

compose by loss of ammonia and give back the starting  $C_3H_6^+$  and its subsequent decomposition products  $C_3H_5^+$  and  $C_3H_3^+$ . The dominant decomposition to  $CH_2NH_2^+$  is expected for the distonic ion but it may also signal that the adduct exists as a mixture of the distonic form (see eq 3) and  $[n-C_3H_7NH_2]^+$ , as has been suggested elsewhere.<sup>13</sup>

In summary, reaction of the cyclopropane cation radical with the nucleophile ammonia produces a new distonic cation radical  $\cdot CH_2CH_2CH_2NH_3^+$  which decomposes to  $CH_2NH_2^+$  and to another distonic species,  $CH_2NH_3^+$ . The generality of this route to distonic ions is now under investigation. Encouragement is offered by reports of the reactivity of other small cyclic cation radicals with nucleophiles.<sup>7d,14</sup>

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**Registry No.** 4, 34496-93-0;  $NH_3$ , 7664-41-7;  $\cdot CH_2CH_2CH_2NH_3^+$ , 20694-02-4;  $\cdot CH_2NH_3^+$ , 21444-88-2;  $CH_2NH_2^+$ , 54088-53-8;  $[n-C_3H_7NH_2]^+$ , 70677-54-2;  $C_3H_8N^+$ , 52018-43-6; cyclopropane, 75-19-4; propylamine, 107-10-8.

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### Proton-Transfer Spectroscopy of Bis[2,5-(2-benzoxazolyl)]hydroquinone in Supersonic Jets: Effect of van der Waals Complexation with Noble Gas Atoms

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Recently we reported on the dual fluorescence of bis[2,5-(2-benzoxazolyl)]hydroquinone (BBXHQ, Figure 1 inset) in a supersonic free jet.<sup>1</sup> The dual, red and blue, fluorescence is caused by excited-state intramolecular proton transfer (ESIPT).<sup>2,3</sup> This paper presents novel observations on the effect of complexation with noble gas atoms on the dual fluorescence of BBXHQ.

The first few bands for excitation of red and blue emission from cold, isolated BBXHQ are shown in Figure 1. Excitation at 4178.1 Å gives blue fluorescence; proton transfer also results in a red fluorescence component. The red to blue fluorescence ratio is greatly reversed for bands at 4175.1 and 4184.7 Å. Several distinct ground-state conformers may, in principle, be present in the jet. However, only the dominant band at 4178.1 Å (and hence only one conformer) shall be discussed here. This band can be assigned to the energetically favored conformer having two  $OH \cdots N$  hydrogen bonds as shown in Figure 1. Briefly, the reasons<sup>4</sup> are the

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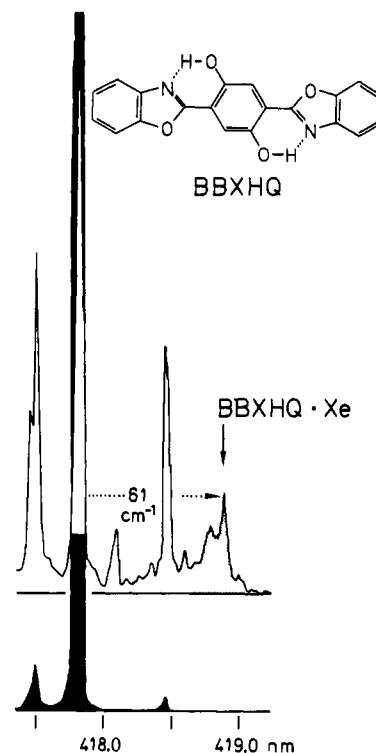


Figure 1. Excitation spectra of BBXHQ in a pulsed supersonic expansion of 6% Xe in He monitoring red (line) and blue fluorescence (solid black). The bands for BBXHQ-Xe are shaded and the microscopic solvent shift is indicated.

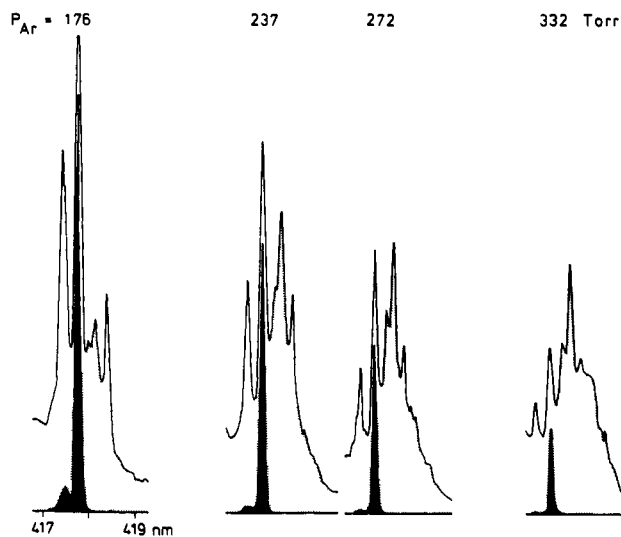


Figure 2. Excitation spectra of BBXHQ in a continuous supersonic expansion of Ar monitoring red (line) and blue fluorescence (solid black). The broadened band due to excitation of BBXHQ-Ar has been shaded.

following: (1) other conformers should have electronic origin transitions at considerably higher energy;<sup>5</sup> (2) the total emission obtained from excitation at 4178.1 Å is stronger than that of nearby bands; (3) H/D exchange shows two successive blue-shifts for this band, by 57  $cm^{-1}$  each, indicating two equivalent strong hydrogen bonds.<sup>6</sup>

The effect of van der Waals complexation of BBXHQ in a continuous expansion of argon is shown in Figure 2. With increasing stagnation pressure, the sharp bands of the bare molecule decrease. A broadened new band appears at 4182.1 Å

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shifted by  $-23\text{ cm}^{-1}$  from the dominant original band. Its formation kinetics establishes that this band is due to complexes of composition  $\text{BBXHQ-Ar}$ .<sup>7</sup> The most striking feature of the new band is that it is only monitored by red fluorescence. Blue fluorescence only observes the original band at  $4178\text{ \AA}$  of the bare molecule, disregarding the overwhelming presence of complexed molecules.

Fluorescence excitation of  $\text{BBXHQ}$  was also examined at higher resolution in pulsed expansions of He mixed with Ne, Ar, Kr, or Xe (Figure 1). Two bands are generally observed—by their red fluorescence only—for complexes  $\text{BBXHQ-R}$  with a single noble atom R. Through the dependence of their spectral position on the polarizability of R, the stronger band must be associated with the original excitation band for dual fluorescence at  $4178\text{ \AA}$ . It is therefore due to a complex formed by the molecule in its favored conformation shown in Figure 1.

Why does complexation with a single noble gas atom R effectively remove the blue fluorescence associated with the excited molecule prior to proton transfer? A possible explanation is the preferred stabilization of the excited tautomer by dipole-induced dipole interaction with R. This should lower the barrier for ES IPT. In cooperation with proton tunneling,<sup>4</sup> a relatively small stabilization would be needed for a strong enhancement of the transfer rate.

Regardless of interpretation, the observations reported here suggest that the relative short-wavelength fluorescence of  $\text{BBXHQ}$  in noble gas matrices may be quite reduced by comparison with the isolated molecule. Conversely, the dual character of fluorescence may be significantly more pronounced in a supersonic jet, for similar molecules<sup>8</sup> which have previously been studied in noble gas matrices.

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### Crystal and Molecular Structure of $[(\text{CH}_3)_2\text{N}]_3\text{S}^+\text{CF}_3\text{O}^-$ . Evidence for Negative Fluorine Hyperconjugation

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Perfluorinated alkoxide anions are well-known reactive intermediates<sup>1</sup> and have been the subject of limited theoretical study,<sup>2</sup> but except for the infrared vibrational frequencies of some  $\text{Cs}^+$  and  $\text{Rb}^+$  salts,<sup>1f,3</sup> no experimental structural data have been re-

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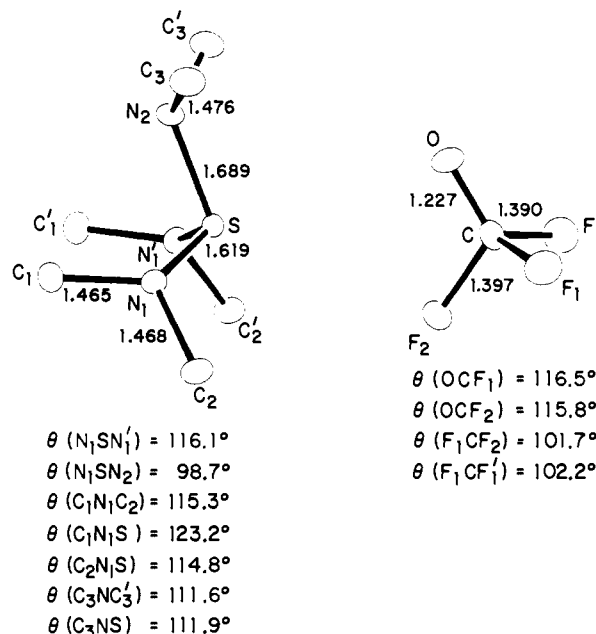


Figure 1. X-ray crystal structure of tris(dimethylamino)sulfonium trifluoromethoxide (1). Bond distances in Å. The mirror plane relates atoms bearing primed and unprimed labels.

ported. We now report the first single-crystal X-ray structure of a perfluoroalkoxide salt, tris(dimethylamino)sulfonium (TAS) trifluoromethoxide, and we present our theoretical studies of the structure and bonding in  $\text{CF}_3\text{O}^-$  and related perfluoroalkoxides.

The X-ray single-crystal diffraction analysis of  $\text{TAS}^+\text{CF}_3\text{O}^-$  (1)<sup>4</sup> shows that the TAS cation and the  $\text{CF}_3\text{O}^-$  anion both lie on a crystallographic mirror plane<sup>5</sup> (Figure 1). The C-F bond lengths (1.390 (3), 1.397 (4) Å) are exceptionally long and the C-O bond length (1.227 (4) Å) is quite short compared with the corresponding gas-phase experimental values for  $\text{CF}_3\text{OR}$  (R = F, Cl,  $\text{CF}_3$ ) derivatives ( $r(\text{C}-\text{F}) = 1.319-1.327\text{ \AA}$ ,  $r(\text{C}-\text{O}) = 1.365-1.395\text{ \AA}$ ).<sup>7</sup> In fact, the C-O bond length in 1 approaches that for the C=O bond in  $\text{CF}_2=\text{O}$  (1.171 Å).<sup>8</sup> Moreover, the FCF bond angles (101.7 (2)°, 102.2 (3)°) are extraordinarily small.<sup>9</sup>

(4) The  $\text{TAS}^+\text{CF}_3\text{O}^-$  salt (1) was prepared by adding  $\text{COF}_2$  to a slurry of 11.0 g (39.5 mmol) of tris(dimethylamino)sulfonium difluorotrimethylsilyl-silicate ( $\text{TASF}^+$ ) in 100 mL of anhydrous tetrahydrofuran at  $-75\text{ }^\circ\text{C}$  until the exothermic reaction subsided. The mixture was warmed to  $25\text{ }^\circ\text{C}$  and filtered with the rigorous exclusion of moisture to give 8.81 g (88%) of 1: mp  $214-216\text{ }^\circ\text{C}$  dec; IR ( $\text{CH}_2\text{Cl}_2$ ) 1553 ( $\nu_1$ ), 805 ( $\nu_2$ )  $\text{cm}^{-1}$ ;  $^{19}\text{F}$  NMR ( $\text{CD}_2\text{Cl}_2$ )  $\delta -21.3$  (br s,  $w_{1/2} = 430$  (23  $^\circ\text{C}$ ), 110 Hz ( $-1\text{ }^\circ\text{C}$ ));  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ )  $\delta 2.88$  (s). Anal. C, H, N, F, S. Crystals for X-ray analysis were grown by slowly diffusing an 8:1 mixture of tetrahydrofuran/diethyl ether into a solution of 1 in 1,2-dichloroethane. The solvent mixture was then removed and replaced with tetrahydrofuran to afford crystals which were mounted in glass capillaries in an atmosphere of dry nitrogen.

(5) Crystal structure information: orthorhombic; space group  $Pnma$  (No. 62);  $a = 14.547$  (2) Å,  $b = 11.125$  (1) Å,  $c = 7.310$  (1) Å,  $V = 1183\text{ \AA}^3$ ,  $Z = 4$ ;  $T = -100\text{ }^\circ\text{C}$ . Data collected on Syntex R3 diffractometer, graphite monochromator, Mo  $K\alpha$ ,  $\lambda = 0.71069\text{ \AA}$ ; 1643 reflections,  $4.6^\circ < 2\theta < 55.0^\circ$ ; 895 unique reflections with  $I > 3.0\sigma(I)$ . Structure solved by direct methods (MULTAN); full-matrix, least-squares refinement. All hydrogens refined isotropically, other atoms, anisotropically. Final  $R = 0.036$ ,  $R_w = 0.039$  for 112 independent variables.

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