[5] a) D. H. R. Barton, M. Ramesh, *J. Am. Chem. Soc.* **1990**, *112*, 891; b) L.-B. Han, K. Ishihara, N. Kambe, A. Ogawa, I. Ryu, N. Sonoda, *J. Am. Chem. Soc.* **1992**, *114*, 7591; c) D. Crich, C. Chen, J.-T. Hwang, H. Yuan, A. Papadatos, R. I. Walter, *J. Am. Chem. Soc.* **1994**, *116*, 8937; d) L. Engman, V. Gupta, *J. Org. Chem.* **1997**, *62*, 157; e) M. A. Lucas, C. H. Schiesser, *J. Org. Chem.* **1998**, *63*, 3032.

[6] Free radical reactions with organotellurium compounds: a) S. Yamago, H. Miyazoe, J. Yoshida, *Tetrahedron Lett.* **1999**, *40*, 2339; b) S. Yamago, H. Miyazoe, J. Yoshida, *Tetrahedron Lett.* **1999**, *40*, 2343; c) S. Yamago, H. Miyazoe, R. Goto, J. Yoshida, *Tetrahedron Lett.* **1999**, *40*, 2347.

[7] Reactivity of silyl telluride under radical conditions was reported recently: C. H. Schiesser, M. Skidmore, *J. Organomet. Chem.* **1998**, *552*, 145.

[8] a) J. E. Drake, R. T. Hemmings, *Inorg. Chem.* **1980**, *19*, 1879; b) K. Sasaki, Y. Aso, T. Otsubo, F. Ogura, *Tetrahedron Lett.* **1985**, *26*, 453.

[9] a) I. Ugi, U. Fetzer, *Chem. Ber.* **1961**, *94*, 1116; b) L. Capuano, C. Wamprecht, W. Hell, *Liebigs Ann. Chem.* **1986**, 132; c) M. Westling, R. Smith, T. Livinghouse, *J. Org. Chem.* **1986**, *51*, 1163.

[10] D. C. Nonhebel, *Chem. Soc. Rev.* **1993**, 347.

[11] While the direct observation of silyl radicals by ESR spectroscopy failed, a spin-trapping experiment with **1** and *N-tert*-butyl-*α*-phenylnitrone (1 equiv) in benzene at 50 °C resulted in detection of the corresponding nitroxyl radical at $g = 2.0059$ with $a_N = 1.41$ mT and $a_H = 0.21$ mT. For spin trapping of trimethylsilyl radicals, see: a) B. B. Adeleke, S.-K. Wong, J. K. S. Wan, *Can. J. Chem.* **1974**, *52*, 2901; b) H. Chandra, I. M. T. Davidson, M. C. R. Symons, *J. Chem. Soc. Perkin Trans. 2* **1982**, 1353.

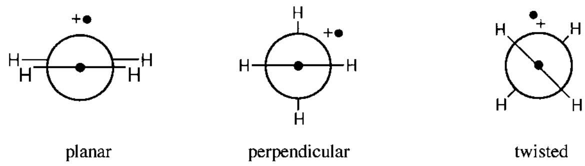
[12] a) D. J. Ager in *Umpoled Synthons* (Ed.: T. A. Hase), Wiley, New York, **1987**, Chap. 2; b) M. Kolb in *Umpoled Synthons* (Ed.: T. A. Hase), Wiley, New York, **1987**, Chap. 3; c) Y. Ito, M. Murakami, *J. Synth. Org. Chem. Jpn.* **1991**, *41*, 184.

[13] Synthetic transformations of C–Te bonds: N. Petragnani, *Tellurium in Organic Synthesis*, Academic Press, London, **1994**.

Structural Characterization of Novel Olefinic Cation Radicals: X-ray Crystallographic Evidence of σ–π Hyperconjugation[**]

Jay K. Kochi*, Rajendra Rathore, Chengjian Zhu, and Sergey V. Lindeman

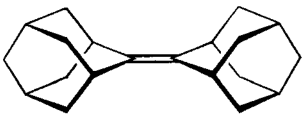
Alkyl-substituted ethylene cation radicals are highly reactive intermediates that occur when a variety of electrophilic addition reactions such as epoxidation, hydroxylation, ozonation, oxidative cleavage, dimerization, and cationic polymerization[1–3] proceed by prior electron transfer. As early as 1947, Mulliken and Roothaane[4] predicted the structure of the parent ethylene cation radical to be twisted by 30° due to the contributions from both the planar structure (normal π bonding) and the perpendicular structure (hyperconjugative bonding) (Scheme 1).



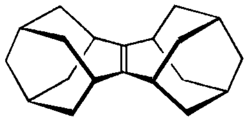
Scheme 1. Predicted structures of the parent ethylene cation radical.

Owing to the importance of ethylene as a precursor in polyethylene production, its cation radical has been subject to scrutiny in great detail using highly sophisticated theoretical methods including extended basis sets.[5] Experimentally, vacuum ultraviolet studies[6] and photoelectron spectroscopy[7] in the gas phase support a nonplanar structure of ethylene cation radical with a twist of 25°. On the other hand, more recent EPR studies[8] in frozen matrices at 4 K conclude that it can be almost planar (8°). In the last two decades, a number of sterically rigid olefinic cation radicals such as those from adamantylideneadamantane, and pagodadiene have been characterized in solution by using a variety of spectroscopic techniques.[9–11] However, despite enormous theoretical and experimental effort,[12] there is a singular lack of definitive X-ray crystallographic information on the structure of any alkyl-substituted olefinic cation radical.[13]

Herein, we report the successful isolation of the novel cation radical derived from the olefinic donor sesquihomoadamantene (SH), an isomer of the well-known adamantylideneadamantane (AA). Sesquihomoadamantene was originally prepared by Wynberg et al.[14] and it contains a tetrasubstituted double bond with rigid cyclic (cage) substituents.[15] Most importantly, sesquihomoadamantene is planar and singularly nonstrained. Therefore its conversion to the cation radical could reveal the typical structural changes that can be expected upon the oxidative conversion of an olefinic donor.



AA



SH

The one-electron oxidation of sesquihomoadamantene (SH) in dichloromethane at −78 °C either electrochemically[16] or chemically (using the well-known one-electron oxidant nitrosonium hexachloroantimonate)[17] yielded a dark purple solution of the corresponding cation radical, the quantitative formation of which was established spectrophotometrically [Eq. (1)].[18]

$$\mathrm{SH} + \mathrm{NO^{+}SbCl_6^{-}} \rightarrow \mathrm{SH^{+\bullet}SbCl_6^{-}} + \mathrm{NO} \qquad (1)$$

The purple salt was isolated as a microcrystalline powder by slow diffusion of toluene into the solution of $\mathrm{SH^{+\bullet}SbCl_6^{-}}$ in dichloromethane at −78 °C; and the purity of the highly colored precipitate was determined to be greater than 98 % by iodometric titration.[17] The identity of the isolated cation

---

[*] J. K. Kochi, R. Rathore, C. Zhu, S. V. Lindeman
Department of Chemistry
University of Houston
Houston, TX 77204-5641 (USA)
Fax: (+1) 713-743-2709
E-mail: jkochi@pop.uh.edu

[**] We thank the National Science Foundation and the Robert A. Welch Foundation for financial support.

0044-8249/00/11220-3817 $ 17.50+.50/0

radical SH$^{+\bullet}$ was further confirmed by its ready ability to quantitatively oxidize a variety of electron-rich organic donors[19] to the corresponding cation radicals. For example, if a solution of SH$^{+\bullet}$ cation radical in dichloromethane (λ_{max} = 360 and 485 nm, $\varepsilon_{360} = 4000 \pm 200\,\text{M}^{-1}\text{cm}^{-1}$)[20] was treated with incremental amounts of neutral CRET,[17] the resulting (UV/Vis) spectral changes (with well-defined isosbestic points at λ_{max} = 335, 449, and 538 nm, see Figure 1) clearly established the concomitant reduction of sesquihomoadamantene cation radical and oxidation of neutral CRET [Eq. (2)]. It should be noted that the highly robust cation radical CRET$^{+\bullet}$ has been well characterized by UV/Vis spectroscopy (λ_{max} = 486 and 518 nm, $\varepsilon_{518} = 7300\,\text{M}^{-1}\text{cm}^{-1}$) as well as by X-ray crystallography.[17]

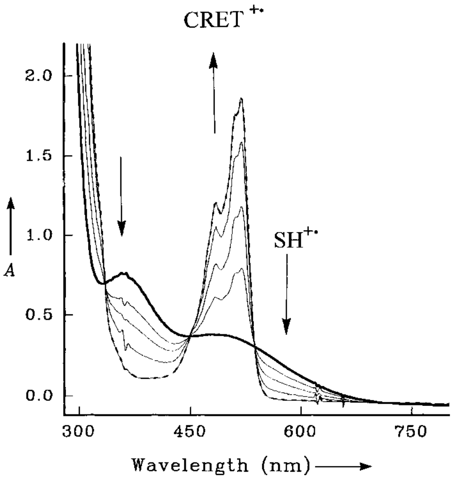
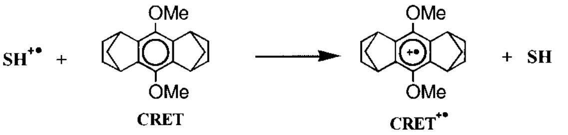


Figure 1. Spectral titration of 0.2 mM SH$^{+\bullet}$SbCl$_6^-$ (7.3×10^{-4} mmol) by incremental additions of neutral CRET (7.3×10^{-4} mmol) in dichloromethane at −78 °C. Note that the CRET$^{+\bullet}$ spectrum (----) remains unchanged upon addition of excess CRET. A = absorbance.



(2)

After repeated attempts to crystallize the powdered salt (especially by varying the solvent and temperature), we have now successfully isolated dark purple (single) crystals by the slow diffusion of hexane into a solution of pure SH$^{+\bullet}$SbCl$_6^-$ in dichloromethane at −50 °C. Single-crystal analysis by X-ray crystallography at −150 °C establishes its molecular structure, which clearly shows the central olefinic bond in the SH$^{+\bullet}$ cation radical to be twisted by 29°,[13] as shown by the sideways ORTEP diagrams in Figure 2 of both SH$^{+\bullet}$ (left) and SH (right). Moreover, a careful comparison of the precise X-ray structures of both neutral SH and its cation radical under identical conditions (see Experimental Section) demonstrates that the pronounced twist cannot be due to relief of steric strain, and thus provides us with the unique opportunity to examine other more subtle structural changes that occur when a single electron is removed from the neutral olefinic donor.

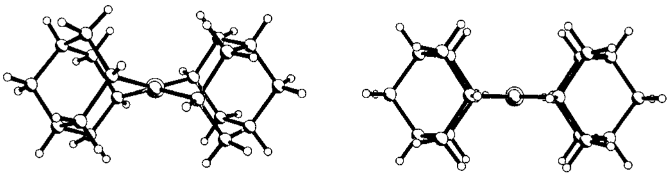
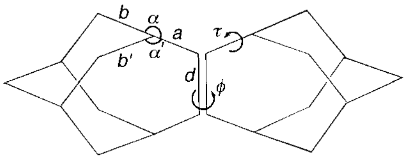


Figure 2. Left) Molecular structure of the cation radical salt SH$^{+\bullet}$SbCl$_6^-$ showing the twist around the central C–C bond. Hexachloroantimonate anion and the solvent molecule omitted for clarity. Right) In comparison, the molecular structure of the neutral SH donor is completely planar.

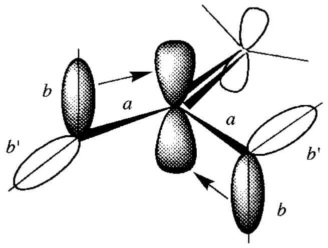
Table 1 summarizes the systematic changes in the bond lengths as well as angular reorganization in sesquihomoadamantene cation radical (SH$^{+\bullet}$) as compared to the neutral olefin. Thus, the central C–C double bond expectedly lengthens by 5 pm. Most notably, however, the four C–C single bonds (α bonds denoted by a) directly attached to the olefinic carbon atoms *shorten* by 3 pm each, and only one of the two C–C bonds (β bonds denoted by b) attached to each allylic carbon atom is elongated by 1.5 pm. (Note that the other C–C bond (denoted by b') remains unchanged.) Moreover, the angles at the allylic carbon atoms undergo significant changes which are accompanied by an increase in the twist (~18 °C) around the a bonds. As a result, the lengthened b bonds position themselves approximately *periplanar* to the (partially occupied) olefinic p orbitals, in a way different from those in the neutral olefin (Scheme 2).[21]

Table 1. Comparison of the principal geometrical parameters of the neutral SH and its cation radical SH$^{+\bullet}$.



Parameter	SH	SH$^{+\bullet}$	Δ (SH → SH$^{+\bullet}$)
d [Å]	1.345(1)	1.397(3)	+0.052
a [Å]	1.526(1)	1.491(3)	−0.035
b [Å]	1.542(1)	1.558(3)	+0.016
b' [Å]	1.542(1)	1.541(3)	−0.001
α [°]	113.3(1)	108.1(2)	−5.2
α' [°]	113.3(1)	115.2(2)	+1.9
ϕ [°]	0.5(1)	29.0(2)	+28.5
τ [°][a]	63.7(1)	82.3(2)	+18.6
τ' [°][a]	−63.7(1)	−43.1(2)	+20.6

[a] τ and τ' are dihedral angles between planes determined by bonds d/a/ab and d/a/ab' respectively.



Scheme 2. Arrangement of the olefinic p orbitals in the sesquihomoadamantene cation radical (SH$^{+\bullet}$).

The latter observation of distinct changes in the bond lengths of the remote β bonds (which lie *periplanar* to the cationic p orbitals), coupled with the substantial shortening of the α bonds represents the first direct experimental evidence for the (classical) hyperconjugative stabilization of cationic charges.[22] We believe that these definitive structural changes in $SH^{+\bullet}$ will also be generally applicable to the characterization of cation radical structures of other olefin donors. As such, we are currently inquiring into the origin and generality of the structural twist and hyperconjugative stabilization in various olefinic cation radicals and carbocations using high-level theoretical calculations.[23]

Experimental Section

A mixture of adamantylideneadamantane (AA) and isomeric sesquihomoadamantene (SH) was prepared according to literature procedures[14] and subjected to the standard conditions of epoxidation using *m*-chloroperbenzoic acid in dichloromethane for 1 h at 0 °C. Aqueous workup followed by chromatographic purification yielded pure sesquihomoadamantene SH (24 %) and adamantylidene – adamantane oxide[14] (51 %). Recrystallization from anhydrous diethyl ether at − 20 °C afforded analytically pure SH, m.p. 202 – 203 °C (lit.[14a] m.p. 199 – 201 °C).

X-ray crystallography: The intensity data were collected at − 150 °C on a Siemens SMART diffractometer equipped with a CCD detector using $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods[24] and refined by full-matrix least-squares procedures.

Crystal data for sesquihomoadamantene cation radical ($SH^{+\bullet}SbCl_6^-$): Brutto formula: $C_{20}H_{28}O_4 \cdot SbCl_6 \cdot CH_2Cl_2$, $M_r = 687.80$, monoclinic $P2_1/n$, $a = 10.4473(4)$, $b = 15.9754(6)$, $c = 15.6397(6)$ Å, $\beta = 93.396(1)°$, $\rho_{calcd} = 1.753\ g\,cm^{-3}$, $V = 2605.7(2)$ Å^3, $Z = 4$. The total number of reflections measured was 37 186, of which 11 429 reflections were symmetrically nonequivalent. Final residuals were $R1 = 0.0339$ and $wR2 = 0.0625$ for 7397 reflections with $I > 2\sigma(I)$.

Crystal data for neutral sesquihomoadamantene (SH): Brutto formula: $C_{20}H_{28}$, $M_r = 268.42$, monoclinic, $P2_1/n$, $a = 6.4547(3)$, $b = 11.9580(6)$, $c = 9.6301(5)$ Å, $\beta = 91.772(1)°$, $\rho_{calcd} = 1.200\ g\,cm^{-3}$, $V = 742.95(6)$ Å^3, $Z = 2$. The total number of reflections measured was 10 380, of which 3266 reflections were symmetrically nonequivalent. Final residuals were $R1 = 0.0421$ and $wR2 = 0.1203$ for 2926 reflections with $I > 2\sigma(I)$. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no.“ CCDC-143380 (neutral SH) and CCDC-143381 ($SH^{+\bullet}$ cation radical). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+ 44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Received: April 19, 2000 [Z15014]

---

[1] a) S. F. Nelsen, *Acc. Chem. Res.* **1987**, *20*, 269, and references therein; b) T. Kim, G. A. Mirafzal, J. Liu, N. L. Bauld, *J. Am. Chem. Soc.* **1993**, *115*, 7653; c) S. F. Nelsen, R. Akaba, *J. Am. Chem. Soc.* **1981**, *103*, 2096; d) E. L. Clennan, W. Simmons, C. W. Almgren, *J. Am. Chem. Soc.* **1981**, *103*, 2098; e) C. M. Jefford, A. F. Boschung, *Tetrahedron Lett.* **1976**, 4771; f) R. Akaba, H. Sakuragi, K. Tokumaru, *Tetrahedron Lett.* **1984**, *25*, 665; g) E. Bosch, J. K. Kochi, *J. Am. Chem. Soc.* **1996**, *118*, 1319.

[2] a) N. L. Bauld, *Tetrahedron* **1989**, *45*, 5307; b) N. L. Bauld, *J. Am. Chem. Soc.* **1992**, *114*, 5800; c) J. P. Dinnocenzo, D. A. Conlon, *J. Am. Chem. Soc.* **1988**, *110*, 2324; d) M. Schmittel, C. Wohrle, *J. Org. Chem.* **1995**, *60*, 8223, and references therein.

[3] a) M. Tabata, A. Lund, P. O. Samskog, S. Lunell, M. B. Huang, *J. Polym. Sci. A* **1988**, *26*, 2725, and references therein; b) see also: N. Salhi-Benachenhou, J. R. Alvarez-Idaboy, S. Lunell, L. A. Eriksson, *Theor. Chem. Acc.* **1997**, *97*, 282; c) H. Zipse, *J. Am. Chem. Soc.* **1995**, *117*, 11 798; d) S. S. Shaik, A. Pross, *J. Am. Chem. Soc.* **1989**, *111*, 4306; e) M. S. Workentin, N. P. Schepp, L. J. Johnston, D. D. Wayner, *J. Am. Chem. Soc.* **1994**, *116*, 1142.

[4] a) R. S. Mulliken, C. C. Roothaane, *J. Chem. Rev.* **1947**, *41*, 219; b) R. S. Mulliken, C. C. Roothaane, *Tetrahedron* **1959**, *5*, 253.

[5] a) S. Lunell, M.-B. Huang, *Chem. Phys. Lett.* **1990**, *168*, 63; b) N. Salhi-Benachenhou, B. Engels, M.-B. Huang, S. Lunell, *Chem. Phys.* **1998**, *236*, 53, and references therein; c) L. A. Eriksson, S. Lunell, R. J. Boyd, *J. Am. Chem. Soc.* **1993**, *115*, 6896; c) O. Takahashi, O. Kikuchi, *J. Chem. Phys.* **1994**, *100*, 1350.

[6] a) A. J. Merer, L. Schoonveld, *J. Chem. Phys.* **1968**, *48*, 522; b) A. J. Merer, L. Schoonveld, *Can. J. Phys.* **1969**, *47*, 1731.

[7] H. Koppel, W. Domcke, L. S. Cederbaum, W. V. Niessen, *J. Chem. Phys.* **1978**, *69*, 4252.

[8] a) K. Toriyama, M. Okazaki, *Appl. Magn. Reson.* **1996**, *11*, 47, and references therein; b) M. Shiotani, Y. Nagata, J. Sohma, *J. Am. Chem. Soc.* **1984**, *106*, 4640; however, see: F. Gerson, G. Gescheidt, S. F. Nelsen, L. A. Paquette, M. F. Teasley, L. Waykole, *J. Am. Chem. Soc.* **1989**, *111*, 5518.

[9] a) F. Gerson, J. Lopez, R. Akaba, S. F. Nelsen, *J. Am. Chem. Soc.* **1981**, *103*, 6716; b) T. Clark, M. F. Teasley, S. F. Nelsen, H. Wynberg, *J. Am. Chem. Soc.* **1987**, *109*, 5719; c) T. Clark, S. F. Nelsen, *J. Am. Chem. Soc.* **1988**, *110*, 868; d) S. F. Nelsen, M. F. Teasley, D. L. Kapp, C. R. Kessel, L. A. Grezzo, *J. Am. Chem. Soc.* **1984**, *106*, 791; e) S. F. Nelsen, C. R. Kessel, *J. Am. Chem Soc.* **1979**, *101*, 2503.

[10] a) H. Prinzbach, G. Gescheidt, H.-D. Martin, R. Herges, J. Heinze, G. K. S. Prakash, G. A. Olah, *Pure Appl. Chem.* **1995**, *67*, 673, and references therein; b) H. Prinzbach, B. A. R. C. Murty, W.-D. Fessner, J. Mortensen, J, Heinze, G. Gescheidt, F. Gerson, *Angew. Chem.* **1987**, *99*, 488; *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 457; c) G. Gescheidt, R. Herges, H. Neumann, J. Heinze, M. Wollenweber, M. Etzkorn, H. Prinzbach, *Angew. Chem.* **1995**, *107*, 1109; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1016; d) M. Etzkorn, F. Wahl, M. Keller, H. Prinzbach, F. Barbosa, V. Peron, G. Gescheidt, J. Heinze, R. Herges, *J. Org. Chem.* **1998**, 63, 6080, and references therein.

[11] a) T. Shida, Y. Egawa, A. Kubodera, T. Kato, *J. Chem. Phys.* **1980**, *73*, 5963; b) M. Kira, H. Nakazawa, H. Sakurai, *J. Am. Chem. Soc.* **1983**, *105*, 6983; c) Y. Itagaki, M. Shiotani, A. Hasegawa, H. Kawazoe, *Bull. Chem. Soc. Jpn.* **1998**, *71*, 2547; d) O. West, *J. Am. Chem. Soc.* **1997**, *119*, 5713; e) A. D. Trifunac, D. W. Werst, *J. Am. Chem. Soc.* **1996**, *118*, 9444; f) H. D. Roth, *Top. Curr. Chem.* **1992**, *163*, 131, and references therein.

[12] a) D. J. Bellville, N. L. Bauld, *J. Am. Chem. Soc.* **1982**, *104*, 294; b) M. J. Shephard, M. N. Paddon-Row, *J. Phys. Chem.* **1995**, *99*, 3101; c) S. D. Chemerisov, D. W. Werst, A. D. Trifunac, *Chem. Phys. Lett.* **1998**, *291*, 262; d) F. Gerson, P. Felder, R. Schmidlin, H. N. C. Wong, *J. Chem. Soc. Chem. Commun.* **1994**, 1659; e) T. Nishinaga, K. Komatsu, N. Sugita, H. J. Lindner, J. Richter, *J. Am. Chem. Soc.* **1993**, *115*, 11642.

[13] Tetraanisylethylene cation radical is the only known example which has been characterized crystallographically and it also shows a twist of 30° around the central C–C bond, see: R. Rathore, S. V. Lindeman, A. S. Kumar, J. K. Kochi, *J. Am. Chem. Soc.* **1998**, *120*, 6931.

[14] a) H. Wynberg, E. Boelema, J. H. Wieringa, J. Strating, *Tetrahedron Lett.* **1970**, 3613; b) E. Boelema, H. Wynberg, J. Strating, *Tetrahedron Lett.* **1971**, 4029

[15] X-ray structure of sesquihomoadamantene has been determined at room temperature, see: W. H. Watson, A. Nagl, *Acta Crystallogr. Sect. C* **1987**, *43*, 2465.

[16] The one-electron oxidation of SH to its purple cation radical can also be carried out electrochemically at $E^{o}_{ox} = 1.36$ V versus SCE in anhydrous dichloromethane (containing tetra-*n*-butylammonium hexafluorophosphate as the supporting electrolyte) at − 78 °C.

[17] For a general procedure for the oxidation of organic donors using $NO^+SbCl_6^-$, see: R. Rathore, J. K. Kochi, *J. Org. Chem.* **1994**, *60*, 4399.

[18] The identity of liberated NO was confirmed by UV/Vis and IR spectroscopy (W. G. Fateley, H. A. Bent, B. Crawford, Jr., *J. Chem. Phys.* **1959**, *31*, 204).

[19] For a list of donors which afford stable cation radical salts, see: R. Rathore, A. S. Kumar, S. V. Lindeman, J. K. Kochi, *J. Org. Chem.* **1998**, *63*, 5847.

[20] In addition, a very weak absorption at $\lambda > 750$ nm (see Figure 1) accounts for the purple color of the cation radical salt. The ESR spectrum of $SH^{+\bullet}SbCl_6^-$ in dichloromethane at − 70 °C was the same as that obtained by Nelsen and co-workers in a mixture of trifluoro-

acetic acid and trifluoroacetic anhydride using the electrochemical method.[9b,c]

[21] Note that the remote *b′* bonds which remain unchanged in the cation radical lie almost orthogonal to the p orbitals and thus do not participate in stabilizing the cationic charge, compare: J. F. King, R. Rathore, *J. Am. Chem. Soc.* **1990**, *112*, 2001.

[22] a) J. Rosenbaum, M. C. R. Symons, *Proc. Chem. Soc.* **1959**, 92; b) see also: S. F. Nelsen, M. F. Teasley, D. L. Kapp, C. R. Kessel, L. A. Grezzo, *J. Am. Chem. Soc.* **1984**, *106*, 791.

[23] Theoretical calculations of olefinic cation radicals are in progress with Professor P. von R. Schleyer.

[24] G. M. Sheldrick, SHELSX-86, program for structure solution, University of Göttingen, Germany, **1986**.

The First Templated Borogermanate $(C_2N_2H_{10})_2[(BO_{2.5})_2(GeO_2)_3]$: Linkage of Tetrahedra of Significantly Different Sizes**

Mike S. Dadachov,* Kai Sun, Tony Conradsson, and Xiaodong Zou*

The classes of microporous materials—tetrahedral- and mixed-framework compounds—with open structures continue to expand in terms of framework-forming elements.[1] The most accomplished and also largest classes of tetrahedral-framework compounds are aluminosilicates (Al-Si-O),[2] aluminophosphates (Al-P-O)[3] as well as their isomorphic substituted forms. Attempts to synthesize frameworks with elements other than Al, Si, and P, especially with transition metals, have resulted in many new classes, such as gallophosphates,[4] titanosilicates,[5] beryllium,[6] zinc,[7] cobalt,[8] iron,[9] vanadium,[10] nickel,[11] and molybdenum[12] phosphates. Since most transition metal atoms are too large to fit comfortably into the hole formed by a van der Waals oxygen tetrahedron, they are often coordinated by additional terminal OH and F groups, forming trigonal bipyramids, square bipyramids, or octahedra in open framework structures. As a consequence, the Me–O bonds become weaker and thus most of these compounds are thermally unstable. Besides the framework compounds containing oxygen, other compounds such as sulfides[13] and a phosphonitride[14] have been reported.

During recent years, attempts have been made to include boron atoms into the ZSM-*n* frameworks. However, very little aluminum/silicon could be replaced by boron.[15] Furthermore, a few templated metal borophosphates were reported.[16]

Open framework germanates are an interesting and expanding class of microporous materials. Germanium forms oxygen polyhedra with 4-, 5-, and 6-coordination, and germanates consisting of both purely tetrahedrally coordinated frameworks[17] and mixed polyhedral frameworks[18] have been reported.

Herein we report the synthesis and structure determination of the first templated borogermanate $(C_2N_2H_{10})_2[(BO_{2.5})_2(GeO_2)_3]$. The hydrothermal reaction of ethylenediamine, boric acid, germanium dioxide, hydrofluoric acid, and pyridine gave transparent platelike crystals of $(C_2N_2H_{10})_2[(BO_{2.5})_2(GeO_2)_3]$ in high yield. X-ray analysis of these crystals[19] revealed a layered structure with large openings in the layers and organic templates between the layers.

There are three unique Ge and two unique B atoms in the structure, all of them tetrahedrally coordinated by oxygen atoms (Figure 1). The structure can be described as undulating borogermanate layers, each one constructed of isolated 3-rings of germanium tetrahedra, $[GeO_2]_3$, connected by pairs of boron tetrahedra, $[BO_{2.5}]_2$ (Figure 2). The borogermanate layers can also be described in terms of large 9-rings formed by alternating two-corner-linked germanium tetrahedra (six in total) and one pair of boron tetrahedra (three pairs in total) (Figure 2). The layers are connected by hydrogen bonding through the two unique charge-compensating diprotonated ethylenediamine cations. One of those cations was found to have two different conformations (Figure 1). Such behavior is not uncommon in this type of structure, since the cations reside in large cavities and possess a considerable freedom of motion.

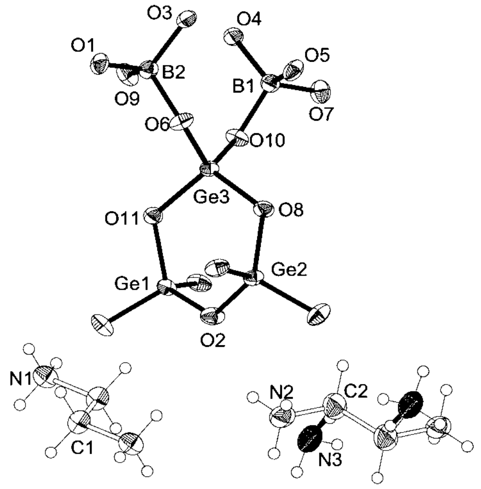


Figure 1. Atom-labeling scheme for all the non-hydrogen atoms of the asymmetric unit of $(C_2N_2H_{10})_2[(BO_{2.5})_2(GeO_2)_3]$ (ORTEP plot; 50% probability ellipsoids). The NH_3 terminal groups (N2 and N3) bonded to C2 are the two different conformations of the diprotonated ethylenediamine.

The bond lengths and angles for both the framework atoms and the guests are unexceptional. All Ge–O distances are between 1.719 and 1.768 Å and the O-Ge-O angles are between 104.27 and 115.18°. All oxygen atoms of the germanium coordination polyhedra are shared either between Ge and Ge or between Ge and B atoms. Three of the four oxygen atoms of each BO_4 tetrahedron are shared between boron and germanium, and one acts as a terminal oxygen atom pointing towards the interlayer. As a consequence, the B–O distances fall into two categories. The three bridging

---

[*] Dr. M. S. Dadachov, Dr. X. D. Zou, Dr. K. Sun, T. Conradsson
Structural Chemistry, Stockholm University
S-106 91 Stockholm (Sweden)
Fax: (+46) 8-16-31-18
E-mail: zou@struc.su.se

[**] This work was supported by the Swedish Natural Science Research Council (NFR).