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Structural Studies of Nonclassical Cyclobutylmethyl Cations by the *ab initio* Method

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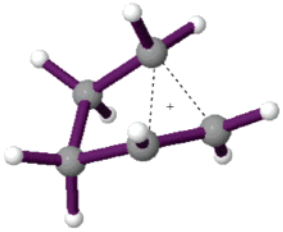

*A*b initio calculations at the MP2/cc-pVTZ level show that the cyclobutylmethyl cation is a nonclassical σ-delocalized species, which is distinct from the global minimum C_2-symmetric cyclopentyl cation (Schleyer, P. v. R.; Carneiro, J. W. de M.; Koch, W.; Raghavachari, K. *J. Am. Chem. Soc.* **1989**, *111*, 5475). Relatively lower level DFT calculations, on the other hand, show that the primary cyclobutylmethyl cation spontaneously collapses into the cyclopentyl cation (Prakash, G. K. S.; Reddy, V. P.; Rasul, G.; Casanova, J.; Olah, G. A. *J. Am. Chem. Soc.* **1998**, *120*, 13362). The secondary 1-cyclobutylethyl cation is also a nonclassical carbocation, as shown by calculations at the MP2/cc-pVTZ level. Two structures having energy minima are identified for the latter cation on the potential energy surface. The conformer in which the methyl group is in the *exo* orientation is a global minimum and is favored over the corresponding *endo* conformer by 1.2 kcal/mol at the MP2/cc-pVTZ//MP2/cc-pVTZ +ZPE level of calculations. The tertiary 1-cyclobutyl-1-methylethyl cation, at this level of calculations, also involves substantial nonclassical σ-delocalization, showing that the nonclassical stabilization is more important for cyclobutylmethyl cations relative to the cyclopropylmethyl cations. The ^{13}C NMR chemical shifts obtained from GIAO-CCSD(T)/tzp/dz calculations further substantiate the nonclassical structures for these carbocations.

Introduction

Nonclassical delocalization involving cyclopropylmethyl cations has been extensively studied experimentally and by ab initio theoretical calculations at correlated levels.[1−14] Relief of the inherent strain in the cyclopropyl ring is the major driving force for the formation of the nonclassical cyclopropylmethyl cations from their corresponding substrates under solvolytic conditions and in superacidic media. The extent of delocalization of the charge into the cyclopropyl ring is markedly diminished in the tertiary carbocations such as α,α-dimethylcyclopropylmethyl cation.[15] There is significant nonclassical stabilization in the secondary cyclopropylmethyl cations, whereas the primary cyclopropylmethyl cation exists as an equilibrating mixture of degenerate nonclassical bicyclobutonium ions, **1** and **2**, with

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(1) Prakash, G. K. S.; Reddy, V. P. Recent studies of long-lived carbocations and carbodications. In *Carbocation Chemistry*; Olah, G. A., Prakash, G. K. S., Eds.; John Wiley: New York, 2004; pp 73−101.

(2) Roberts, J. D.; Mazur, R. H. *J. Am. Chem. Soc.* **1951**, *73*, 3542−3543.

(3) Cacace, F.; Chiavarino, B.; Crestoni, M. E. *Chem.−Eur. J.* **2000**, *6*, 2024−2031.

(4) Olah, G. A.; Reddy, P. V.; Prakash, G. K. S. Long-lived cyclopropylcarbinyl cations. In *Chemistry of the Cyclopropyl Group*; Patai, S., Rappoport, Z., Eds.; John Wiley: New York, 1995; Vol. 2, pp 813−859.

(5) Wiberg, K. B.; Shobe, D.; Nelson, G. L. *J. Am. Chem. Soc.* **1993**, *115*, 10645−10652.

(6) Olah, G. A.; Reddy, V. P.; Prakash, G. K. S. *Chem. Rev.* **1992**, *92*, 69−95.

(7) Childs, R. F.; Kostyk, M. D.; Lock, C. J. L.; Mahendran, M. *J. Am. Chem. Soc.* **1990**, *112*, 8912−8920.

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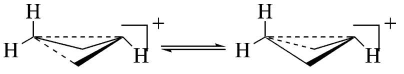
minor contributions from the equilibrating bisected cyclopropylmethyl cation.[8,15,16] Extensive solvolytic, stable ion studies and theoretical calculation support such σ-bridged nonclassical cations in this system.[4,17]



1 **2**

Although relatively less strained when compared to the cyclopropyl group, the cyclobutyl ring, in the puckered conformation, is stereoelectronically well positioned for the formation of nonclassical cyclobutylmethyl cations.[18,19] There is much precedence for the involvement of nonclassical cyclobutylmethyl cations as reaction intermediates based on early solvolytic studies on cyclobutylmethyl substrates.[19−30]

We have recently prepared the first persistent cyclobutylmethyl cation, α,α-dicyclopropylcyclobutylmethyl cation, **4**, in superacid media.[31] The latter carbocation shows distinct absorptions (δ^{13}C) for the cyclopropyl C_α and $C_{\alpha'}$ as well as C_β and $C_{\beta'}$ carbons indicating that it exists as a bisected conformer. The estimated rotational barrier ($\Delta G^\ddagger = 11 \pm 0.5$ kcal/mol at −40 °C) is similar to that of the analogous α,α-dimethylcyclopropylmethyl cation,[32] indicating that the cation is predominantly a charge localized (i.e., classical) species, with significant contribution of σ-delocalization from the neighboring cyclobutyl ring.

TABLE 1. Total Energies (−au), ZPE[a] and Relative Energies (kcal/mol)[b]

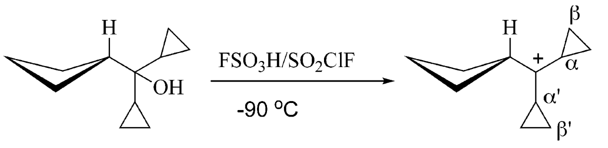
structure	MP2/6-31G*	ZPE	MP2/cc-pVTZ	rel. energy
8	194.89859	77.9	195.15660	10.3
9	194.91416	76.7	195.17117	0.0
10	194.89794	77.5	195.15498	11.0

[a] Zero point vibrational energies (ZPE) at MP2/6-31G*//MP2/6-31G* scaled by a factor of 0.95. [b] Relative energy at the MP2/cc-pVTZ//MP2/cc-pVTZ + ZPE level.

TABLE 2. Total Energies (−au), ZPE[a] and Relative Energies (kcal/mol)[b]

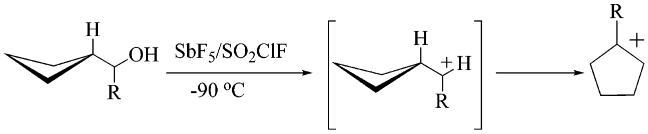
structure	MP2/6-31G*	ZPE	MP2/cc-pVTZ	rel. energy
11	234.07462	95.2	234.38946	1.2
12	234.07677	95.1	234.39115	0.0
13	273.25472	112.0	273.62555	

[a] Zero point vibrational energies (ZPE) at MP2/6-31G*// MP2/6-31G* scaled by a factor of 0.95. [b] Relative energy at the MP2/cc-pVTZ//MP2/cc-pVTZ + ZPE level.



3 **4**

Our attempts to generate the secondary and primary cyclobutylmethyl cations, however, were not successful. In all cases, only the corresponding cyclopentyl cations, **7**, resulting from ring-expansion rearrangements were observed. Our density functional theory (DFT) studies at the B3LYP/6-311+G* level on the primary cyclobutylmethyl cation showed that it is not a minimum on the potential energy surface and spontaneously rearranged into the cyclopentyl cation.[33]



5 **6** **7**

R = CH_3, Ph, cyclopropyl

Although there is strong support for the involvement of nonclassical secondary cyclobutylmethyl cations as the reaction intermediates, from Winstein and co-workers' early solvolysis studies,[20] the structures of the cyclobutylmethyl cations have not been explored at high level ab initio calculations to date.

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(8) Saunders, M.; Laidig, K. E.; Wiberg, K. B.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1988**, *110*, 7652−7659. Cacace, F.; Chiavarino, B.; Crestoni, M. E. *Chem.−Eur. J.* **2000**, *6*, 2024−2031. Siehl, H.-U.; Backes, A. C.; Malkina, O. In *Organosilicon Chemistry IV: From Molecules to Materials*; Auner, N., Weis, J., Eds.; Wiley-VCH: New York, 2000; pp 150−157. Falkenberg-Andersen, C.; Ranganayakulu, K.; Schmitz, L. R.; Sorensen, T. S. *J. Am. Chem. Soc.* **1984**, *106*, 178−182. Abboud, J.-L. M.; Alkorta, I.; Davalos, J. Z.; Muller, P.; Quintanilla, E. *Adv. Phys. Org. Chem.* **2002**, *37*, 57−135. Fuchs, J.-F.; Mareda, J. *THEOCHEM* **2005**, *718*, 93−104. Casanova, J.; Kent, D. R. I. V.; Goddard, W. A., III; Roberts, J. D. *Proc. Natl. Acad. Sci. U.S.A.* **2003**, *100*, 15−19. Wiberg, K. B.; Shobe, D. S. *J. Org. Chem.* **1999**, *64*, 7768−7772. Tian, F.; Battiste, M. A.; Dolbier, W. R., Jr. *Org. Lett.* **1999**, *1*, 193−195. Siehl, H.-U. In *Chemistry of Cyclobutanes*; Rappoport, Z., Ed.; John Wiley: Chichester, UK, 2005; pp 521−547. Vancik, H.; Gabelica, V.; Sunko, D. E.; Buzek, P.; Schleyer, P. v. R. *J. Phys. Org. Chem.* **1993**, *6*, 427−432. Szafran, M.; Karelson, M. M.; Katritzky, A. R.; Koput, J.; Zerner, M. C. *J. Comput. Chem.* **1993**, *14*, 371−377. Schultz, J. C.; Houle, F. A.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1984**, *106*, 7336−7347. 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.

(9) Koch, W.; Liu, B.; DeFrees, D. J. *J. Am. Chem. Soc.* **1988**, *110*, 7325−7328.

(10) McKee, M. L. *J. Phys. Chem.* **1986**, *90*, 4908−4910.

(11) Olah, G. A.; Prakash, G. K. S.; Rawdah, T. N. *J. Org. Chem.* **1980**, *45*, 965−969.

(12) Staral, J. S.; Yavari, I.; Roberts, J. D.; Prakash, G. K. S.; Donovan, D. J.; Olah, G. A. *J. Am. Chem. Soc.* **1978**, *100*, 8016−8018.

(13) Staral, J. S.; Roberts, J. D. *J. Am. Chem. Soc.* **1978**, *100*, 8018−8020.

(14) Okazawa, N.; Sorensen, T. S. *Can. J. Chem.* **1978**, *56*, 2355−2364.

(15) Olah, G. A.; Jeuell, C. L.; Kelly, D. P.; Porter, R. D. *J. Am. Chem. Soc.* **1972**, *94*, 146−156.

(16) Myhre, P. C.; Webb, G. G.; Yannoni, C. S. *J. Am. Chem. Soc.* **1990**, *112*, 8992−8994.

(17) Lenoir, D.; Siehl, H.-U. In *Houben-Weyl Methoden der Organischen Chemie*; Thieme Verlag: Stuttgart, Germany, 1990; Vol. E19c, pp 413 and references therein.

(18) Schindler, M. *J. Am. Chem. Soc.* **1987**, *109*, 1020−1033.

(19) Gassman, P. G.; Armour, E. A. *J. Am. Chem. Soc.* **1973**, *95*, 6129−6131.

(20) Winstein, S.; Holness, N. J. *J. Am. Chem. Soc.* **1955**, *77*, 3054−3061.

(21) Dauben, W. G.; Chitwood, J. L. *J. Am. Chem. Soc.* **1970**, *92*, 1624−1629.

(22) Dauben, W. G.; Chitwood, J. L. *J. Org. Chem.* **1969**, *34*, 726−729.

(23) Dauben, W. G.; Chitwood, J. L.; Scherer, K. V., Jr. *J. Am. Chem. Soc.* **1968**, *90*, 1014−1020.

(24) Roberts, D. D. *J. Org. Chem.* **1984**, *49*, 2521−2526.

(25) Peters, E. N. *J. Org. Chem.* **1977**, *42*, 3015−3017.

(26) Roberts, D. D. *J. Org. Chem.* **1976**, *41*, 486−489.

(27) Roberts, D. D.; Wu, C.-H. *J. Org. Chem.* **1974**, *39*, 3937−3938.

(28) Roberts, D. D.; Wu, C.-H. *J. Org. Chem.* **1974**, *39*, 1570−1575.

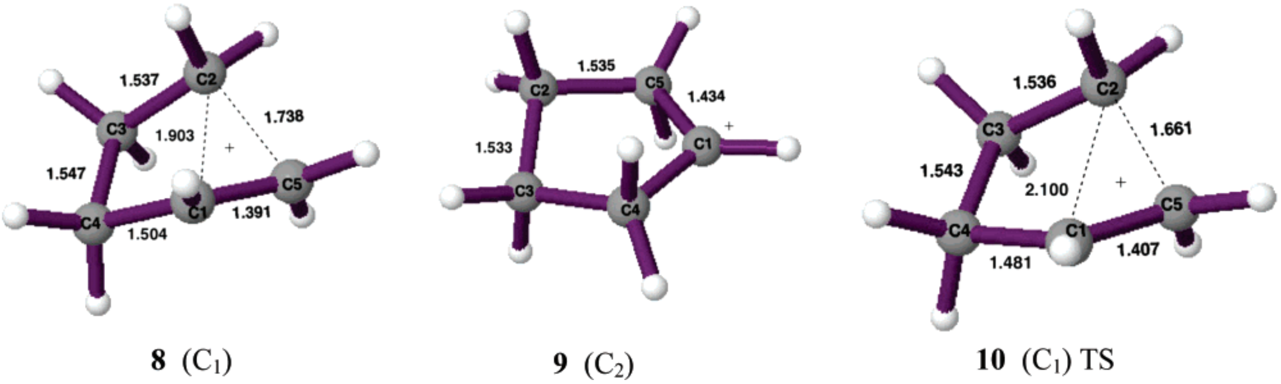
(29) Gajewski, J. J.; Lyle, R. L.; Gajewski, R. P. *Tetrahedron Lett.* **1970**, 1189−1192.

(30) Wiberg, K. B.; Hess, B. A., Jr. *J. Am. Chem. Soc.* **1966**, *88*, 4433−4436.

(31) Prakash, G. K. S.; Reddy, V. P.; Rasul, G.; Casanova, J.; Olah, G. A. *J. Am. Chem. Soc.* **1998**, *120*, 13362−13365.

(32) Kabakoff, D. S.; Namanworth, E. *J. Am. Chem. Soc.* **1970**, *92*, 3234−3235.

(33) Frisch, M. J. et al. *Gaussian 03*, Revision B.04, 2003.



8 (C$_1$)   **9** (C$_2$)   **10** (C$_1$) TS

FIGURE 1. MP2/cc-PVTZ structures of carbocations **8**, **9**, and transition state **10**.

TABLE 3. Calculated[a] and Experimental ^{13}C NMR Chemical Shifts

no.	atom	GIAO-SCF	GIAO-MP2	GIAO-CCSD(T)	exptl
8	C1	198.9	196.6	195.8	
	C2	17.9	26.9	27.3	
	C3	17.8	22.3	21.0	
	C4	19.0	22.9	22.5	
	C5	82.8	90.5	88.7	
9[b]	C1	321.7	318.8	314.8	320.0
	C2,C3	23.3	29.4	28.6	28.0
	C4,C5	61.4	74.2	73.5	71.0
11	C1	139.9	143.8	142.2	
	C2	23.0	33.1	32.8	
	C3	8.1	10.4	9.6	
	C4	12.3	15.8	15.4	
	C5	116.5	120.6	119.4	
	C6	14.8	17.1	16.5	
12	C1	152.8	155.7	154.1	
	C2	28.2	38.5	38.1	
	C3	16.8	21.2	20.0	
	C4	16.5	20.8	20.2	
	C5	117.1	123.5	121.8	
	C6	16.1	18.9	18.2	
13	C1	106.0	115.5		
	C2	34.0	47.0		
	C3	10.5	13.3		
	C4	12.9	17.4		
	C5	164.9	165.2		
	C6	24.4	28.1		
	C7	20.3	22.9		

[a] Referenced to TMS; for numbering scheme please see Figures 1 and 2. [b] Experimental values were taken from ref 42.

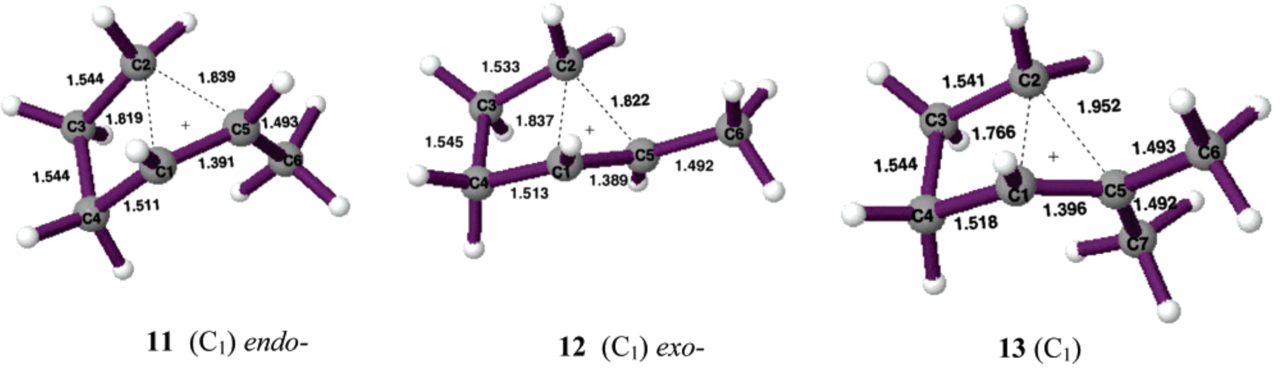
We have therefore sought to obtain structural information on primary, secondary, and tertiary cyclobutylmethyl cations through such high level ab initio calculations. We have also calculated the GIAO-CCSD(T) derived ^{13}C NMR chemical shifts of the selected carbocations to probe the nature and extent of charge delocalization into the cyclobutyl ring.

Calculations

Geometry optimizations and frequency calculations were carried out with the Gaussian 03 program.[33] The geometry optimizations were performed at the MP2/6-31G* level. Vibrational frequencies at the MP2/6-31G*//MP2/6-31G* level were used to characterize stationary points as minima (number of imaginary frequency (NIMAG) = 0) or transition state (NIMAG) = 1) and to evaluate zero point vibrational energies (ZPE), which were scaled by a factor of 0.95. The MP2/6-31G* geometries were further optimized at the higher MP2/cc-pVTZ levels. Final energies were calculated at the MP2/cc-pVTZ//MP2/cc-pVTZ + ZPE level. Calculated energies are given in Table 1. NMR chemical shifts were calculated by the GIAO (Gauge Invariant Atomic Orbitals) method[34−36] using MP2/cc-pVTZ geometries. GIAO-CCSD(T), GIAO-MP2, and GIAO-SCF calculations using the tzp/dz basis set[37−39] have been performed with the ACES II program.[40] The ^{13}C NMR chemical shifts were computed using TMS (calculated absolute shift, i.e., σ(C) = 193.9 (GIAO-SCF), 199.6 (GIAO-MP2), 197.9 (GIAO-CCSD(T)) as a reference.

Results and Discussion

Our earlier DFT calculations at the B3LYP/6-311+G* level showed that the primary cyclobutylmethyl cation is not an energy minimum on the potential energy surface.[31] We have now calculated the structure of the primary cyclobutylmethyl cation at the correlated ab initio MP2/6-31G* and MP2/cc-pVTZ levels, which show a minimum for the σ-bridged nonclassical structure (**8**). The charge delocalization of the latter carbocation



11 (C$_1$) *endo-*   **12** (C$_1$) *exo-*   **13** (C$_1$)

FIGURE 2. MP2/cc-pVTZ structures of carbocations **11**−**13**.

into the cyclobutyl ring is evidenced by significant C_1-C_2 bond elongation (1.903 Å), which is comparable to that of the C_2-C_5 bond (1.738 Å) at the MP2/cc-pVTZ level (Figure 1). Consistent with the nonclassical structure, the C_1-C_5 bond is also significantly shortened (1.391 Å). This structure may also be considered as a nonclassical cyclopentyl cation. However, it is distinctly different from the global minimum C_2-symmetric cyclopentyl cation (**9**), originally calculated at the ab initio MP2-(FU)/6-31G** level by Schleyer and co-workers.[41] We have also calculated the structure of the latter C_2-symmetric cyclopentyl cation at the same level MP2/cc-pVTZ level for a comparison with structure **8**. At the MP2/cc-pVTZ//MP2/cc-pVTZ + ZPE level, the C_2-symmetric cyclopentyl cation (**9**) is favored over the nonclassical primary cyclobutylmethyl cation (**8**) by 10.3 kcal/mol (Table 1).

We have located a transition structure, **10** (Figure 1), for interconversion of nonclassical (**8**) and classical (**9**) structures. Although the global energy minimum for the primary cyclobutylmethyl cation is a classical structure (**9**), it is important to note that the nonclassical structure (**8**) is stabilized relative to the corresponding transition state structure (**10**) by only 0.7 kcal/mol at the MP2/cc-pVTZ//MP2/cc-pVTZ + ZPE level (Table 1). Further, we have calculated the ^{13}C NMR chemical shifts of carbocations **8** and **9** at the GIAO-CCSD(T)/tzp/dz level using MP2/cc-pVTZ geometry (Table 3). For comparison, the ^{13}C NMR chemical shifts were also computed at the GIAO-MP2/tzp/dz and GIAO-SCF/tzp/dz levels (Table 3). The $\delta^{13}C$ obtained at the GIAO-MP2 and GIAO-CCSD(T) levels of calculations for **9** are in much closer agreement with the experimental ^{13}C NMR data[42] than those obtained earlier at relatively lower levels (IGLO/II).[41] The calculated $\delta^{13}C$ for structure **8** are also in agreement with the nonclassical nature of the primary cyclobutylmethyl cation. The $\delta^{13}C$ obtained at the GIAO-MP2 and GIAO-CCSD(T) levels are similar and differ significantly from those obtained at the relatively lower GIAO-SCF level. The GIAO-CCSD(T) $\delta^{13}C$ for the C_2-symmetric classical cyclopentyl cation (**9**) are remarkably similar to that of the experimental data (Table 3). The C_1-symmetric cyclobutylmethyl cation (**8**) shows five distinct absorptions, and the charge is delocalized over C_1 and C_5 carbons ($\delta^{13}C$ 195.8 and 88.7, respectively), showing its bridged nature.

Although our attempts to generate the secondary cyclobutylmethyl cations consistently gave the corresponding substituted cyclopentyl cations, through ring expansion rearrangement, the secondary cyclobutylmethyl cations, **6**, are expected to be minima on the potential energy surface as a result of the relatively lower electron demand for charge delocalization. We have accordingly calculated the structures of the homologous secondary 1-cyclobutylethyl cation at the ab initio MP2/cc-pVTZ level. At this level of calculation we have found that the 1-cyclobutylethyl cation shows energy minima for two conformations. These conformers differ in the stereochemical disposition of the methyl group as either below (*endo* conformer, **11**) or above (*exo* conformer, **12**) the average plane of the cation. The *endo* conformer **11** is relatively less stable than the *exo* conformer **12** by 1.2 kcal/mol at the MP2/cc-pVTZ//MP2/cc-pVTZ + ZPE level. Interestingly both conformers involve nonclassical charge delocalization into the cyclobutyl ring. In the *exo* conformer, **12**, the C_1-C_2 bond is substantially elongated (1.837 Å), whereas the C_2-C_3 bond is relatively unaffected. More importantly the C_2-C_5 bond distance (1.822 Å) of the carbocation **12** is almost equal to that of the C_1-C_2 bond showing that the secondary *exo*-1-cyclobutylethyl cation, **12**, is a true nonclassical structure. Total energies, zero point vibrational energies (ZPE), and relative energies of the calculated structures are shown in Table 2.

Reflecting its relatively higher energy content over that of the *exo* conformer **12**, the C_1-C_2 bond distance (1.819 Å) of *endo*-conformer **11** is relatively smaller than that of the C_2-C_5 bond (1.839 Å). For comparison, we have also calculated the structure of the 1-cyclobutyl-1-methylethyl cation, **13**, at the same level. The latter cation also involves substantial nonclassical delocalization, as shown by its slightly elongated C_1-C_2 bond (1.766 Å), which is significantly shorter than that of the C_2-C_5 bond (1.952 Å). The inductive stabilization of the α-methyl groups seems to be insignificant as the C_5-C_7 (C_5-C_6) bond distances are identical to those of the secondary cations **11** and **12**. The calculated structures of the carbocations **11**, **12**, and **13** are shown in Figure 2. Attempts to find a stable minimum for a possible secondary 2-methylcyclopentyl cation (a classical structure), however, failed because of rearrangement to form a more stable tertiary 1-methylcyclopentyl cation (also a classical structure).

The ^{13}C NMR chemical shifts for *endo* **11** and *exo* **12** conformers of the 1-cyclobutylethyl cation are calculated using GIAO-SCF, GIAO-MP2, and GIAO-CCSD(T) methods (Table 3). The more reliable GIAO-CCSD(T) calculations for conformer **12** show that the C1 carbon is relatively more deshielded ($\delta^{13}C$ 154.1) as compared to that of the *endo* conformer ($\delta^{13}C$ 142.2), indicating relatively more nonclassical stabilization of the *exo* **12**, which is in accord with its relatively elongated C_1-C_2 bond (vide supra). Attempts to find a stable minimum for a possible secondary 2,2-dimethylcyclopentyl cation (a classical structure), however, failed because of rearrangement to form a more stable tertiary 1,2-dimethylcyclopentyl cation (also a classical structure).

Interestingly, the GIAO-MP2 calculated ^{13}C NMR data for the tertiary carbocation **13** indicates that it involves substantial nonclassical charge delocalization into the cyclobutyl ring. Thus, the carbocation center is significantly shielded ($\delta^{13}C(C_5) = 165.2$), showing that the charge is substantially delocalized into the ring, as compared to that of the classical cyclopentyl cation (**9**; $\delta^{13}C$ (expt) = 320.0). The GIAO-CCSD(T) calculations on structure **13** were not possible as a result of the size of the molecule.

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(34) London, F. *J. Phys. Radium* **1937**, *8*, 397−409.

(35) Wolinski, K.; Hinton, J. F.; Pulay, P. *J. Am. Chem. Soc.* **1990**, *112*, 8251−8260.

(36) Ditchfield, R. *Mol. Phys.* **1974**, *27*, 789−807.

(37) Gauss, J. *Chem. Phys. Lett.* **1992**, *191*, 614−620.

(38) Gauss, J. *J. Chem. Phys.* **1993**, *99*, 3629−3643.

(39) Schaefer, A.; Horn, H.; Ahlrichs, R. *J. Chem. Phys.* **1992**, *97*, 2571−2577.

(40) ACES II, Austin-Budapest-Mainz version; Stanton, J. F.; Gauss, J.; Watts, J. D.; Szalay, P. G.; Bartlett, R. J. with contributions from Auer, A. A.; Bernholdt, D. B.; Christiansen, O.; Harding, M. E.; Heckert, M.; Heun, O.; Huber, C.; Jonsson, D.; Jusélius, J.; Lauderdale, W. J.; Metzroth, T.; Ruud, K.; Schiffmann, F.; Tajti, A. and the Integral packages: MOLECULE (Almlöf, J.; Taylor, P. R.), PROPS (Taylor, P. R.), and ABACUS (Helgaker, T.; Aa, H. J.; Jensen H. J. A.; Jørgensen, P. and Olsen, J.). See also: Stanton, J. F.; Gauss, J.; Watts, J. D.; Lauderdale, W. J.; Bartlett, R. J. *Int. J. Quantum Chem. Symp.* **1992**, *26*, 879−894. Current version see *http://www.aces2.de*.

(41) Schleyer, P. v. R.; Carneiro, J. W. d. M.; Koch, W.; Raghavachari, K. *J. Am. Chem. Soc.* **1989**, *111*, 5475−5477.

(42) Myhre, P. C.; Kruger, J. D.; Hammond, B. L.; Lok, S. M.; Yannoni, C. S.; Macho, V.; Limbach, H. H.; Vieth, H. M. *J. Am. Chem. Soc.* **1984**, *106*, 6079−6080.

In conclusion, we have shown by ab initio MP2/cc-pVTZ/GIAO-CCSD(T) ^{13}C NMR chemical shift calculations that the primary cyclobutylmethyl cation is a minimum on the potential energy surface and that it favors a σ-delocalized nonclassical structure (**8**). The secondary 1-cyclobutylethyl cation shows two nonclassical structures as energy minima, which differ in the stereochemical disposition of the α-methyl group. The *exo* conformer **12** is slightly favored over the *endo* conformer **11** by 1.2 kcal/mol at the MP2/cc-pVTZ//MP2/cc-pVTZ + ZPE level. Even the tertiary 1-cyclobutyl-1-methylethyl cation (**13**) shows substantial, although relatively reduced, nonclassical stabilization through delocalization of the positive charge into the neighboring cyclobutyl ring.

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Supporting Information Available: Cartesian coordinates of the structures **8**−**10** and **11**−**13** and the complete citation for ref 33. This material is available free of charge via the Internet at http://pubs.acs.org.

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