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X-ray Crystal Structures of Carbocations Stabilized by Bridging or Hyperconjugation

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Introduction

While the first crystal structures of carbocations stabilized by resonance with π systems (e.g., the trityl cation¹) or with nonbonding electron pairs of heteroatoms (e.g., an iminium ion²) were determined 30 years ago, the first structures of carbocations stabilized by hyperconjugation³ or bridging⁴ were determined only within the last decade. This may be one of the reasons why the debate about the existence of three-center, two-electron (3c, 2e) bonds involving only C or H atoms (i.e., the actual question⁵ behind "the nonclassical ion"⁶ or "the 2-norbornyl cation" problem) lasted so long. The discussion focused mainly on the 2-norbornyl cation⁷⁻¹⁰ (1), which is drawn in Scheme 1 and Chart 1 as a symmetrically bridged species (point group C_s ; the mirror plane is passing through C4, C5, and C6), i.e., a resonance hybrid between 1a, 1b, and 1c.

For many years, it was very difficult to differentiate on the basis of experimental results between this possibility (essentially 1a \leftrightarrow 1b; single minimum potential) and a rapidly equilibrating pair of less symmetrical (point group C_1) classical or partially bridged ions (1a \rightleftharpoons 1b; double minimum potential). The question of the structure of 1 was first discussed by Winstein¹¹ and Roberts,¹² and a huge amount of

Scheme 1

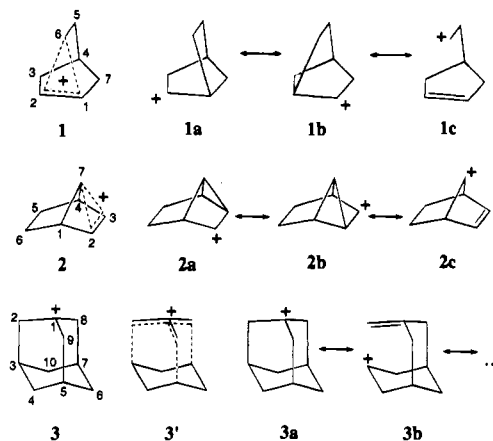
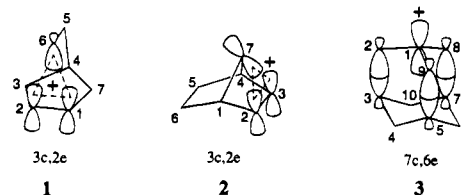


Chart 1. The Most Important AOs Involved in the Charge Delocalization



Thomas Laube (born on September 20, 1952, in Berlin, West Germany) studied chemistry (as well as three semesters of mathematics) and received his diploma in chemistry in 1980 from the Free University of Berlin, West Germany. He then moved to Zürich, Switzerland, and finished his Ph.D. thesis ("Contribution to the Structure and Reactivity of Ester and Amide Lithium Enolates") at the ETH Zürich in 1984. Since 1985, he has worked on the structure of electron-deficient compounds. On the basis of his *Habilitationsschrift* ("Influence of Electronic Effects on the Structure of Alicyclic Carbocations and Related Molecules"), he holds the title of *Privatdozent* (since April 1989) at the ETH Zürich. His major research interests concern the experimental investigation of the structures of reactive intermediates and mathematical problems related to this area.

research effort led to countless publications about this subject since that time. The most often applied experimental methods were solvolysis and, later, NMR studies. Computational studies were carried out at increasing levels of precision. Mainly the similarity of the energy diagrams for the solvolysis reactions of 1 and related substituted ions (the latter were clearly shown to be equilibrating pairs in solution) led Brown

to the conclusion that also **1** may be actually an equilibrating pair¹³ (**1a** \rightleftharpoons **1b**). The NMR experiments in solution at -158 °C (Olah et al.¹⁴) and in the matrix at 5 K (Yannoni et al.¹⁵) as well as the isotopic perturbation method (Saunders et al.¹⁶) and IR measurements (Sunko et al.¹⁷), however, indicate that **1** is either symmetrically bridged as depicted in Scheme 1 or a pair of equilibrating ions with an energy barrier of less than 0.2 kcal/mol (an extremely small value). *Ab initio* calculations also yield a symmetrically bridged species.¹⁸

Winstein^{19,20} and Roberts²¹ concluded that also the norborn-2-en-7-yl cation (**2**) must be bridged, i.e., **2** is a resonance hybrid of **2a**, **2b**, and **2c**. Olah's²² and Winstein's²³ NMR investigations as well as Schleyer's²⁴ *ab initio* calculations support the symmetrical structure.

Bridging and hyperconjugation are related phenomena, but hyperconjugation does not lead to such strong changes of geometry as observed for bridging. There is no clear boundary between the two effects; they are considered as regions in the spectrum of charge delocalization effects between the extreme cases "no charge delocalization" and "strong charge delocalization with bridging". An example of hyperconjugation is the 1-adamantyl cation (**3**).²⁵ It may be mainly

described by resonance formula **3a**, but the three symmetry-related formulas **3b** indicate that, in agreement with NMR results,²⁵ some charge is also found on C3, C5, and C7. Therefore, formula **3'** is in principle more suitable for the description of the 1-adamantyl cation, but this formula is never used, probably because it exaggerates the observed effect. For an approximate description of **3**, one could say that six electrons from three σ_{C-C} bonds are delocalized over seven centers (see Chart 1). Hyperconjugation does not occur with C-C bonds only, but also with C-H bonds, for example.

What are the disadvantages and problems of the crystal structure analyses of carbocations besides the well-known advantages (determination of the geometry, vibrational behavior, sometimes bond electron density and charges)? The biggest disadvantage is the necessity of a well-diffracting crystal; i.e., by far not every cation that can be prepared in solution under superacidic conditions is suitable for crystal growth. Crystal handling is often difficult because of the low thermal stability of many reactive carbocations. Another problem is the question of the potential disorder of structures, which is the direct translation of "the nonclassical ion problem" into the language of structural chemistry; i.e., does the observed structure represent a ground-state or near-ground-state conformation of the carbocation (in a single-minimum potential or in one minimum of a double-minimum potential), or is it a nonresolved or even unresolvable time or space average of carbocations with slightly different structures (double-minimum potential)? Unfortunately, there is another source of potential disorder in many carbocation crystals: the often sphere-like shape of small cations or anions can easily cause orientational disorder leading in the extreme case to plastic phases,²⁶ which have a low diffracting power. And finally, one must ask to what degree an observed crystal structure may be influenced by interactions with neighboring molecules or ions (packing effects).

The following sections show in which cases the difficulties could be overcome and what the answers to the questions are.

Carbocations Stabilized by Hyperconjugation

3,5,7-Trimethyl-1-adamantyl Cation (4). This alicyclic cation was the first whose structure could be determined,³ and a redetermination²⁷ (see Figure 1 and Chart 2) was carried out recently. The average $C_{\alpha}-C_{\beta}$ bond length is 0.063(6) Å smaller and the average $C_{\beta}-C_{\gamma}$ bond length is 0.074(4) Å greater than

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(28) Keller, E. *SCHAKAL92*. Kristallographisches Institut, Universität Freiburg, Hebelstr. 25, D-79104 Freiburg, Federal Republic of Germany.

(29) Bonds involved in hyperconjugation or bridging (as proven by unusual lengths) are drawn as black sticks with the following features: shortened bonds (bond order > 1) are represented by thick sticks, bonds elongated by <0.1 Å by thin sticks, bonds elongated by >0.1 Å and unusually short nonbonding distances by thin and fragmented sticks. Hydrogen atoms are drawn as white spheres, and carbon atoms are labeled by their numbers as given in the original publications. The minor orientations of rotationally disordered methyl groups have been omitted for clarity.

(30) An ORTEP stereo figure is found in ref 27, Figure 2.

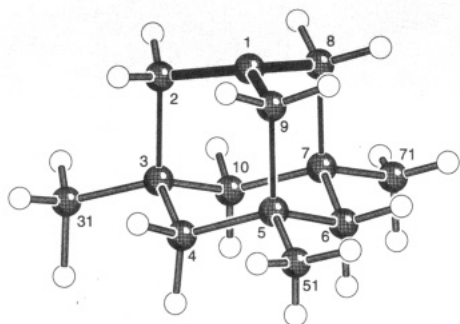
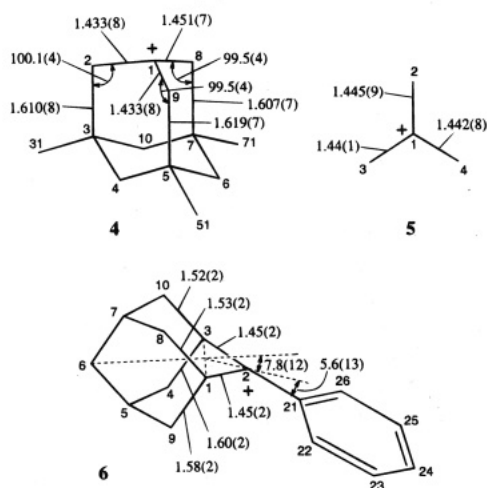
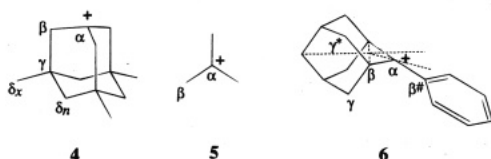


Figure 1. Ball-and-stick model²⁸⁻³⁰ of the crystal structure of 4.

Chart 2. Selected Structural Parameters of Cations 4, 5, and 6^a



^a Distances in Å, angles in deg.



suitable reference values³¹ (see Table 1). The pyramidalization³² $C1-P(2,8,9) \equiv \Delta(C1) = 0.212(5)$ Å is remarkable for an sp^2 -like C atom, and the quaternary C_γ atoms are slightly flattened, if one ignores the $C_\beta-C_\gamma$ bond. The average $C_\gamma-C_{\delta_n}$ and $C_\gamma-C_{\delta_x}$ bond lengths are slightly smaller (by 0.011(3) and 0.015(7) Å) than their reference values.³¹ The average $C_\beta-C_\alpha-C_{\beta'}$ and $C_\alpha-C_\beta-C_\gamma$ bond angles also indicate the unusual geometry about C1. In agreement with the slight flattening of the C_γ atoms, the average $C_\beta-C_\gamma-C_{\delta_n}$ and $C_\beta-C_\gamma-C_{\delta_x}$ angles are slightly smaller, whereas the average $C_{\delta_n}-C_\gamma-C_{\delta_n'}$ and $C_{\delta_n}-C_\gamma-C_{\delta_x}$ angles are slightly larger than the ideal tetrahedral angle of 109.5°. Also the average absolute $C_\gamma-C_{\delta_n}-C_\gamma-C_{\delta_n'}$ torsion angle is smaller than the ideal value. The thermal motion analysis of 4 shows that the displacement parameters of the cation may be roughly explained by the motion of a rigid body.

(31) Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. In *International Tables for Crystallography, Volume C*; Wilson, A. J. C., Ed.; Kluwer Academic Publishers: Dordrecht, 1992; pp 685-706.

(32) (a) $P(i_1, \dots, i_n)$ is the (for $n > 3$: least-squares) plane through C_{i_1}, \dots, C_{i_n} . (b) The pyramidalization Δ of a tricoordinate atom is its distance from the plane through its neighbors.

Table 1. Average Structural Parameters of 4 and Corresponding Reference Parameters^a

av. parameter		ref parameter	
$C_\alpha-C_\beta$	1.439(6)	$C_{sp^3}-CH_2-C_{sp^2}$ ^b	1.502(1)
$C_\beta-C_\gamma$	1.612(4)	$(C_{sp^3})_3C-CH_2-C_{sp^2}$ ^{b,c}	1.538(1)
$C_\gamma-C_{\delta_n}$	1.527(3)	$(C_{sp^3})_3C-CH_2-C_{sp^3}$ ^b	1.538(1)
$C_\gamma-C_{\delta_x}$	1.519(7)	$(C_{sp^3})_3C-CH_3$ ^b	1.534(1)
$C_\beta-C_\alpha-C_{\beta'}$	117.9(3)	ideal $C-C_{sp^2}-C$	120
$C_\alpha-C_\beta-C_\gamma$	99.7(2)	ideal $C-C_{sp^3}-C$	109.5 ^d
$C_\beta-C_\gamma-C_{\delta_n}$	107.4(2)	ideal $C-C_{sp^3}-C$	109.5 ^d
$C_\beta-C_\gamma-C_{\delta_x}$	107.4(2)	ideal $C-C_{sp^3}-C$	109.5 ^d
$C_{\delta_n}-C_\gamma-C_{\delta_n'}$	110.9(4)	ideal $C-C_{sp^3}-C$	109.5 ^d
$C_{\delta_n}-C_\gamma-C_{\delta_x}$	112.2(2)	ideal $C-C_{sp^3}-C$	109.5 ^d
$ C_\gamma-C_{\delta_n}-C_\gamma-C_{\delta_n'} $	56.2(3)	(e.g., diamond lattice)	60
$ \Delta(C_\gamma) $ ^e	0.454(3)	$1/3 \times C_{sp^3}-C_{sp^2}$ ^{b,f}	0.510

^a Lengths are given in Å, angles in deg. ^b Taken from ref 31. ^c The required reference parameter $(C_{sp^3})_3C-CH_2-C_{sp^2}$ is not available. ^d $\arccos(-1/3)$. ^e Bond partners: $C_{\delta_n}, C_{\delta_n'}, C_{\delta_x}$. ^f Ideal $\Delta(C_{sp^3})$ using three bonds.

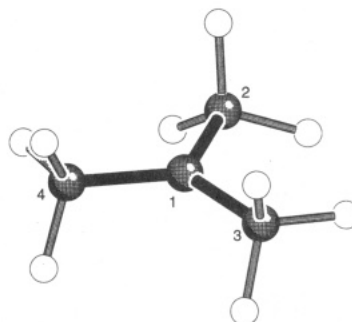


Figure 2. Ball-and-stick model^{28,29,36} of the crystal structure of 5.

The structural features of 4 may be easily explained in terms of a stabilization by C-C hyperconjugation. This was already concluded by Olah et al.²⁵ on the basis of NMR chemical shifts of several 1-adamantyl cations, and also Schleyer et al.^{33,34} explained the computed structure of 3 ($C_\alpha-C_\beta = 1.448$ Å, $C_\beta-C_\gamma = 1.616$ Å, $C_\gamma-C_{\delta_n} = 1.525$ Å) by hyperconjugation. The shortening of the $C_\alpha-C_\beta$ bond agrees with a partial double bond character, the elongation of the $C_\beta-C_\gamma$ bond with a weakened single bond (see resonance formula 3b). The ¹³C data of Olah et al.²⁵ indicate that a significant amount of positive charge is found on the C_γ atoms. Accordingly, these atoms are also slightly flattened in 4, and all $C_\gamma-C_\delta$ bonds are very slightly shortened.

tert-Butyl Cation (5). The structure of 5³⁵ in the crystal is shown in Figure 2. Cation 5 is planar within the limits of accuracy ($\Delta(C1) = 0.007(5)$ Å); its $C_\alpha-C_\beta$ bonds have an average length of 1.442(5) Å (see Chart 2), and the $C_\beta-C_\alpha-C_{\beta'}$ angles are 120(1)°, i.e., the C skeleton has approximate D_{3h} symmetry.

The experimental structure of 5 shows an average $C_\alpha-C_\beta$ shortening of 0.061(5) Å (a normal $C_{sp^2}-CH_3$ bond³¹ has a length of 1.503 Å) and thus agrees with the expectation for a charge delocalization from C1 into the $C_\beta-H$ bonds (C-H hyperconjugation). The observed $C_\alpha-C_\beta$ length agrees well with nutation NMR results of Yannoni et al.³⁷ (1.46 Å) and the *ab*

(33) Buzek, P.; Schleyer, P. v. R.; Sieber, S. *Chem. Unserer Zeit* 1992, 26, 116-128.

(34) Schleyer, P. v. R.; Maercker, C. Submitted to *Pure Appl. Chem.*, special issue, IUPAC 12th Conference on Physical Organic Chemistry, Padova, Italy, Aug 28 to Sep 2, 1994.

(35) Hollenstein, S.; Laube, T. *J. Am. Chem. Soc.* 1993, 115, 7240-7245.

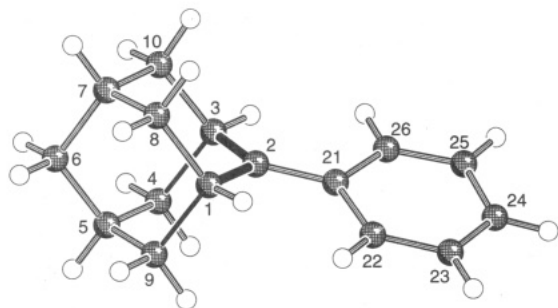


Figure 3. Ball-and-stick model^{28,29,40} of the crystal structure of **6**.

Table 2. Average Structural Parameters of **6 and Corresponding Reference Parameters^a**

av parameter		ref parameter	
$C_{\alpha}-C_{\beta}$	1.45(2)	$(C_{sp^3})_2HC-C_{sp^2}{}^b$	1.510
$C2-C21^c$	1.41(2)	$C_{sp^2}-C_{ar}$ (conjugated) ^b	1.470
$C_{\beta}-C_{\gamma}$	1.59(2)	$(C_{sp^3})_2HC-CH_2(C_{sp^3})^b$	1.531

^a Lengths are given in Å. ^b Taken from ref 31. ^c Only one value available.

initio results of Schleyer et al.^{33,34,38} (1.457–1.459 Å). We have no experimental information about a corresponding C–H lengthening, because all H atoms could only be refined with constraints and were probably disordered.

2-Phenyl-2-adamantyl Cation (6). The structure of **6**³⁹ in the crystal is shown in Figure 3. The most remarkable features of cation **6** (see Chart 2) are the displacement of the C2 bridge out of plane^{32a} $P(1,3,6)$ by 7.8(12)°, the additional bending of the (planar) Ph ring out of plane $P(1,2,3)$ by 5.6(13)° leading to a slight pyramidalization of $\Delta(C2) = 0.049(14)$ Å, and the elongated $C_{\beta}-C_{\gamma}$ bonds (see Table 2). All bonds emanating from C2 are shortened by 0.06(2) Å if compared with reference values³¹ from neutral molecules.

Although most observed deviations of structural parameters of **6** from reference values are only just significant (3σ criterion) due to the large esd's, the structural deformations of **6** are entirely consistent with the assumption of C–C hyperconjugation between C2 and the $C_{\beta}-C_{\gamma}$ bonds, which are on the average elongated by 0.07(2) Å if compared with the $C_{\beta}-C_{\gamma}^*$ bonds. The $C_{\alpha}-C_{\beta}$ bonds are shortened because of a slight double-bond character, and the $C_{\beta}-C_{\gamma}^*$ bonds show no effect because of the bad overlap between the empty p orbital at C2 and the filled $\sigma_{C_{\beta}-C_{\gamma}^*}$ orbitals. These effects were predicted by Sorensen et al.⁴¹ and are also expected from the structures of **4**, **5**, substituted cyclohexanones⁴² (which are in some cases activated by Lewis acids), and an activated adamantane.⁴³ The benzylic resonance in **6** causes the shortening of the $C_{\alpha}-C_{\beta}^{\#}$ bond.

(36) An ORTEP stereo figure is found in ref 35, Figure 1.

(37) Yannoni, C. S.; Kendrick, R. D.; Myhre, P. C.; Bobout, D. C.; Petersen, B. L. *J. Am. Chem. Soc.* **1989**, *111*, 6440–6442.

(38) Sieber, S.; Buzek, P.; Schleyer, P. v. R.; Koch, W.; Carneiro, J. W. d. M. *J. Am. Chem. Soc.* **1993**, *115*, 259–270.

(39) Laube, T.; Hollenstein, S. *Helv. Chim. Acta* **1994**, *77*, 1773–1780.

(40) An ORTEP stereo figure is found in ref 39, Figure 1.

(41) (a) Finne, E. S.; Gunn, J. R.; Sorensen, T. S. *J. Am. Chem. Soc.* **1987**, *109*, 7816–7823. (b) Dutler, R.; Rauk, A.; Sorensen, T. S.; Whitworth, S. M. *J. Am. Chem. Soc.* **1989**, *111*, 9024–9029.

(42) Laube, T.; Hollenstein, S. *J. Am. Chem. Soc.* **1992**, *114*, 8812–8817.

(43) Laube, T.; Stilz, H. U. *J. Am. Chem. Soc.* **1987**, *109*, 5876–5878.

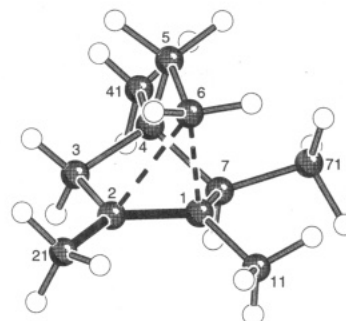
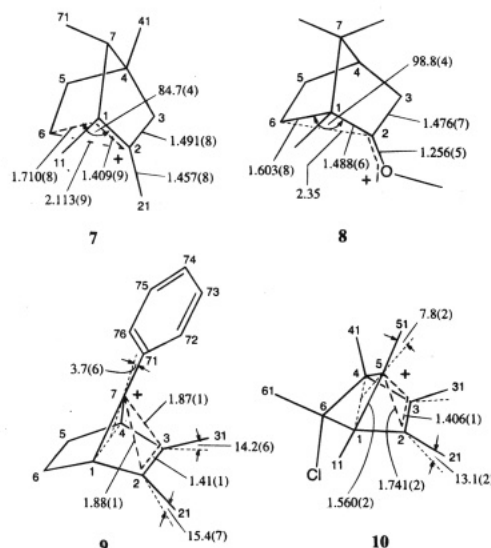


Figure 4. Ball-and-stick model^{28,29,45} of the crystal structure of **7**.

Chart 3. Selected Structural Parameters of Cations **7–10^a**

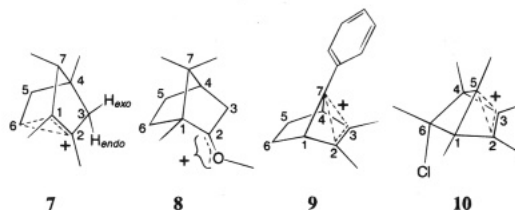


^a Distances in Å, angles in deg.

Common Features of Cations **4–6.** All $C_{\alpha}-C_{\beta}$ bonds involved in C–C or C–H hyperconjugation are shortened by about 0.06 Å (**4–6**), and all $C_{\beta}-C_{\gamma}$ bonds involved in C–C hyperconjugation are lengthened by about 0.06–0.07 Å (**4**, **6**) if compared with reference values³¹ from neutral molecules.

Carbocations Stabilized by Bridging

1,2,4,7-anti-Tetramethyl-2-norbornyl Cation (7). This bridged cation was the first whose structure could be determined,⁴ and a redetermination⁴⁴ (see Figure 4 and Chart 3) was carried out recently. The structure



of **7** deviates strongly from that of a neutral norbornane derivative.^{4,46} The C2–C1 bond is shortened by 0.113(9) Å (see Table 3), C2–C21 is shortened by

(44) Laube, T. *Helv. Chim. Acta* **1994**, *77*, 943–956.

(45) An ORTEP stereo figure is found in ref 44, Figure 1.

(46) Doms, L.; Van Hemelryk, D.; Van de Mierop, W.; Lenstra, A. T. H.; Geise, H. J. *Acta Crystallogr., Sect. B* **1985**, *B41*, 270–274. Fitch, A. N.; Jobic, H. *J. Chem. Soc., Chem. Commun.* **1993**, 1516–1517.

Table 3. Structural Parameters of 7 and Corresponding Reference Parameters^a

parameter		ref parameter ^b	
C2–C1	1.409(9)	$C_{sp^2}-C_{sp^2}(C_{sp^3})_3$	1.522(1)
C2–C21	1.457(8)	$C_{sp^2}-CH_3$	1.503(1)
C1–C11	1.503(8)	$(C_{sp^3})_3C_{sp^3}-CH_3$	1.534(1)
C2–C3	1.491(8)	$C_{sp^2}-CH_2(C_{sp^3})$	1.502(1)
C1–C6	1.710(8)	$(C_{sp^3})_3C_{sp^3}-CH_2(C_{sp^3})$	1.538(1)

^a Lengths are given in Å. ^b Taken from ref 31.

0.046(8) Å, and C1–C11 is shortened by 0.031(8) Å, while C2–C3 is only insignificantly shortened by 0.011(8) Å. The C1–C6 bond is lengthened by 0.172(8) Å. Thermal motion analysis based on a rigid body model does not account well for the observed displacement parameters of **7** ($R = 17.1\%$). Electron and difference density contour diagrams⁴⁴ show that cation **7** is located in a region of elevated diffuse "background" electron density (highest difference density peaks: about $0.9 e \text{ \AA}^{-3}$).

In terms of the MO description, the structural features are the result of the interaction of the empty p orbital at C2 (p_{C2}) with the filled bond orbitals in the neighborhood. The interaction with the ideally aligned σ_{C1-C6} orbital (torsion angle between the symmetry axis of p_{C2} and C1–C6: -7°) leads to an unsymmetrical 3c, 2e bond involving C2, C1, and C6. Simultaneously, p_{C2} is also interacting with the C21 methyl group leading to C–H hyperconjugation (probably somewhat weaker than in **5**, where the average C^+-CH_3 bond length is 1.442(5) Å). The interaction between p_{C2} and the $\sigma_{C3-H_{exo}}$ orbital can only be inferred from the nearly ideal torsion angle between them ($+12^\circ$), while the $p_{C2}/\sigma_{C3-H_{endo}}$ interaction must be worse because of the torsion angle of -46° , in agreement with the fact, that the 3,2-*exo*-H shift in 2-norbornyl cations is much faster than the 3,2-*endo*-H shift.⁴⁷

The structure of **7**·Sb₂F₁₁ contains two hints that **7** is not perfectly ordered: the electron density background in the cation region and the poor agreement of observed and calculated U values. If the highest difference density peak is treated as a C atom, a site occupation factor of 0.12 is obtained. Such a peak can cause positional errors of up to ca. 0.03 Å for the C atoms in the structure of **7**.⁴⁸ However, this error is too small to permit interpretation of the structure of **7** as a superposition of classical cations (see also Disorder and Resolution).

Schleyer et al.³⁴ obtained by *ab initio* methods (BeckeLYP/6–31G*) for the related 1,2-dimethyl-2-norbornyl cation C2–C1 = 1.447 Å, C1–C6 = 1.741 Å, and C6–C1–C2 = 88.5°, i.e., values rather close to those observed in **7**.

2-Methoxy-1,7,7-trimethyl-2-norbornyl Cation (8). The structure of this stabilized 2-norbornyl cation (see Chart 3) has been determined by Montgomery et al.⁴⁹ as the BF₄ salt. The C2–O bond is about 0.05 Å longer than the mean camphor carbonyl distances and at least 0.1 Å shorter than the typical C–O length in ethers, indicating predominant oxonium ion character.

(47) Haseltine, R.; Ranganayakulu, K.; Wong, N.; Sorensen, T. S. *Can. J. Chem.* **1975**, *53*, 1901–1914. Sorensen, T. S. *Acc. Chem. Res.* **1976**, *9*, 257–265.

(48) Laube, T. *Acta Crystallogr., Sect. A* **1992**, *A48*, 158–172.

(49) Montgomery, L. K.; Grendze, M. P.; Huffmann, J. C. *J. Am. Chem. Soc.* **1987**, *109*, 4749–4750.

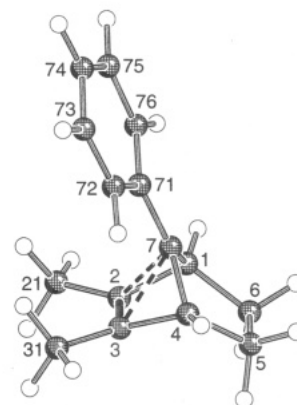


Figure 5. Ball-and-stick model^{28,29,52} of the crystal structure of **9**.

The C1–C6 bond (1.603(8) Å) is about 0.05 Å longer than the average value in simple norbornanes or camphor. The nonbonded distance $C2 \cdots C6 = 2.35 \text{ \AA}$ is about 0.05 Å less than the mean $C2 \cdots C6$ distance in camphor, and the angle $C2-C1-C6 = 98.8(4)^\circ$ is also smaller than in camphor ($C2-C1-C6 = 103.4(12)^\circ$).

The authors explain the C1–C6 lengthening by C–C hyperconjugation or a slight bridging, which agrees with the reduced $C2 \cdots C6$ distance and $C2-C1-C6$ angle if compared with camphor. All important structural deviations from reference values in **8** have the same direction as those observed in **7**, but they are weaker in **8** because of the stabilizing 2-methoxy group.

(deloc-2,3,7)-2,3-Dimethyl-7-phenylnorborn-2-en-7-yl Cation (9). The structure of this cation (see Figure 5) was first reported in 1989,⁵⁰ and the result of an improved refinement on F^2 (see Chart 3) involving a disorder model for the anion was published recently.⁵¹ The most significant features of **9** are the short distances $C2-C7 = 1.88(1) \text{ \AA}$ and $C3-C7 = 1.87(1) \text{ \AA}$. The mutual approach of the C7 and C2=C3 bridges leads to a 5-fold coordination of C7. The former C2=C3 double bond (1.41(1) Å) is significantly lengthened if compared with the reference value³¹ for a $(C_{sp^3})_2C_{sp^2}=C_{sp^2}(C_{sp^3})_2$ bond (1.331 Å). The C2–C21 and C3–C31 bonds are bent by $15.4(7)^\circ$ and $14.2(6)^\circ$ into the *exo* half space of the C2=C3 bond, and the C7–C71 bond is bent by $3.7(6)^\circ$ into the *syn* half space of C7. All other bond lengths have approximately the expected values.

The structure of **9** can be explained by an electronic interaction between the filled π orbital of the C2=C3 bond and the empty p orbital at C7, which is simultaneously part of the conjugated benzyl cation. The result of this interaction is a delocalization of the positive charge about C2, C3, and C7 (and into the phenyl ring) and hence the formation of a bishomocyclopropenyl cation with a symmetrical 3c, 2e bond. The additional bendings of the C2–C21, C3–C31, and C7–C71 bonds may be qualitatively explained by an additional mutual approach of the p orbital symmetry axes at C2, C3, and C7 leading to a higher overlap in the 3c, 2e bond.

Schleyer et al.³⁴ obtained by *ab initio* methods (MP2-FC/6–31G*) for the related 7-phenylnorborn-2-en-7-

(50) Laube, T. *J. Am. Chem. Soc.* **1989**, *111*, 9224–9232.

(51) Laube, T.; Lohse, C. *J. Am. Chem. Soc.* **1994**, *116*, 9001–9008.

(52) An ORTEP stereo figure is found in ref 50, Figure 1.

(53) An ORTEP stereo figure is found in ref 51, Figure 1.

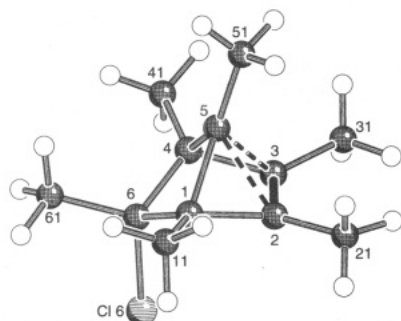


Figure 6. Ball-and-stick model^{28,29,53} of the crystal structure of **10**. The cation contains a crystallographic mirror plane passing through C5, C6, C51, C61, and Cl6.

Table 4. Structural Parameters of **10 and Corresponding Reference Parameters^a**

parameter		ref parameter	
C2=C3	1.406(1)	(C _{sp³}) ₂ C=C(C _{sp³}) ₂ ^b	1.331(1)
C2-C21 ≡ C3-C31 ^c	1.481(2)	C _{sp²} -CH ₃ ^b	1.503(1)
C5-C51	1.485(2)	C _{sp²} -CH ₃ ^b	1.503(1)
Δ(C2) ≡ Δ(C3) ^c	0.126(2)	ideal Δ(C _{sp²})	0
Δ(C5)	0.088(3)	ideal Δ(C _{sp²})	0

^a Lengths are given in Å. ^b Taken from ref 31. ^c Identical values because of the crystallographic mirror plane.

yl cation C2=C3 = 1.385 Å and C2-C7 = 1.901 Å, i.e., values rather close to those observed in **9**.

(deloc-2,3,5)-6-endo-Chloro-1,2,3,4,5,6-exo-hexamethylbicyclo[2.1.1]hex-2-en-5-yl Cation (10**).**

The rather precise structure of the BCl₄ salt of **10** (see Figure 6 and Chart 3) has been determined recently.⁵¹ The most remarkable feature of **10** is the strong bending of the C5 bridge toward the C2=C3 bridge, and thus the C2-C5 (≡ C3-C5) distance is only 1.741(2) Å. The C2=C3 bond is elongated by 0.075(2) Å if compared with a double bond (see Table 4); i.e., C2=C3 has a partial double bond character. The atoms C2, C3, and C5 are strongly pyramidalized,^{32b} if one ignores the C2-C5 and C3-C5 bonds. The C2-C21 (≡ C3-C31) and C5-C51 bonds are slightly shortened by 0.022(2) and 0.018(2) Å.

The structure of **10** deviates so strongly from that of a neutral bicyclo[2.1.1]hexene derivative that it cannot be described as a classical ion without bridging. An equilibrating or disordered pair of tricyclic cations can also be excluded because the cation and the anion behave in the crystal like rigid bodies. Therefore, the description with a 3c, 2e bond as depicted in formula **10** is most suitable. The small shortening of the C2-C21 (≡ C3-C31) and C5-C51 bonds indicates that C-H hyperconjugation does not play an important role in **10**. From the small angle between the cationic bridges in **10** (∠P(1,2,3,4),P(1,4,5) = 75.6(1)°) if compared with **9**^{50,51} (∠P(1,2,3,4),P(1,4,7) = 90.4(5)°) and from the lengths of the partial bonds (**10**, C2-C5 ≡ C3-C5 = 1.741(2) Å; **9**, C2-C7 = 1.88(1), C3-C7 = 1.87(1) Å), it follows that the bishomoaromatic charge delocalization in **10** (Me group at C5) is, as expected, stronger than in **9** (Ph ring at C7). However, the strong pyramidalization of C2 and C3 is comparable in **10** and **9**.

Schleyer et al.³⁴ obtained by *ab initio* methods (SCF/6-31G*) for the deschloro derivative of **10** C2=C3 = 1.393 Å and C2-C5 = 1.734 Å, close to the observed values in **10**.

Common Features of Cations 7–10. All four

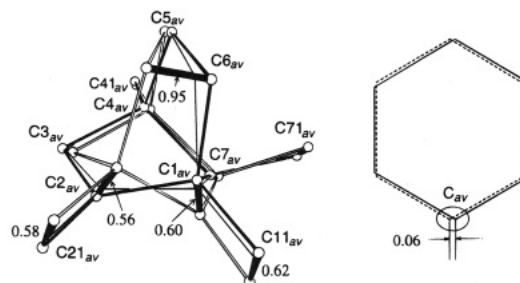
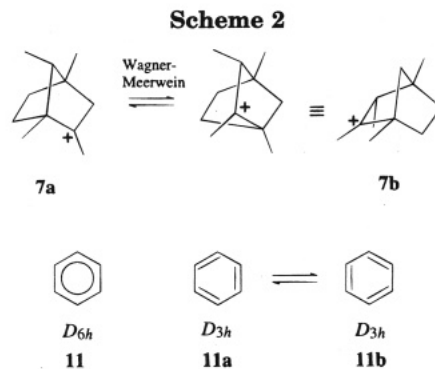


Figure 7. Left: Least-squares superposition⁵⁷ of the hypothetical classical ions **7a** and **7b** (medium-thick black and white bonds). The structure generated by 3:1 averaging of corresponding C positions is represented by thin bonds and atom labels with the subscript *av*. The lines connecting each pair of corresponding atoms in **7a** and **7b** are drawn as thick bars, and distances are given in Å. Right: Superposition of two orientations (solid and dashed bonds, respectively) of a hypothetical cyclohexatriene molecule with localized double bonds (**11a** and **11b**).⁵⁸ The 1:1 averaged structure (not drawn for clarity) has *D*_{6h} symmetry.

structures show deformations if compared with similar neutral molecules, which agree with bridging in a broad range. The weakest bridging is observed in the methoxy-substituted cation **8**, and the strongest bridging is found in **10**, which has Me groups at all atoms involved in the 3c, 2e bond. Bridging is clearly observed in the weakly stabilized cations **7**, **9**, and **10**, although these cations are tertiary (**9** is even benzylic). In the 3c, 2e bonds of these cations, the lengths of the bonds with bond order > 1 are all about 1.41 Å, while the lengths of the bonds with bond order < 1 are in the range 1.71–2.11 Å.

Disorder and Resolution. Cation **7** equilibrates in solution with other cations.^{44,54} Is it possible that the observed crystal structure of **7** is actually a time or space average of the classical⁵⁵ ions **7a** and **7b** (or other ions) whose atomic positions cannot be resolved?⁵⁶ The best superposition (see Scheme 2 and Figure 7, left) shows that C6 would be split into two positions with a distance of 0.95 Å, and C1, C2, C11, and C21 have corresponding distances of ≈0.6 Å, i.e., near to the resolution limit.⁵⁶ Such a superposition would lead to displacement ellipsoids which are elongated along the lines connecting the split positions (thick bars in Figure 7), and for C6, even resolution is possible. While a 3:1 average of **7a** and **7b** has a

(54) Huang, L.; Ranganayakulu, K.; Sorensen, T. S. *J. Am. Chem. Soc.* **1973**, *95*, 1936–1944.

(55) "Classical" means here complete absence of charge delocalization into σ or π bonds. Such a cation has a structure similar to that of a comparable neutral molecule.

(56) The resolution of the crystal structure⁴⁴ of 7-Sb₂F₁₁ is ≈0.7 Å (θ_{max} = 30°, Mo Kα).

(57) The corresponding stereo figure is found in ref 50, Figure 13.

structure similar to that of **7** in the crystal, the directions of the displacement ellipsoids⁴⁵ do not agree with such a superposition. It is possible that minor amounts of other cations or orientations ($\leq 12\%$, see above) are present and responsible for the observed background electron density, but their estimated influence on the atomic positions is small⁴⁸ (≤ 0.03 Å, see above). A similar disorder simulation was carried out for **9**,⁵⁰ and a disorder of classical isomers could be ruled out also here. Fortunately, at least some of the distances between the split positions of disordered molecules are in our cases in the resolution range or greater and not as small as in the (extreme) hypothetical cyclohexatriene/benzene case⁵⁸ (**11a** and **11b**; 0.06 Å, see Figure 7, right), where differentiation between disorder (**11a** and **11b**) and a static molecule (**11**) is not possible by X-ray diffraction.

Crystal-Packing Effects. The interaction of a molecule with its neighbors in a crystal has an influence on the structure. Usually these lattice forces are relatively small, i.e., in the range of 1 or a few kcal/mol. The best known case of a deviation of a crystal structure from a ground state conformation in the gas phase is probably biphenyl.⁵⁹ We have carried out force field⁶⁰ and AM1⁶² calculations on neutral norbornane derivatives related to **7** in order to estimate the energy difference between their ground state (corresponding to the classical ion **7a**) and a structure constrained to resemble **7** in the crystal. The obtained

(58) Ermer, O. *Angew. Chem.* **1987**, *99*, 791–793; *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 782.

(59) Brock, C. P.; Minton, R. P. *J. Am. Chem. Soc.* **1989**, *111*, 4586–4593.

(60) Tripos force field in SYBYL 6.0.⁶¹

(61) SYBYL Version 6.0 for Sun computers, November 1992, Tripos Associates, Inc. (a subsidiary of Evans & Sutherland), St. Louis, MO 63144-2913.

(62) Stewart, J. J. P. MOPAC, version 5.0 (integrated in SYBYL 6.0⁶¹). Program No. 455 from Quantum Chemistry Program Exchange, Indiana University, Bloomington, IN.

energy differences (10–20 kcal/mol) are, even under the assumption of an uncertainty of a factor of 2 (or $1/2$), much higher than expected for a packing effect. The estimation is nevertheless not very safe, because charge delocalization and cation–anion interactions were not taken into account. However, the good agreement between our structures and the *ab initio* results of Schleyer et al.^{33,34} is an indication that our structures are not severely influenced by packing effects.

Concluding Remarks

Although the preparation of carbocations under superacidic conditions and the technique for the manipulation and X-ray measurement of crystals at low temperatures have been known for decades, single-crystal X-ray diffraction of reactive carbocations has been applied successfully only within the last few years. The unusual structural features of aliphatic and alicyclic carbocations were explained with bridging and hyperconjugation; i.e., the direct experimental observation of the cationic intermediates in the crystal provided otherwise unavailable facts for the discussion of the nonclassical ion problem. Our knowledge about the geometry of carbocations is nevertheless still limited if compared with our knowledge about carbocations. We still have no experimental structure data for many types of reactive carbocations. Comprehensive answers to the questions of the influence of substituents, counterions, disorder, and packing effects on the geometry and bond properties of carbocations require that more such structures be determined in the future.

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