

**Table VI.** Acid and Base Parameters for Double-Scale Equation of Enthalpy of Hydrogen Bonding<sup>a</sup>

	$C_A$	$E_A$
Acids <sup>b</sup>		
<i>n</i> -Propyl alcohol	0.183	2.96
Isopropyl alcohol	0.156	2.59
<i>n</i> -Butyl alcohol	0.234	2.72
Isobutyl alcohol	0.259	2.72
<i>sec</i> -Butyl alcohol	0.184	2.58
<i>tert</i> -Butyl alcohol	0.150	2.39
Chloroform	0.159	2.54
Bromoform	0.155	1.95
Bases <sup>b</sup>		
DOE	3.01	1.11
DOTE	7.71	0.34
DOMA	11.50	0.97

<sup>a</sup> See eq 10. <sup>b</sup> Alcohol and base values are revised values; see ref 21.

> DOMA > DOTE. Taken at face value, the results indicate that, for the two haloforms, electrostatic forces account for roughly 85% of the total hydrogen bonding energy with DOE, about 55% with DOMA, and about 40% with DOTE, in accordance with the above sequence. Also, although the absolute electrostatic contribution ( $E_A E_B$ ) to  $-\Delta H$  is greater for the DOE systems, the net  $-\Delta H$  is greater for the DOMA systems, due to the substantial covalent parameter of the amine.

In summary, the simple model leading to eq 4 and 5, the NMR results for hydrogen bonding, auxiliary experimental information, and some useful concepts<sup>3,4,19,22</sup> have permitted us to further resolve and understand thermodynamic data previously determined by GLC for haloform/*n*-donor sys-

tems.<sup>1,2</sup> While the evidence at hand indicates that halogen/*n*-donor interactions do not result in significant complex formation, additional studies are needed to fully clarify the situation.

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## References and Notes

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## <sup>13</sup>C-<sup>1</sup>H Coupling Constants in Carbocations. II.<sup>1</sup> Angular Dependence of <sup>1</sup>J<sub>CH</sub> in Groups Adjacent to Cationic Carbons. A New Criterion for Interpreting NMR Spectra of Carbocations

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**Abstract:** The values of <sup>1</sup>J<sub>CH</sub> in groups adjacent to cationic carbons in classical, static, carbenium ions are dependent upon the dihedral angle between the C-H bond and the unoccupied p orbital of the cationic carbon. This dependence is given by  $\Delta J = A - B \cos^2 \theta$ , where  $\Delta J$  is the difference in <sup>1</sup>J<sub>CH</sub> between that in the cation and that in a neutral model compound (ketone),  $A$  is the maximum inductive enhancement of <sup>1</sup>J<sub>CH</sub> (22.5 Hz), and  $B$  is the maximum hyperconjugative diminution of <sup>1</sup>J<sub>CH</sub> (33.1 Hz). The equation provides another criterion by which chemical shift assignments may be made. In the case of the 2-methylnorbornyl cation, some discrepancies in the previous assignments have been corrected. Comparison of the shift of the methyl carbon of this cation with that in the corresponding alcohol shows that this carbon experiences *no deshielding* upon ion formation. The significance of this finding is discussed. The equation is applicable to some equilibrating classical cations, and can be used to determine conformations in cations, for example, the *tert*-amyl cation.

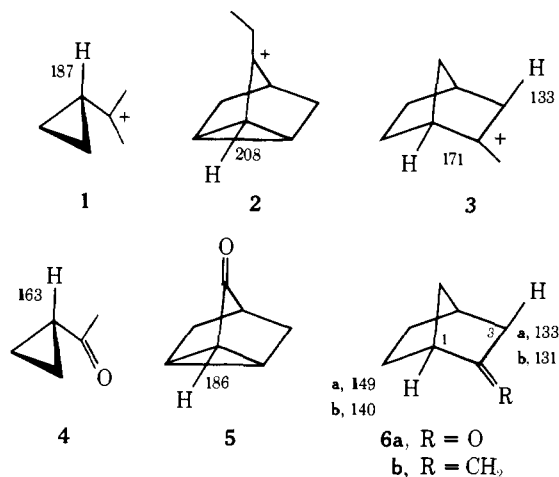
In our investigation of the applicability of <sup>1</sup>J<sub>CH</sub> as a criterion for the presence of  $\sigma$  bridging in cyclopropylcarbinyl cations,<sup>1</sup> it was necessary to determine the effect of the adjacent positive charge on the apical, methine coupling constant in classical (non- $\sigma$  bridged) cyclopropylcarbinyl cations. Thus the <sup>1</sup>J<sub>CH</sub> values increase in the tertiary cations **1** and **2**<sup>3</sup> from those in

the neutral model compounds **4** and **5** by 25 and 22 Hz, respectively ( $\Delta J$ ). The ketones are considered to be appropriate model compounds since they contain a trigonal carbon and are therefore more appropriate models than the corresponding hydrocarbons or carbinols.<sup>1</sup> A similar, large increase occurs for <sup>1</sup>J<sub>CH</sub> in the 2-methylnorbornyl cation **3**<sup>4</sup> from that in 2-

**Table I.**  $^{13}\text{C}$  NMR Parameters for Cations and Model Compounds<sup>a</sup>

Compd	C <sub>1</sub>	C <sub>2</sub>	C <sub>3</sub>	C <sub>4</sub>	C <sub>5</sub>	C <sub>6</sub>	C <sub>7</sub>	CH <sub>3</sub>
<b>3</b>	80.7 d, 171	270.2	55.2 t, 133	42.8 d, 154	23.5 t, 137	35.5 d, d, 145, 149 <sup>b</sup>	40.1 t, 141	27.9 q, 132
<b>6a<sup>c</sup></b>	49.8 d, 149	215.3	45.2 133 <sup>d</sup>	35.4 <i>e</i>	27.3 135 <sup>d</sup>	24.2 138 <sup>d</sup>	36.7 <i>e</i>	
<b>6b<sup>f</sup></b>	45.7 d, 140 <sup>d</sup>	155.4	39.5 t, 131 <sup>d</sup>	37.1 d, 144 <sup>d</sup>	29.9 t, 134 <sup>d</sup>	28.7 t, 133 <sup>d</sup>	38.4 t, 131 <sup>d</sup>	101.9 <sup>g</sup> t, 155 <sup>g</sup>
<b>7</b>	337.9	64.2 t, 129	27.2 t, 139					37.4 q, 132
<b>10</b>	203.1 d, 51	47.4 t, 134	24.0 t, 136					23.4 q, 131
<b>11b<sup>h</sup></b>	152.7	32.9 t, 130	26.6 t, 130					104.2 <sup>g</sup> t, 154.5 <sup>g,i,j</sup>
<b>12<sup>k</sup></b>	134.3 d, 160	129.2 d, 160	40.8 t, 130	35.3 t, 128	25.1 t, 130	32.5 t, 130	40.0, 50.6 <sup>l</sup> d, 134, 135 <sup>l</sup>	
<b>13</b>	220.9 <sup>m</sup>	44.2 d, 124	31.9 t, 132	20.8 t, 133	37.7 t, 130			14.3 q, 127
<b>14</b>	335.5	57.7 t, 123	9.5 <sup>n</sup> q, 131					44.8 q, 132

<sup>a</sup> Chemical shifts are  $\pm 0.2$  ppm from internal TMS (**6a**, **6b**, **11**, **12**, **13**) and from external TMS (**3**, **7**, **10**, **14**). Coupling constants are  $\pm 1$  Hz unless otherwise specified, d = doublet, t = triplet, q = quartet. <sup>b</sup> Nonequivalent protons give rise to doublet of doublets. <sup>c</sup> Chemical shifts have been reported previously by Grutzner et al.<sup>27</sup> and by E. Wenkert, A. O. Clouse, D. W. Cochrane, and D. Doddrell, *Chem. Commun.*, 1433 (1969). <sup>d</sup>  $\pm 3$  Hz, complex multiplets. <sup>e</sup> Overlapping multiplets prevented measurement of coupling constants. <sup>f</sup> Chemical shifts have been reported previously by E. Lippmaa, T. Pehk, J. Paasivirta, N. A. Belikova, and A. F. Plate, *Org. Magn. Reson.*, **2**, 581 (1970). <sup>g</sup> Olefinic methylene carbon. <sup>h</sup> Chemical shifts have been reported previously by J. D. Roberts, D. E. Dorman, and M. Jautelat, *J. Org. Chem.*, **36**, 2757 (1971). <sup>i</sup>  $\pm 0.5$  Hz. <sup>j</sup>  $J_{\text{CCH}} = 4.0$  Hz. <sup>k</sup> Apart from the bridgehead and olefinic carbons, the assignments are tentative and have been based on the expected effect of the double bond on the shifts for octahydropentalene.<sup>37</sup> <sup>l</sup> C<sub>3a</sub>, C<sub>6a</sub>. <sup>m</sup> Partial data also appear in ref 38. <sup>n</sup> Methyl carbon  $\beta$  to cationic carbon.



norbornanone, (**6a**) or the olefin **6b**. Comparison of the  $J_{\text{CH}}$  data for the tertiary and secondary cyclopropylcarbinyl systems with that for the primary cyclopropylcarbinyl cation ( $\Delta J = 17$  Hz) led us to conclude that the primary ion is not  $\sigma$  bridged, since the expected enhancement of  $J_{\text{CH}}$  due to formation of a strained bicyclobutonium structure was not observed.<sup>1</sup> This conclusion was opposite to that based on chemical shift data<sup>5</sup> and indicated the difficulty of applying either criterion to the problem of  $\sigma$  bridging.

We have now extended our examination of the effect of adjacent positive charge on  $J_{\text{CH}}$  to other groups.

## Results and Discussion

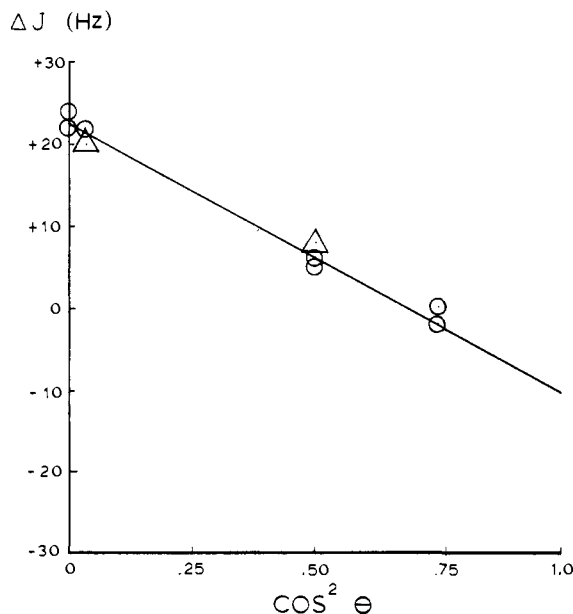
From the data available in the literature<sup>6</sup> and our own work,<sup>1</sup> it is apparent that methyl groups adjacent to cationic carbons generally have their  $J_{\text{CH}}$  values increased by  $6 \pm 1$  Hz ( $\Delta J$ ) over those for the appropriate methyl ketones ( $J_{\text{C}_\alpha\text{H}} = 126$  Hz).<sup>7</sup> In equilibrating systems,<sup>8</sup> the values are slightly less than this. Two exceptions are noted, that in 2-methylnorbornyl

(151.2 Hz)<sup>4</sup> and in 1,2-dimethylcyclopentyl cations (138.0 Hz).<sup>8</sup>

Due to the paucity of  $J_{\text{CH}}$  data for methylene groups, we prepared the methylcyclopentyl cation **7** in high concentration (0.9 M) using syringe techniques<sup>1,9</sup> and measured the coupling constants. The methylene carbons showed couplings of 139 Hz ( $\delta$  27.2) and 129 Hz ( $\delta$  64.2). Since  $J_{\text{C}_\alpha\text{H}}$  of cyclopentanone (**11a**) is 131 Hz, assignment of the lower field resonance to the carbon adjacent to the cationic carbon would result in a value of  $-2$  Hz for  $\Delta J$ , whereas the reverse assignment would give a value of  $+8$  Hz. It was therefore imperative to check the assignments in the methylcyclopentyl cation. This was done by ionizing 1-chloro-1-methylcyclopentane-2,2,5,5-*d*<sub>4</sub> in  $\text{SbF}_5/\text{SO}_2\text{ClF}$  at  $-78$  °C and measuring the spectrum immediately at  $-80$  °C.<sup>10</sup> The spectrum confirmed the lower field resonance to be that due to the methylene group adjacent to the positive charge. 2-Methylnorbornyl yielded a similar result for C<sub>3</sub> (compare **3** and **6**,  $\Delta J = 0$ ). The resonance at  $\delta$  55.2 ( $J_{\text{CH}} = 133$  Hz)<sup>11</sup> was confirmed to be that due to C<sub>3</sub> by observation of a low intensity multiplet in the spectrum of the C<sub>3</sub>-labeled cation (see below).

Thus  $J_{\text{C}_\alpha\text{H}}$  for the ions **3** and **7** remain virtually unaltered from those in the ketones. This conclusion is unaltered by comparison of the  $J_{\text{C}_\alpha\text{H}}$  values with those in the corresponding olefins, methylenecyclopentane (**11b**) and 2-methylenenorbornane (**6b**) (130 and 131 Hz, respectively, Table I).

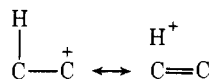
The differences in the  $\Delta J$  values observed here for methine (22–24 Hz), methyl (6 Hz), and methylene groups (0–2 Hz) indicate that effects other than the inductive effect of the positive charge are influencing  $J_{\text{CH}}$ . The presence of an adjacent electronegative substituent (e.g., a positively charged carbon) increases  $J_{\text{CH}}$  by increasing the effective nuclear charge ( $Z$ ) at carbon.<sup>12</sup> An increase in bond angle strain, as previously noted,<sup>1</sup> also causes an increase in  $J_{\text{CH}}$  through changes in hybridization. In this work, the effects of differences in strain between the neutral molecules and the cations have been minimized by using ketones or olefins as the model



**Figure 1.** Angular dependence of  $J_{C\alpha H}$  for classical carbenium ions: (O) static ions, ( $\Delta$ ) equilibrating ions (not included in least-squares analysis).

compounds. Furthermore, all the cations considered so far are static, non- $\sigma$ -bridged carbenium ions.

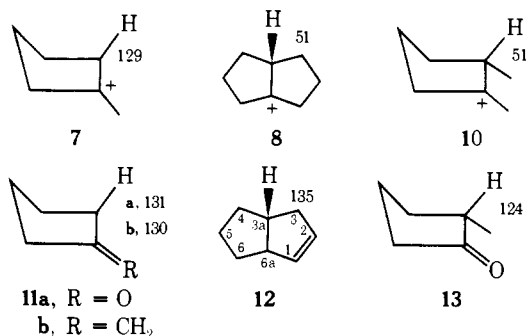
The effects observed above are readily explained in terms of an angle-dependent, electronic interaction between the C-H bonding molecular orbital and the vacant p orbital of the adjacent carbon. In ions **1** and **2**, the  $C_{\alpha}$ -H bond is orthogonal to the vacant p orbital. In this case delocalization of electron density from the C-H bond into the p orbital by hyperconjugation,



would be minimal. As this angle decreases, delocalization into the vacant orbital increases as  $\cos^2 \theta$ .<sup>13</sup> Since this delocalization reduces the bond order between carbon and hydrogen and since coupling constants are directly proportional to the bond order between the coupled nuclei,<sup>14</sup> increasing delocalization will result in *decreasing* values of the C-H coupling constants.<sup>15</sup>

In freely rotating methyl groups,  $\langle \cos^2 \theta \rangle = 0.5$ <sup>13</sup> and  $\Delta J$  is reduced accordingly. For methylene groups adjacent to positive charge, as for  $C_3$ -H in ion **3** and  $C_{\alpha}$ -H in ion **7**,  $\theta$  is further reduced to  $30^\circ$ . At this point ( $\Delta J \approx 0$ ) the hyperconjugative interaction completely nullifies the inductive enhancement of  $J_{CH}$ . The data are plotted in Figure 1. Finally, when the C-H orbital eclipses the vacant p orbital ( $\theta = 0^\circ$ ), large and negative values of  $\Delta J$  should be observed. However, the appropriate cations, for example, bicyclo[3.3.0]octyl (**8**) and bicyclo[4.4.0]decyl, are not static but are rapidly equilibrating between the two tertiary forms.<sup>16</sup> This is perhaps not surprising, since the methine C-H and the vacant p orbitals are most favorably aligned for a 1,2-hydride shift. These ions show reduced methine coupling constants of 51 Hz.<sup>16</sup>

In the absence of a static ion with  $\theta = 0$ , we can use the data for the equilibrating bicyclooctyl ion **8** to calculate  $\Delta J$ . Since the reduced coupling constant is due to an averaging of the two interactions,  $J_{CH}$  and  $J_{CCH}$ , the value in a static ion would be approximately twice the observed value.<sup>17</sup> Using  $J_{C_{3a}H}$  of 1,2,3,3a,4,6a-hexahydropentalene (**12**) as the value for the neutral model compound,  $\Delta J$  is  $-33$  Hz.<sup>18</sup> Similarly, comparison of bicyclo[4.4.0]decyl cation with *cis*-decalin (**9**)<sup>19</sup> gives  $-23$  Hz and of  $J_{C\alpha H}$  for the methine proton of the 1,2-dimethylcyclopentyl cation (**10**)<sup>16</sup> with that for 2-methylcyclopentanone (**13**) gives  $-22$  Hz for  $\Delta J$ .



From the data for the static carbenium ions we obtained the equation

$$\Delta J = A - B \cos^2 \theta \quad (1)$$

where  $A$  is the maximum inductive enhancement of  $J_{C\alpha H}$  (22.5 Hz) and  $B$  is the maximum hyperconjugative diminution of  $J_{C\alpha H}$  (33.1 Hz).<sup>20</sup> The linearity of the plot (Figure 1) indicates that we have successfully eliminated hybridization (steric) factors.

The value of  $\Delta J$  for a static cation with  $\theta = 0$  is predicted to be  $-10$  Hz. We note that the unexpectedly large and negative values for the equilibrating cations ( $-22$  to  $-33$  Hz) are for protons which are associated with two cationic carbons, that is, those which are undergoing rapid 1,2-hydride shifts. However, no such deviation occurs in equilibrating systems for protons adjacent to one of the two carbons sharing the positive charge. For example, the reported value for  $J_{C_1 H}$  of the 2,3-dimethyl-2-norbornyl cation is 159 Hz,<sup>8</sup> which when compared with **6a** leads to a  $\Delta J$  value (10 Hz) approximately half of that observed in **3**.<sup>21</sup> Similarly,  $J_{CH}$  values reported for the methyl groups in 1,2-dimethylnorbornyl and 1,2-dimethylcyclohexyl are 130 Hz,<sup>8</sup> corresponding to a  $\Delta J$  value approximately half that observed in static ions.<sup>22</sup> However, the value for 1,2-dimethylcyclopentyl has been reported as 138.5 Hz.<sup>8</sup> Since there seemed to be no obvious reason for this anomaly, we prepared **10** from the corresponding chloride and measured the <sup>13</sup>C parameters (Table I).  $J_{CH_3}$  is in fact 131 Hz, in keeping with the rest of our results. The coupling constants reported<sup>16</sup> for both  $\alpha$  and  $\beta$  methylene groups also appeared anomalous when compared with those for **7** and **13**. The correct values (134 and 136 Hz, respectively) are consistent with the other data.

The coupling constants of methyl groups adjacent to cationic carbons are thus remarkably constant at 132 Hz for static ions and slightly less in equilibrating ions. However, the value for the methyl group of the 2-methylnorbornyl cation has been reported as 151.2 Hz.<sup>4</sup> Since steric strain in this group is not expected, this value appeared anomalous. We have repeated this work and the spectra are given in Figure 2.

The three lowest field lines (apart from  $C_2$ ) have been assigned to  $C_1$ ,  $C_3$ , and  $C_8$ , presumably on the assumption that carbons adjacent to positive charge will resonate at lower fields than those further removed.<sup>4</sup> However, careful scrutiny of the multiplets centered at 27.9 and 42.8 ppm in the off-resonance (b) and proton coupled spectra (c) show them to be a quartet and doublet, respectively. In the fully coupled spectrum (c) the methyl quartet is clearly visible, with  $J_{CH} = 132$  Hz. There is no doubt that these lines are due to the methyl carbon, since the four lines of the quartet are sharp in comparison with the other lines due to the lack of two-bond <sup>13</sup>C-H coupling ( $^2J_{CH}$ ). There is only one carbon atom in this cation without a proton on an adjacent carbon, the methyl carbon. The resonance at 42.8 ppm ( $J_{CH} = 154$  Hz) is now assigned to  $C_4$ .

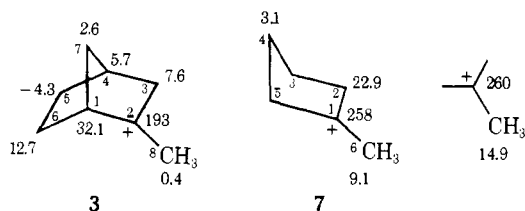
In order to confirm that the peak at 55.2 ppm was due to  $C_3$ , we prepared 2-*exo*-chloro-2-methylnorbornane-3,3-*d*<sub>2</sub> and ionized it in  $\text{SbF}_5/\text{SO}_2\text{ClF}$  at  $-78^\circ\text{C}$ . The spectrum, which

was completed 50 min after ion preparation began, showed a low intensity multiplet centered at 55.2 ppm, confirming that it is due to C<sub>3</sub>.

At -80 °C, no scrambling of the label was apparent. However, when the temperature was raised to -40 °C and the spectrum recorded,<sup>23</sup> significant scrambling had occurred to all positions except C<sub>4</sub> and C<sub>8</sub>.<sup>24</sup> This result is consistent with a series of 3,2-*exo*-H shifts, 6,2-*endo*-H shifts and Wagner-Meerwein rearrangements as shown by Sorensen and co-workers.<sup>26</sup>

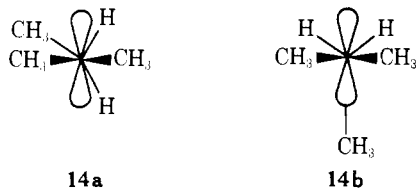
The assignments for C<sub>5</sub>, C<sub>6</sub>, and C<sub>7</sub> as given in Figure 2 were made on the basis of analogy with a large number of 2-substituted norbornyl derivatives in which C<sub>7</sub> is always at lower field than C<sub>5</sub>,<sup>27</sup> and on the fact that of the three appropriate resonances, only that at 35.5 ppm exhibited significant non-equivalent coupling constants (Table I). This resonance was therefore assigned to C<sub>6</sub>.<sup>28</sup>

The observation of the methyl resonance of **3** at 27.9 ppm has an important consequence. The extent of deshielding of a particular carbon upon ionization may be estimated by the difference in chemical shift between that in the cation and that in a neutral precursor. The differences ( $\Delta\delta$ ) between cations **3**, **7**, and *tert*-butyl and their corresponding alcohols are given below, and show that the deshielding experienced by the methyl carbons decreases in the order *tert*-butyl, **7**, **3** to a value essentially zero.<sup>31</sup>



Therefore, the assumption that carbons adjacent to positive charge will be substantially deshielded and to a greater extent than those further removed is invalid in the case of **3**. A similar situation exists in the 2,3,3-trimethylnorbornyl cation, where all three methyl carbons have very similar chemical shifts (18–21.3 ppm).<sup>30</sup> This assumption was applied to the analysis of the proton spectrum of the bicyclo[3.3.0]octyl cation to conclude that the ion was static.<sup>32</sup> This has subsequently been shown to be incorrect.<sup>16</sup> *Chemical shift assignments made on this assumption should therefore be confirmed by other means.*

In order to demonstrate the use of eq 1 in determining conformations of acyclic carbocations, we prepared the *tert*-amyl cation **14** and measured the <sup>13</sup>C parameters.<sup>33</sup> Comparison of  $J_{C_H}$  for the methylene carbon with  $J_{C_3H}$  in 2-butanone<sup>7</sup> gives  $\Delta J = -2$  Hz. We conclude, therefore, that the predominant conformation of this cation is **14a** and not **14b**.



A similar conclusion was reached in the case of 2-butanone from consideration of the geminal H–H coupling constant.<sup>7</sup> However, ab initio MO calculations by Radom, Pople, and Schleyer indicate that **14b** should be ~4 kcal/mol more stable than **14a**.<sup>34</sup>

Application of this concept to the controversial cations, such as cyclopropylcarbanyl,<sup>5</sup> is more difficult. In the above treatment we have eliminated steric factors by choosing appropriate model compounds. However, the formation of a  $\sigma$  bridge in cyclopropylcarbanyl requires not only rotation about C<sub>1</sub>–C<sub>2</sub>,

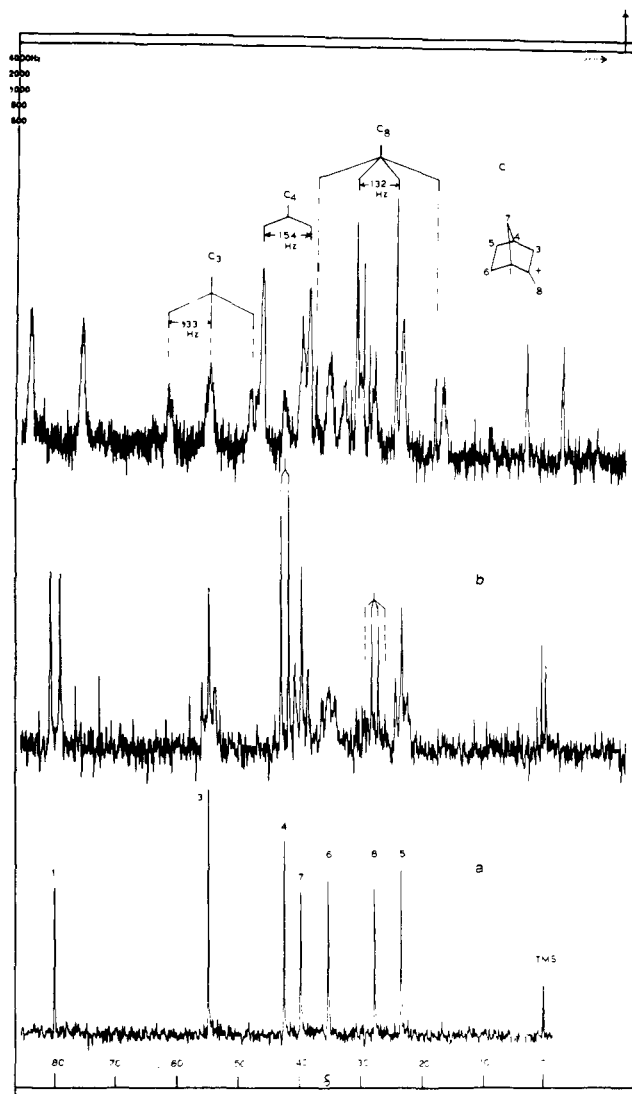
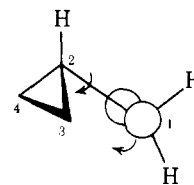


Figure 2. <sup>13</sup>C NMR spectra of 2-methylnorbornyl cation (0.8 M) in SbF<sub>5</sub>/SO<sub>2</sub>ClF (3.8 M) at 20 MHz and -70 °C: (a) proton noise decoupled; (b) single frequency off-resonance decoupled; (c) proton coupled.



but also movement of C<sub>1</sub> toward C<sub>3</sub> and/or C<sub>4</sub>. Rotation about the C<sub>1</sub>–C<sub>2</sub> bond should cause a decrease in  $J_{C_2H}$  (from that observed in the tertiary ion) while inward movement of C<sub>1</sub> should increase  $J_{C_2H}$ . How much each of these two effects contributes to  $J_{C_2H}$  in the case of a rapidly equilibrating,  $\sigma$ -bridged bicyclobutonium structure<sup>5</sup> is difficult to estimate, since we do not have a reliable model for a static  $\sigma$ -bridged cation. The expected value for a  $\sigma$ -bridged species was ~200 Hz,<sup>5</sup> that is, an increase of ~13 Hz over that for the tertiary ion **1**.<sup>35</sup> However, the observed value (180 Hz)<sup>1,3</sup> is less than that in **1**, indicating a large negative contribution to  $J_{C_H}$  (ca. -20 Hz). In classical cations, as we have shown, such a contribution arises when the dihedral angle approaches zero. The proposed bonding in  $\sigma$ -bridged species is sufficiently different to prevent us from drawing any further conclusions about these  $\sigma$ -bridged species at this stage. However, what does follow from our treatment of adjacent positive charge and the observed value of 180 Hz for  $J_{C_2H}$ , is that if the parent cyclopropyl-

carbonyl cation is a rapidly equilibrating set of classical cyclopropylcarbinyl cations, then the structure of the ion must be distorted from the most favorable bisected arrangement<sup>36</sup> by approximately 20° (Figure 1,  $\Delta J = 17$  Hz).<sup>37</sup>

This confirms our earlier conclusion, that it is necessary to proceed with great caution before using <sup>13</sup>C NMR parameters to make a decision on the presence or absence of  $\sigma$  bridging.<sup>1</sup>

## Conclusion

The empirical equation relating  $\Delta J$  and the dihedral angle rationalizes much of the available coupling constant data for groups adjacent to cationic carbons in static and equilibrating carbenium ions, in terms of competing inductive and hyperconjugative interactions.

The equation provides a new criterion for assignment of chemical shifts in carbocations. Of the techniques available to assign shifts, expected charge delocalization and comparison with model compounds, off-resonance decoupling, line broadening, isotopic labeling, and spin-lattice relaxation, only the first two have been used extensively. Since the availability of gated decoupling facilities on most spectrometers makes the measurement of C–H coupling constants almost routine, the use of the  $\Delta J$  equation is an attractive alternative method for making shift assignments.

Although the equation can be used to determine conformations in cations, and is applicable to equilibrating classical systems, it does not allow a clear decision to be made in the case of the cyclopropylcarbinyl cation.

We are continuing to explore the utility of this relationship for determination of conformations in cations where the angles are not so easily evaluated, and as an alternative to <sup>13</sup>C shifts for measurement of charge delocalization.

## Experimental Section

**1-Chloro-1-methylcyclopentane-2,2,5,5-*d*<sub>4</sub>.** Cyclopentanone-2,2,5,5-*d*<sub>4</sub> was prepared by repeated (six times) base catalyzed exchange with D<sub>2</sub>O according to the usual method;<sup>39</sup>  $\delta_{C,TMS}$  (CDCl<sub>3</sub>) 22.8 (C<sub>3,5</sub>) and 37.4 ppm (low intensity multiplet (pentuplet + triplet), C<sub>2,5</sub>). The mass spectrum indicated the following deuterium content (%): 62, *d*<sub>4</sub>; 20, *d*<sub>3</sub>; 4, *d*<sub>2</sub>; and 13, *d*<sub>1</sub>. This ketone was converted to the methyl carbinol by the standard Grignard procedure;  $\delta_{C,TMS}$  (CDCl<sub>3</sub>) 79.4 (C<sub>1</sub>), 40.9 (low intensity multiplet, C<sub>2,5</sub>), 24.0 (C<sub>3,4</sub>), and 28.1 ppm (CH<sub>3</sub>). This alcohol was converted to the chloride using the procedure of Brown and Rei;<sup>40</sup>  $\delta_{C,TMS}$  (CDCl<sub>3</sub>) 77.6 (C<sub>1</sub>), 43.5 (low intensity multiplet, C<sub>2,5</sub>), 23.4 (C<sub>3,4</sub>), and 30.5 ppm (CH<sub>3</sub>).

**2-*exo*-Chloro-2-methylnorbornane-3,3-*d*<sub>2</sub>.** 2-Norbornanone-3,3-*d*<sub>2</sub> was prepared by a modification of the method of Weinberg and Djerrassi<sup>41</sup> using trifluoroacetic anhydride and D<sub>2</sub>O;  $\delta_{C,TMS}$  (CDCl<sub>3</sub>) 45.2 ppm (pentuplet, C<sub>3</sub>). This ketone was converted to 2-*exo*-methyl-norbornan-2-ol as above;  $\delta_{C,TMS}$  (CDCl<sub>3</sub>) 48.0 (C<sub>1</sub>), 76.7 (C<sub>2</sub>), 46.7 (low intensity pentuplet,  $J_{CD} = 2.0$  Hz,  $J_{CH} = 131$  Hz, C<sub>3</sub>), 37.2 (C<sub>4</sub>), 28.2 (C<sub>5</sub>), 21.8 (C<sub>6</sub>), 38.7 (C<sub>7</sub>), and 30.3 ppm (CH<sub>3</sub>). This alcohol was converted to 2-*exo*-chloro-2-methylnorbornane as above;  $\delta_{C,TMS}$  (CDCl<sub>3</sub>) 51.5 (C<sub>1</sub>), 76.3 (C<sub>2</sub>), 50.5 (low intensity pentuplet, C<sub>3</sub>), 37.7 (C<sub>4</sub>), 27.7 (C<sub>5</sub>), 24.2 (C<sub>6</sub>), 38.6 (C<sub>7</sub>), and 29.2 ppm (CH<sub>3</sub>).

**Other Materials.** Methylenecyclopentane (**11b**) and 2-methylenenorbornane (**6b**) were prepared according to literature procedures.<sup>42</sup> A sample of 1,2,3,3a,4,6a-hexahydropentalene was kindly supplied by Dr. R. F. C. Brown of Monash University. 2-Chloro-2-methylbutane was prepared from the alcohol<sup>40</sup> as above. 1-Chloro-1,2-dimethylcyclopentane (mixture of *cis* and *trans* isomers) was prepared from 2-methylcyclopentanone via the methyl carbinols<sup>40</sup> as outlined above. All other materials were commercially available.

**Preparation of Ions.** The ions **3**, **7**, **10**, and **14** were all prepared quantitatively from the corresponding chlorides in SbF<sub>5</sub>/SO<sub>2</sub>ClF at –78 °C using syringe techniques:<sup>1,9</sup> **3** 0.8 M; SbF<sub>5</sub> 3.8 M; **3-*d*<sub>2</sub>** 0.9 M; SbF<sub>5</sub> 3.8 M; **7** 0.6 M; SbF<sub>5</sub> 4.0 M; **7-*d*<sub>2</sub>** 1.0 M; SbF<sub>5</sub> 4.1 M; **10** 0.6 M; SbF<sub>5</sub> 4.0 M; **14** 0.9 M; SbF<sub>5</sub> 4.3 M.

**NMR Spectra.** Spectra of the ions were recorded at –70 to –80 °C either on a Varian CFT-20 spectrometer or on a hybrid Varian HA60-Digilab-PDP-15 spectrometer operating at 15.08 MHz<sup>43</sup> using 8 and 10 mm tubes, respectively. Field stabilization was achieved using a

concentric capillary (3 mm o.d.) of acetone-*d*<sub>6</sub> containing a trace of either benzene or TMS. Spectra of the neutral compounds were recorded at 30 °C in CDCl<sub>3</sub> solutions (~3 M). Chemical shifts are ±0.1 ppm from internal TMS or, in the case of the ions, from external TMS. The proton coupled spectra were obtained by using the gated decoupling technique with a minimum duty cycle of 50%, 8K data points, 45° flip angle, and between 4000 and 6000 transients. Coupling constants were measured by hand from spectra plotted over 500 Hz chart width. In some cases (e.g., **6b**) where there were complex overlapping multiplets, superposition on the chart of the noise decoupled and off-resonance decoupled spectra allowed  $J_{CH/2}$  to be measured. The reported coupling constants are ±1 Hz except where otherwise stated.

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  - (19) Since the value for octahydropentalene is the same as that for **12**,<sup>18</sup> we do not expect a significant difference between that for **9** and the corresponding olefin. *cis*-Decalin (**9**):  $\delta$  ( $J$ ) CDCl<sub>3</sub>, 30 °C; 36.7 (125), C<sub>9,10</sub>, 31.5 (125) C<sub>1,4</sub>, and 24.6 (127) C<sub>2,3</sub>. The parameters for the methylene carbons are averages of those for the two conformers; D. K. Dalling, D. M. Grant, and L. F. Johnson, *J. Am. Chem. Soc.*, **93**, 3678 (1971).
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  - (21) The value for the neutral, model compound in this case should be the average of  $J_{C,H}$  and  $J_{C,H}$ . Since the latter is difficult to extract from the spectrum of **6a**, a value of 142 Hz from norbornene is used. The use of an average value of 146 Hz leads to a slightly larger  $\Delta J$ , 13 Hz.
  - (22) Exactly one-half of  $\Delta J$  (static) (3 Hz) would require a value of 129 Hz in the cation. However, the difference is not significant as the experimental uncertainty in the measurement is ±1 Hz.
  - (23) Total time elapsed, 2.25 h.
  - (24) The peak due to C<sub>2</sub> at 270.2 was almost eliminated. Since C<sub>2</sub> maintains its identity in the rearrangement process previously observed in this cation,<sup>25</sup> the drastic reduction in the intensity of the C<sub>2</sub> signal may be due to an increase in the  $T_1$  value and decrease of the NOE of this carbon. This

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## Correlation Analysis of <sup>13</sup>C and <sup>19</sup>F NMR Substituent Effects in Arylplatinum Complexes

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**Abstract:** <sup>13</sup>C NMR spectra have been obtained for a series of complexes of the type *trans*-(PEt<sub>3</sub>)<sub>2</sub>Pt(C<sub>6</sub>H<sub>5</sub>)X (I). Correlations of the associated chemical shifts and coupling constants with sets of both Taft and modified Swain-Lupton substituent constants were examined. Similarly, correlations involving previously determined <sup>19</sup>F chemical shifts associated with the complexes *trans*-(PEt<sub>3</sub>)<sub>2</sub>Pt(C<sub>6</sub>H<sub>4</sub>F)X (II) were also examined. The observed correlations provide evidence that substituent parameters obtained from organic systems may be used, within limits, to accurately describe the effects of substituents bonded to platinum. An anomalous behavior of the substituents I and Br in these correlations was also noted. Finally, evidence is presented supporting the presence of significant  $\pi$  interactions between platinum and an aryl ligand.

The study of the nature of the aryl-metal bond has been the subject of numerous investigations.<sup>1</sup> Most of these studies have dealt with questions concerning the importance of  $\pi$  bonding in such bonds. However, in spite of the substantial effort devoted to this problem, controversy still surrounds the interpretation of the available physical data. Nevertheless, the problem remains important since an increased understanding of the nature of the aryl-metal bond could have far-reaching implications in the interpretations of such reactivity phenomena as the *trans* effect<sup>2</sup> and metal catalysis.

A significant portion of the work concerned with this problem has involved the study of arylplatinum complexes. Starting with Parshall's study<sup>3</sup> of substituent effects on the <sup>19</sup>F NMR chemical shifts of fluoroarylplatinum complexes, most of this work has employed NMR spectroscopy as a structure probe. However, possible shortcomings to using this technique have recently been documented.<sup>1,32</sup> In this connection, it is also important to note that chemical shifts associated with the aryl group of a series of substituted aryl-metal complexes can, at best, be an approximate measure of the *sensitivity* of the  $\pi$  and  $\sigma$  components of the aryl-metal bond to the effects of substituents. They cannot, without auxiliary information, represent a measure of the *magnitudes* of the  $\pi$  or  $\sigma$  bond orders of these bonds. On the other hand the *existence* of an aryl-metal  $\pi$  interaction may be implied by the observation of a sensitivity to substituent effects characteristic of such interactions.

Recent studies<sup>1,4</sup> have emphasized the use of <sup>13</sup>C NMR spectroscopy to measure substituent effects on aryl carbons. In an important investigation, Clark and Ward<sup>1</sup> examined the <sup>13</sup>C chemical shifts,  $\delta^C$ , and coupling constants, <sup>n</sup>J<sub>PtC</sub>, associated with a series of arylplatinum complexes. On the basis of the chemical shift data they concluded that " $\sigma$  rather than  $\pi$  interactions are dominant in the phenyl-platinum bond."

To gain further insight into the nature of aryl-platinum bonds, we have examined correlations of both <sup>13</sup>C and <sup>19</sup>F NMR substituent effects observed in arylplatinum complexes with substituent parameters derived from organic systems. Furthermore, we have examined these substituent effects as contributions from field/inductive and resonance effects using both a modified Swain-Lupton<sup>5</sup> model and the Taft<sup>6</sup> model for determining the separation of such effects. Arylplatinum metal systems were studied since previous studies<sup>1,3</sup> had demonstrated both their ease of preparation and the additional and valuable information gained through observing spin-spin couplings of <sup>195</sup>Pt (*I* = 1/2, 34% natural abundance) with both <sup>13</sup>C and <sup>19</sup>F.

### Results

**Preparation of Phenylplatinum Complexes.** The phenylplatinum complexes, I, were prepared by conventional methathesis reactions with the exception of I (X = F<sub>2</sub>H) which was