Inorg. Chem. **1991**, *30*, 784–789

Contribution from the Department of Chemistry,
University of Kentucky, Lexington, Kentucky 40506-0055

N-Bonded Triazole Derivatives of Boron: Cyclotetrakis(triazolylboranes)

C. P. Brock, A. L. Companion, L. D. Kock, and K. Niedenzu*

Received June 22, 1990

ASED molecular orbital calculations on the formation of monomeric 1-azolylboranes by the process $BH_3 + Haz \rightarrow H_2 + H_2B(az)$ (Haz = pyrazole, imidazole, 1,2,3-triazole, 1,2,4-triazole, 1,2,5-triazole) indicate that the reaction is energetically favorable and that the charge densities at the nitrogen atoms not involved in bonding to boron are essentially the same as those in the unsubstituted azole. The experimentally observed oligomerizations of 1-triazolylboranes via nonadjacent nitrogen atoms are supported by the calculated data. The oligomerization process is dominated by kinetic rather than thermodynamic factors. The tetrameric 1-triazolylborane $[(CH_3)_2B(ut)]_4$ (Hut = 1,2,3-triazole, **1a**) crystallizes in the monoclinic system in space group *C*2/*c* (No. 15) with $a = 16.541$ (2) Å, $b = 12.819$ (5) Å, $c = 12.615$ (1) Å, $\beta = 105.34$ (1)°, and $Z = 4$ at 296 (1) K. $[(CH_3)_2B(bt)]_4$ (Hbt = benzotriazole, **1b**) crystallizes in the monoclinic system in space group $P2_1/c$ (No. 14) with $a = 9.2125$ (9) Å, $b = 10.282$ (2) Å, $c = 18.897$ (3) Å, $\beta = 93.39$ (1)°, and $Z = 2$ at 296 (1) K. The structures are compared with those of several related porphine-like macrocycles, i.e., tetraoxaquaternanes.

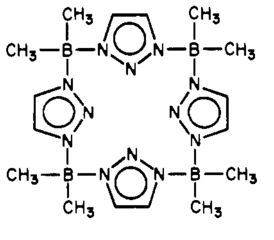
Introduction

It has recently been observed that 1-triazolylboranes form intermolecular acid–base complexes by the preferential engagement of nonadjacent nitrogen atoms of the triazoles as the linking sites to boron.[1] The resultant species were either (presumably) cyclic tetramers or oligomers/polymers of undetermined structure. However, the reaction of $(CH_3)_2BBr$ with $(CH_3)_3Si(ut)$ (Hut = 1,2,3-triazole) was found to yield the tetramer $[(CH_3)_2B(ut)]_4$ as the exclusive product, despite the fact that the $(CH_3)_3Si(ut)$ reagent consisted of a mixture of the 1- and (predominantly) 2-trimethylsilyl isomers. NMR data on the cited tetramer and the corresponding species derived from benzotriazole clearly indicated a high symmetry for the molecule, i.e., suggested the utilization of N(1) and N(3) in the bonding. As a result, the tetramers were presumed to have a cyclic structure containing a central B_4N_{12} ring system resembling that of porphine.[1]

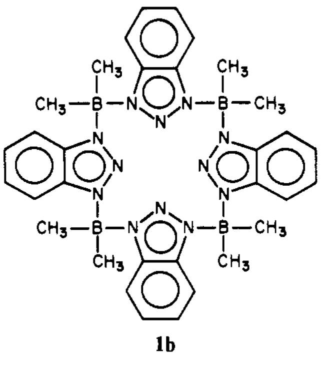
On the other hand, 1-pyrazolylboranes have long been known to form chemically extremely stable dimers = pyrazaboles, which contain a central B_2N_4 ring system.[2] This contrasting behavior between boron derivatives of triazoles and pyrazole has prompted additional studies on 1-triazolylboranes in order to better understand the experimental observations and the chemical features of triazole derivatives of boron. In the present work some theoretical and X-ray diffraction studies on tetrameric 1-triazolylboranes are reported.

Experimental Section

Preparative Data. Both $[(CH_3)_2B(ut)]_4$ (**1a**, where Hut = 1,2,3-triazole) and $[(CH_3)_2B(bt)]_4$ (**1b**, where Hbt = benzotriazole) were prepared as previously described.[1] Crystals of **1a** were grown from cyclohexane: those of **1b** were obtained from a concentrated methylene chloride solution by slow precipitation with a 5-fold volume of *n*-hexane.



1a



1b

Molecular Orbital Calculations. Molecular orbital calculations were carried out with a version of Anderson's ASED MO theory[3] vectorized for the IBM 3090-300E supercomputer. Since the approximations of ASED theory have been appraised in a recent paper,[4] the discussion here is limited to an assessment of the computational differences between ASED and its parent method, EHMO theory, as used in the program FORTICON.[5] ASED differs from EHMO in that the common exponential term $\exp(-0.13R_{ij})$ multiplies the off-diagonal energy matrix term H_{ij} and in that the value of the arbitrary multiplicative constant K or CON is taken as 2.25 rather than the usual 1.75. The practical effect of the exponential term is to decrease the interactive energy as R increases, thus leading to a sharper increase in the potential curve between any two atoms and remedying the well-known problem of the long-tailed diatomic dissociation curve produced by standard EHMO methods. An equivalent interpretation of the effect of the exponential term is that it permits a variation in CON as R_{ij} varies; at a common internuclear distance, such as 2.0 Å, the product CON × $\exp(-0.13R_{ij})$ is approximately 1.75, the usual EHMO value, while at larger R values the product decreases.

Table I. Orbital and Energy Parameters for ASED MO Calculations

atom	orbital	ρ	VSIE, eV
H	1s	1.20	−12.10
B	2s	1.288	−12.93
	2p	1.211	−8.298
C	2s	1.658	−18.50
	2p	1.618	−9.76
N	2s	1.924	−20.33
	2p	1.917	−14.54

The second computational modification of EHMO in the ASED method is the inclusion of a specific pairwise repulsion term derived from consideration of the Hellmann–Feynman theorem. Each pair repulsion energy includes nuclear repulsion terms attenuated by nuclear attraction integrals, the latter computed with classical formulas, but with p and d electrons approximated by spherical distributions. Inclusion of these two modifications significantly improves the validity of EHMO calculations.

In the present supercomputer modification of ASED theory (called ASEDGE), a multiparameter pattern search optimization scheme[6] has been introduced that permits variation of any or all coordinate parameters for a selected number of atoms.

Orbital and energy parameters for atoms in the present work are listed in Table I.

Crystal Structure Determinations. Cyclotetrakis(dimethyl(1,2,3-triazolyl-1-yl)borane) (**1a**), $C_{16}H_{32}B_4N_{12}$, crystallizes as colorless chunks in the monoclinic space group *C*2/*c* (No. 15) with $a = 16.541$ (2) Å, $b = 12.819$ (5) Å, $c = 12.615$ (1) Å, $\beta = 105.34$ (1)°, and $Z = 4$ at 296 (1) K. The individual molecules conform to C_2 symmetry; the symmetry axis passes through two of the four boron atoms. The calculated density is

---

[1] Niedenzu, K.; Woodrum, K. R. *Inorg. Chem.* **1989**, *28*, 4022–4026 and references cited therein.

[2] Niedenzu, K.; Trofimenko, S. *Top. Curr. Chem.* **1986**, *131*, 1–37.

[3] Grimes, R. W.; Anderson, A. B.; Heuer, A. H. *J. Am. Chem. Soc.* **1989**, *111*, 1–7.

[4] Calzaferri, G.; Forss, L.; Kamber, I. *J. Phys. Chem.* **1989**, *93*, 5366–5371.

[5] Howell, J.; Rossi, A.; Wallace, D.; Haraki, K.; Hoffmann, R. FORTICON. Quantum Chemistry Program Exchange No. 344, Indiana University, Bloomington, IN.

[6] Wilde, D. J. *Optimum Seeking Methods*, Prentice-Hall: Englewood Cliffs, NJ, 1979, p 145. Beightier, C. S.; Phillips, D. T.; Wilde, D. J. *Foundations of Optimization*, Prentice Hall: Englewood Cliffs, NJ, 1979, p 236.

0020-1669/91/1330-0784$02.50/0

Table II. Positional Parameters and *B* Values for **1a** and **1b**

atom	*x*	*y*	*z*	*B*, Å^2	atom	*x*	*y*	*z*	*B*, Å^2
				I. $[(CH_3)_2B(ut)]_4$ (**1a**)					
N(1)	0.45614 (6)	0.34288 (7)	0.15301 (9)	3.75 (3)[a]	H(1)	0.5065 (9)	0.3181 (11)	0.0303 (12)	5.3 (3)
N(2)	0.39700 (6)	0.40737 (8)	0.16599 (9)	3.98 (3)[a]	H(2)	0.4022 (10)	0.4610 (12)	−0.0697 (13)	6.0 (4)
N(3)	0.37074 (6)	0.46046 (8)	0.07321 (8)	3.63 (3)[a]	H(3)	0.2562 (09)	0.6419 (11)	0.2436 (11)	5.0 (3)
N(4)	0.33660 (5)	0.63070 (7)	0.14946 (8)	3.42 (3)[a]	H(4)	0.3598 (08)	0.7879 (11)	0.3396 (10)	4.6 (3)
N(5)	0.40689 (6)	0.67966 (8)	0.14794 (8)	3.79 (3)[a]	H(5A)	0.3847 (11)	0.2410 (15)	0.3056 (13)	7.5 (4)
N(6)	0.42143 (6)	0.74891 (8)	0.22903 (8)	3.53 (3)[a]	H(5B)	0.4040 (11)	0.1533 (15)	0.2286 (14)	7.0 (4)
C(1)	0.46714 (10)	0.35537 (12)	0.05186 (12)	4.89 (4)[a]	H(5C)	0.4525 (10)	0.1514 (14)	0.3489 (15)	6.8 (4)
C(2)	0.41327 (9)	0.43016 (12)	0.00146 (12)	4.79 (4)[a]	H(6A)	0.1997 (11)	0.4339 (14)	0.0408 (14)	6.8 (4)
C(3)	0.30636 (8)	0.66945 (11)	0.23009 (11)	4.11 (4)[a]	H(6B)	0.2322 (10)	0.4562 (13)	0.1656 (14)	6.1 (4)
C(4)	0.36021 (8)	0.74444 (11)	0.28067 (11)	4.16 (4)[a]	H(6C)	0.1713 (12)	0.5376 (15)	0.0874 (14)	7.7 (4)
C(5)	0.42953 (10)	0.19821 (13)	0.28520 (18)	5.44 (5)[a]	H(7A)	0.3227 (11)	0.6275 (13)	−0.0814 (13)	6.5 (4)
C(6)	0.21946 (9)	0.48932 (14)	0.09082 (16)	5.16 (5)[a]	H(7B)	0.2519 (13)	0.5466 (16)	−0.1138 (16)	8.3 (5)
C(7)	0.27604 (12)	0.59570 (15)	−0.05951 (14)	5.50 (5)[a]	H(7C)	0.2349 (13)	0.6536 (17)	−0.0638 (15)	8.7 (5)
C(8)	0.50622 (11)	0.89322 (13)	0.35905 (15)	5.40 (5)[a]	H(8A)	0.4603 (11)	0.9397 (14)	0.3475 (14)	7.1 (4)
B(1)	$^1/_2$	0.26524 (16)	$^1/_4$	4.18 (6)[a]	H(8B)	0.5549 (12)	0.9372 (14)	0.3738 (14)	7.7 (5)
B(2)	0.29706 (8)	0.54393 (12)	0.05967 (12)	3.96 (4)[a]	H(8C)	0.5518 (10)	0.8505 (14)	0.4315 (14)	7.4 (4)
B(3)	$^1/_2$	0.82663 (15)	$^1/_4$	4.01 (6)[a]					
				II. $[(CH_3)_2B(bt)]_4$ (**1b**)					
N(1)	0.65052 (17)	0.22286 (16)	0.00808 (8)	2.93 (5)[a]	B(1)	0.6964 (3)	0.2866 (2)	−0.06417 (13)	3.54 (7)[a]
N(2)	0.51880 (17)	0.24318 (16)	0.03071 (8)	3.07 (5)[a]	B(2)	0.3646 (3)	0.1889 (3)	0.13326 (14)	3.62 (7)[a]
N(3)	0.50676 (16)	0.17518 (16)	0.08935 (8)	2.90 (5)[a]	H(5A)	0.880 (3)	0.407 (3)	−0.0912 (16)	8.5 (8)
N(4)	0.32397 (17)	0.03888 (17)	0.14760 (8)	3.20 (5)[a]	H(5B)	0.935 (4)	0.299 (3)	−0.0416 (16)	10 (1)
N(5)	0.34053 (17)	−0.04587 (17)	0.09586 (9)	3.27 (5)[a]	H(5C)	0.852 (3)	0.417 (3)	−0.0142 (15)	8 (1)
N(6)	0.28806 (16)	−0.16031 (7)	0.11419 (8)	3.04 (5)[a]	H(6A)	0.557 (3)	0.449 (3)	−0.0692 (13)	7.1 (8)
C(1)	0.7256 (2)	0.1381 (2)	0.05295 (10)	2.84 (6)[a]	H(6B)	0.597 (2)	0.406 (2)	−0.1430 (12)	5.9 (6)
C(2)	0.6329 (2)	0.1069 (2)	0.10553 (10)	2.93 (6)[a]	H(6C)	0.473 (3)	0.325 (3)	−0.1034 (13)	6.9 (8)
C(3)	0.2569 (2)	−0.0215 (2)	0.20179 (10)	3.32 (6)[a]	H(7A)	0.462 (3)	0.351 (3)	0.1949 (13)	7.5 (7)
C(4)	0.2339 (2)	−0.1494 (2)	0.18030 (10)	3.17 (6)[a]	H(7B)	0.324 (3)	0.287 (3)	0.2290 (15)	7.8 (8)
C(5)	0.8516 (3)	0.3572 (3)	−0.0511 (2)	5.4 (1)[a]	H(7C)	0.480 (3)	0.210 (3)	0.2386 (15)	7.9 (9)
C(6)	0.5681 (4)	0.3741 (3)	−0.09810 (16)	5.1 (1)[a]	H(8A)	0.149 (3)	0.249 (2)	0.1075 (12)	6.1 (6)
C(7)	0.4100 (4)	0.2635 (3)	0.20531 (16)	5.7 (1)[a]	H(8B)	0.214 (3)	0.201 (3)	0.0354 (16)	9 (1)
C(8)	0.2364 (3)	0.2510 (3)	0.08416 (19)	5.2 (1)[a]	H(8C)	0.256 (3)	0.336 (3)	0.0680 (13)	7.2 (7)
C(9)	0.8637 (2)	0.0826 (2)	0.05187 (13)	3.89 (7)[a]	H(9)	0.927 (2)	0.108 (2)	0.0170 (10)	3.9 (5)
C(10)	0.9018 (3)	−0.0035 (3)	0.10462 (13)	4.74 (8)[a]	H(10)	0.998 (3)	−0.041 (2)	0.1060 (12)	6.5 (6)
C(11)	0.8082 (3)	−0.0343 (3)	0.15776 (14)	4.80 (8)[a]	H(11)	0.838 (2)	−0.097 (2)	0.1929 (12)	6.2 (7)
C(12)	0.6728 (3)	0.0195 (2)	0.15986 (11)	3.88 (7)[a]	H(12)	0.609 (2)	0.002 (2)	0.1971 (10)	3.5 (4)
C(13)	0.2123 (3)	0.0224 (3)	0.26732 (13)	4.84 (8)[a]	H(13)	0.226 (2)	0.112 (2)	0.2825 (11)	4.5 (6)
C(14)	0.1438 (3)	−0.0668 (3)	0.30787 (15)	5.9 (1)[a]	H(14)	0.114 (2)	−0.033 (2)	0.3541 (13)	6.6 (6)
C(15)	0.1223 (3)	−0.1949 (3)	0.28604 (15)	5.5 (1)[a]	H(15)	0.076 (3)	−0.253 (3)	0.3155 (13)	6.5 (7)
C(16)	0.1653 (3)	−0.2397 (3)	0.22261 (14)	4.34 (8)[a]	H(16)	0.151 (2)	−0.326 (2)	0.2071 (11)	4.6 (6)

[a] For atoms refined anisotropically, the equivalent displacements parameter is defined as (4/3) Tr(β·G), where $\beta_{ij} = 2\pi^2 a_i^* a_j^* U_{ij}$.

1.122 g cm^{-3}. Data having $k \geq 0$ and $2\theta \leq 55°$ ($h \geq 0$) or $2\theta \leq 50°$ ($h < 0$) were measured on an Enraf-Nonius CAD4 diffractometer using Mo Kα radiation (λ = 0.710 73 Å) and a graphite monochromator. After averaging (2275 reflections observed more than once; *R* factor for averaging 0.019), there were 2965 unique reflections. No correction was necessary for decomposition or absorption (μ = 0.68 cm^{-1}). The structure was solved by using direct methods.[7] Hydrogen atoms were located in difference maps and described with isotropic displacement parameters. The structure was refined[8] to agreement factors *R* and R_w on F_o of 0.035 and 0.042 for 210 variables and the 2016 observations having $I > 3\sigma(I)$; the error in an observation of unit weight is 2.36. The largest peaks in the final difference map have heights <0.14 e Å^{-3} and are located at bond centers. The most significant troughs are no deeper than −0.20 e Å^{-3} and are located near the ring centers. There is no reason to believe that a better description of the structure could be found in the noncentrosymmetric space group *Cc* (No. 9).

Cyclotetrakis(dimethyl(benzotriazol-1-yl)borane) (**1b**), $C_{32}H_{40}B_4N_{12}$, crystallizes as colorless tablets in the monoclinic space group $P2_1/c$ (No. 14) with a = 9.2125 (9) Å, b = 10.282 (2) Å, c = 18.897 (3) Å, β = 93.39 (1)°, and Z = 2 at 296 (1) K. The individual molecules conform to C_i symmetry. The calculated density is 1.182 g cm^{-3}. Data having $h, k \geq 0$ and $2\theta < 55°$ were measured as above. After averaging (1405 reflections observed more than once; *R* factor for averaging 0.019), there were 4082 unique reflections. No correction was necessary for decomposition or absorption (μ = 0.68 cm^{-1}). The structure was solved and refined as outlined above to agreement factors *R* and R_w on F_o of 0.036

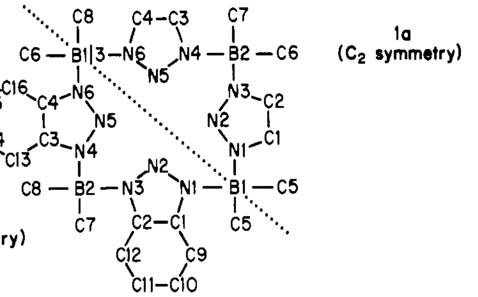


Figure 1. Numbering of atoms in **1a** and **1b** (half of each molecule shown).

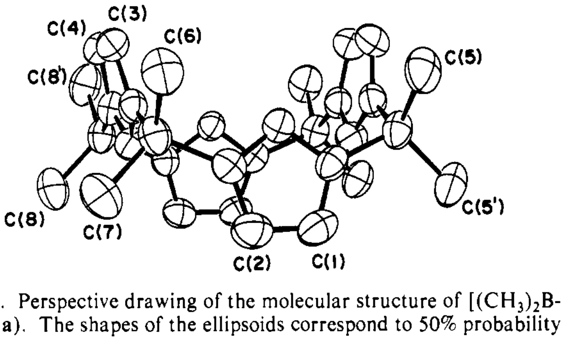


Figure 2. Perspective drawing of the molecular structure of $[(CH_3)_2B(ut)]_4$ (**1a**). The shapes of the ellipsoids correspond to 50% probability contours of atomic displacement. The hydrogen atoms have been omitted for clarity.

---

(7) Main, P.; Lessinger, L.; Woolfson, M. M.; Germain, G.; Declerq, J.-P. MULTAN77. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-Ray Diffraction Data. Universities of York, England and Louvain, Belgium, 1977.

(8) Brock, C. P.; Attig, T. G. *J. Am. Chem. Soc.* **1980**, *102*, 1319–1326.

Table III. Bond Lengths (Å) and Angles (deg) for **1a** and **1b**

	1a	**1b**
N(1)-N(2)	1.324 (1)	1.327 (2)
N(2)-N(3)	1.324 (1)	1.320 (2)
N(4)-N(5)	1.326 (1)	1.325 (2)
N(5)-N(6)	1.327 (1)	1.326 (2)
N(1)-C(1)	1.345 (2)	1.374 (2)
N(3)-C(2)	1.342 (2)	1.376 (2)
N(4)-C(3)	1.342 (2)	1.375 (2)
N(6)-C(4)	1.342 (2)	1.377 (2)
N(1)-B(1)	1.595 (2)	1.594 (3)
N(3)-B(2)	1.597 (2)	1.597 (3)
N(4)-B(2)	1.599 (2)	1.615 (3)
N(6)-B(3/1)[a]	1.603 (2)	1.618 (3)
C(1)-C(2)	1.348 (2)	1.385 (2)
C(3)-C(4)	1.351 (2)	1.389 (3)
C(5)-B(1)	1.603 (2)	1.610 (4)
C(6)-B(2/1)[a]	1.600 (2)	1.590 (4)
C(7)-B(2)	1.595 (2)	1.597 (4)
C(8)-B(3/2)[a]	1.599 (2)	1.592 (4)
C(1)-C(9)		1.396 (3)
C(2)-C(12)		1.397 (3)
C(3)-C(13)		1.402 (3)
C(4)-C(16)		1.400 (3)
C(9)-C(10)		1.364 (3)
C(12)-C(11)		1.367 (3)
C(13)-C(14)		1.372 (4)
C(16)-C(15)		1.365 (4)
C(10)-C(11)		1.398 (3)
C(14)-C(15)		1.390 (4)
N(1)-N(2)-N(3)	107.0 (1)	108.1 (1)
N(4)-N(5)-N(6)	106.6 (1)	109.3 (1)
N(2)-N(1)-B(1)	119.7 (1)	120.4 (2)
N(2)-N(3)-B(2)	120.1 (1)	120.1 (2)
N(5)-N(4)-B(2)	121.0 (1)	117.8 (2)
N(5)-N(6)-B(3/1′)[a]	121.1 (1)	120.9 (2)
C(1)-N(1)-B(1)	130.8 (1)	129.8 (2)
C(2)-N(3)-B(2)	130.0 (1)	129.6 (2)
C(3)-N(4)-B(2)	129.0 (1)	132.5 (2)
C(4)-N(6)-B(3/1′)[a]	129.0 (1)	130.2 (2)
N(2)-N(1)-C(1)	109.4 (1)	109.7 (2)
N(2)-N(3)-C(2)	109.8 (1)	110.2 (2)
N(5)-N(4)-C(3)	109.9 (1)	109.2 (2)
N(5)-N(6)-C(4)	109.8 (1)	108.8 (2)
N(1)-C(1)-C(2)	107.1 (1)	106.3 (2)
N(3)-C(2)-C(1)	106.7 (1)	105.7 (2)
N(4)-C(3)-C(4)	106.9 (1)	106.1 (2)
N(6)-C(4)-C(3)	106.8 (1)	106.6 (2)
N(1)-B(1)-N(1′/6)[a]	102.8 (1)	102.0 (2)
N(3)-B(2)-N(4)	103.5 (1)	102.0 (2)
N(6)-B(3)-N(6′)	103.1 (1)	
N(1)-B(1)-C(5)	109.3 (1)	109.4 (2)
N(1)-B(1)-C(5′/6)[a]	109.8 (1)	110.5 (2)
N(3)-B(2)-C(6/8)[a]	108.7 (1)	109.6 (2)
N(3)-B(2)-C(7)	110.5 (1)	107.7 (2)
N(4)-B(2)-C(6/8)[a]	109.6 (1)	108.0 (2)
N(4)-B(2)-C(7)	108.9 (1)	111.6 (2)
N(6)-B(3/1)-C(8/5)[a]	109.8 (1)	110.1 (2)
N(6)-B(3/1)-C(8′/6)[a]	109.0 (1)	107.9 (2)
C(5)-B(1)-C(5′/6)[a]	115.2 (2)	116.1 (2)
C(7)-B(2)-C(6/8)[a]	115.1 (1)	116.9 (2)
C(8)-B(3)-C(8)′	115.5 (2)	
N(1)-C(1)-C(9)		132.5 (2)
N(3)-C(2)-C(12)		132.3 (2)
N(4)-C(3)-C(13)		132.9 (2)
N(6)-C(4)-C(16)		131.6 (2)
C(2)-C(1)-C(9)		121.1 (2)
C(1)-C(2)-C(12)		122.0 (2)
C(4)-C(3)-C(13)		121.0 (2)
C(3)-C(4)-C(16)		121.8 (2)
C(1)-C(9)-C(10)		116.8 (2)
C(2)-C(12)-C(11)		116.1 (2)
C(3)-C(13)-C(14)		116.5 (3)
C(4)-C(16)-C(15)		116.2 (3)
C(9)-C(10)-C(11)		121.9 (3)
C(12)-C(11)-C(10)		122.2 (2)
C(13)-C(14)-C(15)		122.0 (3)
C(16)-C(15)-C(14)		122.5 (3)

[a] The first number in the pair refers to the atom-numbering scheme in **1a**, and the second refers to the atom-numbering scheme in **1b**.

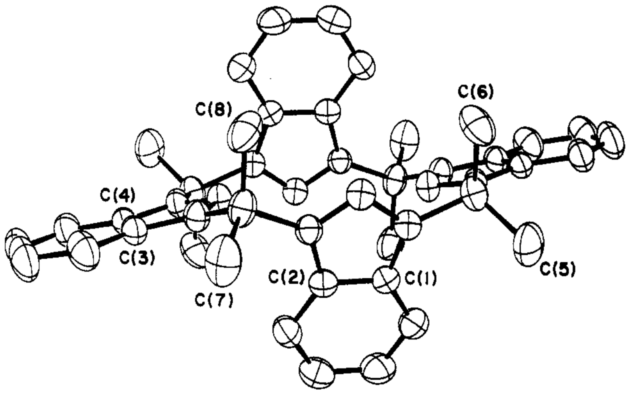


Figure 3. Perspective drawing of the molecular structure of $[(CH_3)_2B(bt)]_4$ (**1b**). The shapes of the ellipsoids correspond to 50% probability contours of atomic displacement. The hydrogen atoms have been omitted for clarity.

Table IV. Calculated Total Energies (eV) for Azoles and Corresponding 1-Azolylboranes and Energy Changes ΔE for Reactions According to Eq 1

	total energy		
	azole	1-azolylborane	ΔE
1,2-diazole[a]	−433.87	−491.50	−1.09[b]
1,3-diazole[c]	−437.14	−494.73	−1.05
1,2,3-triazole	−449.38	−506.70	−0.78
1,2,4-triazole	−454.15	−511.77	−1.08
1,2,5-triazole	−449.62	−505.95	−0.21

[a] Pyrazole. [b] As compared to −2.99 eV obtained by CNDO calculations.[9] [c] Imidazole.

Table V. Selected Calculated Atomic Charges for Azoles and Their Corresponding 1-Azolylboranes

	azole			1-azolylborane			
	N(1)	N(2)	N(3,4,5)	N(1)	N(2)	N(3,4,5)	B
1,2-diazole[a]	−0.22	−0.93		−0.43	−0.94		+0.64
1,3-diazole[b]	−0.54		−1.21	−0.74		−1.20	+0.68
1,2,3-triazole	−0.09	−0.46	−0.76	−0.32	−0.46	−0.72	+0.70
1,2,4-triazole	−0.21	−0.92	−1.20	−0.41	−0.93	−1.19	+0.66
1,2,5-triazole	+0.13	−0.82	−0.84	+0.10	−0.84	−0.86	+0.57

[a] Pyrazole. [b] Imidazole.

and 0.033 for 297 variables and the 1796 observations having $I > 3\sigma(I)$; the error in an observation of unit weight is 1.57. The largest peaks in the final difference map have heights <0.16 e Å^{-3}. The most significant troughs are no deeper than −0.22 e Å^{-3} and are located near ring centers.

The coordinates and B values for the two structures are given in Table II. The numbering of atoms in both **1a** and **1b** is schematically shown in Figure 1. ORTEP plots of the two molecules are presented in Figures 2 and 3, respectively. Bond lengths and angles are listed in Table III.

Results and Discussion

Molecular Orbital Calculations on Monomeric 1-Azolylboranes. The reactions of borane(3) with pyrazole, imidazole, 1,2,3-triazole, 1,2,4-triazole, and 1,2,5-triazole was selected for this particular investigation. Although the first reaction has previously been studied with the CNDO/2 method,[9] it was included here in order to compare the results of the CNDO study with those obtained by ASED-MO calculations. Imidazole was also included due to its structural relationship with 1,2,4-triazole.

The computed energies for the reactions according to eq 1 (Haz = azole) with total energies of −89.11 eV for BH_3 and −32.57 eV for H_2 are summarized in Table IV. As can be seen, all reactions

$$\mathrm{Haz} + \mathrm{BH_3} \rightarrow \mathrm{H_2B(az)} + \mathrm{H_2} \qquad (1)$$

are slightly exothermic with no striking differences. Selected calculated charge distributions in the azoles and the corresponding

---

[9] Companion, A. L.; Liu, F.; Niedenzu, K. *Inorg. Chem.* **1985**, *24*, 1738–1740.

Table VI. Average Bond Lengths (Å) in **1a** and **1b** Compared with Average Bond Lengths (Å) for 1,2,3-Triazoles and Benzotriazoles[a]

bond	1,2,3-triazoles[b]	1a	1b	benzotriazoles[b]
N–N	1.331 (6) (2)[c]	1.325 (2) (1)	1.324 (3) (2)	1.332 (9) (2)
N–C	1.359 (8) (2)	1.343 (2) (1)	1.376 (1) (1)	1.373 (16) (4)
(N)C–C(N)	1.382 (18) (5)	1.350 (2) (2)	1.387 (3) (2)	1.385 (10) (3)
(C)C–C(C) (*o*)			1.399 (3) (1)	1.396 (6) (2)
(C)C–C(C)(*m*)			1.367 (4) (2)	1.367 (9) (2)
(C)C–C(C) (*p*)			1.394 (6) (2)	1.404 (14) (3)

[a] Averages taken by assuming C_{2v} symmetry for the triazole rings. Any distinction between formally double and formally single N–N bonds is lost. Averaging within a ring was performed prior to averaging over several rings and/or fragments. [b] Structures retrieved from Version 4.10 (July 1989) of the Cambridge Structural Database (see text and supplementary material). [c] First number in parentheses is the estimated standard deviation that measures the width of the distribution; the second is the estimated standard deviation of the mean value of the distribution.

1-azolylboranes are given in Table V (calculated charge on boron in BH_3: +0.42).

Two results are of interest here. First of all, there are essentially negligible changes in charge density at the "free" nitrogen atoms in going from the azole to the corresponding 1-azolylborane. Second, in the case of 1-triazolylboranes the nonvicinal nitrogen atom has the highest charge density, suggesting that this atom may favor coordination to another boron atom. This would be in consonance with the experimental data and explain the preferential oligomer formation of 1-triazolylboranes rather than mere dimerization to give a pyrazabole-type structure.

The formation of (cyclic) tetrameric 1-azolylboranes versus that of higher aggregated (linear) species is then apparently a function of the rate at which individual monomers interact. In the case of imidazole, with the relatively high charge on N(3), the reaction may be fast and in random orientation. Thus, a mixture of oligomers is formed[10,11] since the monomers do not have sufficient time for proper orientation to give a cyclic tetramer. The same principle should hold true for the triazoles. Indeed, N-bonded boron derivatives of 1,2,4-triazoles preferentially form oligomers involving N(4) in the bonding, but dimers with bonding via N(2) can also be obtained.[1] However, the latter are usually obtained in low yield, unless steric factors promote dimerization. On the other hand, a dimer was never observed in the case of 1,2,3-triazole, and there is no ready explanation for the sometimes exclusive formation of tetramers rather than that of higher oligomers,[1] unless one assumes that steric effects of the additional boron substituents play a major role during the oligomerization process.

Crystal and Molecular Structures of Cyclotetrakis(dimethyl-(1,2,3-triazol-1-yl)boranes). The molecular structures of **1a** and **1b** are shown in Figures 2 and 3, respectively.

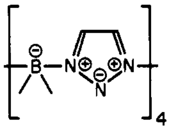
A comparison of the bond lengths in **1a** and **1b** (see Table III) is facilitated by the molecular symmetry; the lengths of most bond types are determined four times in each molecule. The average lengths of the B–C bonds in **1a** and **1b** are 1.599 (3) and 1.597 (9) Å, where the numbers in parentheses are the estimated standard deviations of the means. These bond lengths are typical of bonds between three- or four-coordinate B atoms and sp^3 C atoms (1.597 (22) Å, where the number in parentheses is the sample standard deviation[12]). The B—N bond lengths of 1.598 (2) and 1.606 (6) Å are typical of $X_3B—N(=C)(X)$ bonds (1.611 (13) Å), and are a little longer than the B—N bonds in pyrazaboles (1.549 (15) Å).[12]

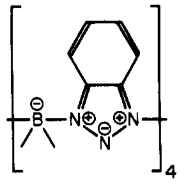
Standard lengths for the N–N, N–C, and C–C bonds in the triazole ring system are not included in the most recent tabulation.[12] A search of Version 4.10 of the Cambridge Structural Database (CSD)[13,14] located coordinates for 11 structures containing the 1,2,3-triazole fragment and coordinates for another 13 structures containing the benzotriazole fragment. In both searches, the crystallographic agreement factor *R* was required to be less than 0.06, and fragments with substituents at the central N atom, i.e., N(2), were excluded. The first search excluded structures in which atoms of the triazole ring are part of the more than one ring system, e.g., benzotriazole. (The search question and the bibliographic references for the retrieved structures are given with the supplementary material.)

There is no evidence of localization of the formally single and double N–N bonds in either **1a** or **1b**. The two independent N–N bonds in each of the triazole rings are nearly the same length, as are the two independent N–C bonds. In the retrieved fragments, however, which are often unsymmetrically substituted, the two N–N and the two N–C bonds may differ by 0.02 Å or more.

The average bond lengths for the N–N, N–C, and N–C bonds in **1a**, **1b**, the 1,2,3-triazoles, and the benzotriazoles are compiled in Table VI. The averaging was performed by assuming C_{2v} symmetry for the fragments; any distinction between single and double N–N bonds has therefore been lost. Inspection of Table VI shows that most of the bond lengths in **1a** and **1b** are typical for those of other 1,2,3-triazoles. The N–C bond in **1a**, however, is a little shorter than average, and the C–C bond is substantially shorter. The degree of localization of the double bonds in the fused benzene ring of **1b** is about the same as in the group of benzotriazoles studied previously.

It is remarkable that the N–C bonds in **1a** are 0.033 (2) Å shorter than those in **1b** while the N–N bonds in the two molecules are nearly the same length. The N–C distances in the two sets of structures retrieved from the CSD also differ, but by a smaller amount (0.014 (4) Å). Presumably the resonance form A, although a minor contributor, is more important to the structure of **1a** than is the quinonoid resonance form B to the structure of **1b**. If this is the case, **1a** may be expected to be the better base of the two.


A


B

The distances between the central N atoms of the four triazole rings depend on the molecular conformation. In **1a** the central N atoms of adjacent rings are separated by 3.505 (2) Å (N(2)···N(2)′), 3.453 (2) Å (N(5)···N(5)′), and 3.504 (2) Å (N(2)···N(5)′); the N···N distance across the macrocycle cavity is 4.918 (2) Å. The corresponding distances in **1b** are 3.645 (2) Å (N(2)···N(5)) and 3.447 (2) Å (N(2)···N(5)′) for adjacent rings, and 5.141 (3) Å (N(2)···N(2)′) and 4.889 (3) Å (N(5)···N(5)′) across the cavity.

No N or C atom in a triazole ring of either **1a** and **1b** deviates from its five-atom least-squares plane by more than 0.004 Å. No C atom in a benzene ring of **1b** deviates from its six-atom plane by more than 0.006 Å. The fused five- and six-membered rings in **1b** are almost but not quite coplanar; the dihedral angles between them are 2.0 and 1.1°, respectively, for the sets of rings containing C(1) and C(3).

---

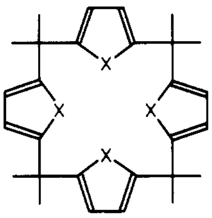
(10) Trofimenko, S. *J. Am. Chem. Soc.* **1967**, *89*, 3903–3904.
(11) Müller, K. D.; Komorowski, L.; Niedenzu, K. *Synth. React. Inorg. Met.-Org. Chem.* **1978**, *8*, 149–155.
(12) Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. J. *J. Chem. Soc., Perkin Trans. 2* **1987**, S1–S19.
(13) Allen, F. H.; Kennard, O.; Taylor, R. *Acc. Chem. Res.* **1983**, *16*, 146–153.
(14) Allen, F. H.; Bellard, S.; Brice, M. D.; Cartwright, B. A.; Doubleday, A.; Higgs, H.; Hummelink, T.; Hummelink-Peters, B. G.; Kennard, O.; Motherwell, W. D. S.; Rodgers, J. R.; Watson, D. G. *Acta Crystallogr., Sect. B: Struct. Sci.* **1979**, *B35*, 2331–2339.

Table VII. Dihedral Angles (deg) between the Four Five-Membered Rings of the Macrocycles and the Plane Defined by the Four Bridging Atoms[a]

		dihedral angle			
compd	imposed sym	ring 1	ring 2	ring 3	ring 4
1a	C_2	−82	82	−76	76
2a		−85	76	−76	82
3		−80	77	−76	79
2a′	C_i	−68	34	68	−34
1b	C_i	−115	12	115	−12
2a″		−70	10	51	68

[a] The dihedral angle is 0° if the five-membered ring is coplanar with the plane of the bridging atoms, and 90° if it is perpendicular. The angle is an approximate measure of the rotation around the vector between the atoms in the 1- and 3-positions of the five-membered ring that would be required to bring the atoms in the 2-position (1) into the plane of the bridging atoms and (2) as close as possible to the center of the macrocycle. The sign of the dihedral angle indicates the sense of the required rotation.

The macrocycle heterocycle common to both **1a** and **1b** is closely related to the ring systems of tetraoxaquaterane (**2a**, also known as tetraoxaporphyrinogen) and of porphyrinogen (**2b**). The three ring systems as well as that of the all-carbon analogue **2c** all contain the same number of electrons, although the boron–nitrogen system differs from the others in the formal location of the double bonds. Since all of the five-membered rings are expected to be planar and of about the same size, the conformational energy surfaces for molecules containing these four ring systems should be similar.



2a: X = O
b: X = NH
c: X = CH_2

Only a few structures of these macrocycles have been determined. The structures of two crystalline forms of tetraoxaquaterane, one of which contains two independent molecules, are known[15] as is the structure of octamethyltetraoxaquaterane.[16] One porphyrinogen structure[17] is included in Version 4.10 (July 1989) of the CSD,[13,14] but no coordinates are available. No structures of molecules containing the all-carbon ring system were located.

It is, therefore, possible to compare the conformations of the ring systems in six molecules: **1a** and **1b**, the three independent molecules of tetraoxaquaterane (**2a**, **2a′**, and **2a″**),[15] and octamethyltetraoxaquaterane (**3**).[16] The dihedral angles between the four five-membered rings in each molecule and the plane of the four bridging atoms linking these rings are shown in Table VII.

None of these six molecules even approaches planarity. Three molecules, **1a**, **2a**, and **3**, adopt a conformation with approximate D_{2d} symmetry (see Figure 1a) in which the five-membered rings are alternately bent up and down by ca. 80° from the plane of the bridging atoms. It seems likely that this conformation corresponds to the global minimum of the potential-energy surface. The conformation adopted by **2a′** is more extended and has inversion symmetry; two five-membered rings make large (68°) angles with the plane of the bridging atoms, but the angles made by the other two five-membered rings are half as big (34°). The very asymmetric conformation found for **2a″** is a sort of hybrid of those described above.

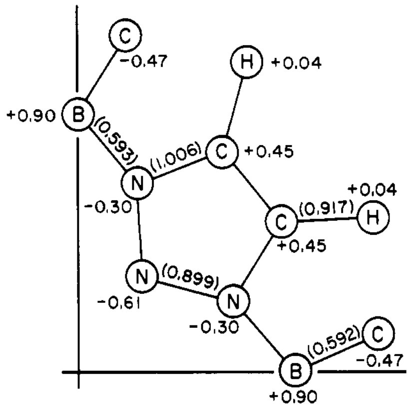


Figure 4. Calculated charge distributions and overlap populations for the smoothed geometry of **1a**.

1b also adopts a conformation with C_i symmetry, but the difference between the two kind of angles is much larger than it is in **2a′**. One pair of triazole rings is nearly parallel to the plane of the boron atoms, while the other is folded so far back that the N(2) atoms point toward the outside of the macrocycle cavity. The unusual orientation of the triazole rings may be an accident of the crystal packing, which is strongly influenced by the fused benzene rings. The B–N bonds to the rings that are nearly planar to the plane of the boron atoms are 0.021 (3) Å longer than the B–N bonds to the other rings, which suggests that there is strain associated with that orientation.

The occurrence of such a variety of conformations for a series of related macrocycles suggests that the ring systems are quite flexible. This is at least clearly evident for the case where the five-membered rings are linked by CH_2 groups. On the other hand, the following MO calculations indicate that linking BR_2 groups seem to impose more rigidity on the macrocycles.

MO Calculations on $[(CH_3)_2B(ut)]_4$ (1a) and $[H_2B(ut)]_4$. ASED MO calculations initially performed on **1a** with crystallographic coordinates indicated small deviations from the expected high symmetry of the molecule in both atomic charges and bond orders (overlap populations). Accordingly, a coordinate transformation was made to a Cartesian system with origin at the center of the molecule and all B atoms in the *xy* plane. All eight nonapical N atoms were found to be essentially coplanar with the four B atoms. Ring system coordinates were adjusted slightly to yield a symmetrical molecule. Subsequent MO calculations on this smoothed geometry resulted in the highly symmetrical charge distributions and overlap populations shown in Figure 4. Except for the reduction in positive and negative charges on the B–N coordinating pair, all other charges and bond orders are quite similar to those in the monomer.

To test for the possible existence of a conformation of **1a** with ring apices all pointed in the same direction, the ring systems were rotated to a common direction at a tilting angle equivalent to that of crystallographic **1a**. The energy of the resultant structure was 22.24 eV above that of crystallographic **1a**. (This geometry was not optimized and the bonds were not permitted to pucker, as observed in the MNDO calculations of tetraoxaquaterane.[18] Nevertheless, the magnitude of the energy change indicates that such a conformation is unlikely.)

To facilitate further studies of conformation changes in **1a**, all eight B-bonded methyl groups were replaced by H atoms, making the model compound $[H_2B(ut)]_4$. The oligomerization reaction

$$4H_2B(ut) \rightarrow [H_2B(ut)]_4$$

where the tetramer has the tilted ring conformation of crystallographic **1a**, was exothermic by 2.26 eV. In this process the charge on B was reduced from +0.64 in the monomer to +0.33

---

(15) Haas, W.; Knipp, B.; Sicken, M.; Lex, J.; Vogel, E. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 409–411.

(16) Hazell, A. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1989**, *C45*, 137–140.

(17) Sawitzki, G.; von Schnering, H. G. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 552.

(18) Cuthbertson, A. F.; Glidewell, C. *J. Mol. Struct.* **1983**, *94*, 407–410.

in the tetramer, and that of N(3) in the monomer (−0.74) was reduced to −0.29 in the tetramer. All other ring charges and overlap populations are consistent with those of crystallographic **1a**.

Two other conformation of $[H_2B(ut)]_4$ were examined: (a) one in which the ring systems were rotated such that all atoms except the H atoms on B were coplanar (8.3 eV above the crystallographic geometry), and (b) one in which ring systems were rotated to a position perpendicular to the *xy* plane (13.62 eV above the observed conformation). These high-energy barriers indicate that there is little likelihood of rotation of the triazole rings in the free molecule from the staggered up–down tilted positions of the crystallographic geometry. In addition, coordination of the four apical N atoms with a metal atom would be unlikely in a square-planar geometry. Instead, the metal would have to be located in the three-dimensional dispheroidal cavity formed by the apical N atoms.

Conclusion. The results of the ASED MO calculations are clearly in consonance with the experimental observations concerning the oligomerization of *N*-triazolylboranes. Furthermore, the calculations illustrate that the approximate D_{2d} conformation of **1a** is indeed near the minimum of the energy surface. Surprisingly, despite the variety of structures observed in the related macrocycles of types **1** and **2**, respectively, which supports the concept of highly flexible systems, MO calculations suggest that the structures in which the five-membered rings are linked by BR_2 groups are more rigid.

Acknowledgment. This work was supported by the Office of Naval Research (K.N.). We also acknowledge support of the University of Kentucky Major Research Instrumentation Bond Program for the purchase of equipment used in this study (Bond ID No. 7E-8E48-25) and a generous grant of free computing time from the University of Kentucky Computer Center. The ASED MO program was formulated for the IBM 3090 by the late David P. Onwood. ASEDGE was written by Vernon C. Hicks.

Supplementary Material Available: Tables of crystallographic data and experimental details of the structure determinations, anisotropic displacement parameters (*U* values), bond lengths and angles involving hydrogen atoms, search questions (Cambridge Structural Database), and bibliographic citations for structures retrieved from the Cambridge Structural Database (11 pages); tables of structure factors (25 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry,
The University of Texas at Austin, Austin, Texas 78712

Novel Synthesis of Unusual Classes of Fluorocarbon Organosulfur Compounds Using Elemental Fluorine as a Reagent

Hsu-Nan Huang, Herbert Roesky, and Richard J. Lagow*

Received February 20, 1990

The reactions of elemental fluorine with branched alkyl mercaptans, alkanesulfonyl fluorides, alkyl thioethers, cyclic alkyl thioethers, alkyl sulfones, and an alkanesultone have been studied. The synthesis and characterizations of perfluoroisobutylsulfur pentafluoride, perfluoroneopentylsulfur pentafluoride, perfluoropropylsulfur pentafluoride, perfluorotetramethylenesulfur tetrafluoride, perfluoro-1,4-thioxane tetrafluoride, perfluoro-2-propanesulfonyl fluoride, 1,1,1,3,3,3-hexafluoro-2-propanesulfonyl fluoride, perfluorotetramethylene sulfone, perfluorobutanesulfonyl fluoride, perfluoro-1,4-butanesultone, and perfluoropropanesulfonyl fluoride are discussed. The ^{19}F and ^{13}C{^{19}F} NMR assignments of the fluorinated products are also reported.

Introduction

In 1977, this laboratory published the first report on temperature and kinetic control of elemental fluorine with sulfur-containing organic molecules such that conditions could be differentiated for obtaining four-coordinate compounds (sulfur tetrafluoride analogues) and six-coordinate compounds (sulfur hexafluoride analogues).[1] Subsequently, Ruppert and others have shown that such oxidative control during fluorination is also possible for organic heteroatom systems containing phosphorus, arsenic, antimony, and bismuth.[2] In this manuscript we present a series of novel sulfur-containing molecules (see Figure 1) that have been preserved by careful fluorination, which are in many ways a study of the current state-of-the-art for such synthetic techniques in organosulfur chemistry. A number of the compounds produced in the study are also potential precursors for use in several areas of materials-related chemistry.

Because they have unusually great acid strength,[3] perfluoroalkanesulfonic acids have been widely used as catalysts in organic reactions and polymerizations.[4] In contrast, derivatives of these acids are attractive for numerous material applications such as electrolytes, surfactants, and coatings due to their high thermal stability, unusual chemical resistance, and surface properties.[5] Syntheses of structurally different perfluorinated precursors such as perfluoroneopentanesulfonyl fluoride, perfluoro-2-propanesulfonyl fluoride, and perfluoro-2-butanesulfonyl fluoride would certainly be important for the purpose of determining how branching affects the overall physical and chemical properties of several classes of sulfuric acid compounds. Electrochemical fluorination has been the major method used for preparation of fluorinated alkanesulfonyl fluorides and is limited to compounds with straight-chain structure unless one is satisfied with very low yields. Additionally, preparation of perfluoroalkylsulfur pentafluorides by this electrolytic cell often results, in low yields,[7] and many of the compounds we report here are inaccessible. Due to their high chemical and thermal stability and usefulness as intermediates, syntheses of perfluoroalkyl derivatives of sulfur hexafluoride have received considerable attention.[8]

Recently, successful direct fluorination of highly branched or even structurally crowded alkyl ethers[9] has led us to continue investigating the synthesis of sulfur-containing perfluorinated organic compounds. Cleavage of the relatively weak C–S bond,[10] a problem giving fragments such as sulfur hexafluoride and

---

(1) Shimp, L. A.; Lagow, R. J. *Inorg. Chem.* **1977**, *16*, 2974.

(2) (a) Ruppert, I.; Bastian, U. *Angew. Chem., Int. Ed. Engl.* **1978**, *16*, 718. (b) Ruppert, I.; Bastian, U. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 214.

(3) In terms of acid strength, trifluoromethanesulfonic acid is 400 times as strong as nitric acid (3M product information).

(4) Howells, R. D.; McCown, J. D. *Chem. Rev.* **1977**, *77*, 69.

(5) Guenther, R. A.; Vietor, M. L. *Ind. Eng. Chem. Prod. Res. Dev.* **1962**, *1*, 165.

(6) (a) Gramstad, T.; Haszeldine, R. N. *J. Chem. Soc.* **1957**, 2640. (b) Burdon, J.; Farazmand, I.; Stacey, M.; Tatlow, J. C. *J. Chem. Soc.* **1957**, 2574.

(7) Burdon, J.; Tatlow, J. C. *Adv. Fluorine Chem.* **1960**, *1*, 129.

(8) (a) Baba, H.; Kodaira, K.; Nagase, S.; Abe, T. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 1891. (b) Abe, T.; Nagase, S.; Baba, H. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 3845.

(9) Persico, D. F.; Huang, H. N.; Lagow, R. J. *J. Org. Chem.* **1985**, *50*, 5156.

(10) The average bond energy for C–S is 65 kcal/mol and for C–H is 98.7 kcal/mol: Cottrell, T. L. *The Strengths of Chemical Bonds*, 2nd ed.; Butterworths Scientific Publications: London, 1958.