(↑) and spin down (↓) orbitals undergo a large spin polarization splitting, with five occupied predominantly Fe↑ orbitals stabilized and the Fe↓ counterparts higher in energy and unoccupied, consistent with high-spin ferric calculations.[20] The NO $\Pi^*$ orbitals also split with the occupied $\Pi^*$↓ stabilized below the Fe↓ orbitals due to their spin pairing with the Fe↑ $d_{xz}$,$d_{yz}$ electrons. The $\Pi^*$↑ set is higher in energy and unoccupied. This calculation therefore gives five uncompensated spin up electrons on the Fe (ferric) and two spin down electrons in the NO $\Pi^*$ orbitals ($NO^-$). These are spin paired due to direct orbital overlap. Thus an experimentally and theoretically consistent electronic structure has been generated for the $\{FeNO\}^7$ $S = {}^3/_2$ system, which can be described as high-spin $Fe^{3+}$($S = {}^5/_2$) antiferromagnetically coupled to $NO^-$($S$ = 1) to produce the $S = {}^3/_2$ ground state. This new bonding description provides a general understanding of the interaction of NO with the high-spin ferrous site, and the spectral features can be quantitated to provide insight into differences in bonding and electron distribution which can be related to dioxygen activation by non-heme iron enzymes.

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# Synthesis and X-ray Crystal Structure of 11-Bromo-*endo*-9-chloro-7-ethoxybicyclo[5.3.1]undec-1(11)-ene. A Stable, Highly Strained Anti-Bredt Olefin

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Strained and twisted double bonds[1] have fascinated chemists ever since Bredt formulated his famous rule which "forbids" the existence of bridgehead double bonds in the so-called anti-Bredt olefins;[2] current interest is illustrated by recently described, highly strained and "unlikely" representatives of this class.[3,4] Strain leads to increased reactivity,[5] and therefore experimental structures are very rare;[1] in the bridgehead *trans*-cyclooctene family, only one X-ray crystal structure of an uncomplexed member is known.[3,6,7]

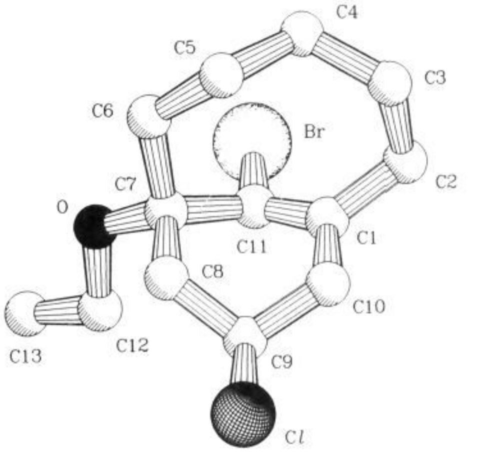


**Figure 1**. PLUTON drawing of **1** with hydrogen atoms removed for clarity. Selected bond lengths (Å) and bond angles (deg): C1–C2, 1.502 (9); C2–C3, 1.555 (9); C3–C4, 1.541 (8); C4–C5, 1.554 (9); C5–C6, 1.545 (9); C6–C7, 1.554 (9); C7–C11, 1.502 (8); C7–C8, 1.559 (9); C8–C9, 1.520 (8); C9–C10, 1.521 (9); C1–C10, 1.504 (9); C1–C11, 1.319 (8); C2–C1–C10, 117.0 (5); C11–C1–C2, 123.1 (6); C11–C1–C10, 118.6 (5); Br–C11–C7, 112.9 (4); C1–C11–Br, 121.3 (4); C1–C11–C7, 122.9 (5); C1–C2–C3, 105.7 (5); C6–C7–C11, 105.5 (5).

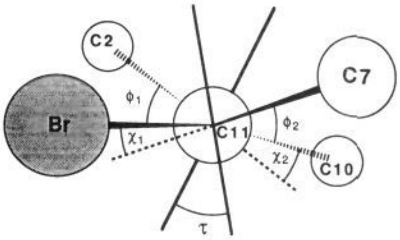
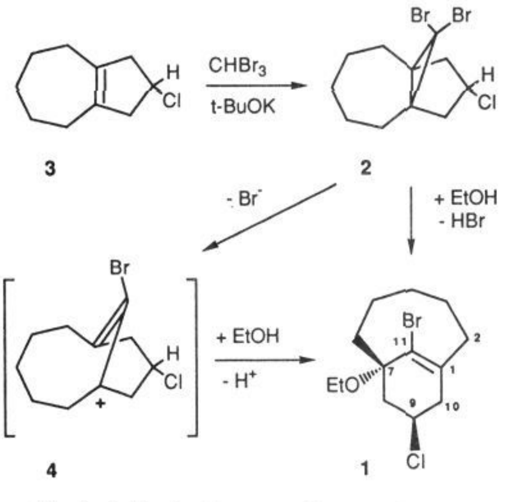


**Figure 2**. View along the double bond C11═C1. $\chi_1$: 180° − ∠BrC11C1C7 = 20.8 (7)°. $\chi_2$: 180° − ∠C10C1C11C2 = 13.4 (6)°; $\phi_1$: ∠BrC11C1C2 = 25.6 (8)°. $\phi_2$: ∠C7C11C1C10 = 33.0 (8)°. $\tau$: $0.5(\phi_1 + \phi_2)$ = 29.3°. $\theta_1$: ∠C7C11C1C2 = 133.6 (6)°. $\theta_2$: ∠BrC11C1C10 = 167.8 (4)°.

**Scheme I**



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We now report the synthesis and X-ray crystal structure of 11-bromo-*endo*-9-chloro-7-ethoxybicyclo[5.3.1]undec-1(11)-ene (**1**), which has the eight-membered-ring double bond in the particularly unfavorable position toward the smallest, i.e., one-carbon, bridge.

Compound **1** was unexpectedly obtained in quantitative yield from the propellane **2** on attempted crystallization from boiling ethanol; **2**, a somewhat unstable compound, was prepared in 16% yield by dibromocarbene addition ($CHBr_3$/KO-*t*-Bu in pentane[8]) to 9-chlorobicyclo[5.3.0]dec-1(7)-ene (**3**)[9] (Scheme I). The formation of **1** can be rationalized by invoking electrocyclic ionization and ring opening of **2** to furnish the intermediate cation **4**, which is intercepted by the solvent. This type of solvolysis has ample precedent in the work or Warner et al. involving the isomeric bicyclo[4.4.1]undecane system where, incidentally, the primary solvolysis products analogous to **1** contain a *trans*-cycloheptane ring and therefore were not stable enough to be isolated.[1a]

Several crystallizations of **1**[10] from ethanol yielded colorless crystals suitable for X-ray crystal structure determination[11] (Figure 1).

Analysis of the X-ray data shows one of the most distorted C=C double bonds experimentally observed so far. This is most clearly seen on inspection of Figure 2. Note, e.g., the large torsion between C2 and C7 ($180 - \theta_1 = 46.4\ (6)°$). In comparison with other highly strained olefins,[3,4,7] it is remarkable that the strain in **1** is revealed not so much by pyramidalization of the olefinic carbon atoms ($\chi_m = 0.5(\chi_1 + \chi_2) = 17.1\ (7)°$) as by an unusually high degree of torsion ($\tau = 29.3°$). This must at least in part be a consequence of the geometrical restrictions imposed by the bicyclo[5.3.1]undecene skeleton. Per degree of deformation, torsion requires more energy than pyramidalization,[7b,c] and therefore geometrically less restricted alkenes respond preferentially by pyramidalization; however, placing the double bond in the shortest bridge of **1** obviously enforces torsion which can be alleviated by pyramidalization only to a minor extent. Interestingly, semiempirical calculations such as MNDO[12] overemphasize this effect by predicting even higher torsion ($\tau = 36.9°$) at the expense of pyramidalization ($\chi_m = 9.6°$). An additional factor may be the bromine substituent at position 11 interacting with C4-H(exo) of the pentamethylene bridge.

Intuitively, one would expect that torsion should weaken the double bond due to decrease of the π-overlap; the calculations seem to support this ($d = 1.36$ Å). Surprisingly, like in other strained olefins,[3,4,7] this is actually not the case in **1**, which has a rather short double bond ($d$(C1=C11) = 1.319 (8) Å!).

Contrary to other strained anti-Bredt compounds,[1] **1** is not reactive toward oxygen and moisture. Further chemical and physical properties of **1** are presently being investigated.

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**Registry No. 1**, 143841-68-3; **2**, 143841-69-4; **3**, 102836-25-9.

**Supplementary Material Available:** Tables of crystal data and details of the structure determination, all atomic coordinates and thermal parameters, bond lengths, and bond angles and a thermal motion ellipsoid plot (9 pages); listing of observed and calculated structure factors (19 pages). Ordering information is given on any current masthead page.

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(10) **1**: mp 130 °C; $^1$H NMR (200 MHz; $CDCl_3$) $\delta$ 1.02 (m, 1 H), 1.28 (t, $^3J_{HH} = 7$ Hz, 3 H, Me), 1.6–2.0 (m, 5 H), 2.0–2.3 (m, 4 H), 2.5–2.9 (m, 3 H), 3.18 (m, 1 H), 3.37 (dq, $^3J_{HH} = 7$ Hz, $^2J_{HH} = 8$ Hz, 1 H, $OCH_2$), 3.49 (dq, $^3J_{HH} = 7$ Hz, $^2J_{HH} = 8$ Hz, 1 H, $OCH_2$), 4.11 (m, 1 H, CHCl); $^{13}$C NMR (50.3 MHz; $CDCl_3$) $\delta$ 15.5 (q, $J_{CH} = 126$ Hz, Me), 25.6 (t, $J_{CH} = 124$ Hz), 25.9 (t, $J_{CH} = 124$ Hz), 36.6 (t, $J_{CH} = 127$ Hz), 38.1 (t, $J_{CH} = 134$ Hz), 43.3 (t, $J_{CH} = 135$ Hz), 43.8 (t, $J_{CH} = 132$ Hz), 48.6 (t, $J_{CH} = 129$ Hz), 53.4 (d, $J_{CH} = 152$ Hz, CHCl), 59.4 (t, $J_{CH} = 140$ Hz, $OCH_2$), 83.2 (s), 128.9 (s), 143.7 (s); HRMS ($C_{13}H_{20}O^{81}Br^{35}Cl$) calcd 308.0364, found 308.031.

(11) Crystal data for **1**: $C_{13}H_{20}BrClO$, plate-shaped crystal, monoclinic, space group $P2_1/a$, $V = 1340.15\ (15)$ Å$^3$, $Z = 4$, $\mu$(Mo K$\alpha$) = 32.2 cm$^{-1}$, 3076 independent reflections ($1.3° < \theta < 27.5°$, $T = 298$ K, Zr-filtered Mo K$\alpha$ radiation). Data were corrected for Lp, observed linear decay, absorption, and extinction. The structure was solved by automated direct methods (SHELXS86). Refinement on $F$ by full-matrix least-squares techniques (SHELX76); $R = 0.0497$, $wR = 0.0246$, $w^{-1} = \sigma^2(F)$, $S = 1.47$ for 1339 reflections with $I > 2.5\sigma(I)$. Non-hydrogen atoms were refined with anisotropic thermal parameters; hydrogen atoms were included on calculated positions (C–H = 0.98 Å) in riding mode. No residual density outside −0.47 and 0.61 e Å$^{-3}$.

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# Negative Ion Photoelectron Spectroscopy of $CH_2$=SiH and $CH_3$–Si

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Simple organosilicon radicals are of interest as intermediates in the gas-phase reactions occurring during chemical vapor deposition of silicon carbide,[2] as astrochemically important species,[3] and as benchmarks for theoretical models of silicon–carbon multiple bonding.[4] The electron affinities of several silicon hydrides[5,6] and $Si_n$ clusters[7,8] have been measured by negative ion photoelectron spectroscopy, and values for a number of $R_3Si$ radicals have been obtained by electron photodetachment spectroscopy.[9] We report here the 488-nm photoelectron spectra of the isomeric organosilicon anions $CH_3$–$Si^-$ and $CH_2$=$SiH^-$. These data yield electron affinities for $CH_3$–Si (0.852 ± 0.010 eV) and $CH_2$=SiH (2.010 ± 0.010 eV), as well as vibrational frequencies for both molecules. The measured electron affinities are used to estimate Si–H gas-phase acidities of 372 ± 3 kcal/mol for $CH_3$–SiH and 364 ± 5 kcal/mol for $CH_2$=$SiH_2$. These results provide the first spectroscopic data for $CH_3$–Si, $CH_2$=SiH, and their negative ions and illustrate of the ability of this experimental technique to identify isomeric structures.

The experimental apparatus employed in these studies has recently been described in detail.[10] Negative ions were prepared at 0.5 Torr in a flowing afterglow ion source by seeding a small amount (1–10 std cm$^3$/min) of tetramethylsilane-$H_{12}$ or -$D_{12}$ into a fast flow of helium (~8 std l/min) just downstream of a 2.45-GHz microwave cavity. Similarly, a $[Si,C,H_3]^-$ anion was prepared from methylsilane in a previous flowing afterglow study of this system.[11] In the present study, anions sampled from the plasma were mass selected, and the 43 (protonated) or 46 amu

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