compounds raise the question of whether the Zr_6X_{12} unit can (or ever does) exist empty.

We do not think it likely that there is any atom occupying the Zr_6 cage in $Zr_6Cl_{12}(PMe_2Ph)_6$. The presence of C, N, or any heavier atom could scarcely escape our notice. The presence of Be or B seems unplausible for chemical reasons alone. Only H (or H_2) might be chemically possible and crystallographically acceptable.

The $Zr_6Cl_{12}(PMe_2Ph)_6$ molecule has a mean Zr–Zr distance of 3.223 (3) Å, and there are 12 electrons for Zr_6 cluster bonding. In the occupied cages mentioned above, there are generally 14 electrons and Zr–Zr distances of ca. 3.21 Å. The addition of two electrons would increase the Zr–Zr bond order only from 0.50 to 0.58 which does not seem inconsistent with the slight change in Zr–Zr distance.

Acknowledgment. We thank the National Science Foundation and the Robert A. Welch Foundation for support.

Supplementary Material Available: Tables of atomic positional and isotropic equivalent thermal parameters, anisotropic thermal parameters, and bond distances and bond angles for **1**, **2**, and **3** (28 pages). Ordering information is given on any current masthead page.

The ab Initio Energy Difference Favoring the Nonclassical over the Classical Structure of the Bicyclo[2.1.1]hexyl Cation. Comparison of Calculated (IGLO) and Experimental ^{13}C Chemical Shifts

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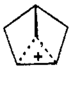
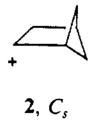
Despite the inherent investigational advantage that both nonclassical **1** and classical **2** forms possess C_s symmetry, the 2-bicyclo[2.1.1]hexyl cation[1] has received only a fraction of the attention[1-3] afforded its infamous homolog, the 2-norbornyl cation, **3**[4] (**4** is a hypothetical species).[5] Nevertheless, data pertinent to the structure (**1** vs **2**) of the bicyclohexyl cation are rather extensive, but there has been disagreement regarding the intepretation.[1-3,6-12] The problem is not a simple one. As all three methylene groups are equivalent on the NMR time scale at −110°, and no CMR line broadening is observed, the energy difference between **1** and **2** must be 3 kcal/mol or less.[6,7,9] The isotopic perturbation method clearly indicates that the stable ion has the bridged structure.[9] Kirmse's impressive recent double labeling experiments indicated that **1** should be about 3 kcal/mol more

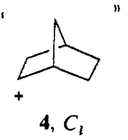


1, C_s



2, C_s

3, C_s



4, C_1

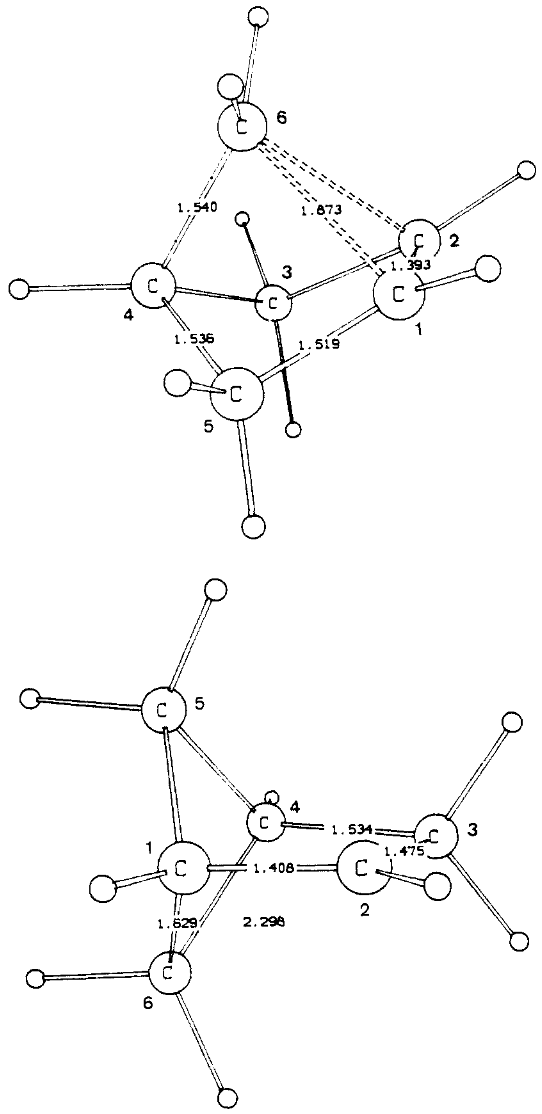


Figure 1. MP2(FULL)/6-31G* geometries of the bridged **1** (top) and classical **2** (botton) 2-bicyclo[2.1.1]hexyl cations. For bicyclo[2.1.1]hexane **5** at the same level, $r(C_1C_2)$ = 1.533, $r(C_1C_6)$ = 1.546, and $r(C_2C_3)$ = 1.557 Å.

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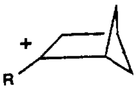
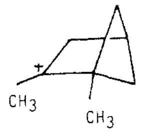
Table I. Comparison of Experimental and Calculated (IGLO)[a] ^{13}C NMR Chemical Shifts, ppm (vs TMS)

					
	classical			bridged	
ring positns	expt, R = CH_3[b] **6**	calcd, R = H[a] **2**	expt,[c] **7**	expt[b] **1**	calcd[a] **1**
1	81.6	80.6	*e*	*e*	158.5
2	322.0	334.2[d]	*e*	*e*	158.5
1, 2 av	201.8	207.4[d]	199.5	157.8	158.5
3	*e*	57.1	*e*	*e*	36.1
5	*e*	60.8	*e*	*e*	36.1
6	*e*	60.8	*e*	*e*	64.8
3, 5, 6 av	56.0	59.6	60.6	49.1	45.7
4	35.5	30.4	34.6	43.4	37.5

[a] IGLO method, DZ basis set on the MP2/6-31G* geometries (see ref 18). [b] Reference 7. [c] Reference 10. [d] These values would be lowered by methyl substitution, as in the experimentally examined systems. [e] Only average signals for these carbons are observed.

stable than **2** in nucleophilic media.[3]

Extensive calculational studies of carbocation potential energy surface have established the levels of theory needed for problems of this type.[5,13,14] Use of a CRAY XMP Computer and the GAUSSIAN 82 program[14] permitted MP2FULL/6-31G* (FULL = all electrons correlated) optimizations of **1** and **2**; 3-21G and 6-31G* optimizations were carried out as well. Frequency analysis at 6-31G* showed both **1** and **2** to be minima (no imaginary frequencies). MINDO/3 gives the same result, with a barrier of only 0.3 kcal/mol.[11] Whether or not this also is the case at the correlated levels (e.g., MP2) could not be established, but the potential energy surface between **1** and **2** evidently is quite flat.

The MP2FULL/6-31G* geometries (Figure 1) were then employed for MP3FC/6-31G* single point computations (by using the frozen core approximation, FC) on **1** (−232.92392 au) and **2** (−232.91673 au). As expected,[5,13,14] the relative stability of the bridged ion is underestimated at HF/3-21G and at HF/6-31G*, but the correlated MP2 and MP3 levels give quite similar results and favor **1** over **2** by 5.2 and 4.5 kcal/mol, respectively. After correction for the zero-point energy differences, the bridged form **1** is 4.0 kcal/mol more stable than the open isomer **2**. Kirmse's recent estimate of about 3 kcal/mol[3] is only slightly smaller, and Sorensen's results[10] also are in line. Theoretical estimates of the stabilization energy of the 2-norbornyl cation due to bridging (**3** vs **4**) are higher, in the 10–15 kcal/mol range, but are derived more arbitrarily.[5a] Stabilization energy estimates around 11 kcal/mol are obtained from gas-phase data.[16]

Experimental ^{13}C chemical shifts now provide a sensitive structure probe, since these values now can be calculated reliably for different structural models (e.g., **1** and **2**). The IGLO[17] results (DZ//MP2FULL/6-31G*) on **1** and **2** are compared with the experimental ^{13}C chemical shifts for the parent secondary **1** and two tertiary 2-methyl **6** and 1,2-dimethylbicyclo[2.1.1]hexyl **7** cations in Table I. As all three of the experimental systems are rapidly equilibrating at the temperatures investigated, only average signal positions of C(3), C(5), and C(6) are reported. C(1) and C(2) also either are identical (e.g., as in **1**) or averaged (e.g., as in **2**). IGLO clearly differentiates between these possibilities: For **1**, the experimental (157.8 ppm) and calculated (158.5 ppm) values are nearly identical but do not correspond to the IGLO chemical shift for **2** (207.4 ppm). However, the latter is in good agreement with the C(1)–C(2) average ^{13}C chemical shift found in **7**. For **6**, both C(1) and C(2) can be observed; note the close agreement between theory and experiment shown in Table I (also for C(4) and for the C(3), C(5), and C(6) averages).

Both on the basis of the calculated energies and the IGLO results, we conclude that the 2-bicyclo[2.1.1]hexyl cation prefers the symmetrically bridged **1** over the **2** structure. The energy difference, about 4 kcal/mol, appears to be lowered only slightly in solution (if at all), judging from Kirmse's 3 kcal/mol estimate[3] and that from the NMR line broadening experiments. This supports Kirmse's conclusion that "nucleophilic solvation does not appreciably effect the relative stabilities of bridged and open ions". The tertiary 2-methylbicyclo[2.1.1]hexyl cation **6** is classical and the 1,2-dimethyl analogue **7** equilibrates rapidly between two equivalent classical tertiary structures. These results calibrate and demonstrate the reliability of similar evidence[5,16] indicating the 2-norbornyl cation to be a *symmetrically* bridged species with a *single sharp* energy minimum.

7

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Photoactivable Fluorophores. 3. Synthesis and Photoactivation of Fluorogenic Difunctionalized Fluoresceins[1,2]

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The design and synthesis of new fluorescent probe molecules have been essential aspects in the continuing development and application of biophysical tracer methods.[3] In this paper we describe the synthesis and photoactivation of a new type of probe molecule, the photoactivable fluorophore (PAF), designed for tracer studies of molecular transport and diffusion in biological systems.

Photoactivable fluorophores are stable, nonfluorescent molecules with latent fluorescent characteristics that can be revealed by photoinduced processes.[4,5] Photoactivable fluorophores attached to biological macromolecules or other species of interest may be converted to ultimate fluorophores within a confined spatial region

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