B, proton noise decoupled; C, proton noise coupled.

Table I. ^1H NMR Data[a] of Fulvenium Ions in SO_2ClF or SO_2F_2 Solutions at −80 or −70 °C

Ions	Shifts
16	8.5 (b, 1 H, H_a), 8.2 (d, 1 H, H_c, $J_{H_cH_b}$ or $J_{H_aH_b}$ = 12 Hz), 7.4 (b, 1 H, H_b), 3.9 (broad singlet, 2 H, H_d), 2.0–3.0 (b, 10 H, Cpr protons)
15	8.8–9.1 (m, 2 H, H_a and H_c), 7.7–8.3 (m, 11 H, aromatic protons), 4.3 (s, 2 H, H_d)
18	8.8–9.1 (b, 2 H, H_a and H_c), 7.7–8.3 (b, 6 H, H_b and aromatic protons), 4.2 (s, 2 H, H_d), 3.2 (s, 3 H, CH_3)
17	9.9 (b, 1 H, H_a), 9.1 (d, 1 H, H_c, $J_{H_cH_b}$ or $J_{H_aH_b}$ = 8 Hz), 7.8 (b, 1 H, H_b), 4.2 (b, 3 H, H_d and proton at 2′), 3.6 (b, 1 H, proton at 2′), 1.9–2.8 (broad multiplet, 12 H, protons at 3′, 4′, and 5′)
19	8.6 (d, 1 H, H_a, $J_{H_aH_b}$ or $J_{H_bH_c}$ = 8 Hz), 8.2 (b, 1 H, H_c), 7.2–7.9 (broad multiplet, 6 H, H_b and aromatic protons), 4.2 (broad singlet, 2 H, H_d), 2.9–3.3 (m, 1 H, CH of Cpr), 1.9–2.5 (m, 4 H, CH_2 of Cpr)

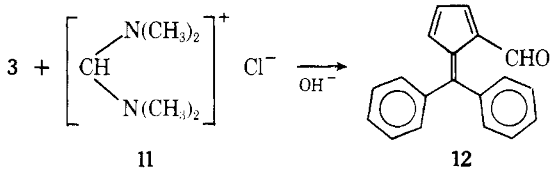
[a] Shifts are in δ values from external capillary Me_4Si.

polar structure **10**. The contribution of the dipolar structure can be assessed from the dipole moments, UV absorptions, and NMR shifts. Further, the contribution of **10** is also dependent on the nature of the substituents on the exocyclic α-carbon atom C_6. The effect of substituents on the tendency of aromatization of the cross-conjugated system can also be studied by varying substituents. It has been reported that fulvenes undergo Diels–Alder reactions, both as dienes and as dienophiles, add halogens, and form peroxides, all characteristic olefinic properties.[2c,d] Fulvenes as cyclic conjugated isomers of benzenoid compounds also undergo substitution reactions. Nucleophilic reagents such as alkyllithiums attack fulvenes at the exocyclic carbon atom C_6 to form alkylcyclopentadienyl compounds. The driving force for this reaction is the gain in resonance energy originating from the transition of the cross-conjugated system to a cyclic Hückeloid 6π-aromatic system.

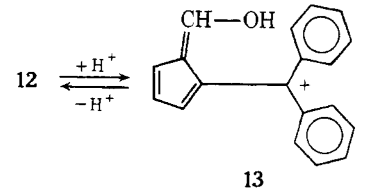


9 **10**

Electrophilic reactions of fulvenes have not yet attracted much attention. However, fulvenes should be as susceptible to electrophilic reactions as other nonbenzenoid cyclic conjugated compounds. **3** is known to undergo formylation with ease and in high yield by treatment with Wilsmeier's complex **11**.[9,10] In accordance with theoretical electron density distribution calculations,[11] the electrophilic reagent attacks at C_2 of the cross-conjugated system. The fulvenaldehyde **12** undergoes facile reversible protonation to give the conjugated acid **13**.[2c] There was only a reference to an otherwise unpublished Ph.D. Thesis[12] by Hafner[2c] to have achieved protonation (as well as alkylation and nitrosation) of fulvenes **2** and **3** to corresponding σ complexes of type **14** which were stable only below −80 °C. For a systematic study of the protonation of fulvenes under stable ion conditions with ^1H and ^{13}C NMR spectroscopy, we synthesized a series of 6,6-disubstituted fulvenes and carried out their protonation under superacid conditions at low temperatures.



11 **12**



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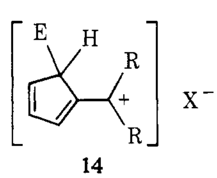

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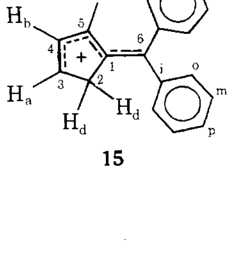
Fulvene **3** underwent facile protonation in FSO_3H/SO_2ClF at −78 °C at C_2 to give fulvenium ion **15**. The ion is stable up



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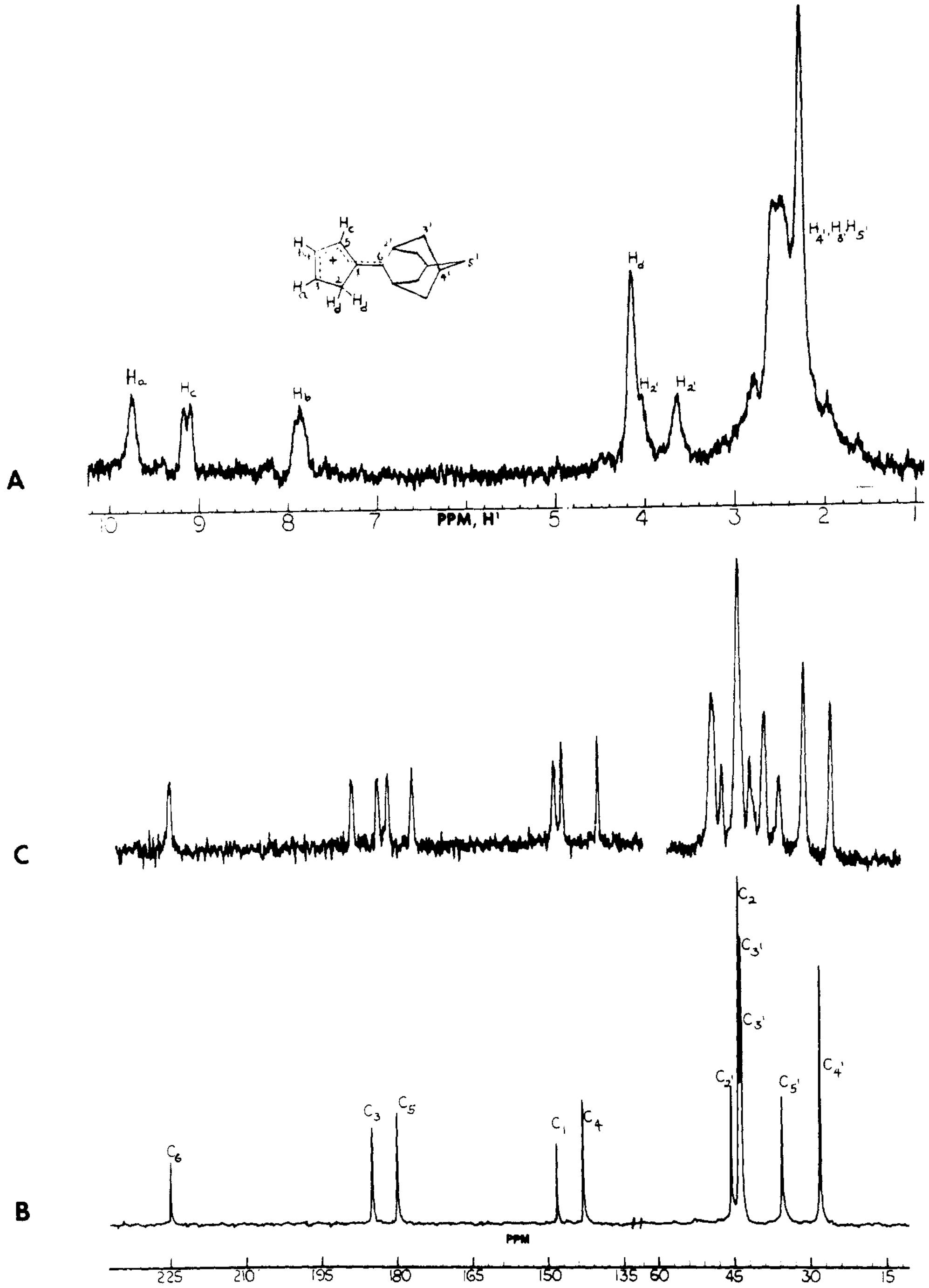

Figure 2. (A) ^{1}H NMR spectrum of ion **17** in FSO_3H/SO_2ClF at −70 °C. (B, C) ^{13}C NMR spectrum of ion **17** in FSO_3H/SO_2ClF at −70 °C: B, proton noise decoupled; C, proton noise coupled.

to −40 °C. In the ^{1}H NMR spectrum H_a and H_c protons absorb around δ 8.8–9.1 and H_b absorbs along with the aromatic protons around δ 7.7–8.3, showing a shift pattern characteristic of an extended conjugated allyl cationic system. The H_d protons absorb at δ 4.3. In the ^{13}C NMR spectrum the most deshielded C_6 carbon absorbs at δ^{13}C 189.9 followed by $\delta^{13}C_3$ 182.5, $\delta^{13}C_5$ 179.2, $\delta^{13}C_1$ 152.1, and $\delta^{13}C_4$ 142.7. This indicates that the charge is highly dispersed along the C_3 to C_6 carbon centers. The para carbons of the phenyl rings are deshielded as compared to the precursor and both the phenyl rings are magnetically equivalent. In the ^{13}C NMR spectrum of the precursor the C_6 carbon is deshielded over the C_1 carbon by 7.9 ppm, which justifies the dipolar nature of the C_1–C_6 bond.

Fulvene **1** was also protonated in FSO_3H/SO_2F_2 at −120 °C to give the C_2 protonated fulvenium ion **16**, which is stable up to −40 °C (in a sealed NMR tube). In the ^{1}H NMR spectrum of the ion at −70 °C, H_a absorbed at δ 8.5, H_c at δ 8.2 with a coupling of $J_{H_cH_b}$ or $J_{H_aH_b}$ = 12 Hz with the neighboring proton H_b. H_b absorbs at δ 7.4 as a multiplet. The aliphatic methylene proton absorption is at δ 3.9 as a singlet, which is rather shielded when compared to that in ion **15**. The cyclopropyl protons (both α and β) absorb around δ 2.0–3.0. The spectrum is shown in Figure 1. The ^{1}H shifts clearly indicate the formation of the ion **16** with maximum charge centered

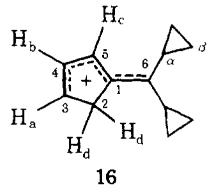

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Table II. ^{13}C **NMR Shifts**[a] **of Fulvenium Ions in** FSO_3H/SO_2ClF **or** SO_2F_2 **Solutions at −70 or −80 °C**

Ions	C_1	C_2	C_3	C_4	C_5	C_6	Substituents at C_6
17	148.7	44.4	185.5	143.6	180.5	225.3	$C_{2'}$ 45.7, 44.4; $C_{3'}$ 43.8, 43.6; $C_{5'}$ 35.7; $C_{4'}$ 28.2
16	143.0	44.6	165.2	138.6	164.3	224.8	C_α 31.9, 21.7; C_β 32.4, 22.2
19	155.2	42.8	179.2	140.6	175.7	207.1	C_i 132.1; C_p 132.1; C_o 128.8; C_m 128.0; C_α 31.4; C_β 25.2
18	154.5	49.2	186.3	143.8	180.9	196.3	C_i 139.9; C_p 138.6; C_o 133.6; C_m 130.1; CH_3 26.6
15	152.1	47.9	182.5	142.7	179.2	189.1	C_p 140.5; C_i 139.1; C_o 137.9, 136.8; C_m 129.8

[a] Shifts are in parts per million from external capillary Me_4Si.

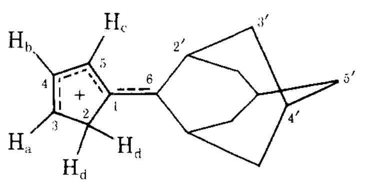
Table III. ^{13}C **NMR Shifts**[a] **of Precursor Fulvenes in** $CDCl_3$ **at 37 °C**

Fulvenes	C_1	C_2	C_3	C_4	C_5	C_6	Subtituents at C_6
8	137.1	131.6	120.5	120.5	131.6	167.3	$C_{2'}$ 41.3; $C_{1'}$ 40.9; $C_{4'}$ 38.4; $C_{3'}$ 29.4
7	135.6	129.9[c]	120.5	120.5	128.8[c]	163.3	$C_{1'}$ 43.9; $C_{3'}$ 38.8; $C_{7'}$ 38.4; $C_{4'}$ 35.7; $C_{6'}$ 28.7[c]; $C_{5'}$ 27.3[c]
1	144.9	131.2	121.7	121.7	131.2	160.4	C_α 16.3; C_β 8.8
6	145.0	130.6[b]	124.5[c]	121.5[c]	128.6[b]	157.0	C_i 138.2; C_p 133.0; C_o 130.6; C_m 128.2; C_α 17.9; C_β 8.0
5	143.9	131.0[c]	121.3[b]	121.0[b]	130.3[c]	155.4	CH_3 15.5; C_α 18.4; C_β 8.4
3	144.9	129.6	125.4	125.4	129.7	152.8	C_i 142.3; C_p 133.4; C_o 133.1; C_m 128.7
2	132.7	131.3	121.3	121.3	131.3	139.3	CH_3 23.4
4	144.6	130.3[b]	124.8	122.2	129.3	150.7	C_i 143.1; C_p 133.0; C_o 132.6; C_m 129.0; CH_3 23.6

[a] Shifts are in parts per million from external capillary Me_4Si. [b,c] Assignment interchangeable.

at C_6. The ^{13}C NMR spectrum also substantiates this conclusion. In the ^{13}C NMR spectrum C_6 absorbs at $\delta^{13}C$ 224.8 followed by $\delta^{13}C_3$ 165.2, $\delta^{13}C_5$ 164.3, $\delta^{13}C_1$ 143.0, and $\delta^{13}C_4$ 138.5. C_6 is substantially deshielded as compared to previously discussed ion **15** even if one takes into account the unusually large neighboring group deshielding effect by the cyclopropyl groups adjacent to a carbocationic center.[14] The C_α and C_β carbons of the two cyclopropyl groups show nonequivalence and are also substantially deshielded compared to the precursor **1**. The corresponding ^{13}C NMR shifts are $\delta^{13}C_\alpha$ 31.9 and 21.7 and $\delta^{13}C_\beta$ 32.4 and 22.4, respectively. The large difference within the C_α and C_β shifts indicates that one of the cyclopropyl groups is delocalizing charge better than the other. In the ^{13}C NMR spectrum of **1** C_α absorbs at $\delta^{13}C$ 16.3 and C_β at $\delta^{13}C$ 8.8. The difference between C_6 and C_1 shifts ($\delta^{13}C_6 - \delta^{13}C_1 = 15.6$) demonstrates the increased dipolar nature of **1** over **3**, which is indeed the case.[8b]

The symmetrical and highly hindered fulvene **8** in FSO_3H/SO_2ClF at −78 °C gave fulvenium ion **17**. The ^1H and



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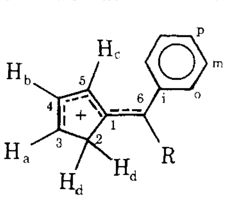
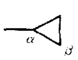
^{13}C NMR spectra of the ion **17** are shown in Figure 2. In the ^1H NMR spectrum H_a absorbs at δ 9.9, H_c at δ 9.1 with a coupling $J_{H_cH_b}$ or $J_{H_aH_b}$ = 8 Hz, and H_b at δ 7.8. The methylene protons absorb at δ 4.2. The shift pattern clearly shows that more positive charge is present in the five-membered ring (along C_3 to C_1) than in the previously discussed ions **15** and **16**. The two bridgehead protons $H_{2'}$ are also substantially deshielded compared with the corresponding shifts of the precursor **8** (absorptions at δ 4.2 and 3.2, respectively). The ^{13}C NMR spectrum shows C_6 absorption at $\delta^{13}C$ 225.3 followed by $\delta^{13}C_3$ 185.5, $\delta^{13}C_5$ 180.5, $\delta^{13}C_1$ 148.7, and $\delta^{13}C_4$ 143.6. The large deshielding of C_6 may also be due to the rigidity of the adamantyl ring skeleton. C_3 and C_5 centers also show considerable charge delocalization as compared to ions **15** and **16**. In the ^{13}C NMR spectrum of the precursor **8**, C_6 is substantially deshielded compared to C_1, the shift difference being $\delta^{13}C_6 - \delta^{13}C_1 = 30.2$, which also demonstrates the rigidity of the adamantane cage system as well as the dipolar nature of the species.

Fulvenes **4** and **6**, being unsymmetrical, can undergo protonation at either C_2 or C_5 to give rise to two different ions. We protonated the two precursors **4** and **6** in FSO_3H/SO_2ClF at −120 °C and obtained only a single ion in each case; we tentatively assign to the ions structures **18** and **19**, respectively.



18, R = CH_3

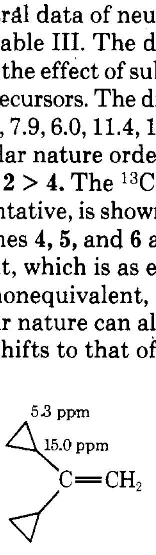
19, R = 

However, our data do not allow us to determine the site of protonation with certainty. The two different ionic species formed by the protonation at C_2 or C_5 can become equivalent if the barrier of rotation along the C_1–C_6 bond becomes low due to charge dispersion. In the ^1H NMR spectrum of the ion **18**, the H_a and H_c protons absorb around δ 8.8–9.1; H_b absorbs along with aromatic protons at δ 8.3. The methylene absorption occurs at δ 4.2 and the methyl absorption at δ 3.2. In the precursor **4** the methyl group absorbs at δ 1.85. This shows that substantial positive charge is present at C_6. In the ^{13}C NMR spectrum C_6 absorbs at $\delta^{13}C$ 196.3 followed by $\delta^{13}C_3$ 186.3, $\delta^{13}C_5$ 180.9, $\delta^{13}C_1$ 154.5, and $\delta^{13}C_4$ 143.8. The aromatic carbons (ortho and para) are notably deshielded as compared to those of the corresponding shifts in precursor **4**, indicating greater participation of the phenyl ring to share the positive charge. Considerable charge is also dispersed over the C_3–C_5 centers as indicated by their ^{13}C NMR shifts.

Fulvenium ion **19** shows particularly interesting features. In its ^1H NMR spectrum, H_a absorbs at δ 8.6, H_c at δ 8.2, and H_b absorbs along with aromatic protons at δ 7.2–7.9. The methylene absorption (H_d) is at δ 4.2. The α and β protons of the cyclopropyl group are also deshielded compared to the precursor, indicating substantial positive charge in the three-membered ring. In the ^{13}C NMR spectrum C_6 absorbs at $\delta^{13}C$ 207.1, falling in between the C_6 shifts of ions **15** and **16**, indicating a characteristic shift pattern of the effect of cyclopropyl substitution over that of phenyl. A similar shift pattern is observed in many cyclopropyl, phenyl substituted carbinyl cations.[15] The C_3 carbon absorbs at $\delta^{13}C$ 179.2 followed by $\delta^{13}C_5$ 175.7, $\delta^{13}C_1$ 155.2, and $\delta^{13}C_4$ 140.5. These shifts also fall midway between the shifts of ions **15** and **16**. The cyclopropyl carbons (both α and β) are substantially deshielded as compared to precursor **6** shifts, i.e., $\delta^{13}C_\alpha$ 31.40 and $\delta^{13}C_\beta$ 25.2. It is also interesting to note that little change is observed with aromatic carbon shifts over those of the precursor shifts. This further demonstrates the superiority of cyclopropyl over phenyl groups to share the positive charge in these extended conjugated systems.

Comparing the fulvenium ions **15**, **16**, **17**, **18**, and **19**, it is evident that positive charge distribution over the C_3–C_6 centers is considerably altered depending upon the nature of the substituents at C_6. Cyclopropyl groups at C_6 tend to decrease the charge over the C_3–C_5 positions with a subsequent smaller effect by phenyl and methyl groups. In these extended conjugated cationic systems the cyclopropyl group delocalizes charge better than a phenyl group which in turn is much more effective than a methyl group. The same trend was also observed in our previous studies on allylic cation systems.[14] In the highly strained adamantylidene substituent in **17**, the positive charge is highly dispersed over C_3–C_5 centers. Fulvenes **2**, **5**, and **7** did not give identifiable ions upon protonation in any of the superacidic systems, i.e., FSO_3H, $FSO_3H + SbF_5$, HF/SbF_5, HF, $HF + BF_3/SO_2ClF$, or SO_2F_2, even at −120 °C. They obviously undergo protonation, but tend to react further with excess, yet unprotonated, precursor to give rise to polymeric products.

The ^{13}C NMR spectral data of neutral fulvene precursors **1–8** are tabulated in Table III. The difference in the C_6 and C_1 shifts demonstrates the effect of substituents as well as the dipolar nature of the precursors. The difference in C_6–C_1 shifts from **1** to **8** are 15.6, 6.6, 7.9, 6.0, 11.4, 13.0, 27.7, and 30.2 ppm, respectively. The dipolar nature order can be estimated as **8** > **7** > **1** > **6** > **5** > **3** > **2** > **4**. The ^{13}C NMR spectrum of the precursor **7**, as representative, is shown in Figure 1. In the ^{13}C NMR spectra of fulvenes **4**, **5**, and **6** all the fulvene ring carbons are nonequivalent, which is as expected. In the case of **7** only C_2 and C_5 are nonequivalent, whereas C_3 and C_4 are equivalent. The dipolar nature can also be demonstrated by comparing ^{13}C NMR shifts to that of 1,1-disubstituted ethylenes. For example, when comparing cyclopropyl α and β carbon shifts of fulvene **1** to that of 1,1-dicyclopropylethylene **20**, it is found that α carbon is deshielded by 1.3 ppm and the β carbon by 3.6 ppm. This indicates the increased dipolar nature of **1** over **20**. This effect was also demonstrated to some degree by the ^1H NMR shifts by Linde and co-workers.[8b]



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Conclusions

Our study on fulvenium ions shows that protonation occurs exclusively at the C_2 position of the fulvene ring in accordance with calculated electron density distributions. The charge dispersion pattern is governed by the nature of the substituents at C_6 position. Data also show that in the fulvenium ions the ability of neighboring substituent groups adjacent to carbenium center in delocalizing positive charge is $c\text{-}C_3H_5 > Ph > CH_3$ in accordance with previous studies.[14,15] The increase in the C_1–C_6 carbon chemical shift difference in the neutral precursors indicate their increased dipolar nature.

Experimental Section

Fulvenes **1**, **2**, **3**, and **4** were prepared by reported methods.[8]

6-Cyclopropyl-6-methylfulvene (5). To a stirred solution of 6.9 g (0.3 mol) of sodium in 75 ml of absolute ethanol under dry nitrogen gas was slowly added a mixture of freshly distilled cyclopentadiene (13.2 g, 0.2 mol) and 16.8 g of cyclopropyl methyl ketone (0.2 mol). After the mixture was stirred for 8 h at room temperature, it was quenched with crushed ice; the product was extracted with methylene chloride, the organic layer washed with water and dried over anhydrous $MgSO_4$, and the solvent evaporated. The yellow liquid obtained was immediately distilled under vacuum using a 15-cm fractionating column. The fraction distilling at 68 °C (2 mm) was collected, 7.2 g (27.2%), air-sensitive yellow liquid (stable at −78 °C for months). The infrared spectrum (neat, cm^{-1}) showed $\delta_{C=C}$ at 1630 (s), 1615 cm^{-1} (m). The UV spectrum (cyclohexane) showed maxima at 284 nm (log ε 4.31) and 367.5 (2.59). The mass spectrum showed m/e 132 (100, M^+). The ^1H NMR spectrum (60 MHz, $CDCl_3$, from external capillary Me_4Si, 37 °C) showed absorptions at δ 5.6–5.9 (s, b, 4 H, H_a, H_b, H_c, and H_d), 1.9–2.3 (m, 1 H, CH of Cpr), 1.65 (s, 3 H, CH_3), 0.7–0.95 (unsymmetric doublet, 4 H, CH_2 of Cpr).

Anal. Calcd for $C_{10}H_{12}$: C, 90.90; H, 9.09. Found: C, 90.89; H, 9.04.

6-Phenyl-6-cyclopropylfulvene (6). The reaction was carried out as described previously with sodium (4.6 g, 0.20 mol), absolute ethanol (60 ml), freshly distilled cyclopentadiene (6.6 g, 0.1 mol), and phenyl cyclopropyl ketone (14.6 g, 0.1 mol). The mixture was stirred for 10 h and then worked up with methylene chloride. The product was distilled under vacuum and the dark orange-yellow liquid distilling at 111–112 °C (0.65 mm) collected, 8.6 g (43%), air-sensitive liquid. The infrared spectrum (neat) showed $\nu_{C=C}$ 1600 (m), 1610 cm^{-1} (s). The UV spectrum (cyclohexane) showed maxima at 287.5 nm (log ε 4.35), 370 (2.60). The mass spectrum showed m/e 194 (100, M^+). The ^1H NMR spectrum (60 MHz, $CDCl_3$, from external capillary Me_4Si, 37 °C) showed peaks at δ 7.3–7.7 (b, 5 H, aromatic protons), 7.1 (m, 1 H, H_a or H_d), 6.9 (m, 1 H, H_a or H_d), 6.5 (m, 1 H, H_b or H_c), 6.0 (m, 1 H, H_b or H_c), 4.5–4.9 (m, 1 H, CH of Cpr), and 0.8–1.3 (m, 4 H, CH_2 of Cpr).

Anal. Calcd for $C_{15}H_{14}$: C, 92.78; H, 7.21. Found: C, 92.76; H, 7.24.

6,6-Adamantylidenefulvene (8). To a solution of sodium metal (4.6 g, 0.2 mol) in 75 ml of absolute ethanol under dry nitrogen, 6.6 g (0.1 mol) of freshly distilled cyclopentadiene was added followed by immediate addition of adamantanone (15.0 g, 0.1 mol). Stirring was continued at room temperature for 3 h and thereafter the reaction mixture was very carefully quenched with crushed ice, the product extracted with methylene chloride and dried, and the solvent evaporated. The yellow solid obtained was recrystallized from hot ethanol, 16.0 g (81.8%), mp 91–92 °C. The infrared spectrum (CCl_4) showed $\nu_{C=C}$ 1638 cm^{-1} (s). The UV spectrum (cyclohexane) showed maxima at 273.0 nm (log ε 4.34), 281.5 (4.32), and 360.0 (2.52) and a shoulder at 290.5 nm. The mass spectrum showed m/e 198 (100, M^+). The ^1H NMR spectrum (60 MHz, $CDCl_3$ from external capillary Me_4Si, 37 °C) showed absorptions at δ 7.93 (s, 4 H, ring protons), 2.67 (2 H, protons at 2′ of adamantane), 1.07–1.57 (b, 12 H, protons of adamantane at 3′, 4′, and 5′).

Anal. Calcd for $C_{15}H_{18}$: C, 90.90; H, 9.09. Found: C, 90.88; H, 8.97.

6,6-(2-Norbornylidene)fulvene (7). To a stirred solution of sodium metal (2.3 g, 0.1 mol) in 40 ml of absolute ethanol under nitrogen, 3.3 g (0.05 mol) of freshly distilled cyclopentadiene was added followed by 5.5 g (0.05 mol) of norcamphor. The stirring was continued for 14 h and the reaction mixture was worked up as described earlier. The product was fractionated under vacuum. The yellow, oily fraction distilling at 80–81 °C (0.5 mm) was collected, 4.2 g (53%), air-sensitive liquid. The infrared spectrum (neat) showed $\nu_{C=C}$ 1656 (s), 1620 cm^{-1} (m). The UV spectrum (cyclohexane) showed maxima at 276.5 nm (log ϵ 4.30), 283.5 (4.28), 365 (2.49), and a shoulder at 295 nm. The mass spectrum showed *m/e* 158 (100, M$^+$). The ^{1}H NMR spectrum (60 MHz, CDCl$_3$ from external capillary Me$_4$Si, 37 °C) showed absorptions at δ 6.8 (s, 4 H, ring protons), 3.7 (b, 1 H, bridgehead proton at 1′), 2.9 (b, 3 H, methylene protons at 3′ and bridgehead proton at 4′), 1.6–2.4 (b, 6 H, methylene protons at 5′, 6′, and 7′).

Anal. Calcd for C$_{12}$H$_{14}$: C, 91.14; H, 8.86. Found: C, 91.06; H, 8.90.

Preparation of Fulvenium Ions. Freshly distilled FSO$_3$H was dissolved in about twofold amount of SO$_2$ClF or SO$_2$F$_2$ at dry ice/acetone temperature (ca. −78 °) or ethanol/liquid nitrogen temperature (ca. −120 °C). To this solution was slowly added with vigorous stirring a cooled slurry of the appropriate fulvene precursor in SO$_2$ClF or SO$_2$F$_2$, to give an approximately 10% solution of the ion.

^{1}H NMR spectra were obtained on a Varian Model A56/60A spectrometer equipped with variable temperature probes and external capillary Me$_4$Si was used as the reference.

^{13}C NMR spectra were obtained using a Varian Model XL-100 NMR spectrometer equipped with an FT accessory with variable temperature probe as previoulsy described.[16]

The infrared spectra were obtained on a Beckman IR-10 spectrophotometer, the ultraviolet spectra were recorded on a Beckman DB-G spectrophotometer, and the mass spectra on a Du Pont Model 21-094 GC/MS system operating at a filament current of 70 eV.

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Registry No.—**1**, 4479-62-3; **2**, 2175-91-9; **3**, 2175-90-8; **4**, 2320-32-3; **5**, 61010-59-1; **6**, 61010-60-4; **7**, 61010-61-5; **8**, 16668-82-9; **15**, 61010-54-6; **16**, 61010-55-7; **17**, 61010-56-8; **18**, 61010-57-9; **19**, 61010-58-0; cyclopentadiene, 542-92-7; cyclopropyl methyl ketone, 765-43-5; phenyl cyclopropyl ketone, 3481-02-5; adamantanone, 700-58-3; norcamphor, 497-38-1.

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(13) In the studied fulvenium ions from **15** to **19** it was not possible to differentiate H$_a$ from H$_c$ or C$_3$ from C$_5$ in both ^{1}H and ^{13}C NMR spectra as H$_a$ lacked any coupling with H$_d$ protons. Hence we have tentatively assigned H$_a$ and C$_3$ to be more deshielded than H$_c$ and C$_5$. However, this does not alter any of our conclusions.

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Carbon-13 Nuclear Magnetic Resonance. Steric and Electronic Effects on the α, β, and γ Shifts in Norcarane Derivatives

Takashi Ishihara, Teiichi Ando,* Takeshi Muranaka, and Koichi Saito

Department of Industrial Chemistry, Faculty of Engineering, Kyoto University, Kyoto 606, Japan

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Fourier transform carbon-13 nuclear magnetic resonance spectra were measured for a number of endo- and exo-7-substituted and 7,7-disubstituted norcaranes. The substituent shift parameters were calculated from a series of 7-monosubstituted norcaranes and were used for predicting the shifts of stereoisomers of some 7,7-disubstituted norcaranes. The agreement between the observed and the calculated shifts was satisfactory, proving the validity of this general approach. Interpretation of the observed substituent shifts in terms of steric and electronic effects has shown that (1) the α and β substituent effects as well as the γ gauche and anti effects are dependent on the relative orientation of the substituent on the α carbon, and (2) a long-range γ anti effect produced on the γ carbon nuclei by the exo 7 substituent can be explained more reasonably by the back-lobe interaction mechanism than by the hyperconjugative interaction mechanism. Several ^{13}C–^{19}F and ^{13}C–^{1}H coupling constants are also reported and interpreted in terms of the s character of the C–F and C–H bonds, respectively.

The carbon-13 magnetic resonance spectra of a number of molecules containing hetero substituents have been recorded and interpreted in terms of inductive, steric, and bond delocalization effects.[1-8] In the literature, however, there is no systematic investigation on the conformational and substituent factors, which affect carbon-13 shieldings, in cyclopropyl ring systems possessing hetero substituent(s).

Now we have determined the carbon chemical shifts for a series of norcarane derivatives. These compounds were chosen because the norcaryl skeleton provides a relatively rigid and stereochemically defined framework suitable for the investigation of substituent effects. Our aim was to determine steric and substituent shift factors and to investigate their variations due to the orientational changes of a substituent on the norcaryl skeleton. This will make it possible to test quantitatively the validity of the theories and speculations which have been advanced to explain carbon-13 shieldings on an electronic ground.

Experimental Section[9]

Materials. All 7,7-disubstituted norcaranes except 7-chloro- (and -bromo-) 7-methoxycarbonylnorcarane were obtained by the addition of the corresponding halocarbene (or carbenoid) to cyclohexene.[10] 7-Chloro- (and -bromo-) 7-methoxycarbonylnorcarane was prepared