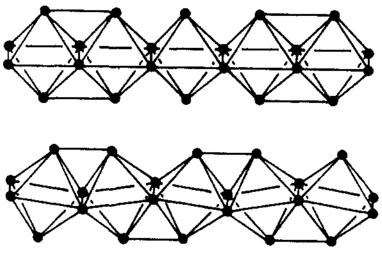
Table II. Parameters Used in the Extended-Hückel Calculations

orbital		H_{ii} (eV)	ζ_1 (C_1^a)	ζ_2 (C_2^a)
Mo	4d	−11.06	4.54 (0.5899)	1.90 (0.5899)
	5s	−8.77	1.96	
	5p	−5.60	1.90	
In	5s	−12.60	1.903	
	5p	−6.19	1.677	
O	2s	−32.3	2.275	
	2p	−14.8	2.275	
H	1s	−13.6	1.40	

[a] Coefficients in the double-ζ d orbital expansion.

The relevant levels of $Mo_{22}O_{34}^{8-}$, labeled b_{2g} and $1b_{3u}$ in Figure 8, become b_g and b_u in the distorted structure and cannot mix. In fact, both levels drop in energy with octahedral tilting. The bonding situation for Mo pairing or octahedral tilting in $Mo_{22}O_{34}^{8-}$ is succinctly summarized in **20**. **20** shows that pairing and tilting each form four strong Mo–Mo bonds between apical molybdenums.



20

Conclusions

Mo–Mo bonding in $Mo_{18}O_{28}^{7-}$ was analyzed in detail, in terms of parallel metal chains at the apex or in the basal planes of the component octahedra. The experimentally observed variation in Mo–Mo bond lengths parallel to the chain was attributed to the occupation of x^2-y^2 levels of C_{2v} ML_4 (basal molybdenums) and C_{4v} ML_5 (apical Mo) fragments. The basal x^2-y^2 levels are low in energy and filled through the level with one node perpendicular to the chain, similar to the π system of butadiene. Like the carbon atoms in butadiene, basal molybdenums in $Mo_{18}O_{28}^{7-}$ pair up at the ends of the chain.

Apical Mo x^2-y^2 orbitals appear near the HOMO–LUMO gap and suggest several interesting distortions to form apical Mo–Mo bonds, depending on the d electron count at the metal. The energy gap that opens up below the singly occupied $5a_g$ orbital in $Mo_{18}O_{28}^{7-}$, as well as a LUMO for $Mo_{22}O_{34}^{8-}$ that appears slightly below $5a_g$, suggests that the experimentally observed clusters may be better formulated as $Mo_{18}O_{28}^{6-}$ and $Mo_{22}O_{34}^{9-}$. It will be difficult to test this prediction experimentally since singly occupied orbitals on $Mo_{18}O_{28}^{7-}$ or $Mo_{22}O_{34}^{9-}$ both have b_{3u} symmetry and differ only in the extent of delocalization along the chain.

Several possible distortions exist for the $Mo_{22}O_{34}^{8-}$ cluster as well, depending on electron count. Predicted distortions—a simple pairing of apical molybdenums or a tilting of octahedra—are summarized for both molecules, for a variety of different electron counts, in Table I.

$Mo_{18}O_{28}^{n-}$ shows a definite preference for the pairing or for the tilting distortion, whereas $Mo_{22}O_{34}^{n-}$ often finds Mo pairing or octahedron tilting equally favorable. The preference of $Mo_{18}O_{28}^{6-,7-}$ for pairing was traced to orbital topology. For a chain such as $Mo_{18}O_{28}$—with an even number, N, of octahedra—pairing apical molybdenums forms N metal–metal bonds, but tilting of octahedra can only form $N-1$ bonds. For odd N, both pairing and tilting form the same number of strong Mo–Mo bonds and are equally favorable. The energy difference between pairing and tilting can be removed for even N by emptying one bonding level. In $Mo_{18}O_{28}^{6-}$ the orbital that is emptied on going to $Mo_{18}O_{28}^{4-}$ is the singly noded $1b_{2g}$ level. The difference between even- and odd-member chains is an "end effect" that decreases as N increases, as the chain grows longer.

The pairing of apical molybdenums along the chain and basal Mo–Mo bonding perpendicular to the chain are electronically coupled. An empty level with a substantial contribution from basal molybdenums at the ends of the chain mixes with occupied levels when apical molybdenums pair. The mixing strengthens primarily those basal Mo–Mo bonds (perpendicular to the chain) that are located at the chain ends.

Acknowledgment. We thank Susan A. Jansen and Jing Li for helpful discussions and the Cornell University Materials Science Center for funding through Grant No. DMR 87422702 from the NSF.

Appendix

Extended-Hückel calculations[23] were carried out with use of the parameters listed in Table II. Molybdenum[21a] and indium[29] exponents and Coulomb integrals were taken from previous publications. Cluster geometries were idealized, with Mo–Mo distances of 2.80 Å along the chain axis and 2.75 Å between apical and basal molybdenums; Mo–O distances were taken as 2.00 Å.

The $C_4H_7^+$ Cation. A Theoretical Investigation

Wolfram Koch,*,† Bowen Liu,† and Douglas J. DeFrees‡

Contribution from IBM Almaden Research Center, 650 Harry Road,
San Jose, California 95120-6099, and Molecular Research Institute, 701 Welch Road,
Palo Alto, California 94304. *Received March 10, 1988*

Abstract: The potential energy surface of the $C_4H_7^+$ cation has been investigated with ab initio quantum chemical theory. Extended basis set calculations, including electronic correlation, show that cyclobutyl and cyclopropylcarbinyl cation are equally stable isomers. The saddle point connecting these isomers lies 0.6 kcal/mol above the minima. The global $C_4H_7^+$ minimum corresponds to the 1-methylallyl cation, which is 9.0 kcal/mol more stable than the cyclobutyl and the cyclopropylcarbinyl cation and 9.5 kcal/mol below the 2-methylallyl cation. These results are in excellent agreement with experimental data.

The structures, reactions, and energetics of the $C_4H_7^+$ cation have received continued attention ever since the discovery of facile interconversion of cyclopropylcarbinyl, cyclobutyl, and allylcarbinyl derivatives in aprotic solvents by Roberts, more than 35 years ago.[1-4] In solution, it is now firmly established that $C_4H_7^+$ generated from cyclopropylcarbinyl or cyclobutyl derivatives has more than one structure. Available experimental information can

---

† IBM Almaden Research Center.
‡ Molecular Research Institute.

(1) Richey, G. In *Carbonium Ions*; Olah, G. A., Schleyer, P. v. R., Eds.; Wiley Interscience: New York, 1972; Vol III, Chapter 25.
(2) Wiberg, K. B.; Hess, B. A.; Ashe, A. J. In *Carbonium Ions*; Olah, G. A., Schleyer, P. v. R., Eds.; Wiley Interscience: New York, 1972; Vol. III, Chapter 26.

0002-7863/88/1510-7325$01.50/0

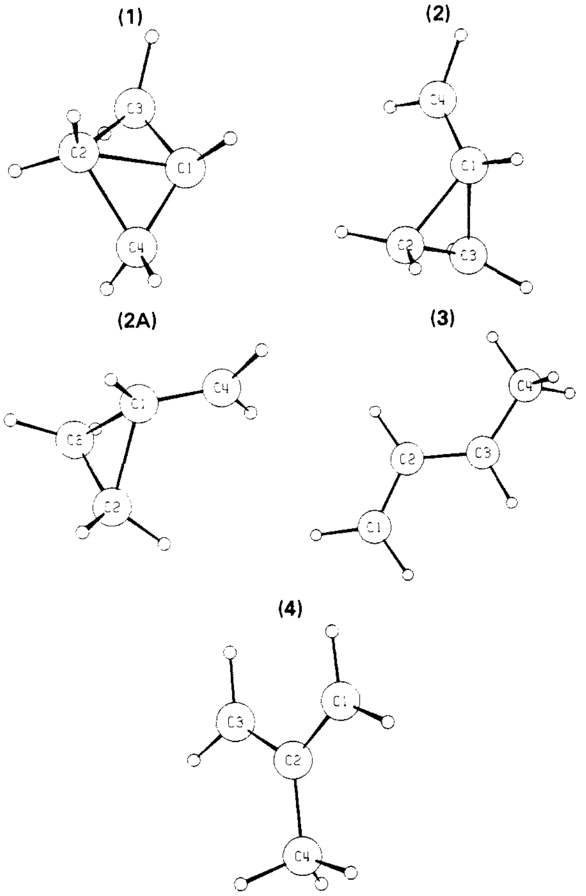


Figure 1. Geometries for **1**, **2**, **2a**, **3**, and **4**.

Table I. Previous Theoretical Results for Structures **1**, **2**, and **2a**[a]

	1 (C_s) *E* (NIMAG)	**2** (C_s) *E* (NIMAG)	**2a** (C_1) *E* (NIMAG)	ref
STO-3G	collapses to **2**	0.0 (0)	-	13, 14
3-21G	10.2 (1)	0.0 (0)	0.0 (0)	4, 16
4-31G	10.9 (1)	0.0 (0)	1.5 (0)	15
6-31G*	2.5 (1)	0.0 (1)	-0.01 (0)	4, 7, 16
MP2/6-31G*	-1.8 (-)	0.0 (-)	-	7, 16
MP3/6-31G*[b]	-1.3	0.0	0.0	7
MP4SDQ/6-31G*[b]	-0.7	0.0	-	16
MINDO/3	-5.6 (0)	0.0 (0)	-	17

[a] $E = E_{rel}$ in kcal/mol. NIMAG = number of imaginary frequencies, i.e., number of negative eigenvalues, in the corresponding force constant matrix. [b] At MP2/6-31G* optimized geometries.

Table II. Selected Optimized Geometrical Parameters[a]

	6-31G*	6-31G**	6-311G**	MP2/ 6-31G*	MP2/ 6-31G**
			Structure **1** (C_s)		
R(C1C2)	1.687	1.684	1.686	1.650	1.649
R(C1C3)	1.417	1.417	1.417	1.424	1.424
R(C2C3)	1.646	1.646	1.652	1.649	1.647
A(C3C1C4)	111.8	111.8	112.0	112.9	112.7
A(C3C2C4)	90.9	90.9	90.7	92.0	92.1
A(C1C3C2)	66.4	66.2	66.1	64.5	64.5
			Structure **2** (C_s)		
R(C1C2)	1.647	1.647	1.654	1.646	1.644
R(C2C3)	1.408	1.407	1.407	1.415	1.414
R(C1C4)	1.351	1.350	1.347	1.356	1.355
A(C2C1C3)	50.6	50.6	50.3	50.9	51.0
A(C4C1X23[b])	120.3	120.2	120.0	119.5	119.4
			Structure **2a** (C_1)[c]		
R(C1C2)	1.690	1.690	1.717	1.715	1.713
R(C1C3)	1.604	1.604	1.593	1.519	1.520
R(C1C4)	1.351	1.350	1.348	1.368	1.367
R(C2C4)	2.543	2.544	2.528	2.301	2.308
R(C3C4)	2.563	2.561	2.559	2.509	2.509
A(C2C1C3)	50.7	50.6	50.4	53.0	52.9
A(C4C1C2)	113.0	112.6	110.6	95.9	96.4
A(C4C1C3)	120.1	120.0	120.8	120.6	120.6
			Structure **3** (C_s)		
R(C1C2)	1.360	1.359	1.358	1.372	1.371
R(C2C3)	1.391	1.391	1.391	1.397	1.396
R(C3C4)	1.472	1.470	1.469	1.458	1.457
A(C1C2C3)	118.6	118.6	118.6	118.3	118.1
A(C2C3C4)	125.4	125.4	125.5	125.3	125.4
			Structure **4** (C_s)		
R(C1C2)	1.377	1.377	1.377	1.388	1.388
R(C2C4)	1.514	1.514	1.513	1.503	1.502
A(C1C2C3)	114.1	114.1	114.0	113.8	113.8
A(C1C2C4)	122.4	122.3	122.5	122.5	122.5

[a] *R* = bond distance in Å, *A* = bond angle in deg. [b] X23: midpoint of the C2C3 bond. [c] Corresponds to a minimum on 6-31G*, 6-31G**, and 6-311G**, but to the saddle point connecting **1** and **2** on MP2/6-31G**.

best be interpreted in terms of a rapid equilibrium involving two structural isomers of $C_4H_7^+$. The identities of these isomers, however, are not well established. ^{13}C NMR studies strongly point to the pentacoordinated bicyclobutonium cation **1** as the more stable of the participating isomers.[5] (Since there is no clear-cut distinction between a puckered cyclobutyl and a bicyclobutonium structure, we will refer to both structures as **1**.) The bisected cyclopropylcarbinyl ion **2** has been tentatively assigned to the higher energy species. The two isomers are nearly equal in energy, with a small interconversion barrier of 1.0 ± 0.5 kcal/mol.[5] This interpretation of the results is supported by a recent theoretical calculation of NMR chemical shifts, which show that the best agreement with experimental results is achieved by assuming a mixture of bicyclobutonium cation and cyclopropylcarbinyl cation, with the former being the major species.[6,7] Deuterium isotope effects also suggest **1** as the dominant species in the equilibrium.[8,9]

Many experiments have also been performed on $C_4H_7^+$ in the gas phase. A mass spectrometric investigation of kinetic energy release and collision activation spectra of Br loss from several C_4H_7Br precursors indicated that, besides 1- and 2-methylallyl cations (**3** and **4**), a cyclobutyl-like cation is also a stable isomer of $C_4H_7^+$.[10] The same conclusion was reached in radiochemical experiments by Cacace and Speranza.[11] The β decay of tritiated cyclobutyl and cyclopropylcarbinyl derivatives in the presence of nucleophiles like H_2O or NH_3 produced cyclobutanol (cyclobutylamine) and cyclopropylcarbinol (cyclopropylcarbinylamine) among other products. Lifetimes in excess of 10^{-9} s were estimated for cyclobutyl- (or bicyclobutonium-) and cyclopropylcarbinyl-like cations. A recent, detailed photoelectron spectroscopy investigation of isomers of the C_4H_7 radical by Beauchamp and co-workers[12] provides energetical details of some $C_4H_7^+$ isomers. By combining known heats of formation of the radicals with measured adiabatic ionization energies, they found the 1-methylallyl cation **3** to be the most stable $C_4H_7^+$ isomers, with a heat of formation of 203.1 ± 1.4 kcal/mol. The 2-methylallyl cation, **4**, is less stable by 9.1 ± 1.5 kcal/mol. In accord with the other gas-phase experiments

---

(3) Brown, H. C. (with comments by P. v. R. Schleyer) *The Nonclassical Ion Problem*; Plenum: New York, 1977; Chapter 5.

(4) Hehre, W., Radom, L., Schleyer, P. v. R., Pople, J. A. *Ab initio Molecular Orbital Theory*; Wiley Interscience: New York, 1986.

(5) Staral, J. S.; Yavari, I.; Roberts, J. D.; Prakash, G. K. S.; Donovan, D. J.; Olah, G. A. *J. Am. Chem. Soc.* **1978**, *100*, 8016.

(6) Schindler, M. *J. Am. Chem. Soc.* **1987**, *109*, 1020.

(7) Saunders, M.; Laidig, K. E.; Wiberg, K. B.; Schleyer, P. v. R. *J. Am. Chem. Soc.*, following paper in this issue.

(8) Saunders, M.; Siehl, H. U. *J. Am. Chem. Soc.* **1980**, *102*, 6868.

(9) Brittain, W. J.; Sqillacote, M. E.; Roberts, J. D. *J. Am. Chem. Soc.* **1984**, *106*, 7280.

(10) Bowen, R. D.; Williams, D. H.; Schwarz, H.; Wesdemiotis, C. *J. Chem. Soc., Chem. Soc.* **1979**, 261.

(11) Cacace, F.; Speranza, M. *J. Am. Chem. Soc.* **1979**, *101*, 1589.

(12) Schultz, J. C.; Houle, F. A.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1984**, *106*, 7336.

Table III. Total, Relative, and Zero-Point Vibrational Energies

comp. level	**1** (C_s)	**2** (C_s)	**2a** (C_1)	**3** (C_s)	**4** (C_s)
6-31G*^{a}	−155.22382	−155.22779	−155.22781	−155.25312	−155.23517
E_{rel}	18.4	15.9	15.9	0.0	11.3
6-31G**^{a}	−155.23618	−155.24008	−155.24009	−155.26538	−155.24720
E_{rel}^b	18.3	15.9	15.9	0.0	11.4
6-311G**^{a}	−155.26047	−155.26485	−155.26491	−155.29087	−155.27262
E_{rel}^b	19.1	16.3	16.3	0.0	11.4
MP2/6-31G*^{a}	−155.74766	−155.74471	−155.74404	−155.75538	−155.73918
E_{rel}^b	4.8	6.7	7.1	0.0	10.2
MP2/6-31G**^{a}	−155.80216	−155.79926	−155.79863	−155.80975	−155.79400
E_{rel}^b	4.8	6.6	7.0	0.0	9.9
ZPVE	63.6	63.1	63.2	62.1	62.0
MP4/6-311G**^{a}	−155.89090	−155.89007	−155.88940	−155.90290	−155.88753
E_{rel}^b	7.5	8.0	8.5	0.0	9.6
E_{rel}^c	9.0	9.0	9.6	0.0	9.5
experiment	<22.0 ± 1.3^d	ca. 9^e	10.0 ± 0.5^f	0.0	9.1 ± 1.5^d

^{a} In atomic units. ^{b} In kcal/mol. ^{c} In kcal/mol, including zero-point energies. ^{d} Reference 12. ^{e} Reference 24. ^{f} Reference 5.

Table IV. Harmonic Frequencies and IR Intensities Computed at MP2/6-31G**

structure		Harmonic frequencies^a (IR intensities^b)
1	a′:	409 (0), 610 (5.7), 792 (28), 914 (1), 1100 (2), 1126 (0), 1158 (8), 1196 (35), 1292 (2), 1481 (4), 1584 (9), 3239 (36), 3252 (17), 3277 (6), 3358 (3), 3371 (55)
	a″:	136 (92), 927 (2), 955 (3), 991 (37), 1161 (0), 1185 (1), 1296 (0), 1484 (6), 1578 (4), 3248 (15), 3361 (5)
2	a′:	393 (1), 726 (72), 828 (4), 945 (6), 1103 (30), 1147 (8), 1306 (17), 1345 (9), 1473 (41), 1598 (4), 1671 (32), 3236 (6), 3251 (15), 3328 (6), 3351 (13), 3372 (31)
	a″:	83 (33), 424 (24), 617 (1), 1037 (5), 1119 (1), 1147 (8), 1166 (26), 1260 (1), 1528 (14), 3248 (11), 3358 (21)
3	a′:	303 (0), 522 (0), 907 (34), 1028 (22), 1235 (14), 1323 (108), 1359 (25), 1394 (34), 1409 (42), 1510 (72), 1593 (53), 1706 (331), 3090 (88), 3236 (0), 3241 (3), 3280 (13), 3303 (6), 3358 (9)
	a″:	121 (5), 164 (1), 550 (1), 842 (2), 1042 (35), 1104 (0), 1144 (21), 1489 (21), 3155 (16)
4	a′:	394 (0), 457 (0), 879 (2), 1014 (1), 1087 (1), 1108 (10), 1462 (5), 1478 (72), 1493 (13), 1545 (15), 1623 (20), 1677 (105), 3154 (1), 3231 (6), 3233 (4), 3270 (1), 3348 (6), 3351 (8)
	a″:	47 (0), 214 (9), 486 (8), 671 (0), 1086 (2), 1147 (27), 1159 (1), 1536 (16), 3253 (0)

^{a} In cm^{-1}. ^{b} In km/mol.

described above, the cyclobutyl cation was found to be a stable isomer, with an estimated heat of formation of 225.1 ± 1.1 kcal/mol. However, since the Franck–Condon factors may not be favorable enough for the 0–0 transition to be observed, Beauchamp et al.[12] interpret this heat of formation as an upper limit for the true ΔH_f value. The other cyclic $C_4H_7^+$ isomer, i.e., the cyclopropylcarbinyl cation **2**, could not be studied, due to the facile ring opening of the parent cyclopropylcarbinyl radical.

While experimental investigations almost unanimously point to the existence of two stable, cyclic $C_4H_7^+$ isomers, theoretical studies have produced less harmonious results, which are summarized in Table I.[4,7,13-16] Hehre et al.[15] found that, at the HF/4-31G level, the asymmetric structure **2a** corresponds to a minimum, while **1** corresponds to a saddle point. Interconversion of **2** and **2a** was then thought to explain the NMR results. The best basis set used so far is 6-31G*. McKee[16] and Schleyer et al.[7] found that, at this level, both **1** and **2** are transition states, in distinct contrast to experimental results. Both papers suggested that one or even both ring structures may turn out to be stable when electron correlation effects are included in the theoretical treatment. Schleyer et al. supported this supposition by showing that MP2/6-31G* energies increase when the HF/6-31G* transition-state structures are distorted slightly along their respective reaction coordinates.[7] However, no force constants including the effect of electronic correlation have been reported yet for $C_4H_7^+$ isomers. Consequently, the final characterization of the cyclic isomers is still missing.

Semiempirical MINDO/3 calculations reported recently by Dewar and Reynolds[17] show both **1** and **2** as minima, with **2** being more stable by 5.6 kcal/mol. While this is in qualitative agreement with experiments, the computed energy difference between the two is most likely significantly too high.

In this paper we present a detailed ab initio study of the most important isomers of $C_4H_7^+$ and some of the transition states connecting them. The smallest basis set used in this study, 6-31G*, is the largest basis used in all previous studies of $C_4H_7^+$. Effects of electronic correlation were included in both molecular structure determination and vibrational frequency and infrared intensity calculations. Relative energies of the isomers were obtained by using an extended basis set and full fourth-orderMøller–Plesset perturbation theory.

Calculations

Standard ab initio calculations were performed with the vectorized IBM version of the Gaussian 86 program.[18] Geometry optimization was performed at RHF/6-31G*, RHF/6-31G**, RHF/6-311G**, MP2/6-31G*, and MP2/6-31G** levels of theory.[19] Force constants, harmonic frequencies, zero-point vibrational energies (ZPVE), and infrared intensities were determined analytically for the Hartree–Fock wave functions and by numerically differentiating the analytical first derivatives for the MP2 wave functions. Single-point energy calculations were performed, at MP2/6-31G** optimized geometries, using the 6-311G** basis set and full fourth-order Møller–Plesset perturbation theory. This calculation, including zero-point energy correction, may be denoted as MP4(SDTQ)/6-311G**//MP2/6-31G** + ZPVE.

All calculations were performed on a IBM 3090 Model 200 at the IBM Washington Systems Center. The MP4(SDTQ)/6-311G** calculation for structure **3** required approximately 410 min of CPU time.

Results and Discussion

Geometries of cyclobutyl cation (**1**), bisected cyclopropylcarbinyl cation (**2**), the asymmetric structure (**2a**), 1-methylallyl cation (**3**), and 2-methylallyl cation (**4**) are presented in Figure 1. Selected bond lengths and angles are listed in Table II. Table III shows total, relative, and zero-point energies of $C_4H_7^+$ isomers,

---

(13) Hehre, W. J.; Hiberty, P. C. *J. Am. Chem. Soc.* **1972**, *94*, 5917.

(14) Hehre, W. J.; Hiberty, P. C. *J. Am. Chem. Soc.* **1974**, *96*, 302.

(15) Levi, B. A.; Blurock, E. S.; Hehre, W. J. *J. Am. Chem. Soc.* **1979**, *101*, 5537.

(16) McKee, M. L. *J. Phys. Chem.* **1986**, *90*, 4908.

(17) Dewar, M. J. S.; Reynolds, C. H. *J. Am. Chem. Soc.* **1984**, *106*, 6388.

(18) Gaussian 86: Frisch, M. J.; Binkley, J. S.; Schlegel, H. B.; Raghavachari, K.; Melius, C. F.; Martin, R. L.; Stewart, J. J. P.; Bobrowicz, F. W.; Rohlfing, C. M.; Kahn, L. R.; DeFrees, D. J.; Seeger, R.; Whiteside, R. A.; Fox, D. J.; Fluder, E. M.; Pople, J. A. Carnegie-Mellon Quantum Chemistry Publishing Unit, Pittsburgh, PA, 1984.

(19) For a description of the various basis sets and Møller–Plesset perturbation theory, see Chapter 4 in ref 4.

while Table IV gives MP2/6-31G** harmonic frequencies and IR intensities. The global minimum on the $C_4H_7^+$ surface correponds to the 1-methylallyl cation (**3**) (only the more stable trans form of **3** has been considered). It is calculated to be 9.5 kcal/mol more stable than the 2-methylallyl cation (**4**), in excellent agreement with the experimental gas-phase energy difference of 9.1 ± 1.5 kcal/mol obtained by Beauchamp and co-workers. The cyclobutyl cation and the cyclopropylcarbinyl cation are close energetically. On the basis of total energies, **1** is 0.5 kcal/mol more stable than **2**. After correction for zero-point energies the two isomers are equally stable, 9.0 kcal/mol above the global minimum. The MP2/6-31G** optimized geometries of **1** and **2** differ insignificantly from the MP2/6-31G* structures reported previously.[7,16] As noted by McKee,[16] **1** is best interpreted as a nonclassical, pentacoordinated bicyclobutonium cation with strong transannular bonding. The C1–C3 transannular distance, 1.65 Å, is the same as the C2–C3 distance and significantly longer than a normal C–C single bond. The cyclopropylcarbinyl structure is, as expected, bisected. The (formal) cationic center in this structure, at the methylene group, is stabilized by the Walsh orbitals of the cyclopropyl ring. This is reflected in the structure of the cyclopropyl ring, which has two abnormally long (1.64 Å) and one relatively short (1.41 Å) C–C bonds.[20]

The most striking finding of our study is the critical importance of electronic correlation in determining the potential energy surface of $C_4H_7^+$. Structures **1** and **2** correspond to local minima at the MP2/6-31G** level of theory, while both correspond to saddle points at the HF/6-31G* level. Both structures are stabilized by inclusion of electron correlation effects. Compared to **3**, **1** is stabilized by about 10 kcal/mol and **2** by about 15 kcal/mol. This is not surprising, since it is well known that electron correlation is particularly important for small rings and nonclassical cations.[21-23] We carried out additional calculations to verify that the 6-31G* result is a sufficiently accurate approximation to the Hartree–Fock limit. The imaginary frequencies of **1** and **2** change from 162i and 64i, respectively, at the 6-31G* level to 167i and 56i at the 6-31G** level and to 224i and 79i at the 6-311G** level. Further extension of the basis will not change these results qualitatively. Thus, accurate description of the ring structures of $C_4H_7^+$ requires explicit inclusion of electronic correlation effects.

We also studied the asymmetric cyclopropylcarbinyl-like cation **2a** which Hehre and collaborators used to interpret the experimental results.[15] At all three Hartree–Fock levels described above, **2a** is a local minimum slightly lower in energy than the C_s symmetric ion, **2**. At the MP2/6-31G* and MP2/6-31G** levels, however, this structure turned out to have one imaginary frequency. It represents the transition state for a reaction connecting structures **1** and **2** as indicated by the transition mode which corresponds to a motion of C4 toward C2 and a twisting of the $C4H_2$ methylene group (see Figure 1). With this, the barrier to interconversion between the bicyclobutonium ion and the cylopropylcarbinyl ion is predicted to be 0.6 kcal/mol.

Although a direct comparison between the theoretical barrier height, which applies to isolated molecules at 0 K, and NMR experiments conducted in aprotic solvents is problematic, it is encouraging that the NMR studies predict **1** and **2** to be close in energy and separated by a barrier of 1 ± 0.5 kcal/mol.[5] In the gas-phase photoelectron spectroscopy experiments, the relative energy of **1** with respect to **3** was estimated to be 22.0 ± 1 kcal/mol. This value is significantly larger than our theoretical value of 9.0 kcal/mol. However, as noted by Beauchamp et al.[12] this experimental energy difference should only be viewed as an upper limit to the true value. Because of the large structural difference between the almost planar cyclobutyl radical and the strongly puckered bicyclobutonium cation, it is very likely that the 0–0 transition was not observed and that the onset of the photoelectron band does not correspond to the adiabatic ionization energy. For the cyclopropylcarbinyl cation, **2**, only a tentative experimental heat of formation of 212 kcal/mol is documented in the literature.[24] With use of this ΔH_f value, **2** is placed about 9 kcal/mol above **3** in near perfect agreement with our predicted energy difference.

Summary

We have presented, for the first time, a consistent picture of the structural isomers of the $C_4H_7^+$ cation. Our results are in excellent agreement with available experimental information. Cyclobutyl cation, which is better described as a nonclassical pentacoordinated bicyclobutonium ion, and bisected cyclopropyl cation are both stable isomers lying 9.0 kcal/mol above the global minimum, the 1-methylallyl cation. The activation barrier for isomerization between the two cyclic isomers is 0.6 kcal/mol. 2-Methylallyl has also been found as a stable isomer lying 9.5 kcal/mol above the 1-methylallyl cation. The effects of electron correlation are of critical importance for a proper description of these species. The minimum level of theory capable of a correct qualitative description appears to be MP2/6-31G*.

Acknowledgment. We thank L. W. Ivester of the IBM Washington Systems Center for making available the computing resource for this study and K. M. Goin and W. J. McShea of the same organization for facilitating our calculations. We thank P. v. R. Schleyer for a copy of ref 7 prior to publication and M. L. McKee for valuable comments.

Registry No. 1, 19067-43-7; **2**, 14973-56-9; **3**, 17171-49-2; **4**, 17542-17-5.

---

(20) For a detailed discussion see Section 7.3.1.c(iii) in ref 4.

(21) Lischka, H.; Köhler, H. J. *J. Am. Chem. Soc.* **1978**, *100*, 5297.

(22) Raghavachari, K.; Whiteside, R. A.; Pople, J. A.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1981**, *103*, 5649.

(23) Yoshimine, M.; McLean, A. D.; Liu, B.; DeFrees, D. J.; Binkley, J. S. *J. Am. Chem. Soc.* **1983**, *105*, 6185.

(24) As described in ref 12 the heat of formation has been obtained from the proton affinity of the olefin taken from: Aue, D. H.; Bowers, M. T. In *Gas Phase Ion Chemistry*; Bowers, M. T., Ed.; Academic: New York, 1979; Vol. II, Chapter 9.