Structures and Energies of Ions Derived from Bicyclo[1.1.1]pentane

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Abstract: The structures of bicyclo[1.1.1]pentane and of the following derivatives were calculated at the HF/6-31G* and MP2/6-31G* theoretical levels: the 1-cation, the anion, and the radical, the 1,3-dication, the radical cation, and the molecular dication. Comparison data also are provided for cyclopropane, cyclobutane, bicyclo[1.1.0]butane, and [1.1.1]propellane derivatives. Higher level calculations, carried out at the MP2/6-31G* geometries, indicate that the bicyclo[1.1.1]pentyl 1-cation is formed more easily from its parent hydrocarbon than the *tert*-butyl cation, in agreement with experimental observations. The calculated C–H bond dissociation energies of methane, cyclopropane, cyclobutane, bicyclobutane, and bicyclopentane were in good accord with the available data, and the same is true for the homolytic bond dissociation energies leading to the corresponding anions. The calculated ionization potentials of cyclopropane, cyclobutane, bicyclobutane, and [1.1.1]propellane, both adiabatic and vertical, were in very good accord with experiment. The charge distributions in some of the ions were studied using two different procedures, atoms in molecules and natural population analysis. The ^{13}C chemical shifts for the hydrocarbons and closed-shell ions were calculated using IGLO.

Introduction

Bicyclo[1.1.1]pentane (**1**) has the shortest known 1–3 nonbonded C–C distance (1.85 Å).[2-4] We have been interested in the nature of the 1–3 nonbonded interaction in **1**[5] because it has a number of chemically interesting consequences. Some time ago, we found that the long-range coupling constant between the bridgehead hydrogens was remarkably large, 18 Hz.[6] Subsequently, other large coupling constants between atoms attached to the bridgehead carbons have been observed: 71 Hz for H···F,[7] 30–60 Hz for H···P,[8,9] and 156–180 Hz for H···Sn.[8] A long-range interaction has been found with the bridgehead radical.[10] Calculations for the bridgehead cation also suggest a strong bridgehead–bridgehead interaction.[11]

In order to gain further information on the bridgehead–bridgehead interactions, we have carried out ab initio calculations for bicyclo[1.1.1]pentane (**1**) and a series of ions derived from **1** that include the 1-cation (**2**), the 1,3-dication (**3**), the radical cation (**4**), and the hydrocarbon dication (**5**). The 1-cation has been studied previously, but only at lower levels of theory.[11] For a comparison with the cationic species, the bridgehead radical (**6**) and anion (**7**) also were studied. The latter was of interest because the large bridgehead ^{13}C–H NMR coupling constant (164 Hz)[6] anticipated the observation of enhanced acidity in the gas phase.[12] The optimizations were carried out at the RHF/6-31G* or UHF/6-31G* level as appropriate. The energies are summarized in Table I. It is known that the structures and relative energies of cationic species are often affected by correction for electron correlation. Therefore the geometries also were calculated at the MP2/6-31G* level of theory, which is known to generally give very satisfactory structures.[13] These data are given in Figure 1. The effect of higher level corrections for electron correlation was examined by obtaining MP3 and MP4(SDTQ)/6-31G* energies at the MP2/6-31G* geometries. Finally, in order to evaluate the effect of increasing the flexibility of the basis set, MP3/6-311G* energies were obtained at the MP2/6-31G* geometries. The use of a triple-ζ basis set for the valence electrons should significantly improve the relative energies. MP3/6-31+G*, which includes diffuse functions at carbon, was used with the anions so that the lone-pair electrons would be better represented.[13,14]

Structure of Bicyclo[1.1.1]pentane

Two electron diffraction studies[2,3] have been reported for bicyclo[1.1.1]pentane, leading to significantly different structural parameters (Table II). A microwave study also is available for the 1-chloro derivative,[4] but it is flawed by the necessity of assumptions about the methylene group geometry. The MP2/6-31G*-optimized geometry of **1** is compared with the experimental data in Table II. There is an excellent agreement between the calculated geometry and the results of the more recent electron diffraction study. The latter also is in better agreement with the rotational constants derived from the rotational components of the infrared spectrum of bicyclo[1.1.1]pentane.[15]

We were interested in comparing bicyclo[1.1.1]pentane (**1**) with some related carbocyclic systems. Therefore, the structures of cyclopropane, cyclobutane, bicyclo[1.1.0]butane, and [1.1.1]propellane also were obtained at the MP2/6-31G* theoretical level. Again the calculated geometries were in good agreement with the available experimental data (Table III).

Bridgehead Cations

1-Chlorobicyclo[1.1.1]pentane has been found to solvolyze more rapidly than *tert*-butyl chloride[16] despite the usual observations of markedly reduced reactivity of bridgehead halides.[17] Such high S_N1 reactivity also has been found with 1-bromobicyclo[1.1.1]pentane[18] and was originally thought to be derived from

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Table I. Calculated Energies (H)

species	HF/6-31G* //HF/6-31G*	MP2/6-31G* //MP2/6-31G*	MP3(fc)/6-31G* //MP2/6-31G*	MP4(fc)/6-31G* //MP2/6-31G*	MP3(fc)/6-311G** //MP2/6-31G*	MP3(fc)/6-31+G* //MP2/6-31G*
bicyclo[1.1.1]pentane (**1**)	−193.905 68	−194.582 33	−194.593 30	−194.627 56	−194.661 78	−194.600 51
1-cation (**2**)	−193.042 41	−193.702 07	−193.708 07	−193.743 84	−193.768 07	
1,3-dication (**3**)	−191.737 27	−192.342 35	−192.356 92	−192.393 25	192.413 06	
1-anion (**7**)	−193.201 64	−193.887 88	−193.895 59	−193.933 57		−193.929 01
1-radical (**6**)	−193.263 78	−193.917 35	−193.928 14	−193.962 07	−193.995 56	
(projected)		−193.918 58	−193.928 88	−193.962 81		
radical cation (**4**)	−193.558 21	−194.231 82	−194.238 96	−194.274 76	−194.302 06	
(projected)		−194.235 97	−194.241 25	−194.277 05		
(vertical)		−194.197 25	−194.204 35	−194.240 71	−194.268 17	
(vertical, proj)		−194.200 56	−194.206 04	−194.242 40		
dication (**5**)	−193.000 02	−193.687 19	−193.687 33	−193.726 15	−193.746 72	
cyclopropane	−117.058 87	−117.462 83	−117.476 83	−117.494 77	−117.519 36	−117.482 82
anion	−116.349 75	−116.758 47	−116.769 94	−116.790 09		−116.802 78
radical	−116.415 54	−116.791 97	−116.804 82	−116.822 09	−116.847 54	
(projected)		−116.793 58	−116.805 93	−116.823 20		
radical cation	−116.742 56	−117.109 31	−117.127 95	−117.144 63	−117.166 23	
(projected)		−117.110 61	−117.128 65	−117.145 33		
(vertical)		−117.092 07	−117.109 18	−117.108 41	−117.128 35	
(vertical, proj)		−117.075 97	−117.092 74	−117.110 18		
cyclobutane	−156.097 03	−156.637 06	−156.655 84	−156.680 53	−156.713 26	
cation	−155.223 81	−155.747 66	−155.760 30	−155.786 47	−155.810 46	
radical	−155.467 26	−155.978 36	−155.998 32	−156.021 63	−156.054 02	
(projected)		−155.980 86	−155.999 77	−156.023 07		
bicyclo[1.1.0]butane	−154.871 77	−155.409 48	−155.417 70	−155.443 81	−155.470 60	−155.425 46
1-anion	−154.190 68	−154.735 79	−154.740 77	−154.769 88		−154.774 65
1-radical	−154.218 82	−154.723 55	−154.730 62	−154.760 62	−154.784 88	
(projected)		−154.725 40	−154.731 77	−154.761 76		
radical cation	−154.601 84	−155.097 60	−155.112 46	−155.137 82	−155.159 53	
(projected)		−155.103 26	−155.116 11	−155.141 47		
(vertical)		−155.077 67	−155.091 72	−155.116 90	−155.138 36	
(vertical, proj)		−155.082 46	−155.094 71	−155.119 89		
[1.1.1]propellane	−192.691 06	−193.374 71	−193.370 43	−193.410 89	−193.435 53	
radical cation	−192.397 81	−193.022 08	−193.031 78	−193.066 07	−193.089 61	
(projected)		−193.030 93	−193.037 24	−193.071 53		
(vertical)		−193.018 83	−193.028 57	−193.062 62	−193.086 40	
(vertical, proj)		−193.027 55	−193.033 94	−193.067 99		
isobutane	−157.298 98	−157.847 77	−157.873 35	−157.897 84	−157.934 56	
tert-butyl cation	−156.442 41	−156.959 54	−156.984 92	−157.009 29	−157.038 65	
tert-butyl radical	−156.675 01	−157.195 79	−157.222 29	−157.245 45	−157.281 57	
(projected)		−157.197 97	−157.223 57	−157.246 73		
methane	−40.195 17	−40.337 04	−40.348 62	−40.354 79	−40.365 96	−40.350 15
methyl cation	−39.230 64	−39.329 44	−39.341 93	−34.346 18	−39.354 52	
methide ion	−39.466 84	−39.607 01	−39.617 31	−39.624 31	−39.657 36	−39.662 01
methyl radical	−39.558 99	−39.673 03	−39.684 63	−39.689 36	−39.701 32	
(projected)		−39.675 04	−39.685 84	−39.690 56		
hydrogen atom	−0.498 23	−0.498 23	−0.498 23	−0.498 23	−0.499 81	
hydride ion	−0.422 44	−0.428 91	−0.430 67	−0.431 17	−0.479 41	−0.430 67

Table II. Structure of Bicyclo[1.1.1]pentane (**1**)

parameter	ED(1)[a]	ED(2)[b]	MP2/6-31G*[c]
R(C–C), Å	1.545 (6)	1.557 (2)	1.552
R(C–H), Å	1.100 (10)	1.097 (16)	1.090
∠CCC, deg	73.3 (10)	74.2 (2)	74.5
∠HCH, deg	103.9 (50)	111.2	112.0

[a] Reference 2. [b] Reference 3. [c] This work.

strain relief in a ring opening which accompanied ionization.[16] However, in view of the recent demonstrations that the solvolysis of the cyclobutyl derivative proceeds via bicyclobutonium ion intermediates,[19] along with the previous calculations for **2** which suggest a delocalized electronic structure,[11] it now appears likely that the high reactivity is another manifestation of the strong interaction between the bridgehead carbons.

The HF/6-31G*-calculated structure of the bridgehead cation (**2**) was remarkably different from that of **1**.[11d] The 1–3 nonbonded distance was found to decrease to 1.537 Å, close to that of a normal C–C bond. Reoptimization at MP2/6-31G* reduced the bridgehead–bridgehead distance further to 1.525 Å, which is not surprising since electron correlation is known to generally favor delocalized structures.[13,20] The structure resembles that of [1.1.1]propellane and might best be described as a proton attached to the nonbonded charge distribution at one of the bridgehead carbons of the propellane.[21] The vibrational frequencies of **2** at MP2/6-31G* revealed one degenerate imaginary mode (325*i* cm^{-1})[22] corresponding to C3 and its hydrogen moving perpendicular to the original C_{3v} axis. This would lead to ring opening to the bicyclo[1.1.0]butyl-1-carbinyl cation,[23] which ultimately gives the observed 3-methylenecyclobutyl products.[24]

The energy of **2** can best be compared with that of the *tert*-butyl cation by using a homodesmotic reaction which tends to cancel errors.[25] Even though **2** is a transition state and the *tert*-butyl

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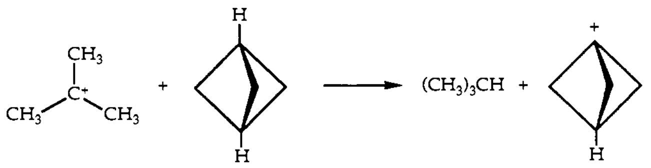
Table III. Calculated Structures of Hydrocarbons[a]

compound	unit	HF/ 6-31G*	MP2/ 6-31G*	obs[b]
cyclopropane	*R*(C–C)	1.497	1.502	1.514 ± 0.002
	R(C–H)	1.076	1.084	1.082 ± 0.003
	∠HCH	114.0	114.2	116.5
cyclobutane	*R*(C–C)	1.549	1.543	1.548 ± 0.003
	R(C–H)	1.085	1.094	1.092 (av)
	∠CCC	89.01	87.90	~87.2
	∠CCH_e	117.08	118.45	
	∠CCH_a	112.30	110.97	
	∠HCH	108.18	108.75	
	α^c	14.96	30.8	~25
bicyclo[1.1.0]-butane	*R*(C1–C2)	1.488	1.492	1.489 ± 0.004
	R(C1–C3)	1.467	1.496	1.497 ± 0.003
	R(C1–H)	1.070	1.080	1.071 ± 0.004
	R(C2–H_e)	1.078	1.088	1.093 ± 0.008
	R(C2–H_a)	1.082	1.092	1.093 ± 0.008
	∠C1C2C3	58.90	60.16	59.96
	∠C3C1H	132.51	128.14	128.4 ± 0.2
	∠C1C2He	117.10	116.94	
	∠C1C2Ha	119.50	119.23	
	∠HC2H	113.98	114.08	115.57
	α^c	120.9	122.4	122.7 ± 0.5
[1.1.1]-propellane	*R*(C1–C2)	1.544	1.592	1.596 ± 0.005
	R(C1–C3)	1.503	1.514	1.525 ± 0.002
	R(C–H)	1.076	1.088	1.106 ± 0.005
	∠HCH	114.6	114.9	116.0 ± 1.9

[a] Angles in degrees; bond lengths in angstroms. [b] Cyclopropane: Jones, W. J.; Stoicheff, B. P. *Can. J. Phys.* **1964**, *42*, 2259. Cyclobutane: Almennigen, A.; Bastiansen, O.; Skanke, P. N. *Acta Chem. Scand.* **1961**, *15*, 711. Bicyclobutane: Cox, K. W.; Harmony, M. D.; Nelson, G.; Wiberg, K. B. *J. Am. Chem. Soc.* **1968**, *90*, 3395. [1.1.1]Propellane: Hedberg, L.; Hedberg, K. *J. Am. Chem. Soc.* **1985**, *107*, 7257. [c] Ring-puckering angle.

cation is an intermediate, their rates of formation should largely be controlled by their relative energies.



The data for isobutane and the *tert*-butyl cation are included in Table I, and the estimated energy changes are summarized in Table IV. The reaction is calculated to be endothermic at the HF level but is found to be exothermic at all correlated levels. The increased stabilization of the bridged ion is expected when correction is made for electron correlation.[13,20] The results indicate that **2** has slightly greater (~2 kcal/mol) stabilization than the *tert*-butyl cation and are in very good agreement with the experimental observations on the relative rates of solvolysis.

As a check, the energy change for the corresponding reaction for cyclobutane was calculated, giving the data summarized in Table IV. The cyclobutyl cation is now well established to have a nonclassical bicyclobutonium ion structure.[19] Here, the reaction was found to be endothermic at all theoretical levels. Again, there was a considerable difference between the HF result and those obtained by including electron correlation. The ion was found to be destabilized with respect to the *tert*-butyl ion by about 4 kcal/mol. The results are in good accord with experiment, where it is known that cyclobutyl derivatives are significantly less reactive than the corresponding *tert*-butyl derivatives.[26]

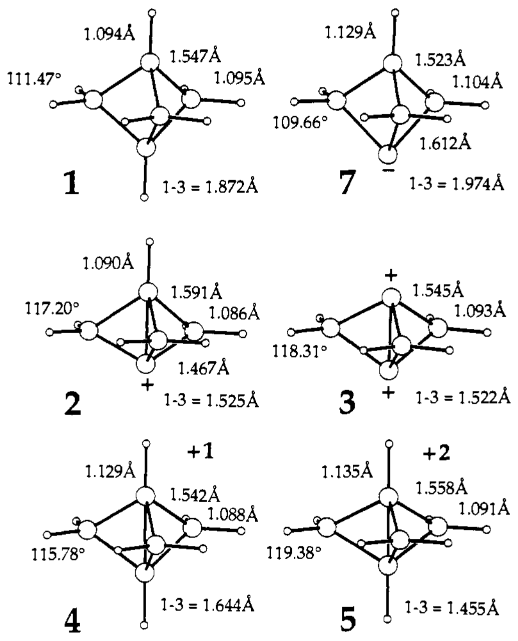


Figure 1. MP2/6-31G*-calculated structures of bicyclo[1.1.1]pentane and of the ions derived from it.

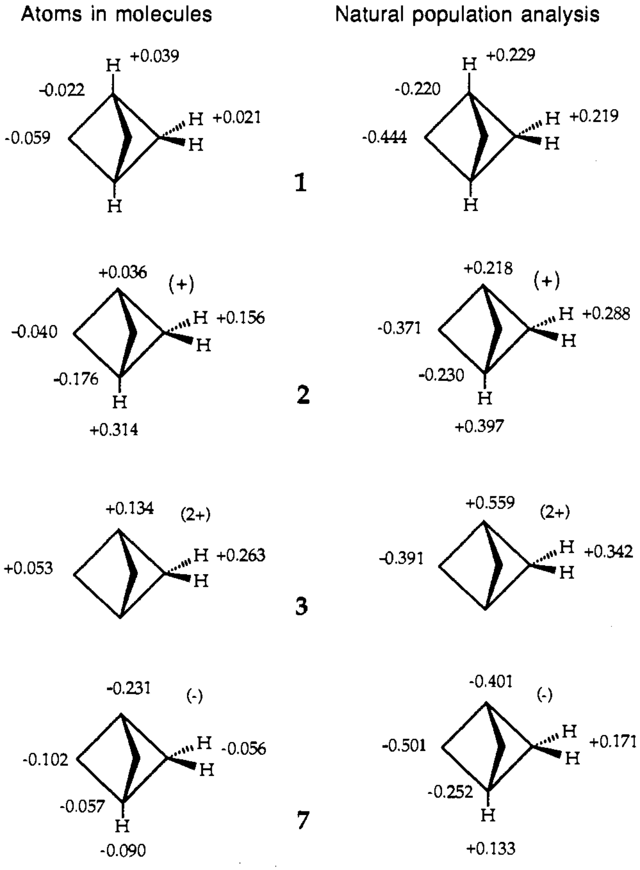


Figure 2. Atomic charges derived from the calculated electron populations using two different procedures: atoms in molecules and natural population analysis. The atoms in molecules populations were derived from MP2/6-31G* wave functions, and the natural populations were derived from MP4/6-31G* wave functions.

Table IV. Isodesmotic Reactions with the *tert*-Butyl Cation and Isobutane[a,b]

cation	HF/6-31G*	MP2/6-31G*	MP3/6-31G*	MP4/6-31G*	MP3/6-311G*
bicyclo[1.1.1]pentyl	4.2	−5.0	−2.0	−3.0	−1.4
cyclobutyl	10.4	0.7	4.5	3.5	4.3

[a] $R\text{-}H + t\text{-}C_4H_9^+ \rightarrow R^+ + i\text{-}C_4H_{10}$. [b] The HF calculations were carried out with the HF/6-31G*-optimized geometries, and the MP calculations were carried out using the MP2/6-31G*-optimized geometries.

Table V. Electron Populations and Atom Energies for Bicyclo[1.1.1]pentane and Its Ions (MP2/6-31G*)

species	atom	*n*[a]	*L*[b]	*E*[c]
bicyclo[1.1.1]pentane (**1**)	C1	6.0216	0.0025	−37.9410
	H	0.9615	0.0001	−0.5909
	C2	6.0570	−0.0046	−37.9703
	H	0.9791	0.0001	−0.6012
	sum	37.9992		−194.5819
bicyclopentyl 1-cation (**2**)	C1	5.9637	−0.0007	−38.0206
	C2	6.0396	−0.0016	−37.9756
	H	0.8440	0.0001	−0.5461
	C3	6.1756	0.0018	−38.0232
	H	0.6859	0.0001	−0.4579
	sum	36.0080		−193.7051
bicyclopentyl 1,3-dication (**3**)	C1	5.8662	−0.0008	−37.8402
	C2	5.9468	0.0000	−37.8960
	H	0.7375	0.0001	−0.4951
	sum	33.9978		−192.3390
bicyclopentyl 1-anion (**7**)	C1	6.2307	−0.0029	−37.7580
	C2	6.1022	−0.0029	−37.9499
	H	1.0563	0.0001	−0.6255
	C3	6.0568	−0.0028	37.9224
	H	1.0895	0.0001	−0.6226
	sum	38.0214		−193.9057
cyclobutane	C	6.0391	0.0011	−37.9520
	H	0.9806	0.0001	−0.6031
	H	0.9793	0.0001	−0.6043
	sum	31.9960		−156.6376
cyclobutyl cation	C1	6.0018	0.0010	−38.0370
	H	0.8165	0.0001	−0.5394
	C2	6.0505[d]		
	H	0.8301	0.0001	−0.5407
	H	0.8395	0.0001	−0.5467
	C3	6.1584	0.0020	−37.9868
	H	0.8163	0.0001	−0.5355
	H	0.7669	0.0001	−0.5129
	sum	30.0000		

[a] Electron population. [b] Integral of $-(h/4m)\nabla^2\rho$, which would be zero if the integration for the kinetic energy were exact. [c] Atom energy, given by the negative of the calculated kinetic energy, corrected for the small virial defect in the MP2 calculation. [d] It was not possible to obtain a satisfactory integration for this carbon, and the value was obtained by difference.

What is the nature of bonding in these compounds, and where does the positive charge reside in the cations? There are two basically different approaches to the calculation of atomic charges. In the first, electron populations are derived by an analysis of orbital contributions, partitioning the overlap component in some fashion between the two centers involved. The two major problems with this approach are (1) the orbitals have components in other than the bonding direction and some part of a given orbital may actually "belong" to a different atom, and (2) it is difficult to obtain an appropriate way of partitioning the part in the overlap region. An early approach of this type is the Mulliken population analysis,[27] and a more modern and considerably improved procedure is the natural population analysis of Weinhold and Reed.[28] The second makes use of an analysis of the charge density, which has the advantage of eliminating the assignment of orbitals to specific atoms. The major problem here is determining the appropriate volume elements to be assigned to atoms. Hirshfeld[29] has developed one of the earlier approaches of this type, and more recently a procedure has been developed by Bader[30] in his theory of atoms in molecules, which allows the atoms to be defined in a fashion that may be derived from first principles. The present compounds would be expected to have a wide distribution of atomic charges and appeared to provide a good opportunity to compare the charges assigned by the more modern versions of the two basic approaches.

Making use of the theory of atoms in molecules, surfaces are first located which uniquely separate two atoms forming a bond. The set of these surfaces served to separate a molecule into atomic domains. Integration of the charge density over a domain gives the electron population, and other properties, such as the kinetic energy, may also be derived by integration of the appropriate function of the charge density.

Along the 1–3 nonbonded axis of **1** there is a cage critical point, being a minimum in charge density in all directions. The value of ρ at the critical point is 0.0983 e/B^3. The 1-cation (**2**) has a bond critical point along the C1–C3 axis with ρ = 0.177 e/B^3, indicating that a bond has indeed been formed. We have integrated the charge density to give the electron populations for the atoms in **1** and **2**, and they are summarized in Table V. The atomic charges thus derived are summarized in Figure 2.

The considerable charge transfer to the other bridgehead substituent in **2** is in good accord with the observation that 1,3-diiodobicyclo[1.1.1]pentane is relatively unreactive.[8,31] The iodine would reduce the ability of the center to participate in bonding with C1. The same effect was observed in our study of the 3-substituted cyclobutyl tosylates, where it was found that a chlorine substituent prevented the normal S_N1 reaction and that it gave only a much slower S_N2 reaction with inversion of configuration.[32] The large amount of charge transfer from the methylene hydrogens also is of interest.

The atomic charges derived from natural population analysis also are shown in Figure 2. A major difference between the results of the two population analyses can be seen with bicyclo[1.1.1]pentane itself. The atoms in molecules approach leads to small charges at carbon and hydrogen, in good accord with the general idea that the electronegativities of carbon and hydrogen are quite similar. On the other hand, the natural population analysis leads to larger charges, e.g. −0.444 at the methylene carbon and +0.219 at the methylene hydrogens. But the trends are the same for the two methods of calculating electron populations and lead to the same conclusions concerning the changes in charge on going from the hydrocarbon to the mono- and dications.

A calculation for the dication **3** gave a slightly longer central bond, 1.561 Å, still much smaller than that in **1**. The inclusion of electron correlation further reduced the distance to 1.522 Å. While the MP3/6-311G* energies give the second ionization step as 288 kcal/mol greater than the first, the structure of **3** does not reflect a strong 1–3 repulsive interaction.

Bridgehead Anion

The calculations suggest that the formation of the 1-bicyclo[1.1.1]pentyl anion leads to increased 1–3 nonbonded repulsion because the distance lengthens to 1.970 Å. As noted above, an increased acidity of the bridgehead hydrogens of **1** is expected, since they have a rather large ^{13}C–H coupling constant (164 Hz),[6] suggesting relatively high s-character in the C–H bond. A comparison with cyclopropane, which has enhanced acidity,[33] and with bicyclo[1.1.0]butane, which forms a very stable anion in the gas phase,[34] also was of interest. Again, homodesmotic reactions provide useful comparions:

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(26) Raber, D. J.; Harris, J. M.; Hall, R. E.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1971**, *93*, 4821.

(27) Mulliken, R. S. *J. Chem. Phys.* **1962**, *36*, 3428. Cf.: Mulliken, R. S.; Politzer, P. *J. Chem. Phys.* **1971**, *55*, 5135.

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(29) Hirshfeld, F. L. *Theor. Chim. Acta* **1977**, *49*, 129. Cf.: Ritchie, J. P *J. Am. Chem. Soc.* **1985**, *107*, 1829.

(30) Bader, R. F. W. *Acc. Chem. Res.* **1985**, *18*, 9. Bader, R. F. W. *Atoms in Molecules: A Quantum Theory*; Oxford University Press: Oxford, U.K., 1990.

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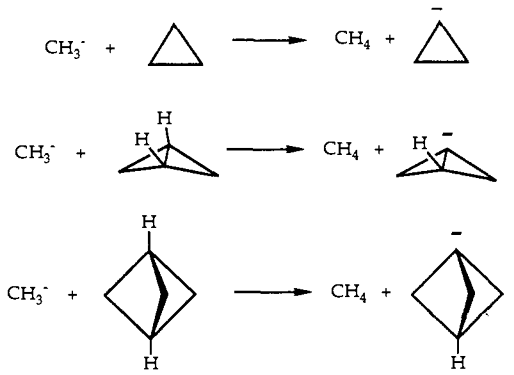
(34) Kass, S. R.; Chou, P. K. *J. Am. Chem Soc.* **1988**, *110*, 7899.



The calculated energy changes are summarized in Table VI.

The calculated relative energies depend on electron correlation, but with the 6-31G* basis set, the level of correlation correction had little effect. The use of a larger basis set including diffuse functions and the MP3 correction led to significant changes in the calculated reaction energies. It is well recognized that diffuse functions are required for the proper description of anions,[13,14] and this effect can easily be seen in the data for methane and methide ion in Table I. The MP3/6-311G* energy is lower than that at MP3/6-31+G* for methane whereas the reverse is true for the anion. The difference in deprotonation energies for methane and cyclopropane calculated using MP3/6-31+G* is close to the experimental value (see Table VI). We believe that the MP3/6-31+G* relative energies are reasonably accurate whereas the available carbanion experimental data have large error bars.[12]

In the case of bicyclo[1.1.0]butane, the reaction with methide ion is estimated to be exothermic by 23 kcal/mol. This is in accord with the observations that a bridgehead proton may be removed by reagents such as phenyllithium[35] and with the large ^{13}C–H NMR coupling constant (205 Hz).[36] The acidity of bicyclobutane has recently been measured in the gas phase, and from this datum, the reaction with methide ion is exothermic by −19 ± 3 kcal/mol.[33] Our estimate is in good agreement with this result.

Bicyclo[1.1.1]pentane should be less acidic than bicyclobutane, as judged by the ^{13}C–H coupling constant of **1** (164 Hz).[6] The reaction of **1** with methide ion was estimated to be 13 kcal/mol less exothermic than that of bicyclobutane, in very good agreement with the experimental results.[12]

Ionization Potentials

Photoelectron spectroscopy has proven to be a very useful tool in studying organic compounds.[37] The ionization potentials are usually discussed in terms of Koopmans' theorem,[38] which relates the ionization potentials approximately to the molecular orbital energy levels. However, this does not give much detailed information about the radical cation state which is formed in the process. Therefore, a direct study of the radical cations is useful.

The geometrical changes observed with the bridgehead cation also are found in the radical cation formed by loss of an electron from **1** to give **4** (Figure 1). The 1–3 distance in **4** is quite short (1.643 Å). Furthermore, the calculated central bond length decreased to 1.453 Å in the dication (**5**) formed by removing two electrons from **1**! This leads to a C–C–C bond angle at the methylene group of 56°. However, the dication (**5**) had degenerate imaginary frequencies and is not expected to be an observable species.

The ionization potential of **1** does not appear to have been determined, and therefore the IP's of some related compounds were calculated in order to see how well they may be estimated.

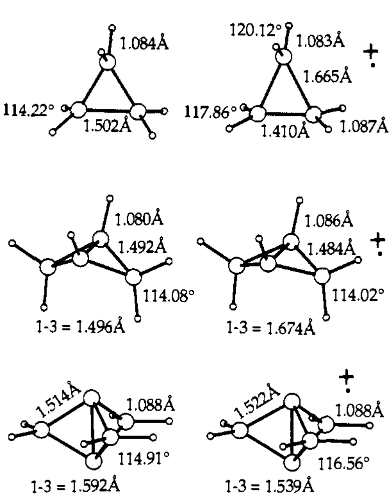


Figure 3. MP2/6-31G*-calculated structures for hydrocarbons (left) and their radical cations (right).

The compounds were cyclopropane, bicyclo[1.1.0]butane, and [1.1.1]propellane (Figure 3), all of which have been studied via photoelectron spectroscopy.[39] The structures of the radical cations were first obtained at the UHF/6-31G* level, and then geometry optimization was carried out at the UMP2/6-31G* level. In all cases, spin contamination was small and was eliminated by projecting out the contamination. In the case of the UMP energies derived using the 6-31G* basis set, the energies obtained both before and after projecting out the spin contamination are given.

The structures of the radical cations are compared with those of the parent hydrocarbons in Figure 3. The highest occupied MO's of bicyclobutane and of the propellane were nondegenerate, and the symmetries of both radical cations were reasonably assumed to be the same as those of the hydrocarbons. With bicyclobutane,[40] the expected lengthening of the central C–C bond on removal of an electron was found, but with propellane, the central bond was calculated to be shorter in the radical cation than in the parent. In the case of cyclopropane, the highest occupied MO is degenerate, and the radical cation was assumed to have a lower symmetry because of Jahn–Teller distortion.[41] Here, two of the C—C bonds lengthened considerably, and the third shortened to a value similar to that of a C═C bond. The structure resembles a CH_2^+ unit coordinated with a double bond and is similar to that of a corner-protonated cyclopropane.[42]

The MP4/6-31G* and MP3/6-311G* energies were obtained both at the MP2/6-31G* geometries, giving the adiabatic ionization potential, and at the MP2/6-31G* geometries of the parent hydrocarbons, giving the vertical ionization potentials. The calculated ionization potentials are compared with the experimental values in Table VII. It can be seen that the agreement is fairly good. Of more importance, it is known that the vertical and adiabatic ionization potentials for [1.1.1]propellane are unusually close,[39c] whreas a more normal difference is found for bicyclobutane. Cyclopropane gives a large difference due to Jahn–Teller distortion in the radical cation. These differences are reproduced by the calculations. The predicted ionization potentials for bicyclo[1.1.1]pentane are 9.8 eV (adiabatic) and 10.7 eV(vertical).

Since we are able to reproduce the experimental ionization potentials, the wave functions should lead to a good description of the charge density distribution. The latter has been calculated

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(36) Christl, M. *Chem. Ber.* **1975**, *108*, 2781.

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(38) Koopmans, T. A. *Physica* **1983**, *1*, 104.

(39) (a) Cyclopropane: Basch, H.; Robin, M. B.; Kuebler, N. A.; Baker, C.; Turner, D. W. *J. Chem. Phys.* **1969**, *51*, 52. (b) Bicyclobutane: Bombach, R.; Dannacher, J.; Stadelmann, J.-P.; Neier, R. *Helv. Chim. Acta* **1983**, *66*, 701. (c) [1.1.1]Propellane: Honegger, E.; Huber, H.; Heilbronner, E.; Dailey, W. P.; Wiberg, K. B. *J. Am. Chem. Soc.* **1985**, *107*, 7172.

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Table VI. Energy Changes in Reaction with the Methide Ion (kcal/mol)

compound	6-31G*	MP2/6-31G*	MP3/6-31G*	MP4/6-31G*	MP3/6-31+G*	expt
cyclopropane	−12.1	−16.1	−15.3	−16.2	−5.1[a]	−10 ± 7.5[b]
bicyclobutane	−29.6	−35.4	−34.1	−35.5	−23.4	−19.3 ± 3[c]
bicyclopentane	−15.2	−22.3	−21.1	−22.9	−10.4	−7 ± 7[d]

[a] The MP2/6-31+G*//6-31G* value is −4.0 kcal/mol (Schleyer, P. v. R.; Spitznagel, G. W.; Chandrasekhar, J. *Tetrahedron Lett.* **1986**, *27*, 4411). [b] Reference 32. [c] Reference 33. [d] Reference 12.

Table VII. Ionization Potentials (eV)

	calc IP[a]				
	MP4/ 6-31G*		MP3/ 6-311G*		obs[b]
compound	adiab	vert	adiab	vert	vert
cyclopropane	9.48	10.43	9.58	10.60	10.6
bicyclo[1.1.0]butane	8.20	8.78	8.44	9.01	9.1
[1.1.1]propellane	9.20	9.30	9.38	9.47	9.7
bicyclo[1.1.1]pentane	9.51	10.45	9.76	10.67	

[a] The MP4 ionization potentials are corrected for spin contamination in the radical cation, and the MP3 ionization potentials are not corrected. The correction would reduce the MP3 ionization potentials by about 0.05 eV. [b] Reference 38.

from the MP2/6-31G* wave functions for the hydrocarbons and the ions formed in the vertical excitation. Three-dimensional charge density difference plots were calculated for the 0.01 e/au^3 level and are shown in Figure 4. The solid contours show regions of charge concentration in the radical cation whereas the dashed contours show regions of charge depletion.

The vertical radical cation of cyclopropane has a concentration of charge between C1 and C2 but a decrease in the C1–C3 and C2–C3 bonds. There are a significant charge increase near the carbon nuclei and charge withdrawal from the hydrogens and the C–H bonds. Thus, the vertical radical cation is on its way toward a CH_2^+ group interacting with an ethylene unit.

The radical cation from bicyclobutane shows a significant charge depletion in the bent bond joining the bridgehead carbon atoms. This should lead to a weakening of the central bond and an increase in its length along with an increase in the angle between the two cyclopropane rings in the adiabatic ion. These changes are observed. As in the case of cyclopropane, there is charge accumulation near all of the carbon nuclei at the expense of the hydrogens and the back lobes of the bridgehead bent bond.

The radical cation from bicyclo[1.1.1]pentane shows charge concentration near the carbon nuclei and a diffuse accumulation in the internuclear region between the bridgehead carbons. In addition, there is a significant depletion of charge in the bridgehead C–H bonds. The changes suggest that there should be a decrease in the bridgehead C1–C3 distance on going to the adiabatic radical cation, and this is found.

The charge density difference plot for [1.1.1]propellane is quite similar to that for bicyclo[1.1.1]pentane. Charge is accumulated near the carbon nuclei, mainly at the expense of the bridgehead nonbonded charge concentration. The effect on the methylene groups is smaller than that for bicyclopentane. However, the propellane radical cation does not have much of a change in charge between the bridgehead carbons as compared to the propellane. The small changes that occur in this region lead to the small geometry change found on going to the adiabatic cation.

Most of the charge depletion on going to the radical cations may be attributed to the HOMO, and for these systems they involve the bent bonds and some C–H bonds. The geometrical distortions that occur on going to the adiabatic ions are easily related to the changes in charge density.

Bridgehead Radical

The bicyclo[1.1.1]pentyl bridgehead radical (**6**), derived from **1**, has been observed experimentally and has been found to exhibit a large cross-ring interaction.[10] Such interactions (which can lead to substantial hyperfine coupling) have even been observed with the 1-norbornyl and 1-bicyclo[2.2.2]octyl radicals, in which the cross-ring distances are much larger.[43] The radical **6** has been studied theoretically by several groups.[44–46] Feller and Davidson[46] found the first bridgehead C–H bond dissociation energy to be 106 kcal/mol and the second to be 46 kcal/mol (i.e., forming [1.1.1]propellane), leading to a bridgehead–bridgehead bond energy of 60 kcal/mol in the propellane. This is in very good agreement with the bond energy estimated in other ways.[47]

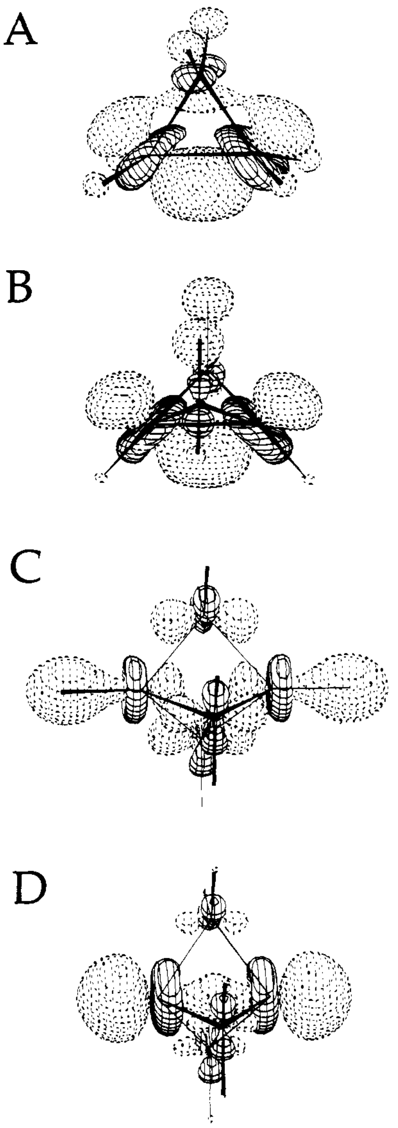

Figure 4. Charge density differences on going from the hydrocarbons to their vertical radical cations. The 0.01 e/au^3 contours are shown. The compounds are as follows: A, cyclopropane; B, bicyclo[1.1.0]butane; C, bicyclo[1.1.1]pentane; D, [1.1.1]propellane.

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[46] Feller, D.; Davidson, E. R. *J. Am. Chem. Soc.* **1987**, *109*, 4133.

[47] Wiberg, K. B.; Dailey, W. P.; Walker, F. H.; Waddell, S. T.; Crocker, L. S.; Newton, M. *J. Am. Chem. Soc.* **1985**, *107*, 7247.

Table VIII. Calculated Bond Dissociation Energies (kcal/mol)[a]

compound	HF 6-31G*	MP2 6-31G*	MP3 6-31G*	MP4 6-31G*	rel BDE	MP3 6-311G*	rel BDE	expt rel BDE[b]
cyclopropyl-H	91.1	107.3	108.4	108.8	+4.6	107.9	+4.5	+1
cyclobutyl-H	82.5	99.1	99.0	99.9	−4.3	100.0	−3.4	−7
1-bicyclo[1.1.0]butyl-H	97.1	116.6	117.8	115.3	+11.3	116.7	+12.3	na
1-bicyclo[1.1.1]pentyl-H	90.2	103.9	104.3	104.6	+0.4	104.4	+1.0	na
methyl-H	86.6	102.8	103.3	104.2	0.0	103.4	0.0	0
tert-butyl-H	78.9	95.1	95.1	95.9	−8.3	96.1	−7.3	−9

[a] The BDE's for the UMP/6-31G* calculations were obtained using energies obtained after spin contamination was projected out. In the case of the UMP3/6-311G* calculations, spin contamination was not projected out. The estimated change in BDE upon spin projection is 0.5–0.7 kcal/mol. The values are not corrected for zero-point energy changes. [b] Methyl and *tert*-butyl: Russell, J. J.; Seetula, J. A.; Timonen, R. S.; Gutman, D.; Nova, D. F. *J. Am. Chem. Soc.* **1988**, *110*, 3084. Cyclopropyl and cyclobutyl: Reference 49. These authors give the BDE of cyclobutane as equal to that of propane, and for consistency with methyl and *tert*-butyl, it was taken as 98 kcal/mol. The uncertainty in the relative energies is on the order of ±2 kcal/mol.

Consistent with our other calculations, the structure of the radical **6** was optimized at both UHF/6-31G* and UMP2/6-31G* followed by UMP4/6-31G* and UMP3/6-311G* calculations using the UMP2/6-31G* geometry. The 1–3 nonbonded distance was found to be 1.797 Å.[48] For comparison with other small-ring compounds, the structures of the cyclopropyl, cyclobutyl, and 1-bicyclobutyl radicals also were optimized at these levels. In addition, data for the methyl and *tert*-butyl radicals were obtained. The calculated bond dissociation energies are given in Table VIII. The bond dissociation energy of cyclopropane was calculated to be 108 kcal/mol, which may be compared with the measured value, 106 kcal/mol.[49] Our value for the bridgehead C–H bond dissociation energy for bicyclopentane was 104 kcal/mol, in good agreement with the value computed by Feller and Davidson. The bridgehead C–H bond dissociation energy for bicyclobutane (117 kcal/mol) was the largest of the group; this fits well with the large ^{13}C1–H NMR coupling constant which implies unusually high s-character. Bond dissociation energies are known to increase with increasing s-character.[50] The smallest C–H bond dissociation energy was found with cyclobutane, and it is like that of an ordinary methylene group.

Although the calculated dissociation energies appear to be in reasonable agreement with experiment, it must be remembered that there is a zero-point energy (ZPE) change of about 9 kcal/mol associated with the cleavage of a C–H bond. It is known that quantitative calculations of bond dissociation energies are difficult to achieve and require both larger basis sets and a higher level of correction for electron correlation, such as MP4 or QCI.[51] With methane, for example, the bond dissociation energy calculated at the MP4/6-311++G** theoretical level was 108.5 kcal/mol,[52] and after correction for the zero-point energy change, it is close to the experimental value. Nevertheless, our calculations are useful in estimating the relative bond dissociation energies from which more accurate BDE's can be derived.

Bicyclobutane had the largest calculated bridgehead C–H bond dissociation energy and also has the largest ^{13}C–H NMR coupling constant of any compound in the group studied. These characteristics exceed those of a C–H bond in ethylene. The latter has a bond dissociation energy of 110 kcal/mol[49] and a $J(^{13}C\text{–}H)$ of 160 Hz. Thus, the large dissociation energy of bicyclobutane is in good accord with other properties of this molecule.

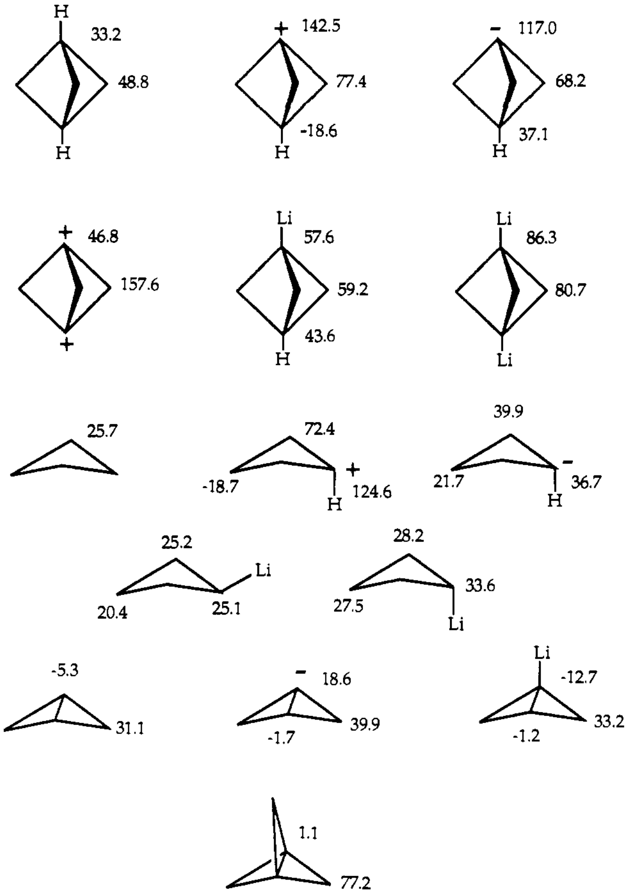

Figure 5. Calculated ^{13}C NMR chemical shifts.

NMR Chemical Shifts

It has been found that ^{13}C NMR chemical shifts of hydrocarbons and their closed-shell ions can be satisfactorily estimated using the IGLO procedure of Kutzelnigg and Schindler,[53] provided accurate geometries (e.g. for the cations those obtained at correlated levels of ab initio theory) are used.[19,54] During the last years the IGLO method has been established to be an important tool for the determination of the exact structures of carbocations, being the link between ab initio geometry optimization and NMR data. Since gegenion and solvent effects play a minor role in carbocation NMR spectroscopy, calculations on the isolated

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(48) The full structural information for **6** as well as the other compounds is available as supplementary material.

(49) DePuy, C. H.; Gronert, S.; Barlow, S. E.; Bierbaum, V. M.; Damrauer, R. *J. Am. Chem. Soc.* **1989**, *111*, 1968.

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(51) Curtiss, L. A.; Pople, J. A. *J. Chem. Phys.* **1988**, *88*, 7405; **1989**, *91*, 2420. Montgomery, J. A., Jr.; Petersson, G. A. *Chem. Phys. Lett.* **1990**, *168*, 75.

(52) At the MP4(sdtq)/6-311++G**//MP2/6-31G* level, methane had $E = -40.42543$, methyl radical had $E = -39.75270$, and the hydrogen atom had $E = -0.49982$ kcal/mol. Higher level corrections add about 3.7 kcal/mol to the calculated bond dissociation energies: Pople, J. A.; Head-Gordon, M.; Fox, D. J.; Raghavachari, K.; Curtiss, L. A. *J. Chem. Phys.* **1989**, *90*, 5622. The zero-point energy change for the dissociation of methane is 9.4 kcal/mol. With these two corrections, the calculated bond dissociation energy is 102.8 kcal/mol, in good agreement with the 0 K experimental value of 103.2 kcal/mol.

(53) (a) Kutzelnigg, W. *Isr. J. Chem.* **1980**, *19*, 193. (b) Schindler, M.; Kutzelnigg, W. *J. Chem. Phys.* **1982**, *76*, 1919. (c) Kutzelnigg, W. *J. Mol. Struct.* **1989**, *202*, 11.

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Table IX. ^{13}C Chemical Shifts Calculated Using MP2/6-31G* Geometries

species	atom	IGLO/DZ	IGLO/DZ+sp(C)	IGLO/II	expt
bicyclo[1.1.1]pentane (**1**)	C1	30.96		32.23	33.59[a]
	C2	47.82		48.84	50.75[a]
bicyclo[1.1.1]pentyl 1-cation (**2**)	C1	146.98		142.54	
	C2	83.34		77.38	
	C3	−13.23		−18.57	
bicyclo[1.1.1]pentyl 1-anion (**4**)	C1	96.27	117.01		
	C2	51.75	68.24		
	C3	28.62	37.10		
bicyclo[1.1.1]pentyl 1,3-dication (**7**)	C1	55.29		46.81	
	C2	174.64		157.55	
bicyclo[1.1.1]pentyl-1-lithium	C1	60.09	57.60		
	C2	53.41	59.19		
	C3	35.04	43.57		
1,3-dilithiobicyclo[1.1.1]pentane	C1		86.28		
	C2		80.67		
cyclobutane	C1	18.13		25.65	22.40[b]
cyclobutyl cation	C1	127.02		124.57	
	C2	73.17		72.38	
	C3	−22.40		−18.66	
cyclobutyl anion	C1	36.64	36.70		
	C2	46.86	39.87		
	C3	19.92	21.70		
cyclobutyllithium, equat[g]	C1	25.10[c]			
	C2	25.20[c]			
	C3	20.40[c]			
cyclobutyllithium, axial[g]	C1	33.60[c]			
	C2	28.20[c]			
	C3	27.50[c]			
bicyclo[1.1.0]butane	C1	0.91		−5.30	−3.00[d]
	C2	31.76		31.06	33.00[d]
1-bicyclo[1.1.0]butyl anion	C1	37.21	18.58		
	C2	38.18	39.26		
	C3	5.69	−1.70		
1-bicyclo[1.1.0]butyllithium[g]	C1		−4.99	−12.73	−14.80[e]
	C2		34.21	33.16	33.40[e]
	C3		0.18	−1.16	7.20[e]
1-bicyclo[1.1.0]butyllithium dimer[g]	C1		−2.80[c]	−14.95	−14.80[e]
	C2		28.40[c]	24.91	33.40[e]
	C3		13.20[c]	11.62	7.20[e]
[1.1.1]propellane	C1	18.64		1.08	1.00[f]
	C2	80.61		77.16	74.20[f]

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molecules give a reasonable model.

In contrast to carbocations, very few organometallic compounds exist as separated ions. Hence calculations on isolated carbanions are not reasonable models for the species in solution. Moreover, they often exhibit various degrees of aggregation and solvation.[55] For this reason and for comparison with available experimental data, the corresponding lithiated species have been computed. Recently we showed that even IGLO chemical shifts calculated for isolated monomers give acceptable agreement with the experimental values for aggregated species.[56]

We have applied the IGLO method to the MP2/6-31G* geometries given in Tables II and III and Figure 1, using the IGLO basis sets DZ (double ζ) and II (triple ζ plus polarization functions for C and H) for the cations and neutrals and the DZ+sp(C) (double ζ plus diffuse s and p functions for carbon) basis sets for the anions. The data are summarized in Figure 5 and Table IX.

Since it is well-known[57] that the smallest IGLO basis set we employed (DZ) fails with highly strained molecules, those systems were recalculated with the larger basis II. The calculated chemical shift of carbon C1 in [1.1.1]propellane improves by more than 17 ppm from DZ to II and becomes very close to the experimental value (IGLO/II//MP2/6-31G* 1.1 ppm vs experimental 1.0 ppm). This problem seems to be even more serious with our cationic species. Even with the large basis II, no reasonable results could be obtained for the bicyclobutyl cation and the [1.1.1]-propellane dication.

The IGLO results on cyclobutane, bicyclobutane, bicyclo[1.1.1]pentane, and [1.1.1]propellane fairly well reproduce the available data,[56] deviations up to 5 ppm being within both experimental and IGLO error. The chemical shifts for the bicyclobutonium–cyclopropylcarbinyl ion interconversion equilibrium were predicted by IGLO[19a] before values for the cations became available (by 5 K CPMAS-NMR spectroscopy).[19c]

Large differences of the calculated chemical shifts between anions and the corresponding lithiated species show the importance of the metal ion. Experimental data are available for only one of the investigated compounds, bicyclo[1.1.0]butyllithium. Our IGLO/II//MP2/6-31G* results are in acceptable agreement with experiment. For the reasons mentioned above, again IGLO basis II was employed for this strained system and resulted in reasonable improvement over the DZ basis set calculations. A comparison with the dimer (see Table IX) shows that, at least for those systems, aggregation effects are nearly negligible.

No other experimental data exist for the other species investigated in this work, so our calculated chemical shifts have to serve as predictions for future experiments.

Conclusions

The calculations presented herein have proven to be remarkably successful in reproducing the available experimental data for cation

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formation, anion formation, ionization potentials, and other properties of these small-ring systems. They have provided useful insights into the structures and charge distributions of small-ring compounds and the ions derived from them. They have also provided an impetus for futher experimental studies.

We are in the process of examining substituent effects on the bicyclo[1.1.1]pentyl 1-cation (**2**) and the bicyclo[1.1.1]pentyl 1-radical (**5**) both experimentally and theoretically. In the case of the radical, we are especially interested in the effect of substituents on the spin density distribution. We also are studying the transition states for the ring opening of both the cation and the radical.

Calculations

The ab initio calculations at Yale (HF and MP2 optimizations, MP3 larger basis set) were carried out using GAUSSIAN 90 and a Trace 7/200 computer, and those at Erlangen (MP4) were carried out using GAUSSIAN 88 and a Convex computer. The atoms in molecules charge distributions were obtained using PROAIM; the natural population analysis was carried out using a modified GAUSSIAN 88 program, Convex version, installed by Dr. Alan Reed, and the NMR chemical shifts were estimated using the IGLO program, Convex version, as supplied by Dr. Michael Schindler.

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Registry No. 1, 311-75-1; **2**, 22907-79-5; **3**, 141398-00-7; **4**, 37908-33-1; **5**, 71490-77-2; **6**, 141398-01-8; **7**, 141435-29-2; cyclopropane, 75-19-4; cyclopropane anion, 2417-82-5; cyclopropane radical cation, 34496-93-0; cyclobutane, 287-23-0; cyclobutane cation, 19067-43-7; cyclobutane radical, 4548-06-5; bicyclo[1.1.0]butane, 157-33-5; bicyclo-[1.1.0]butane 1-anion, 96666-81-8; bicyclo[1.1.0]butane 1-radical, 95694-51-2; bicyclo[1.1.0]butane radical cation, 85915-57-7; [1.1.1]-propellane, 35634-10-7; [1.1.1]propellane radical cation, 141398-02-9; isobutane, 75-28-5; *tert*-butyl cation, 14804-25-2; *tert*-butyl radical, 1605-73-8; methane, 74-82-8; methyl cation, 14531-53-4; methyl ion, 15194-58-8; methyl radical, 2229-07-4; hydrogen, 12385-13-6; hydride ion, 12184-88-2.

Supplementary Material Available: MP2/6-31G*-optimized geometries in Z-matrix format (4 pages). Ordering information is given on any current masthead page.

An Energy Criterion for Determining Relative σ and π Contributions in Transition Metal–Carbonyl Bonding

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Abstract: In this paper a new criterion is presented for determining the contribution of a particular class or group of orbitals to a chemical bond. The new criterion is the diatomic energy contribution of particular orbitals in a particular bond (any diatomic atom pair) to the total molecular energy. It is a unique feature of NDO (neglect of diatomic overlap) type procedures that the total energy can be divided entirely into monatomic and diatomic energy terms. Here this method is applied to determining the contribution of σ and π orbitals to the cohesive energy of CO adsorbed on a cluster of 12 iron atoms. While recent theoretical calculations have tended to downplay the role of the σ orbitals in metal–CO bonding, the results here show that the largest contribution to the stability of the metal–carbon bond is provided by the σ electrons.

Introduction

There is great interest in the adsorption and reaction of CO on transition metal surfaces. In addition, the hydrogenation of CO to hydrocarbon and alcohol fuels is of considerable commercial interest. Iron in various forms is one of the most commonly used Fischer–Tropsch catalysts and so is chosen for this work. Because CO adsorbs strongly on many clean metal surfaces, it is readily studied by many physical techniques, so there is a wealth of data for chemisorbed CO. It has been shown that a simple molecular orbital model would qualitatively explain variations in adsorbed C–O stretching frequencies from one metal to another and the effect of other adsorbates on the chemisorbed CO.[1,2]

The adsorption of carbon monoxide on a metal surface is a classical case of CO σ donation and metal π back-bonding. The CO σ orbitals form a covalent bond with the σ orbitals of the metal. The $2\pi^*$ orbital in gas-phase carbon monoxide is empty but it is a fairly low lying orbital and therefore the metal π orbitals can donate charge to it. Charge donation from the metal to the CO 2π orbitals weakens the CO bond, strengthens the metal–carbon bond, and thereby shifts the C-O stretching frequency to a lower value. The relative amounts of σ donation and π back-bonding vary from metal to metal. The strength of the metal–CO bond increases as one moves to the left and to the top of the transition metals. This correlates well with the above description of the metal–CO bonding, since the $d\pi$ electrons are held less tightly by the metals on the left side of the periodic table. As one moves to the left, the ratio of the size of the d orbitals to the sp orbitals increases. These two contributions increase metal to CO back-bonding, and therefore the metal–CO bond strength increases as one moves to the left of the periodic chart.[3]

The published[4] calculational results using MINDO/SR show that the breakdown of the adsorption energy into monatomic and diatomic terms indicates a complex interaction in which a large Fe–C diatomic energy term of 325 kcal/mol for CO in an on-top site is needed to obtain a net adsorption energy of 23 kcal/mol because adsorption destabilizes the C–O bond and the Fe–Fe bonds in Fe_{12}. The cluster d band is shifted by adsorbate–adsorbent charge transfer even though the d orbitals overlap only very weakly with the adsorbate. While the interaction of CO with its nearest neighbor dominates the interaction energy, the energy for the interaction with the other cluster atoms is necessary for a quan-

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