Communications to the Editor

Crystal Geometry of the Bifluoride Anion

Sir:

The bifluoride anion HF_2^- has received considerable interest, not only because it contains the strongest[1] hydrogen bond but also because of the possibility[2] of a double-minimum potential for the H atom. Ab initio calculations[3-5] on the isolated anion all predict only a single minimum, although Kollman and Allen[4] found a double minimum for larger F-F distances. One expects then that in symmetric environments the hydrogen atom would have its equilibrium position midway between the two fluorines, and structural studies for the NH_4^+ cation,[6] the Na^+ cation,[7] and the K^+ cation[8] have all come to this conclusion.

Denne and Mackay[9] have reported an X-ray structure for *p*-toluidinium bifluoride which crystallizes in the orthorhombic space group *Pbca*. They interpreted their data as indicating the bifluoride ion to be linear and symmetric, to within experimental error. Recently, Williams and Schneemeyer[10] have reexamined the same system using neutron diffraction and found the $(F-H-F)^-$ ion to be linear but with very different H-F bond lengths. Their derived distances are 1.235 Å for *R*, the F(1)-H distance, and 1.025 Å for *r*, the F(2)-H distance.

The structure is composed of discrete $CH_3C_6H_4NH_3^+$ cations and FHF^- anions. In attempting to determine whether the asymmetry in the anion can be explained solely on the basis of the asymmetric crystal field, we have calculated the effect of an external point charge on the bifluoride geometry using minimal basis STO-3G[11] and split valence shell 4-31G[12] ab initio wave functions. Figure 1 shows the two bond lengths as a function of the position of a unit positive point charge placed along the axis, a fixed distance from the H atom. As expected, both fluorine atoms move toward the positive charge shortening one H-F bond and lengthening the other. The effect is much enhanced with the larger, more polarizable 4-31G basis set.

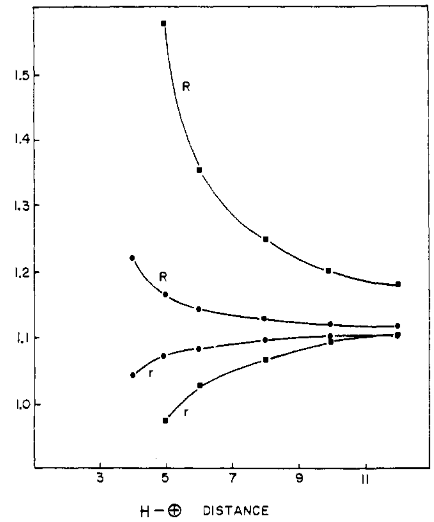

Figure 1. Variation of bond lengths *R* and *r* with the distance of a point charge from the H atom. Point charge is along axis and all distances are in ångströms (●, STO-3G; ■ 4-31G).

Table I. Coordinates (Å) of the Crystal Calculation

	X	*Y*	*Z*
F(1)	0.0	0.0	0.0
F(2)	0.0	0.0	2.27645
+	2.51035	0.88748	−0.29955
+	−2.33126	−1.17646	3.23301
+	1.45576	1.92081	4.06615
+	−1.62110	−0.14586	−2.06097

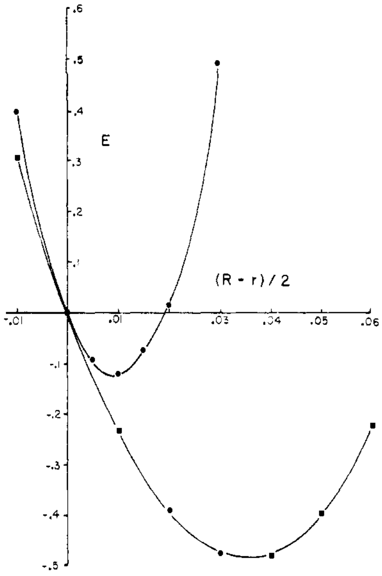

Figure 2. The relative energy *E* (kJ mol^{-1}) as a function of the displacement $(R - r)/2$ (Å) of the H atom from its symmetric position (●, STO-3G; ■-4-31G).

Having found that a point charge will markedly affect the geometry of HF_2^-, we have simulated the crystal field of *p*-toluidinium bifluoride by replacing the $CH_3C_6H_4NH_3^+$ cation with a point charge at the position of the nitrogen atom. The coordinates of F(1), F(2), and the four closest nitrogen atoms, calculated from the positional parameters of the X-ray study,[9] are shown in Table I. The next closest nitrogen atom is considerably further away. The energy relative to a symmetric H atom is shown in Figure 2, as a function of the position of the H atom along the axis, between the two fluorine atoms. In agreement with experiment, the H atom is displaced toward F(2), although the experimental value of the displacement $(R - r)/2$ is three times (0.105 Å) the 4-31G value of 0.035 Å.

The asymmetric geometry of the bifluoride ion in *p*-toluidinium bifluoride can thus be explained, at least in part, by its asymmetric crystal field, without invoking electronic interactions with its neighbors nor the detailed structure of the cation. The effect increases markedly as the basis set increases and the description of the polarizability of the anion, in the presence of a point charge, is improved. More accurate calculations which include polarization functions, d orbitals on F and p orbitals on H, are required to obtain the limit of this effect.

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References and Notes

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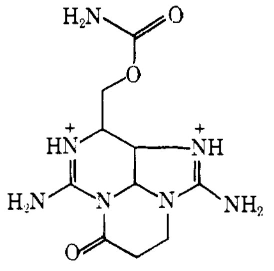
The Structure of Saxitoxin[1]

Sir:

Saxitoxin is the neurotoxin isolated from toxic Alaska butter clams (*Saxidomus giganteus*), toxic mussels (*Mytilus californianus*), and axenic cultures of *Gonyaulax catanella*.[2] Recently it was also found to be present in aged extracts of scallops collected during a *G. tamarensis* bloom.[2] It is among the most toxic substances known with an LD_{50} of 5-10 μg/kg (mouse, ip). The chemistry of saxitoxin has been complicated by its noncrystalline, highly polar, nonvolatile nature and even the molecular formula has been a subject of debate.[3b] As a result of extensive chemical and spectroscopic work, structures **1**[3a] and **2**[3b] have previously been reported in the literature. We have succeeded in crystallizing the *p*-bromobenzenesulfonate saxitoxin and now wish to report the structure deduced from a single-crystal X-ray diffraction study as **3**.



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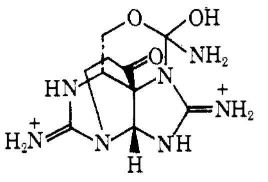

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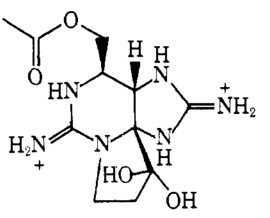

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Purified saxitoxin hydrochloride ($C_{10}H_{17}N_7O_4\cdot 2HCl$) was dissolved in water and 2 equiv of sodium *p*-bromobenzenesulfonate was added. The crystals resulting from this were washed and recrystallized from water. A satisfactory biological assay (4088 mu/mg) was obtained.[4] These crystals were subjected to a single-crystal X-ray diffraction study. A crystal of 0.1 × 0.2 × 0.6 mm was mounted in a Lindemann capillary with mother liquor. The crystals formed in the common, chiral, unambiguously determined, space group $P2_12_12_1$ with $a = 31.095$ (4), $b = 12.180$ (1), $c = 7.8057$ (9) Å. A calculated density of 1.74 g/cm^3 (for $Z = 4$ and mol wt = 773) was interpreted to mean that one unit of $C_{10}H_{19}N_7O_4\cdot 2C_6H_4BrSO_3$ formed the asymmetric unit. Reflection data for all unique diffraction maxima with $2\theta \le 114°$ were collected on a fully automated four-circle diffractometer using an ω-scan technique because of the pronounced spread of the reflections. A total of 2340 reflections were measured and after correction for Lorentz, polarization, and background effects 1895 (81%) were judged observed ($F_o \ge 3\sigma(F_o)$).

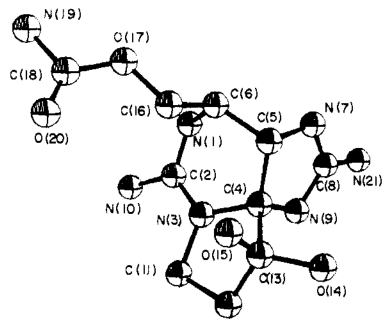

Figure 1. A computer generated perspective drawing of saxitoxin crystallized as the *p*-bromobenzenesulfonate. For clarity the hydrogen atoms of the saxitoxin portion and all atoms of the sulfonate are omitted. The absolute configuration is as shown.

The bromine and sulfur atoms were easily located and three-dimensional electron density syntheses revealed all 43 non-hydrogen atoms.[7] Least-squares refinements with anisotropic temperature factors lowered the conventional discrepancy index to 6.3%. Placement of all hydrogens followed by further least-squares refinement lowered the discrepancy index to 5.6%. Inclusion of anomalous scattering factor contributions for Br and S, followed by still further least-squares refinement lowered the discrepancy index to the current value of 5.2% for the structure and 5.7% for its mirror image, a statistically significant difference.[8] A careful remeasurement of the 20 most enantiomorph sensitive reflections also indicated that the structure and not its mirror image was the correct absolute configuration. Figure 1 shows a computer generated drawing of the final X-ray model. Tables I, II, III, and IV contain the final fractional coordinates, bond distances, bond angles, and structure factors, respectively, and can be found in the supplemental material.

In general the bond distances and angles agree well with accepted values. Saxitoxin contains three rings and is conveniently described as a 3,4,6-trialkyl tetrahydropurine. The 3 and 4 positions are bridged by a three-carbon fragment to form the third ring which contains a hydrated ketone as a novel structural element. The 2 and 8 positions of the purine ring contain NH_2 groups which form the two guanidine moieties of saxitoxin. Position 6 is substituted by a $-CH_2OCONH_2$ fragment which adopts a pseudo-axial configuration. The crystal structure reveals 13 possible H bonds but none of these is intramolecular. There is a close approach between O(14) and N(9) of 2.82 Å but the hydrogen of O(14) is turned away from N(9).

The five-membered ring containing the guanidine group is planar with a maximum deviation from the least-squares plane of 0.001 Å. In addition, four (N(3), C(4), C(11), and C(12)) of the five atoms in the other five-membered ring