# The Prop-2-yl Cation is Chiral

**Paul von Ragué Schleyer,*[a] Wolfram Koch,*[b,c] Bowen Liu,[c] and Ulrich Fleischer[d]**

[a] *Institut für Organische Chemie, Henkestr. 42, Universität Erlangen-Nürnberg, D-8520 Erlangen, Federal Republic of Germany*

[b] *IBM Heidelberg Scientific Center, Tiergartenstr. 15, D-6900 Heidelberg, Federal Republic of Germany*

[c] *IBM Almaden Research Center, San José, CA 95120-6099, U.S.A.*

[d] *Lehrstuhl für Theoretische Chemie, Ruhr-Universität Bochum, D-4630 Bochum, Federal Republic of Germany*

The prediction made by high level *ab initio* theory (MP4/6-311G**//MP2/6-311G** + ZPE) that the prop-2-yl cation prefers a twisted structure with $C_2$ symmetry is supported by the excellent and unique correspondence of the experimental and Individual Gauge for Localized molecular Orbitals (IGLO) calculated $^{13}C$ n.m.r. chemical shifts for that conformation.

Although carbocations tend to prefer geometries in which the cationic carbon and its three attached atoms lie in one plane, this plane need not be a plane of symmetry for the entire molecule. We now demonstrate that the simplest secondary carbocation, the prop-2-yl cation, prefers a chiral structure. The overall molecular symmetry of the lowest energy prop-2-yl cation conformation is $C_2$, with the methyl groups twisted in the same direction (**1**). This geometry, predicted by high level *ab initio* molecular orbital calculations[2] using large basis sets and including electron correlation effects (MP4/6-311G**),[3] is established by a comparison of the $^{13}C$ n.m.r. chemical shifts found experimentally in super acid media with those calculated for various conformations by the IGLO (Individual Gauge for Localized molecular Orbitals) method.[4]

Only two structures (Figure 1) for the prop-2-yl cation, both with $C_{2v}$ symmetry, (**2**) and (**3**), have been considered in prior computational investigations.[3,5] The latter structure, (**3**), is considerably more stable than structure (**2**) for reasons analysed by Cremer *et al.*[6] However, frequency analyses[3] at the MP2(full)/6-311G** level reveal both (**2**) and (**3**) have two negative eigenvalues in the force constant matrices. This means that these forms are chemically irrelevant higher order stationary points rather than viable structural candidates. The $C_2$ structure (**1**) is the only minimum found computationally among the prop-2-yl cation conformers. Indeed, (**1**) is the global minimum on the $C_3H_7^+$ energy surface.[7] The rotational transition structure (**4**) for conversion of chiral (**1**) into its enantiomer has $C_s$ symmetry with a mirror plane bisecting the methyl groups. However, (**4**) is not shown explicitly in Figure 1 as it resembles (**3**) very closely, and has nearly the same energy. While the rotational barrier is less than 4 kJ mol$^{-1}$, only (**1**) will have a significant population at low temperatures. A second $C_s$ prop-2-yl cation form, (**5**), with the three carbon atoms and the central hydrogen coplanar, is also a saddle point for methyl rotation, but is energetically less favourable than (**4**). The chirality of the prop-2-yl cation will have little consequence for experiments on a long time scale (*e.g.* solvolysis), but can be demonstrated convincingly by an analysis of experimental n.m.r. data in solution.

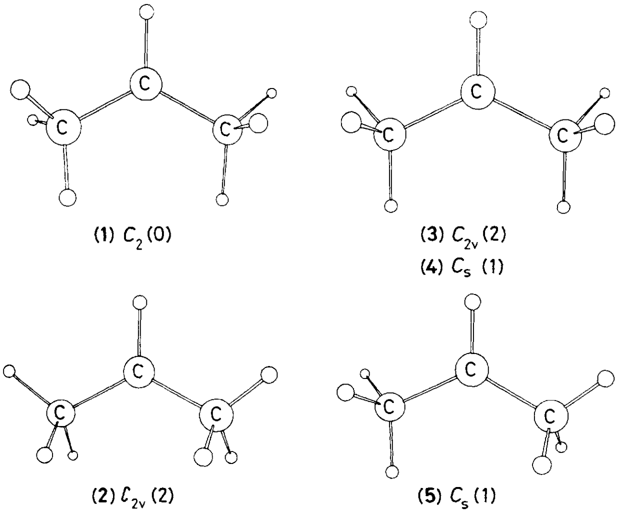
(1) $C_2$(0)
(3) $C_{2v}$(2)
(4) $C_s$ (1)
(2) $C_{2v}$(2)
(5) $C_s$(1)

**Figure 1.** Prop-2-yl cation MP2(FU)/6-311G**-optimized geometries. The number of imaginary frequencies computed at HF/6-31G* are given in parentheses. The MP4FC/6-311G** energies (with zero point corrections), relative to (**1**) in kJ mol$^{-1}$ are: (**2**), 15.9 (15.1); (**3**) 2.5 (1.3); (**4**) 2.3 (1.7); (**5**) 6.0 (5.4).

The method we are employing[8] is to compare the experimental $^{13}C$ n.m.r. chemical shifts for both the carbenium and the methyl carbons with those calculated by the IGLO method[4] for (**1**)—(**5**). The large differences for the five conformations predicted by IGLO is striking: only one form, (**1**) agrees with experiment (Table 1).

C–H Hyperconjugation is responsible both for the preferred conformation (**1**) and the large chemical shift differences between (**1**) and (**2**)—(**5**) revealed by IGLO. In order to understand the situation, consider the ethyl cation. At adquately high levels of theory, there is no classical minimum.[5] Instead, the methyl hydrogen aligned with the vacant orbital at C-1 moves to a symmetrically bridging position and the $C_{2v}$ form of $C_2H_5^+$ results. In the prop-2-yl cation of $C_2$ symmetry (**1**), single hydrogens on each of the two methyl groups are also aligned almost perfectly (within 1.4°) with the vacant orbital at C-2. While the hyperconjugative interaction is not as strong as in the ethyl cation, the two critical C–C–H angles in (**1**) are reduced to 92.7° and the C–H bonds are elongated to 1.121 Å.† This double partial hydrogen bridging in the isopropyl cation (**1**) results in enhanced delocalisation of the charge away from C-2, not only to these partially bridging hydrogens but also to the methyl carbons.

**Table 1.** IGLO (basis set II)[a] and experimental[b] $^{13}C$ chemical shifts (*vs* $CH_4$, p.p.m.) for prop-2-yl cation conformations (MP2FU/6-311G** geometries)

| Atom | expt[b] | (1) | (2) | (3) | (5) |
|---|---|---|---|---|---|
| *C*H | 323.9 | 324.6[c] | 340.9 | 356.2 | 346.4 |
| *C*$H_3$ | 53.8 | 44.5[c] | 42.7 | 38.2 | 40.3, 42.7 |

[a] Ref. 4. [b] Ref. 9: 2.3 p.p.m. was added to the $Me_4Si$ values. [c] The GIAO (Gauge Invariant Atomic Orbitals) method gives nearly identical values; P. Pulay, personal communication.

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† The MP2(full)/6-311G** bond lengths are: C–C 1.437; C–H 1.089, 1.092, and 1.121 Å. ∠CCC 125.2°.

As a consequence, the $^{13}C$ n.m.r. chemical shift for C-2 does not exhibit as high a degree of deshielding for **(1)** as is indicated by IGLO for the other conformations **(2)**—**(5)** in Table 1.

Such hyperconjugative distortions can be shown to be a general feature of carbocation structures.[10] When evaluated by these demanding n.m.r. chemical shift criteria, very few fully classical carbocations exist.

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