

## Influence of $\text{BF}_4^-$ Position on the $\text{N}=\text{N}$ Distance of Trialkyldiazonium Cation Salts

Stephen F. Nelsen,\* Hao Chang, J. Jens Wolff, and Douglas R. Powell

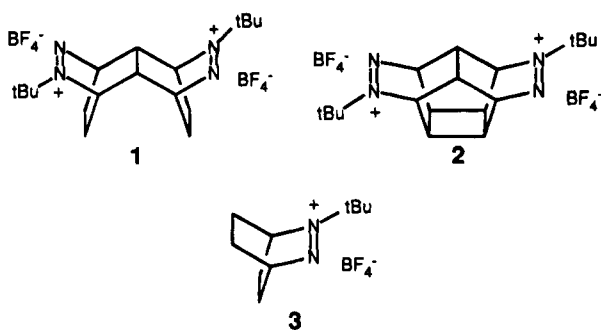
S. M. McElvain Laboratories of Organic Chemistry, Department of Chemistry, University of Wisconsin, 1101 W. University Avenue, Madison, Wisconsin 53706-1396

Received April 26, 1994<sup>Ⓢ</sup>

The crystal structures of two bis(trialkyldiazonium) bis(tetrafluoroborate) salts, **1** and **2**, are reported. The structure of **2** provides eight chemically identical but crystallographically different 2-*tert*-butyl-2-azonia-3-azabicyclo[2.2.2]oct-2-ene units for examining the effects of the neighboring  $\text{BF}_4^-$  groups on the  $\text{N}=\text{N}$  geometry. Each bis(cation) has one  $\text{N}=\text{N}$  group with two neighboring  $\text{BF}_4^-$  and a second  $\text{N}=\text{N}$  group with only one nearby  $\text{BF}_4^-$  group. The twelve  $\text{BF}_4^-$  groups nearest to the  $\text{N}=\text{N}$  groups of **2** ( $\text{B}_\text{br}\text{N}$  distances  $< 4.14 \text{ \AA}$ ) are oriented above or below the  $\text{R}_2\text{N}=\text{NR}$  planes having  $\text{BN}^\oplus\text{N}^+\text{C}_\text{br}$  torsion angles  $|\text{92.9}|$  to  $|\text{108.6}|^\circ$ . The  $\text{N}=\text{N}$  distances cluster into two groups with six values ranging from 1.241(4) to 1.251(4)  $\text{Å}$  and two values of 1.257(4) and 1.261(4)  $\text{Å}$ . The  $\text{N}=\text{N}$  bonds in **1** are 1.244(4) and 1.245(4)  $\text{Å}$ . The 0.020  $\text{Å}$  difference in the  $\text{N}=\text{N}$  distances in **2** corresponds to a Pauling  $\text{N}=\text{N}$  bond order decrease from 2.0 for the shorter  $d(\text{N}=\text{N})$  units to 1.9 for the longer ones. It appears unlikely that  $\text{F}_\text{br}\text{N}^\oplus$  bonding is involved in causing the bond length change.

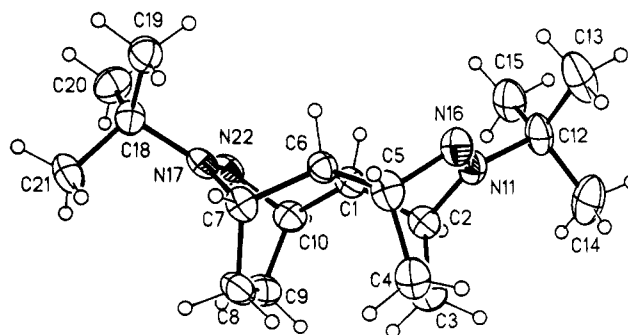
### Introduction

We prepared the tetracyclic **1**<sup>1</sup> and hexacyclic **2**<sup>2</sup> bis-(diazonium cation tetrafluoroborate) salts as precursors of bis(hydrazyl) and bis(hydrazine) radical cations which would be organic analogues of transition metal intervalence complexes. These molecules contain two 2-*tert*-butyl-2-azonia-3-azabicyclo[2.2.2]octene cation (**3**) units *anti*-fused to each other and only differ by the presence of two extra CC bonds in the hexacyclic compound **2**. Optical and ESR studies of the radical cation oxidation states of species derived from **1** and **2** have been published separately.<sup>2</sup> In this work, we describe the X-ray structures of these dications, which prove interesting in their own right, as they reveal an unexpected effect of  $\text{BF}_4^-$  position upon the  $\text{N}=\text{N}$  bond length.



### Results

The X-ray structures of **1** (Figure 1) and **2** (Figure 2) have been determined (see Experimental Section). **1** crystallized in the monoclinic  $P2_1/c$  system with four equivalent dication units in the unit cell, so there are two crystallographically different substituted **3** units present. Although **2** crystallized in the same space group,



**Figure 1.** Thermal ellipsoid plot (50% probability) drawing of the X-ray structure of the dication unit of **1**.

it has sixteen molecules in the unit cell and four different unsymmetrical dication units. One of the  $\text{BF}_4^-$  ions of **1** and two of the eight of **2** are disordered. A particular point of interest for the electron transfer studies was establishing the distance between the linked dinitrogen units in these compounds. In agreement with conclusions from semiempirical calculations on these dications,<sup>2</sup> the presence of the four-membered ring of **2** tilts the dinitrogen units apart slightly relative to **1**. The average distance between the  $4\sigma$ -bond linked nitrogen atoms is 0.13  $\text{Å}$  (2.8%) larger in **2** than in **1** (see Table 1). Table 1 also compares the geometries about the nitrogens of these compounds. As expected, all are planar at the trisubstituted nitrogen, and their bicyclic rings have little torsion. The  $\text{C}_\text{br}\text{N}_\text{C}_\text{br}$  twist angles vary from  $-0.6$  to  $+1.4^\circ$  for **2**, but are slightly larger for the less constrained compound **1**,  $+1.4$  and  $+3.1^\circ$ , estimated standard deviations,  $\sigma = 0.4^\circ$ . The crystal structure of **4**, the neutral azo analogue of **3**, has a twist angle of  $1.5^\circ$ , and its cyclobutanated analogue **5**,  $0^\circ$ .<sup>3</sup> The  $d(\text{N}=\text{N})$  values of

<sup>Ⓢ</sup> Abstract published in *Advance ACS Abstracts*, September 1, 1994.

(1) Nelsen, S. F.; Wolff, J. J.; Chang, H.; Powell, D. R. *J. Am. Chem. Soc.* **1991**, *113*, 7882.

(2) Nelsen, S. F.; Chang, H.; Wolff, J. J.; Adamus, J. J. *J. Am. Chem. Soc.* **1993**, *115*, 12276.

(3) (a) Ottersen, T.; Romming, C.; Snyder, J. P. *Acta Chem. Scand. Ser. B* **1976**, *30*, 407. (b) Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc., Perkin Trans. 2* **1987**, S1. (c) The  $d(\text{BF})$  range for the six nondisordered  $\text{BF}_4^-$  groups of **2** is 1.355–1.397  $\text{Å}$ , mean 1.384  $\text{Å}$ . This is near the center of the most often found distribution of  $d(\text{BF})$  reported for  $\text{BF}_4^-$  (Figure 3, ref 3b), which is unusually broad and asymmetrical, presumably because  $\text{BF}_4^-$  is so frequently disordered.

Table 1. Comparison of Geometries about the Nitrogen Atoms for 3 Derivatives<sup>a</sup>

	tetracyclic 1 <sup>b</sup>		hexacyclic 2 <sup>c</sup>				
		av	a12,a34	b12,b34	c12,c34	d12,d34	av
Nonbonded N,N Distances							
d(N <sup>o</sup> ,N <sup>+</sup> ), Å	4.730,4.736	4.733	4.864,4.853	4.862,4.882	4.852,4.865	4.872,4.865	4.864
d(N <sup>+</sup> ,N <sup>+</sup> ), Å	4.867		4.961	4.976	4.965	4.971	4.968
d(N <sup>o</sup> ,N <sup>o</sup> ), Å	4.915		4.070	5.085	5.067	5.081	5.076
Bonded Distances							
d(NN), Å	1.245,1.244	1.244	1.250,1.244	1.246,1.261	1.241,1.257	1.251,1.247	1.250
d(N <sup>o</sup> C <sub>br</sub> ), Å	1.486,1.480	1.483	1.461,1.466	1.467,1.458	1.462,1.4531	1.463,1.462	1.462
d(N <sup>+</sup> C <sub>br</sub> ), Å	1.494,1.489	1.492	1.464,1.466	1.466,1.466	1.471,1.465	1.461,1.471	1.466
d(N <sup>+</sup> C <sub>tb</sub> ), Å	1.530,1.530	1.530	1.523,1.528	1.526,1.520	1.524,1.525	1.533,1.529	1.526
Bond Angles							
∠(C <sub>br</sub> N <sup>+</sup> N <sup>o</sup> ), deg	118.4,118.6		119.5,119.5	119.3,119.1	119.3,119.2	119.7,119.4	
∠(C <sub>br</sub> N <sup>+</sup> C <sub>q</sub> ), deg	121.7,122.1		120.3,120.4	121.2,121.3	121.3,121.0	120.4,120.1	
∠(N <sup>o</sup> N <sup>+</sup> C <sub>q</sub> ), deg	119.9,119.3		120.2,120.2	119.5,119.4	119.4,119.8	119.8,120.5	
Torsional Angles							
∠(N <sup>o</sup> N <sup>+</sup> ,C <sub>tb</sub> Me), deg	-0.7,-5.1		-2.4,+0.5	+0.4,-6.5	+1.9,-5.9	-2.3,1.2	
∠(C <sub>br</sub> N <sup>+</sup> ,N <sup>o</sup> C <sub>br</sub> ), deg	+3.1,+1.4		+0.9,-0.6	-0.6,+0.4	0.7,+0.5	+1.4,-0.4	

<sup>a</sup> N<sup>+</sup> refers to a *tert*-butylated nitrogen, N<sup>o</sup> to a disubstituted nitrogen, C<sub>tb</sub> to a bridgehead tertiary carbon, C<sub>br</sub> to a bridgehead carbon, and C<sub>q</sub> to a quaternary carbon of a *tert*-butyl group. <sup>b</sup> Distances, ±0.005 Å, angles, ±0.3°, torsional angles ±0.5°. <sup>c</sup> Distances, ±0.004 Å, angles, ±0.3°, torsional angles ±0.4°.

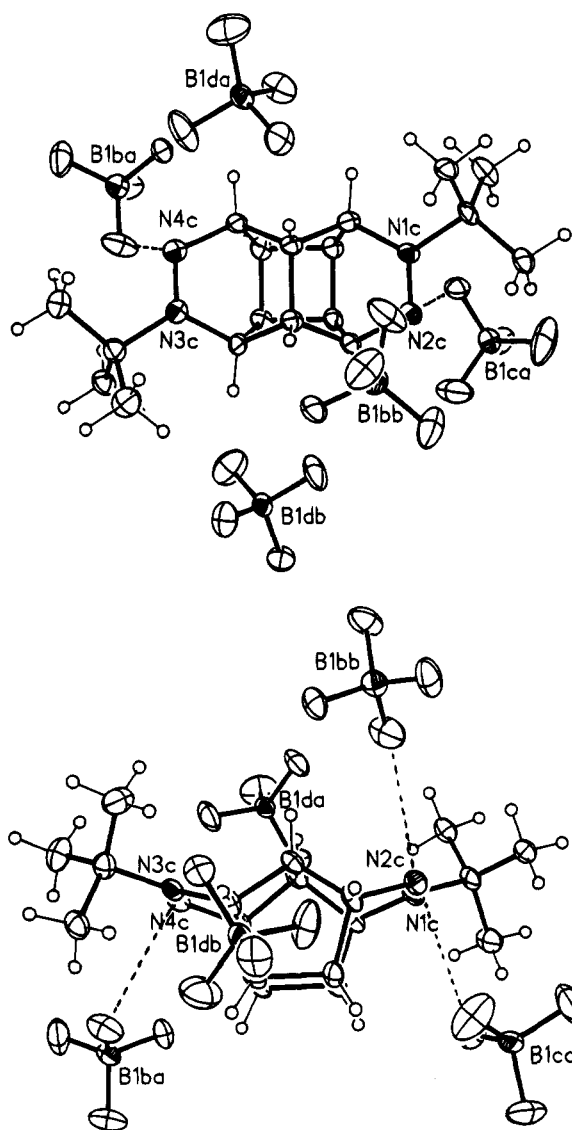
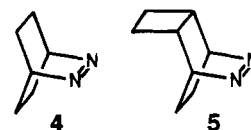


Figure 2. Thermal ellipsoid plot (50% probability) drawing of the X-ray structure of dication 2 showing one of the four independent unsymmetrical units in the crystal (c), with its closer BF<sub>4</sub><sup>-</sup> groups. The dotted lines show closest N<sup>o</sup>,F approach (see Discussion).

1.244(4) and 1.245(4) Å observed for 1 are indistinguishable and slightly shorter than the 1.255(4) Å of both 4 and 5,<sup>3a</sup> but near the 1.240 Å mean d(N=N) for neutral



azo compounds.<sup>3b</sup> The presence of eight crystallographically different 3 units in 2 provides an unusual opportunity for consideration of structural variation within these units, using exactly comparable crystal data. We found it intriguing that the d(N=N) values for 2 vary appreciably, from 1.241(4) to 1.261(4) Å, and that both values for 1 fall in the lower quarter of this range. Furthermore, the range of d(N=N) for 2 (0.020 Å) is larger than that of any of its N-C single bond lengths (0.009–0.013 Å). There is of course experimental uncertainty in these numbers, but finding greater variation in the length of the strongest bond to nitrogen in these systems surprised us, and we became interested in why this might occur.

## Discussion

The principal difference we found in examining the positions of the bonded atoms between the different diazenium cation units of 2 is in the torsional angle at the *tert*-butyl groups. As expected, the *tert*-butyl groups are oriented to nearly eclipse one methyl group with the N=N bond, which minimizes steric interaction of the other two methyl groups with the bicyclic ring. For clarity the divalent nitrogens will be designated N<sup>o</sup> and the trivalent ones N<sup>+</sup>, using their formal charges. The smallest N<sup>o</sup>N<sup>+</sup>,C<sub>q</sub>Me torsional angles vary from -6.5 to +1.9°,  $\sigma = 0.4^\circ$ , a rather small range. An unexpectedly linear correlation of d(N=N) with the torsional angle nevertheless occurs: see Figure 3. The maximum deviation in d(N=N) from the regression line is 0.0015 Å, although  $\sigma$  values for the N=N distances are 0.004 Å. The N-C single bond lengths do not correlate well with *tert*-butyl group torsional angle. Both the  $\pi$  and  $\pi^*$  molecular orbitals of the trialkyldiazonium cation unit should be unusually stabilized compared to carbon-

Table 2. Environments of the Divalent Nitrogens for 1 and 2

diazonium unit	N=N dist	<i>t</i> -Bu twist	BF <sub>4</sub> <sup>-</sup>	B,N <sup>o</sup> dist	∠BN <sup>o</sup> N <sup>+</sup>	∠BN <sup>o</sup> , N <sup>+</sup> C <sub>br</sub>	closest F to N <sup>o</sup>		
							d(FN)	∠FNN	∠FNNC <sub>br</sub>
Tetracyclic Compound 1(BF <sub>4</sub> <sup>-</sup> ) <sub>2</sub>									
N17=N22	1.244	-5.1	2*	4.114	107.1	122.7			
			2*	4.247	108.3	125.5			
			2a*	4.191	86.0	-99.8			
N11=N16	1.245	-0.7	1	4.719	93.5	111.2			
			2*	4.603	85.8	-91.2			
Hexacyclic Compound 2(BF <sub>4</sub> <sup>-</sup> ) <sub>2</sub>									
c12	1.241	+1.9	c	3.750	100.2	99.6	3.184	80.6	91.4
			b	4.001	107.7	-97.2	3.111	90.3	-99.7
a34	1.244	+0.5	a	3.624	102.4	103.2	3.081	82.1	94.7
			e	3.998	103.3	-96.7	3.092	86.6	-99.8
b12	1.246	+0.4	h*	3.816	103.4	-107.8	*		
			f	4.133	100.5	92.9	3.566		
d34	1.247	-1.2	g*	3.889	102.0	-108.6	*		
			d	4.011	102.5	95.7	3.376		
a12	1.250	-2.4	h*	3.958	106.4	99.2	*		
			[f	4.331	135.1	-69.7]			
d12	1.251	-2.3	g*	3.867	108.5	99.8	*		
			[c	4.795	135.2	-61.1]			
c34	1.257	-5.9	b	3.713	114.4	100.1	2.994	94.2	102.5
			[d	4.214	132.9	-74.7]			
b34	1.261	-6.5	e	3.784	115.2	99.0	2.997	95.8	100.7
			[a	4.667	134.2	-64.8]			

\* The asterisks mark disordered BF<sub>4</sub><sup>-</sup> groups. The brackets enclose data for 2(BF<sub>4</sub><sup>-</sup>) groups which are not oriented for association with the N=N π\* bond; all have B,N<sup>o</sup> distances > 4.2 Å.<sup>7</sup>

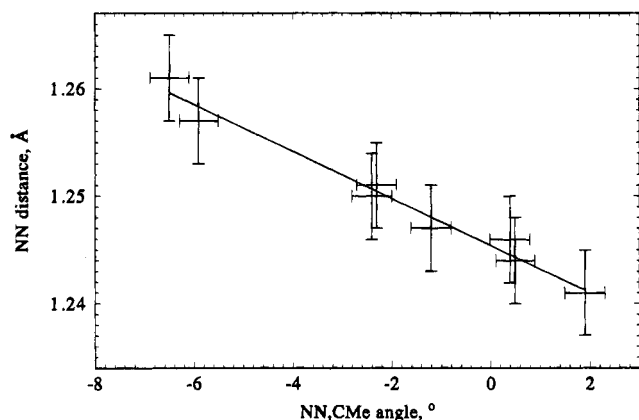


Figure 3. Plot of  $d(\text{N}=\text{N})$  vs *tert*-butyl group torsional angle for 2. The error bars show  $\sigma$  values from the crystal structure, 0.004 Å for  $d(\text{N}=\text{N})$ , 0.4° for torsional angles.

centered double bonds because they are centered on relatively electronegative nitrogens, which also share a formal positive charge.<sup>4</sup> We would expect  $\sigma, \pi^*$  mixing effects to be unusually large,<sup>5</sup> but the approximately three-fold local symmetry of the *tert*-butyl group should make its interaction with the  $\pi$  system nearly isotropic, and one would not expect the importance of  $\sigma, \pi^*$  mixing to vary significantly with *tert*-butyl group rotation angle. This is the result obtained for cation 3 by AM1 semiempirical calculations, for which the N=N bond length only changes by 0.0001 Å for N<sup>o</sup>N<sup>+</sup>, C<sub>q</sub>Me torsional angle increase from the energy minimum 0° value to 10°, which is calculated to destabilize this cation by only 0.12 kcal/mol. We conclude that *tert*-butyl torsional angle is not a plausible cause of the  $d(\text{N}=\text{N})$  variation and presume

that more subtle, multiatom interactions in the crystal must be involved in causing both the "stiff" N=N bond length change and the "soft" N<sup>o</sup>N<sup>+</sup>, C<sub>q</sub>Me torsional angle change, and that the fact that they correlate well with each other is basically an accident.

The placement of the BF<sub>4</sub><sup>-</sup> counterions relative to the trialkyldiazonium units varies substantially in these crystals, as indicated in Table 2. Although two of the eight BF<sub>4</sub><sup>-</sup> groups of 2 are disordered, the crystal data were successfully modeled using two BF<sub>4</sub><sup>-</sup> units with superimposed boron atom positions, and we shall assume that the boron positions are reasonably well known. The B-F distances in these structures vary from about 1.37 to 1.40 Å,<sup>3c</sup> so the maximum BF<sub>4</sub><sup>-</sup> van der Waals (vdW) radius is about 2.84–2.87 Å, and the maximum vdW sum for contact with nitrogen is about 4.39–4.42 Å,<sup>6</sup> but it costs little energy to achieve closer approach by rotating the BF<sub>4</sub><sup>-</sup> to place the nitrogen in the crevices between fluorines. No B,N<sup>o</sup> distances under 4.11 Å are present for 1. The BF<sub>4</sub><sup>-</sup> groups of 2 having B,N<sup>o</sup> distances greater than vdW contact distance (including the four closer ones shown in square brackets in Table 2 which have  $d(\text{B},\text{N}^o)$  in the range 4.21–4.80 Å) are clearly not oriented for interaction with the N=N π systems (as for B1d of Figure 2).<sup>7</sup> In contrast, all twelve BF<sub>4</sub><sup>-</sup> groups having  $d(\text{B},\text{N}^o)$  under 4.14 Å are oriented roughly for contact with the N=N π (or π\*) orbital, having BN<sup>o</sup>, N<sup>+</sup>C<sub>br</sub> torsional angles in the range ±(92.9–108.6°), and BN<sup>o</sup>N<sup>+</sup> angles between 100.2 and 115.2°. The BF<sub>4</sub><sup>-</sup>, (N=N)<sup>+</sup> interaction appears to be highly anisotropic, because the bicyclic alkyl substituents encumber π approach (BN<sup>o</sup>, N<sup>+</sup>C<sub>br</sub> torsional angle ±90°), and there appears to be more room to accommodate a BF<sub>4</sub><sup>-</sup> group near N<sup>o</sup> in the plane of the diazenium units (torsional angle near 180°). The  $d(\text{B},\text{N}^o)$

(4) For discussion of NMR evidence for nearly equal charges at the nitrogens of trialkyldiazonium cations, see Nelsen, S. F.; Blackstock, S. C. *J. Org. Chem.* **1984**, *49*, 1134.

(5) For discussion of lone pair,  $\sigma^*$  mixing effects, see (a) David, S.; Eisenstein, O.; Hehre, W. J.; Salem, L.; Hoffmann, R. *J. Am. Chem. Soc.* **1973**, *95*, 3806. (b) Schleyer, P. v. R.; Kos, H. J. *Tetrahedron* **1983**, *39*, 1141. (c) Schleyer, P. v. R.; Jemmis, E. D.; Spitznagel, G. W. *J. Am. Chem. Soc.* **1985**, *107*, 6393.

(6) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.

(7) The four longer N=N units, a12, d12, c34, and b34, have B atoms 4.21–4.80 Å from N<sup>o</sup>, with BN<sup>o</sup>N<sup>+</sup> angles of 132.9–135.2° and BN<sup>o</sup>, N<sup>+</sup>C<sub>br</sub> dihedral angles -61.1° to -74.4°, placing them near the central CH-CH unit of the molecule (see B1da of Figure 2). The next closer BF<sub>4</sub><sup>-</sup> groups are >5.4 Å from N<sup>o</sup> of the shorter N=N distance units, c12 and b12, but are slightly closer to N<sup>+</sup> of the other N=N unit of the molecule (see B1db of Figure 2).

unit	d(N=N)		closer B positions	closest F positions
b34	1.261	—	3.78 / 115	3.00 / 96
c34	1.257	—	3.71 / 114	2.99 / 94
d12	1.251	—	[3.87 / 109]	
a12	1.250	—	[3.96 / 106]	
d34	1.247	—	[3.89 / 102] ; 4.01 / 103	
b12	1.246	—	[3.82 / 103] ; 4.13 / 101	
a34	1.244	—	3.62 / 102 ; 4.00 / 103	3.08 / 82 ; 3.09 / 87
c12	1.241	—	3.75 / 100 ; 4.00 / 108	3.18 / 81 ; 3.11 / 90

**Figure 4.** Summary of closer boron and closest fluorine positions for **2** as a function of N=N bond length. The numbers listed are X,N<sup>o</sup> distance (Å)/XN<sup>o</sup>N<sup>+</sup> angles (deg), rounded from the data in Table 2. The numbers in brackets are for disordered BF<sub>4</sub><sup>-</sup> groups, for which fluorine positions are not known.

and BN<sup>o</sup>N<sup>+</sup> angle data for each diazenium unit are summarized in Figure 4, and we note that there are two different motifs for BF<sub>4</sub><sup>-</sup> orientation. The four shorter d(N=N) units have BF<sub>4</sub><sup>-</sup> groups <4.14 Å away on both π faces of the N=N bond (as for **c12** of Figure 2, right, d(N=N) 1.241 Å), but the four longer ones only have one close BF<sub>4</sub><sup>-</sup> group (as for **c34** of Figure 2, left, d(N=N) 1.257 Å). The four shorter d(N=N) units have B,N<sup>o</sup> distances as small as those of the longer d(N=N) units, but have smaller BN<sup>o</sup>N<sup>+</sup> angles (100.2–103.4°). The two longest d(N=N) units, **b34** and **c34**, have larger BN<sup>o</sup>N<sup>+</sup> angles (115.2° and 114.4°, respectively) than those for the two intermediate ones with only one close BF<sub>4</sub><sup>-</sup> group, **d12** (1.251 Å and 108.5°) and **a12** (1.250 Å and 106.4°). We conclude that the clearly different BF<sub>4</sub><sup>-</sup> orientations relative to the diazenium units are the likely cause of the N=N bond length (and *tert*-butyl group torsional angle) changes observed for **2**.

It is obviously F,N<sup>o</sup> contact which should be examined, but this is not possible for all eight diazenium units because the closest BF<sub>4</sub><sup>-</sup> group is disordered for the four N=N units having intermediate d(N=N) values, and their fluorine positions are not known at all accurately. Disorder was not detected for the nearest BF<sub>4</sub><sup>-</sup> groups of the four diazenium units at the extremes of the d(N=N) ranges, and we shall consider only these units below. The differences in d(N=N) between the “long” units, **b34** and **c34**, and the “short” units, **c12** and **a34**, are 0.013–0.020 Å, (3–5)σ. The “long” units have d(F,N<sup>o</sup>) 2.99–3.00 Å, somewhat shorter than the 3.02 sum of N and F Bondi vdW radii,<sup>6</sup> while the “short” units have d(F,N<sup>o</sup>) of 3.08–3.18 Å, a difference of (10–45)σ from the “long” units. The FN<sup>o</sup>N<sup>+</sup> angles of the “long” units are 94.2° and 95.8°, while those of the “short” ones are 80.6–90.3°, a difference of (13–50)σ.

The closest fluorine positions for the “long” d(N=N) units are very reminiscent of those for amino nitrogens which are held close to the carbonyl carbons of ketones in crystals, which as Dunitz and co-workers pointed out,<sup>8</sup> may be usefully interpreted as mapping the energy

surface for nucleophilic addition to the carbonyl group. Six crystals with d(N,C) of 2.91–1.49 Å showed a relatively constant NCO angle of 107 ± 5°, and analysis of d(N,C) based upon Pauling's prediction that bond distance varies linearly with log(*n*), where *n* is the bond order, employing the pyramidality at the carbonyl carbon gave *n*<sub>N,C</sub> values of 0.15–0.26 for d(N,C) of 2.91–2.56 Å, which are 0.34–0.69 Å shorter than the vdW radii sum. Analysis of C=O bond distances for these cases using the Pauling formula,<sup>9a</sup>  $r(n) = r(1) - k \log(n)$ , gave *n*<sub>CO</sub> values ≥ 1.96.<sup>8</sup>

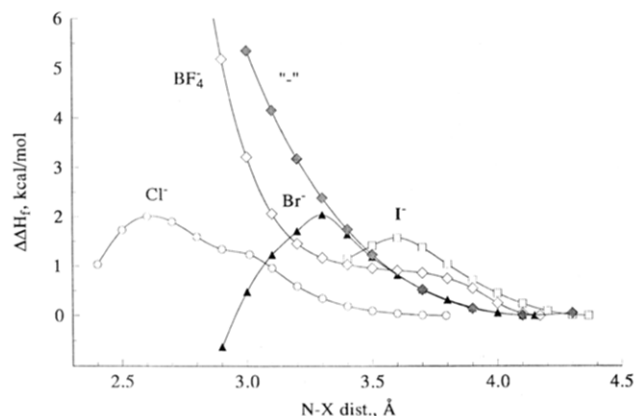
Although both the N=N and F,N<sup>o</sup> distance differences between the “long” and “short” d(N=N) units are small, the more easily deformed bond angles show considerably greater differences. The FN<sup>o</sup>N<sup>+</sup> angles are significantly smaller for the “short” **c12** and **a34** units, as might be expected for a π complex of BF<sub>4</sub><sup>-</sup> with the (N=N)<sup>+</sup> unit, than they are for the “long” **b34** and **c34** units. If the latter structures did represent the beginning of the reaction coordinate for addition to the (N=N)<sup>+</sup> bond, one would expect a larger angle of approach corresponding to orientation for interaction with the π\*(N=N) orbital. The large distances to which nucleophile, electrophile angular correlation are maintained were emphasized by Dunitz and co-workers<sup>8</sup> and have been more recently discussed in connection with consideration the extent and type of aryl, silicon interaction implied by Lambert and coworkers' Et<sub>3</sub>Si<sup>+</sup>,BPh<sub>4</sub><sup>-</sup>,(toluene)<sub>2</sub> X-ray structure and subsequent work.<sup>10</sup> We believe it is especially noteworthy that for **2**, a relatively small increase in N,F distance between **b34/c34** (2.99–3.00) and **c12/a34** (3.08–3.18), occurring near the Bondi ΣvdW radii (3.02), is associated with both a large change in FN<sup>o</sup>N<sup>+</sup> angle, from that expected for orientation with π\*(N=N) to that expected for a π complex, and loss of detectable (N=N) bond lengthening. A Pauling analysis of d(N=N) for **2** using  $r(2) = 1.240$  and  $r(1)$  in the range 1.45 to 1.50 Å<sup>9b</sup> gives *n*<sub>NN</sub> very close to 2 for the “short” d(N=N) units (1.99–2.00 for **c12**, 1.97–1.98 for **a34**), but smaller values for the “long” d(N=N) units (1.87–1.89 for **b34**, 1.89–1.91 for **c34**). Despite the approximate nature of vdW radii, it seems clear that approach of a fluoroborate fluorine to N<sup>o</sup> of under 0.03 Å less than the sum of the Bondi vdW radii is associated with a larger change in d(N=N) than is the considerably closer approach of R<sub>3</sub>N to (C=O). The charges present in the diazenium salts are presumably responsible for this difference.

The d(F,N<sup>o</sup>), for which change in BF<sub>4</sub><sup>-</sup> orientation is accompanied by detectable (N=N)<sup>+</sup> bond length increase for **2**, is large, making it seem quite unlikely to us that significant σ-bonding would be present for either motif of BF<sub>4</sub><sup>-</sup> orientation. We also would not expect significant charge transfer from BF<sub>4</sub><sup>-</sup> to diazenium cation units and have carried out semiempirical calculations to see if such interaction is predicted. To consider what the change in

(8) (a) Bürgi, H. B.; Dunitz, J. D.; Shefter, E. *J. Am. Chem. Soc.* **1973**, *95*, 5065. (b) For similar O,C=O interactions covering a wide range of O nucleophile structure, see Bürgi, H. B.; Dunitz, J. D.; Scheffer, E. *Acta Crystallogr.* **1974**, *B30*, 1517. For reviews of this and related work see: (c) Bürgi, H. B.; Dunitz, J. D.; Lehn, J. M.; Wipf, G. *Tetrahedron* **1974**, *30*, 1563. (d) Menger, F. M. *Ibid.* **1983**, *39*, 1013. (e) Kirby, A. J. *Adv. Phys. Org. Chem.* **1994**, *29*, 87.

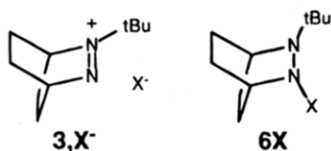
(9) (a) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed., Cornell: Ithaca, NY, 1963; p 246. (b) Taking  $r(2)$  as the mean azo compound value,<sup>9b</sup> but using a larger range for  $r(1)$ , because from more recent data,<sup>9b</sup> the 1.45 Å quoted<sup>9b</sup> for saturated hydrazines is probably too small for ones with bicyclooctyl substituents. (c) Nelsen, S. F.; Wang, Y.; Powell, D. R.; Hayashi, R. K. *J. Am. Chem. Soc.* **1993**, *115*, 5246.

(10) (a) Lambert, J. B.; Zhang, S.; Stern, C. L.; Huffman, J. C. *Science* **1993**, *260*, 1973. (b) Reed, C. A.; Xie, Z.; Bau, R.; Benesi, R. *Science* **1993**, *262*, 402. (c) Schleyer, P. v. R.; Buzek, P.; Müller, T.; Apeloig, Y.; Siehl, H.-U. *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1471. (d) Pauling, L. *Science* **1994**, *263*, 983. Olah, G. A.; Rasul, G.; Li, X.-y.; Buchholz, H. A.; Sandford, G.; Prakash, G. K. S. *Ibid.* **1994**, *263*, 984. Lambert, J. B.; Zhang, S. *Ibid.* **1994**, *263*, 984. Reed, C. A.; Xie, Z. *Ibid.* **1994**, *263*, 985.



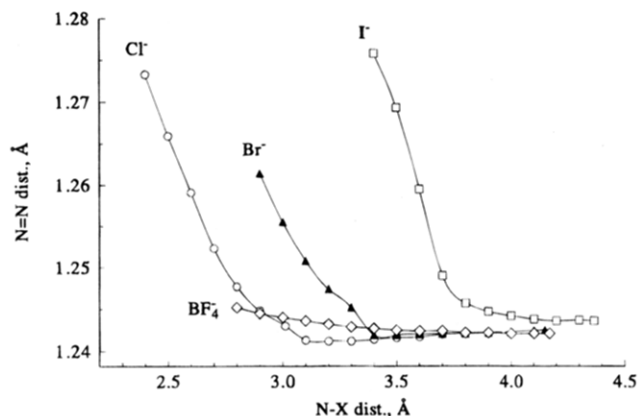
**Figure 5.** Enthalpy curves calculated by AM1 for  $3, X^-/4X$  as a function of  $N^{\circ}, X^-$  distance. “—” is the negative “sparkle” (see text).

$d(N=N)$  ought to be in the gas phase as a function of counterion ( $X^-$ ) position, AM1 calculations of **3** with various  $X^-$  and the covalently bonded forms **6X** have been carried out. **3**, halide<sup>11a</sup> pairs with large enough  $N^{\circ}, X^-$



separations that there is no  $N, X$  covalent bonding optimize to structures having the counterion slightly closer to  $N^+$ , a hydrogen bond to a methylene hydrogen for  $Cl^-$ , and to both a methylene hydrogen and a *tert*-butyl hydrogen for the larger  $Br^-$  and  $I^-$ . Stretching the  $N-X$  bond of **6X** results in  $N^{\circ}-X$  bond cleavage and eventually gives the  $3, X^-$  ion pair. Figure 5 shows a plot of the AM1 enthalpy curves as a function of the  $N^{\circ}, X^-$  distance. Decreasing the  $N^{\circ}, X^-$  distance in  $3, X^-$  results in crossing from the ion pair to the **6X** energy surface for both  $X = Cl^-$  and  $Br^-$  (in the distance region where the break in the energy plots occurs,  $\sim 2.9$  Å for  $X = Cl^-$ , and  $3.1$  Å for  $X = Br^-$ ), but the iodide remained higher in energy at a given  $N, I^-$  distance and did not cross to the **6I** surface in the calculations done.  $d(N=N)$  is calculated to start to increase rather sharply as the  $N-X$  distance is decreased, see Figure 6, which is accompanied by significant transfer of charge from  $X^-$  to **3**. The distances involved for maximum calculated  $\Delta H_f$  as well as the increase in  $d(N=N)$  are compared to sum of the  $N$  and  $X$  vdW radii in Table 3, where it will be noted that the change in the amount of charge transfer is calculated to occur at larger distances relative to the sum of the vdW radii as the polarizability of the halide is increased.  $BF_4^-$  is calculated to behave significantly differently from the halides as the  $N, B$  distance is decreased (Figures 5 and 6). At the energy minimum, one fluorine of  $BF_4^-$  is pointed at the  $N=N$  group, but as the  $N, B$  distance is decreased, the  $BF_4^-$  group rotates until eventually two F atoms are nearly equidistant from  $N$ . Apparently as a result, the  $N, B$  distance is calculated to be extremely

(11) (a) The fluoride counterion could not be investigated computationally because allowing fluoride to approach **3** results in proton transfer to give HF and the aminoaziridine derivative, while stretching the  $N-F$  bond of **4F** produces the azo compound, HF, and isobutylene upon  $N-F$  bond cleavage. (b) The entire description of the negative sparkle in both the AMPAC and MOPAC manuals is “a 100% ionic halogen-like atom”.



**Figure 6.**  $d(N=N)$  Calculated by AM1 for  $3, X^-/4X$  as a function of  $N^{\circ}, X^-$  distance.

**Table 3.** AM1 Calculations for Decreasing the  $N^{\circ}, X^-$  Distances in  $3, X^-$  Pairs

halide	$N^{\circ}, X^-$ dist, $\Delta H_f$ max <sup>a</sup>	$N^{\circ}, X^-$ dist, C.T. Onset <sup>b</sup>	VdW( $N+X$ ) <sup>c</sup>
$Cl^-$	2.6	3.1	3.30
$Br^-$	3.2	3.4	3.40
$I^-$	3.6	3.8	3.53

<sup>a</sup> For maximum  $\Delta H_f$  of the ion pair. <sup>b</sup> Where  $N=N$  bond length starts to increase sharply (see Figure 5), which is accompanied by significant charge transfer from  $X^-$  to **3**. <sup>c</sup> Sum of the vdW distances for nitrogen and halogen.<sup>6</sup>

“soft”, the energy only increasing about 1 kcal/mol between the minimum  $\Delta H_f$  structure at  $d(N, B) = 4.15$  and  $3.4$  Å. Decreasing the  $N, B$  distance further results in an increasingly sharp enthalpy rise which is not accompanied by either a sharp increase in  $N=N$  bond length (Figure 6) or calculated transfer of charge from  $BF_4^-$  to **3**, and a covalently bonded **6BF<sub>4</sub>** structure could not be found. Also shown in Figure 5 is the curve produced by using the “negative sparkle” of AM1, which is a negative charge with the same potential as  $Br^-$ , but which is prohibited from transferring charge, so it cannot produce a bond. The behavior of the  $\Delta \Delta H_f$  vs  $N-X$  distance curves for the negative sparkle and  $BF_4^-$  are similar, although the sharp energy increase for  $BF_4^-$ , which has a smaller effective radius, occurs at a somewhat shorter distance. AM1 calculations thus predict that in the gas phase, charge transfer from  $BF_4^-$  to the trialkyldiazonium unit does not occur at any distance, and that even large changes in  $N^{\circ}, BF_4^-$  distance do not affect  $d(N=N)$  significantly. The X-ray structures indicate that at least the latter prediction is incorrect for crystals. It is of course quite possible that AM1 calculations treat  $BF_4^-$  so poorly that the calculated results are meaningless,<sup>12</sup> but we know of no other computational evidence that  $BF_4^-$  could transfer charge to an electrophile.

## Conclusion

The crystal structure of **2** shows that the difference in  $BF_4^-$  placement between the **c12** and **a34** units and the

(12) AM1 does calculate the anisotropy of  $BF_4^-$ , diazenium cation interaction seen in the crystals, getting the in-plane  $BF_4^-$  structure over 8 kcal/mol higher in enthalpy than the minimum. The (gas phase) AM1 enthalpy minimum structure does not, however, much resemble any of the X-ray structures; it has  $d(N, N^{\circ})$  4.17 Å,  $\angle BN^{\circ}N^+$  69.3°, and  $\angle BN^{\circ}N^+C_{br}$  (-)98.6°;  $BF_4^-$  is calculated to be closer to the formally positively charged nitrogen and to the bicyclic rings than observed for any such units in the crystals. We have not attempted *ab initio* calculations.

**b34** and **c34** units results in a  $d(\text{N}=\text{N})$  increase which corresponds to a 0.1 decrease in NN Pauling bond order. This change occurs at a distance which is longer in terms of vdW radii than that for which significant changes in C=O bond length are observed for  $\text{R}_3\text{N}, \text{R}_2\text{CO}$  pairs in crystals, a case for which nucleophilic addition to the C=O bond occurs. It appears unlikely that significant  $\text{F}, \text{N}^\ominus$  bonding is actually involved for **2**, but the fluoride placement for the longer (N=N) units of **2** is similar to those which have been interpreted as being on the pathway for nucleophilic addition to carbonyl groups. The charged units involved for **2** are presumably responsible for the effect seen, but it is not clear how.

### Experimental Section

**Crystallography.** Preparation of **1** and **2** has been previously reported.<sup>1,2</sup> Intensity data were measured with a Siemens P3f diffractometer using graphite monochromated Cu K $\alpha$  radiation ( $\lambda = 1.54178 \text{ \AA}$ ). Crystal data and refinement parameters are summarized in Table 4. The structures were solved using the SHELXS-86 program<sup>13</sup> and refined using the SHELXL-93 program,<sup>14</sup> which refines on  $F^2$  values. The disordered  $\text{BF}_4^-$  group for **1** was modeled with two sites for the boron atom, with two sets of fluorine sites for each boron site. The occupancies of the fluorine sites are as follows: F(5): 0.356(13), F(5a): 0.247(14), F(5'): 0.232(13), F(5'a): 0.161(13). Borons B(2) and B(2a) had to be modeled as sitting on the same site and have a combined occupancy of 0.603(14); borons B(2') and B(2's) are sitting on the same site and have a combined occupancy of 0.393(12). Note that the sum of the occupancies is equal to 1.0 within less than one esd. The two disordered  $\text{BF}_4^-$  groups for **2** were modeled with one site for each boron atom and two sets of fluorine sites for each boron site.

**AM1 Calculations**<sup>15</sup> were carried out using Clark's VAMP 5.0 program.<sup>16</sup>

(13) Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467.

(14) Sheldrick, G. M. *J. Appl. Crystallogr.*, in preparation.

**Table 4. Summary of Crystal Data and Refinement Parameters**

compound number	<b>1</b>	<b>2</b>
empirical formula	$(\text{C}_{18}\text{H}_{32}\text{N}_4)^{2+}2(\text{BF}_4)^-$	$(\text{C}_{18}\text{H}_{28}\text{N}_4)^{2+}2(\text{BF}_4)^-$
temperature, K	123(2)	113(2)
space group	monoclinic, $P2_1/c$	monoclinic, $P2_1/c$
Z	4	16
a, $\text{\AA}$	15.408(5)	13.6902(8)
b, $\text{\AA}$	10.637(3)	13.7896(7)
c, $\text{\AA}$	13.809(6)	45.391(6)
$\beta$ , deg	93.26(3)	95.730(8)
volume, $\text{\AA}^3$	2259.6(14)	8526.2(13)
density(calcd), $\text{g/cm}^3$	1.405	1.477
$F(000)$	1000	3936
crystal size, mm	$0.60 \times 0.35 \times 0.25$	$0.50 \times 0.30 \times 0.20$
reflections collected	3181	12027
independent reflect. <sup>a</sup>	3025(0.0311)	11460(0.0453)
final R indices <sup>b</sup>	0.0630/0.1395	0.0519/0.1311
R indices (all data)	0.0817/0.1508	0.0751/0.1421
goodness of fit on $F^2$	1.013	0.977
data/restraints/parameters	3025/626/320 <sup>c</sup>	11460/2550/1187 <sup>c</sup>
largest diff map peaks <sup>d</sup>	0.330 and $-0.405$	0.457 and $-0.413$

<sup>a</sup> In parentheses:  $R_{\text{int}}$ . <sup>b</sup>  $R_1/wR_2$ , [ $I > 2\sigma(I)$ ]. Full-matrix least-squares refinement on  $F^2$ . <sup>c</sup>  $\text{BF}_4^-$  restraints. <sup>d</sup> In  $\text{\AA}^{-3}$ .

Atomic coordinates, bond lengths and angles for compounds **1** and **2** have been deposited with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, upon request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.

**Acknowledgment.** We thank the National Institutes of Health for partial financial support of this work under grant GM 29541, and the funds from NSF grant CHE-9105497 and the University of Wisconsin for the purchase of X-ray instruments and computers.

(15) Dewar, M. J. S.; Zoebisch, E. G. F.; Healey, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902.

(16) VAMP 5.0, modified for use on a Stardent computer was supplied by Timothy Clark. Rauhut, G.; Chandrasekhar, J.; Alex, A.; Steinke, T.; Clark, T. *VAMP 5.0*, Oxford Molecular, Oxford, 1994.