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Proposed Intermediates in the Tautomerization of Benzofurazan 1-Oxide

Morgan Ponder

Department of Chemistry, Samford University, Birmingham, Alabama 35229

Joseph E. Fowler and Henry F. Schaefer III*

Center for Computational Quantum Chemistry, University of Georgia, Athens, Georgia 30602

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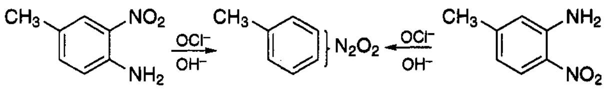
An *ab initio* quantum mechanical study of benzofurazan 1-oxide (BFO) and the possible intermediates of its tautomerization reaction has been completed. Optimum geometries for BFO and five possible intermediates have been obtained at the double-ζ plus polarization (DZP) self-consistent field (SCF) level of theory. A sixth possible intermediate has been studied with a minimal basis set. DZP second-order perturbation theory (MP2) energies for BFO, *anti*-1,2-dinitrosobenzene (DNB), and *amphi*-DNB suggest that *anti*-DNB lies 12.0 kcal/mol above BFO whereas *amphi*-DNB lies 12.9 kcal/mol above BFO. The peroxide, bridged, three-ring, and cyclobutadiene-like structures lie considerably higher in energy. Reported are geometrical parameters, harmonic vibrational frequencies, infrared intensities, and total and relative energies. Among the higher energy structures, the DNB predictions appear to provide the best match to several experimetal infrared frequencies.

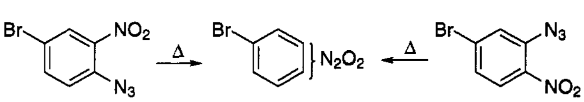
Introduction

Although benzofurazan 1-oxide (BFO) (or benzofuroxan) was first synthesized over 100 years ago,[1] considerable disagreement over its structure plagued researchers for many years. Structures **1**–**5** were those most commonly proposed. The currently accepted structure, **1**, was first proposed in 1912,[2] but its acceptance was hindered by the fact that synthetic procedures that would be expected to produce BFO substituted at either C-4 or C-5 in fact yielded the same compound. For instance, hypochlorite oxidation of 3-amino-4-nitrotoluene and 4-amino-3-nitrotoluene leads to the same methylbenzofurazan 1-oxide[3] (eq 1).



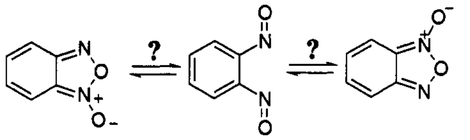
(1)

Also, 4-bromo-2-nitrophenyl azide and 5-bromo-2-nitrophenyl azide produce the same monobromosubstituted BFO upon heating[4] (eq 2).



(2)

This evidence seemed to favor a symmetric structure for the N_2O_2 group, such as *anti*-DNB or the peroxide or bridged structures. However, proton NMR results[5–10] for BFO showed an ABCD pattern at low temperatures that coalesced into an A_2B_2 pattern at higher temperatures. These observations led to the currently accepted view, which is that BFO rapidly interconverts between two tautomeric forms through a symmetric intermediate (eq 3).



(3)

anti-Dinitrosobenzene (DNB) and the peroxide, bridged, three-ring, and cyclobutadiene-like structures have been suggested as possible intermediates for this tautomerization.[5,11–14] (Also, it is reasonable to assume that BFO would pass through a structure such as *amphi*-DNB on its path to a symmetric intermediate.) *anti*-DNB has clearly been the favorite candidate, but arguments on its behalf were until lately only indirect because the proposed intermediate had not been experimentally observed. (However, two groups have reported results that could be explained on the basis of trapping of *anti*-DNB.)[15,16] In 1991 and 1992, three different groups reported the photochemical formation of a compound at cryogenic temperatures (argon matrix at 14 K) from BFO that may be the long-awaited intermediate.[17–19] This compound was formed by irradiation of BFO at about 350 nm, and the progress of its formation could be monitored by the growth of new peaks in both the IR and UV

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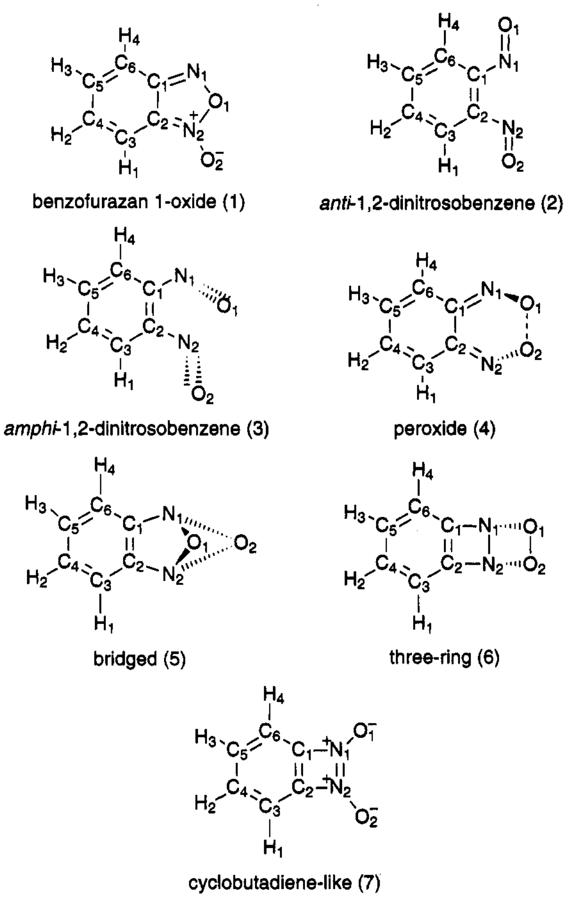
Chart 1



benzofurazan 1-oxide (1)

anti-1,2-dinitrosobenzene (2)

amphi-1,2-dinitrosobenzene (3)

peroxide (4)

bridged (5)

three-ring (6)

cyclobutadiene-like (7)

spectra. In particular, a strong IR band at about 1516 cm^{-1} was observed for this compound, a band that is characteristic of aromatic nitroso compounds. This led all three groups to identify this new compound as *anti*-DNB.

The goal of the present work was two-fold. First, we report *ab initio* ground-state energies of BFO and the proposed intermediates. Prior to this work, the only geometrical information available for any of the structures considered here was the crystal structure of BFO.[20] Thus the stationary point structures reported here will provide concreteness to future discussion of the BFO isomers. Second, we report vibrational frequencies and infrared intensities for each of these compounds. The latter information should help in the elucidation of the structure of the intermediate of the tautomerization of BFO.

Methods

Molecular electornic energies were determined by optimizing structures using restricted Hartree–Fock self-consistent field (SCF) analytic gradient techniques.[21,22] Residual Cartesian and internal coordinate gradients did not exceed 10^{-6} au. Analytic second-derivative methods[23] were used to determine the quadratic force constants and resulting harmonic vibrational frequencies at the SCF level.

Table 1. Geometrical Parameters for Benzofurazan 1-Oxide (structure 1). Bond Lengths Are in Angstroms, and Bond Angles Are in Degrees. This Structure Has C_s Symmetry

bond lengths, *r*	STO-3G SCF	DZP SCF	exptl[a]	bond angles, θ	STO-3G SCF	DZP SCF	exptl[a]
N_1-O_1	1.409	1.359	1.381	$C_1-C_6-C_5$	117.8	116.6	117.4
N_2-O_1	1.408	1.329	1.464	$C_2-C_3-C_4$	116.8	115.6	116.3
N_2-O_2	1.288	1.222	1.235	$C_6-C_5-C_4$	122.9	123.3	122.2
C_1-N_1	1.334	1.292	1.327	$C_3-C_4-C_5$	121.5	121.9	122.3
C_2-N_2	1.365	1.309	1.319	$C_2-C_1-C_6$	118.1	119.1	119.8
C_1-C_2	1.424	1.418	1.418	$C_3-C_2-C_1$	122.8	123.5	122.0
C_6-C_1	1.456	1.444	1.416	$C_4-C_3-H_1$	123.1	123.6	124
C_3-C_2	1.436	1.433	1.426	$C_5-C_6-H_4$	122.7	122.8	119
C_5-C_6	1.340	1.346	1.347	$C_4-C_5-H_3$	117.3	117.4	117
C_4-C_3	1.342	1.346	1.337	$C_5-C_4-H_2$	117.9	118.0	109
C_5-C_4	1.461	1.462	1.441	$C_2-C_1-N_1$	112.3	110.4	111.9
C_6-H_4	1.082	1.075	0.95	$C_1-C_2-N_2$	105.5	105.2	107.3
C_3-H_1	1.083	1.075	0.87	$C_1-N_1-O_1$	105.1	105.2	105.9
C_5-H_3	1.084	1.077	1.04	$C_2-N_2-O_1$	107.9	108.6	106.7
C_4-H_2	1.082	1.076	0.96	$N_1-O_1-N_2$	109.2	110.6	108.2
				$C_2-N_2-O_2$	133.5	132.6	136.7

[a] Reference 20.

Table 2. Geometrical Parameters for *anti*-1,2-Dinitrosobenzene (structure 2). Bond Lengths Are in Angstroms, and Bond Angles Are in Degrees. This Structure Has C_{2v} Symmetry

bond lengths	STO-3G SCF	DZP SCF	bond angles, θ	STO-3G SCF	DZP SCF
N_1-O_1	1.234	1.182	$C_1-C_6-C_5$	119.9	119.5
C_1-N_1	1.508	1.447	$C_6-C_5-C_4$	120.2	120.3
C_1-C_2	1.396	1.392	$C_2-C_1-C_6$	119.9	120.2
C_6-C_1	1.390	1.393	$C_5-C_6-H_4$	121.0	121.1
C_5-C_6	1.386	1.383	$C_4-C_5-H_3$	119.9	119.8
C_5-C_4	1.390	1.396	$C_6-C_1-N_1$	122.3	122.0
C_6-H_4	1.083	1.074	$C_1-N_1-O_1$	111.8	114.2
C_2-H_3	1.083	1.077			

Two basis sets were used. The first set, for exploratory purposes only, was the minimal STO-3G basis set of Hehre *et al.*[24] The second set used was designated double-ζ plus polarization (DZP) and is the source of our reliable structural predictions. Specifically, for carbon, nitrogen, and oxygen the Huzinaga–Dunning[25–27] (9s5p/4s2p) sets were augmented with a set of five pure angular momentum d-like functions with exponents $\alpha_d(C) = 0.75$, $\alpha_d(N) = 0.80$, and $\alpha_d(O) = 0.85$; and for hydrogen a set of p functions with exponent $\alpha_p(H) = 0.75$ was added to the (4s/2s) set. Electron correlation effects for BFO, *anti*-DNB, and *amphi*-DNB were estimated through the use of second order perturbation theory (MP2)[28] in conjunction with the DZP basis set. The MP2 computations were completed through use of the TURBOMOLE programs[29] while all other work was done with the PSI program system.[30]

Results and Discussion

Tables 1–7 show the geometrical parameters obtained for structures **1** through **7**, and Table 8 shows the energies obtained for these structures.

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Table 3. Geometrical Parameters for *amphi*-1,2-Dinitrosobenzene (Structure 3). Bond Lengths Are in Angstroms, and Bond Angles Are in Degrees. This Structure Has C_1 Symmetry

bond lengths and angles	STO-3G SCF	DZP SCF	bond angles	STO-3G SCF	DZP SCF
$r(N_1-O_1)$	1.235	1.180	$\theta(C_4-C_3-C_2)$	120.0	120.0
$r(N_2-O_2)$	1.234	1.181	$\theta(C_4-C_5-C_6)$	120.2	119.8
$r(C_1-N_1)$	1.507	1.440	$\theta(C_5-C_4-C_3)$	120.1	120.3
$r(C_2-N_2)$	1.506	1.445	$\theta(C_1-C_6-H_4)$	119.2	118.8
$r(C_1-C_2)$	1.396	1.398	$\theta(C_2-C_3-H_1)$	119.0	119.1
$r(C_6-C_1)$	1.389	1.386	$\theta(C_6\text{-}C_5\text{-}H_3)$	119.9	120.0
$r(C_3-C_2)$	1.390	1.387	$\theta(C_3-C_4-H_2)$	119.8	119.6
$r(C_5-C_6)$	1.386	1.389	$\tau(C_2-C_1-N_1-O_1)$	34.9	28.8
$r(C_4-C_3)$	1.386	1.389	$\tau(C_3-C_2-N_2-O_2)$	20.2	28.7
$r(C_4-C_5)$	1.389	1.389	$\tau(C_1-C_2-C_3-C_4)$	0.3	0.6
$r(C_6-H_4)$	1.083	1.076	$\tau(C_2-C_3-C_4-C_5)$	−0.7	−1.0
$r(C_3-H_1)$	1.083	1.075	$\tau(C_3-C_4-C_5-C_6)$	0.1	0.0
$r(C_5-H_3)$	1.083	1.076	$\tau(C_4-C_5-C_6-C_1)$	0.7	1.5
$r(C_4-H_2)$	1.083	1.077	$\tau(C_5-C_6-C_1-C_2)$	−1.1	−1.9
$\theta(C_1-N_1-O_1)$	112.1	115.2	$\tau(C_6-C_1-C_2-C_3)$	0.5	0.9
$\theta(C_2-N_2-O_2)$	112.0	114.2	oop (N_1)[a]	−0.9	0.7
$\theta(C_2-C_1-N_1)$	123.1	124.9	oop (N_2)[b]	−3.2	−5.6
$\theta(C_1-C_2-N_2)$	118.3	119.4	oop (H_1)[c]	−0.3	−1.0
$\theta(C_6-C_1-C_2)$	120.0	120.2	oop (H_2)[d]	−0.4	−0.8
$\theta(C_3-C_2-C_1)$	119.8	119.6	oop (H_3)[e]	−0.2	−0.5
$\theta(C_5-C_6-C_1)$	119.9	120.0	oop (H_4)[f]	0.5	0.9

[a] oop (N_1) = angle between the C_1—N_1 bond and the plane defined by C_6, C_1, and C_2. [b] oop (N_2) = angle between the C_2—N_2 bond and the plane defined by C_1, C_2, and C_3. [c] oop (H_1) = angle between the C_3—H_1 bond and the plane defined by C_2, C_3, and C_4. [d] oop (H_2) = angle between the C_4—H_2 bond and the plane defined by C_3, C_4, and C_5. [e] oop (H_3) = angle between the C_5—H_3 bond and the plane defined by C_4, C_5, and C_6. [f] oop (H_4) = angle between the C_6—H_4 bond and the plane defined by C_5, C_6, and C_1.

Table 4. Geometrical Parameters for the Peroxide Structure (structure 4). Bond Lengths Are in Angstroms, and Bond Angles Are in Degrees. This Structure Has C_2 Symmetry

bond lengths and angles	STO-3G SCF	DZP SCF	bond angles	STO-3G SCF	DZP SCF
$r(O_1-O_2)$	1.433	1.383	$\tau(C_3-C_4-C_5-C_6)$	−3.1	−3.0
$r(N_1-O_1)$	1.411	1.372	$\tau(C_4-C_5-C_6-C_1)$	−1.4	−1.4
$r(C_1-N_1)$	1.292	1.263	$\tau(C_5-C_6-C_1-C_2)$	9.7	9.6
$r(C_1-C_2)$	1.488	1.480	$\tau(C_6-C_1-C_2-C_3)$	−13.6	−13.8
$r(C_6-C_1)$	1.483	1.464	$\tau(N_2-C_2-C_1-N_1)$	−20.4	−20.8
$r(C_5-C_6)$	1.324	1.333	$\tau(C_2-C_1-N_1-O_1)$	−2.7	−1.4
$r(C_5-C_4)$	1.482	1.475	$\tau(C_1-N_1-O_1-O_2)$	45.8	42.0
$r(C_6-H_4)$	1.083	1.075	$\tau(N_1-O_1-O_2-N_2)$	−70.6	−65.7
$r(C_5-H_3)$	1.083	1.077	oop (H_4)[a]	−2.5	−2.7
$\theta(C_1-C_6-C_5)$	119.7	118.9	oop H($_3$)[b]	−0.5	−0.7
$\theta(C_6-C_5-C_4)$	122.0	122.0			
$\theta(C_2-C_1-C_6)$	117.6	118.4			
$\theta(C_5-C_6-H_4)$	122.9	122.9			
$\theta(C_4-C_5-H_3)$	117.3	117.9			
$\theta(C_2-C_1-N_1)$	120.8	120.1			
$\theta(C_1-N_1-O_1)$	111.1	112.7			
$\theta(N_1-O_1-O_2)$	110.2	111.9			

[a] oop (H_4) = angle between the C_6—H_4 bond and the plane defined by C_5, C_6, and C_1. [b] oop (H_3) = angle between the C_5—H_3 bond and the plane defined by C_4, C_5, and C_6.

For the initial STO-3G SCF studies, all structures except the bridged structure were, at first, constrained to be planar, with BFO and *amphi*-DNB belonging to the C_s point group and *anti*-DNB and the peroxide, three-ring, and cyclobutadiene-like structure belonging to the C_{2v} point group. For the bridged structure, all atoms except the oxygens were assumed to lie in the same plane, with each oxygen lying equidistant on either side of this plane. This structure has C_{2v} symmetry. At the SCF level of theory, harmonic vibrational frequencies for each structure were obtained though the use of analytic second derivatives. All structures except *amphi*-DNB, the peroxide, and the three-ring structures were found to be minima. Vibrational frequencies for the planar versions of *amphi*-DNB and the peroxide structure showed one imaginary frequency, whereas those for the three-ring structure included two imaginary frequencies. The imaginary frequency for *amphi*-DNB corresponded to an out-of-plane motion of the oxygen atoms. Therefore the STO-3G geometry optimization was repeated for *amphi*-DNB with no symmetry. The imaginary frequency for the peroxide structure corresponded to the puckering of the nitrogen-containing ring, a mode of a_2 symmetry in the C_{2v} point group. Because the a_2 representation in the C_{2v} point group preserves symmetry

Table 5. Geometrical Parameters for the Bridged Structure (structure 5). Bond Lengths Are in Angstroms, and Bond Angles Are in Degrees. This Structure Has C_{2v} Symmetry

bond lengths, r	STO-3G SCF	DZP SCF	bond angles, θ	STO-3G SCF	DZP SCF
N_1-O_1	1.471	1.425	$C_1-C_6-C_5$	115.6	114.8
C_1-N_1	1.520	1.461	$C_6-C_5-C_4$	121.8	121.9
C_1-C_2	1.394	1.386	$C_2-C_1-C_6$	122.6	123.3
C_6-C_1	1.365	1.356	$C_5-C_6-H_4$	121.4	121.9
C_5-C_6	1.407	1.415	$C_4-C_5-H_3$	119.3	119.1
C_5-C_4	1.382	1.382	$C_2-C_1-N_1$	101.8	101.0
C_6-H_4	1.083	1.076	$C_1-N_1-O_1$	97.2	98.1
C_5-H_3	1.083	1.077	$N_1-O_1-N_2$	86.4	86.0
			$O_1-N_1-O_2$	85.2	85.2

Table 6. Geometrical Parameters for the Three-Ring Structure (structure 6). Bond Lengths Are in Angstroms, and Bond Angles Are in Degrees. This Structure Has C_s Symmetry

bond lengths, r	STO-3G SCF	DZP SCF	bond angles	STO-3G SCF	DZP SCF
O_1-O_2	1.420	1.404	$\theta(C_1-C_6-C_5)$	114.0	113.0
N_1-O_1	1.469	1.422	$\theta(C_6-C_5-C_4)$	122.5	122.7
N_1-N_2	1.537	1.475	$\theta(C_2-C_1-C_6)$	123.5	124.2
C_1-N_1	1.504	1.448	$\theta(C_5-C_6-H_4)$	121.9	122.3
C_1-C_2	1.380	1.365	$\theta(C_4-C_5-H_3)$	118.6	118.3
C_6-C_1	1.374	1.374	$\tau(C_4-C_5-C_6-C_1)$	0.6	1.1
C_5-C_6	1.399	1.399	$\tau(C_5-C_6-C_1-C_2)$	−0.6	−1.2
C_5-C_4	1.393	1.401	oop (O)[a]	72.3	70.5
C_6-H_4	1.083	1.075	oop (N)[b]	−3.0	−3.9
C_5-H_3	1.083	1.077	oop (H_4)[c]	0.3	0.3
			oop (H_3)[d]	−0.2	−0.5

[a] oop (O) = angle between the N_1—O_1 bond and the plane defined by C_1, N_1, and N_2. [b] oop (N) = angle between the C_1—N_1 bond and the plane defined by C_6, C_1, and C_2. [c] oop (H4) = angle between the C_6—H_4 bond and the plane defined by C_5, C_6, and C_1. [d] oop (H3) = angle between the C_5—H_3 bond and the plane defined by C_4, C_5, and C_6.

Table 7. Geometrical Parameters for the Cyclobutadiene-Like Structure (structure 7). Bond Lengths Are in Angstroms, and Bond Angles Are in Degrees. This Structure Has C_{2v} Symmetry

bond lengths, r	STO-3G SCF	bond angles, θ	STO-3G SCF
N_1-O_1	1.298	$C_1-C_6-C_5$	113.3
N_1-N_2	1.377	$C_6-C_5-C_4$	122.6
C_1-N_1	1.502	$C_2-C_1-C_6$	124.1
C_1-C_2	1.407	$C_5-C_6-H_4$	121.7
C_6-C_1	1.343	$C_4-C_5-H_3$	119.4
C_5-C_6	1.440	$C_2-C_1-N_1$	89.4
C_5-C_4	1.362	$C_1-N_1-O_1$	138.3
C_6-H_4	1.082		
C_5-H_3	1.083		

Table 8. Total Energies (in Hartrees) and Relative Energies (in kcal/mol) for Each of the Stationary Points

			STO-3G SCF		DZP SCF		DZP MP2	
structure	designation	point group	total energy	relative energy	total energy	relative energy	total energy	relative energy
1	BFO	C_s	−481.75033	0.0	−488.04877	0.0	−489.49382	0.0
2	*anti*-DNB	C_{2v}	−481.76175	−7.2	−488.06955	−13.0	−489.47466	12.0
3	*amphi*-DNB	C_1	−481.76078	−6.6	−488.06655	−11.2	−489.47326	12.9
4	peroxide	C_2	−481.76552	−9.5	−487.99287	35.1		
5	bridged	C_{2v}	−481.76945	−12.0	−487.94439	65.5		
6	three-ring	C_2	−481.58798	101.9				
		C_s	−481.73932	6.9	−487.90319	91.4		
7	cyclobutadiene	C_{2v}	−481.60246	92.8				

about the C_2 axis, the STO-3G SCF geoemtry optimization was repeated for the peroxide structure constrained only to the lower symmetry group C_2. For the three-ring structure, one of the imaginary vibrational frequencies corresponded to an out-of-plane twist of the nitrogens, which has a_2 symmetry, and the other imaginary frequency corresponded to the in-phase, out-of-plane movement of the oxygens, a mode of b_1 symmetry. Therefore, the three-ring structure was allowed to drop to lower symmetry (C_2 to account for the nitrogen out-of-plane motion and C_s to account for the oxygen out-of-plane motion), and two separate minima were located at the STO-3G SCF level.

The departure of the peroxide and three-ring structures from planarity is probably caused by repulsion between the nonbonding and the bonding electrons on the nitrogen atoms. These structures can only increase the distance between the nonbonding and the bonding electrons by twisting the ring or rings. It is interesting to note that the bridged structure can increase the distance between nonbonding and bonding electrons on the nitrogen atoms without breaking the symmetry of the molecule. The departure of *amphi*-DNB from planarity is probably caused by repulsion between the nonbonding electrons on O-1 and the nonbonding electrons on N-2.

Experimental geometries have been published for only one of the structures studied in this work. Britton and Olson[20] have published a geometry for BFO obtained from X-rya crystallography. The results of their work are included in Table 1. Their structure for BFO was slightly nonplanar. The largest observed deviation from nonplanarity (O-2) was just over 3°.

From the relative energies at the STO-3G SCF level, shown in Table 8, it can be seen that the cyclobutadiene-like structure and the three-ring structure in the C_2 point group are considerably higher in energy than the other proposed intermediates. Therefore, higher levels of theory were not applied to these two structures. It should be noted that at this level of theory, several of the proposed intermediates actually have *lower* energies than the parent compound BFO.

Comparison of the relative energies obtained from the DZP SCF level of theory reveals that BFO, *anti*-DNB, and *amphi*-DNB decreased in energy in going from STO-3G SCF to DZP SCF much more than did any of the other strucutres. At this level of theory, only *anti*-DNB and *amphi*-DNB appear to be reasonable candidates for the tautomerization intermediate, with *anti*-DNB lying about 2 kcal/mol lower in energy than amphi-DNB. In fact, at the DZP SCF level, both *anti*-DNB and *amphi*-DNB still have lower energies than BFO.

The relative energy ordering of *anti*-DNB, *amphi*-DNB, and BFO is rather dramatically reversed upon the inclusion of electron correlation. This inclusion was carried out at the MP2 level using the DZP basis set. The large difference in the energy drop experienced by the three compounds is similar to that observed by Politzer and co-workers for furazan 1-oxide isomers.[31] These workers found that the energy gaps between furazan 1-oxide and *anti*- or *amphi*-*cis*-dinitrosoethylene (BFO, *anti*-DNB, and *amphi*-DNB without the fused benzene rings) increased substantially between Hartree−Fock and MP2 calculations, with the *amphi* form lying 3−4 kcal/mol higher in energy than the *anti* form. They suggested that this increase may be due to the relative abundance of strongly electronegative heteroatoms and their accompanying lone pairs.[32,33]

On the basis of the calculated energies at the DZP MP2 level, *anti*-DNB appears to be the most likely candidate for the tautomerization intermediate. At this level of theory, *anti*-DNB lies 12.0 kcal/mol above BFO. If *anti*-DNB is the intermediate in the BFO tautomerization, one would expect that the energy of *anti*-DNB would be only slightly lower than the energy of the transition state between BFO and *anti*-DNB. The energy difference between BFO and the transition state, which is of course the energy of activation, has been measured by various groups as 16.1 ± 0.5,[34] 17.2 ± 1.5,[35] and 14.0 ± 0.2[36] kcal/mol. The fact that our predicted value of the energy difference between BFO and *anti*-DNB (12.0 kcal/mol) is only slightly smaller than the measured activation energy for the tautomerization of BFO is consistent with the identification of *anti*-DNB as the intermediate in the BFO tautomerization.

The quantitative results shown in Table 8 support the qualitative arguments presented by Mallory and co-workers[12] as to the relative stabilities of some of the proposed intermediates. For instance, they pointed out that the peroxide structure lacks aromaticity and includes a weak peroxide bond, and the three-ring and cyclobutadiene-like structures should exhibit considerable ring strain. The bridged structure should have considerable ring strain, as well.

Previous *ab initio* results from the 3-21G HF level have been reported for *anti*-DNB and *amphi*-DNB by Marriot and co-workers.[37] Our predicted total energy for both structures at the DZP SCF level is about 3 Hartrees lower than the value reported by these workers at the 3-21G HF level. The energy difference between *anti*-DNB and *amphi*-DNB that we found at the DZP SCF level is

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Table 9. Comparison of Theoretical and Experimental Vibrational Frequencies for Benzofurazan 1-Oxide (structure 1). This Structure Has C_s Symmetry

exptl[a]	theoret[b]	diff[c]	theoret inten[d]	symmetry	mode
1622 s	1692	70	130.8	a'	6-mem ring def
1598 s	1607	9	120.7	a'	C—N asym stretch
1589 s	1580	−9	14.2	a'	6-mem ring def
1545 s	1531	−14	904.0	a'	N_2—O_2 stretch
1492 m	1491	−1	137.4	a'	6-mem ring def
1446 w	1430	−16	23.6	a'	6-mem ring def
1427 w	1386	−41	6.8	a'	sym C—C—H bend
1358 w	1307	−51	5.1	a'	asym C—C—H bend
1205 w	1204	−1	29.3	a'	asym C—C—H bend
1151 vw	1150	−1	4.3	a'	sym C—C—H bend
1126 w	1120	−6	51.9	a'	N—O sym stretch
1020 m	983	−37	110.1	a'	N—O asym stretch
895 w	903	8	10.4	a'	6-mem ring def
837 w	843	6	1.7	a''	H oop
760 w	764	4	7.0	a''	6-mem ring pucker
746 m	754	8	83.5	a''	H oop
739 w	736	−3	31.0	a'	6-mem ring breathing
669 w	660	−9	12.1	a''	O oop

[a] s = strong; m = medium; w = weak; vw = very weak. Reference 17. [b] Theoretical frequencies have been multipled by 0.91. [c] Average absolute difference = 16 cm^{-1}. [d] km/mol.

Table 10. Comparison of Theoretical Vibrational Frequencies of *anti*-1,2-Dinitrosobenzene (structure 2) with Experimental Frequencies for Photochemically Produced Compound. This Structure Has C_{2v} Symmetry

possible exptl[a]	theoret[b]	diff[c]	theort inten[d]	symmetry	mode
1516 s	1618	102	69.9	b_2	ring stretch
1423 w	1457	34	9.0	b_2	C—C—H bend
1257 w	1270	13	43.6	b_2	C—C—H bend
1162 w	1182	20	89.1	a_1	C—N stretch
1108 m	1173	65	15.0	b_2	C—C—H bend
1077 w	1113	36	4.7	a_1	asym ring def
805 w	803	−2	42.3	a_1	C—N—O bend
772 w	784	12	86.8	b_1	H oop
622 vw	610	−12	12.6	a_1	ring bend

[a] s = strong; m = medium; w = weak; vw = very weak. Reference 17. [b] Theoretical frequencies have been multipled by 0.91. [c] Average absolute difference = 33 cm^{-1}. [d] km/mol.

similar to that found by Marriot *et al.* at the 3-21G HF level. All bond lengths reported by these workers agree within 0.01 Å with those we obtained except for the N—O bond length. Our value is about 0.04 Å shorter than that reported by Marriot *et al.* (The bond lengths that we obtianed for *anti*-DNB and *amphi*-DNB are identical to within 0.001 Å.) Marriot and co-workers apparently assumed planar structures for both *anti*-DNB and *amphi*-DNB. Because they did not report vibrational frequencies, we cannot tell whether they determined that these planar structures were minima.

Table 11. Comparison of Theoretical Vibrational Frequencies of *amphi*-1,2-Dinitrosobenzene (structure 3) with Experimental Frequencies for Photochemically Produced Compound. This Structure Has C_1 Symmetry

possible exptl[a]	theoret[b]	diff[c]	theoret inten[d]	mode
1516 s	1612	98	20.8	asym ring def
1423 w	1454	34	4.5	C—C—H bend
1257 w	1270	16	16.2	C—C—H bend
1162 w	1185	24	55.4	C—N stretch
1108 m	1175	68	19.8	C—N stretch
1077 w	1111	35	4.8	asym ring def
805 w	818	14	29.6	C—NßbdO bend
772 w	774	5	79.4	H oop
622 vw	626	4	7.8	ring pucker

[a] s = strong; m = medium; w = weak; vw = very weak. Reference 17. [b] Theoretical frequencies have been multipled by 0.91. [c] Average absolute difference = 31 cm^{-1}. [d] km/mol.

Table 12. Comparison of Theoretical Vibrational Frequencies of the Peroxide Structure (structure 4) with Experimental Frequencies for Photochemically Produced Compound. This Structure Has C_2 Symmetry

possible exptl[a]	theoretl[b]	diff[c]	theoret inten[d]	symmetry	mode
1516 s	1620	104	0.7	a	asym def
1423 w	1441	18	27.2	a	C—C—H bend
1257 w	1351	94	1.0	a	C—C—H bend
1162 w	1153	−9	2.5	a	C—C—H bend
1108 m	1074	−34	43.9	a	O—O stretch
1077 w	1022	−55	10.4	b	N—O stretch
805 w	842	37	7.4	a	H oop
772 w	749	−23	43.0	b	H oop
622 vw	636	14	1.8	a	hetero ring def

[a] s = strong; m = medium; w = weak; vw = very weak. Reference 17. [b] Theoretical frequencies have been multiplied by 0.91. [c] Average absolute difference = 43 cm^{-1}. [d] km/mol.

Table 13. Comparison of Theoretical Vibrational Frequencies of the Bridged Structure (structure 5) with Experimental Frequencies for Photochemically Produced Compound. This Structure Has C_{2v} Symmetry

possible exptl[a]	theoret[b]	diff[c]	theoret inten[d]	symmetry	mode
1516 s	1463	−53	10.9	a_1	C—C—H bend
1423 w	1461	38	8.1	b_2	C—C—H bend
1257 w	1284	27	0.6	b_2	C—C—H bend
1162 w	1197	35	3.2	a_1	hetero ring def
1108 m	1136	28	5.3	b_2	C=N stretch
1077 w	1066	−11	18.4	a_1	N—O stretch
805 w	852	47	11.8	a_1	ring breathing
772 w	781	9	69.5	b_1	H oop
622 vw	641	19	33.5	b_1	O oop

[a] s = strong; m = medium; w = weak; vw = very weak. Reference 17. [b] Theoretical frequencies have been multipled by 0.91. [c] Average absolute difference = 30 cm^{-1}. [d] km/mol.

Table 9 compares the theoretical vibrational frequencies for BFO and the experimental vibrational frequencies reported for BFO by Dunkin and co-workers[17] (Hacker[18] and Murata and Tomioka[19] also reported vibrational frequencies for BFO; the values reported by these two groups are essentially identical to those reported by Dunkin *et al.*) For comparison to the experimental values, the theoretical frequencies have been scaled by 0.91, as recommended by Grev *et al.*[38] The matching of a particular calculated frequency with a particular experimental frequency is somewhat arbitrary because mode assignments have not been made for the experimental frequencies; we placed somewhat more emphasis on trying to match our frequencies calculated to have the largest intensities with particular experimental frequencies rather than matching the frequencies as closely as possible. The discrepancies between the theoretical and the experimental frequencies range from less than 1 cm^{-1} to nearly 70 cm^{-1}, with an average difference of about 16 cm^{-1}. The match of relative intensities is reasonably good for BFO; that is, there is a reasonably good corespondence between the calculated frequencies of highest intensity and the strongest experimental frequencies.

Tables 10−14 compare the harmonic vibrational frequencies calculated at the DZP SCF level of theory for *anti*-DNB, *amphi*-DNB, and the peroxide, bridged, and

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[38] Grev, R. S.; Janssen, C. L.; Schaefer, H. F. *J. Chem. Phys.* **1991**, *95*, 5128.

Table 14. Comparison of Theoretical Vibrational Frequencies of the Three-Ring Structure (structure 6) with Experimental Frequencies for Photochemically Produced Compound. This Structure Has C_s Symmetry

possible exptl[a]	theoret[b]	diff	theoret inten[c]	sym-metry	mode
1516 s	1478	−38	29.0	a'	C—C—H bend
1423 w	1475	52	5.1	a''	C—C—H bend
1257 w	1279	22	2.4	a''	C—C—H bend
1162 w	1159	−3	2.6	a'	C—N stretch
1108 m	1101	−7	0.3	a'	sym ring def
1077 w	1070	−7	6.2	a'	O—O stretch
805 w	831	26	4.8	a'	ring breathing
772 w	767	−5	83.1	a'	H oop
622 vw	593	−29	13.2	a'	ring bending

[a] s = strong; m = medium; w = weak; vw = very weak. Reference 17. [b] Theoretical frequencies have been multipled by 0.91. [c] Average absolute difference = 21 cm^{-1}. [d] km/mol.

three-ring structures with the set of experimental frequencies reported by Dunkin and co-workers for the compound formed photochemically from BFO. (Again, the results reported by Hacker and by Murata and Tomioka for this compound are essentially identical to those of Dunkin *et al.*) For none of the five candidates do the calculated frequencies appear to match the experimental data for the photochemically produced compound as well as the theoretical frequencies for BFO match the experimental frequencies for BFO. However, the best agreement seems to occur with *anti*-DNB. The average difference between theoretical and experimental frequencies is about 33 cm^{-1} for *anti*-DNB, while it ranges from about 21 to about 43 cm^{-1} for the other four compounds. The primary reason that we believe *anti*-DNB matches the experimental IR spectrum better than any other proposed intermediate is the fact that *anti*-DNB has a stronger intensity vibration in the vicinity of the experimental vibration at 1516 cm^{-1} than any other proposed intermediate. The peak at 1516 cm^{-1} is the strongest peak in the spectrum of the compound photochemically produced from BFO and is believed to be due to the nitroso group. It should, however, be noted that for *anti*-DNB, the strong intensity theoretical peak (1618 cm^{-1}) to which we refer is about 100 cm^{-1} away from the 1516 cm^{-1} experimental peak.

Conclusions

In summary, the predicted relative energies of six proposed intermediates in the tautomerization of BFO suggest that *anti*-1,2-dinitrosobenzene is the most likely candidate. This identification is consistent with previous speculation by various workers. The predicted vibrational frequencies also suggest that *anti*-DNB is the intermediate, even though discrepancies between theoretical and experimental frequencies render this evidence somewhat more ambiguous than the energy results.

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