Synthesis, Spectroscopy and Structure of the Parent Furoxan $(HCNO)_2$

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The parent furoxan (1,2,5-oxadiazole 2-oxide), synthesized from glyoxime and NO_2(g), has been investigated in the gas phase for the first time by mid-infrared and He I photoelectron spectroscopy, and in the liquid phase by Raman spectroscopy. The ground-state geometry has been obtained from quantum-chemical calculations at the B3LYP, MPn ($n = 2-4$), CISD, QCISD, CCSD, CCSD(T), RSPTn ($n = 2,3$), MRCI, and MR-AQCC levels using 6-311++G(2d,2p), cc-pVTZ, aug-cc-pVTZ, cc-pCVTZ, and cc-pVQZ basis sets. Furoxan is predicted to be planar, with a strong exocyclic and a relatively weak endocyclic N−O bond. The furoxan moiety is electron rich, indicated e.g. by a large negative NPA charge (−0.46 e). According to various aromaticity indices, furoxan is nearly as aromatic as furan and furazan. Unlike alkyl- and cyano-substituted furoxans, the parent furoxan, upon thermolysis, does not cleave to the monomer nitrile oxide, yielding only HNCO, HCN, CO_2, CO, NO, and H_2O decomposition products.

Introduction

Furoxans (1,2,5-oxadiazole 2-oxides) have a long and fascinating history with much debate and controversy.[1−3] The first furoxan, dibromofuroxan, was prepared in 1858 from mercury fulminate and bromine,[4] unknowingly as it turns out, for the reaction product was believed to be dibromonitroacetonitrile. After a century of debate, NMR spectroscopy and X-ray crystallography clarified the general form of furoxans as planar five-membered rings with an exocyclic *N*-oxide group,[5,6] and furoxans became important synthetic precursors and found application as high energy materials[7] and biologically active[8] compounds. Their pharmacological properties have been recently reviewed.[9]

In spite of the enormous growth of furoxan chemistry in the 20th century, the parent furoxan ($H_2C_2N_2O_2$, **1**) was unknown until 1994,[10] when it was prepared from glyoxime by oxidizing with N_2O_4 in dichloromethane. The structure was confirmed by NMR, MS and X-ray crystallography, with IR and UV spectra in KBr(s) and CH_2Cl_2(l) also recorded.[10] The condensed phase IR spectrum was also studied in 1994.[11] No other experimental investigations exist, despite the fact that **1** is the key to understanding the structure, properties and chemistry of all the electron-rich furoxans.

As the electron-rich parent furoxan, **1** has attracted some theoretical investigations. Early *ab initio* calculations limited to the Hartree−Fock (HF) and MP2 levels with modest (3-21G, 4-31G, 4-31G*, 6-31G*) basis sets[12,13] correctly suggested the planar frame, but failed to describe the structure, especially the endocyclic N−O bond. Rauhut and co-workers pointed out later that furoxans were sensitive with respect to dynamical correlation effects and thus calculations based on MP2 and HF geometries were inherently in error.[14,15] Calculations on **1** and substituted derivatives indicate that density functional theory (DFT) using the B3LYP functional can provide a correct description of the furoxan geometry,[15−17] providing a viable and cost-effective computational approach.

In this paper, we report the first gas-phase investigation of **1** using IR and photoelectron (PE) spectroscopies, Raman and IR spectroscopy of the liquid complement the gas-phase IR. A detailed investigation of the *ab initio* and DFT equilibrium structure is undertaken with the intension of testing a range of methods to assess the importance of dynamical and nondynamical electron correlation effects in describing the structure. Of particular interest are the structure, spectroscopy, aromaticity, and thermal decomposition of **1**.

Experimental Section

Synthesis of Furoxan. 1. A 20 g sample of dry glyoxime (Fluka, dried at 60 °C in a drying box) and 200 mL of dichloromethane were placed in a flask equipped with magnetic stirrer, reflux condenser, and gas inlet tube with gas dispersion disk at the end. The suspension was brought to reflux and nitrogen dioxide gas introduced slowly until most of the solid glyoxime disappeared (ca. 1.5 h). The NO_2 introduction was stopped, the mixture was stirred for another 30 min, and then filtered. The filtrate was washed three times with 200 mL of water, dried over magnesium sulfate, and the solvent was removed by distillation. 4.6 g of **1** (raw product) was obtained as a pale yellow liquid with a purity of higher than 95%, according to NMR. Attempts to purify this by column chromatography (silica gel, eluent: dichloromethane:methanol = 20:1) led to partial decomposition. **1** was thus purified by distillation (42 °C/2 mbar). Pure **1** is a colorless liquid at room temperature, which slowly turns light yellow upon standing. NMR (Bruker DRX 500 spectrometer, room temperature,

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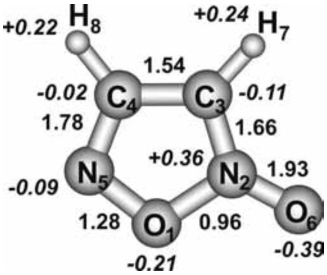


Figure 1. NPA charges, bond orders (B3LYP/6-311++G(2d,2p) level), and numbering of atoms.

reference tetramethylsilane): ^{1}H NMR ($CDCl_3$): $\delta = 7.13$ (s, H_7), $\delta = 8.33$ (s, H_8). ^{13}C NMR ($CDCl_3$): $\delta = 103.5$ (s, C_3), 144.7 (s, C_4); see Figure 1.

Gas-phase IR spectra (resolution 0.5 cm^{-1}) were obtained on a Nicolet Nexus 870 FTIR using a flow-through, single-pass (20 cm) cell and a room temperature DTGS detector. The cell, with KBr windows, gave a spectral range from 4000 to 400 cm^{-1}. Spectra were recorded at ca. 900 mTorr. The IR spectrum (resolution 2.0 cm^{-1}) of a liquid film between KBr windows was collected at room temperature on a Perkin-Elmer System 2000 Fourier-transform spectrometer equipped with a liquid nitrogen cooled mercury cadmium telluride (MCT) detector. The Raman spectrum of liquid **1** was recorded, using Nd:YAG excitation (1064 nm), on a Bruker RFS 100 FT-Raman spectrometer at 2 cm^{-1} resolution.

The He I ultraviolet photoelectron spectrum (UPS) of gaseous **1** was recorded using an Atomki ESA-32 photoelectron spectrometer described in detail elsewhere.[18] The spectrum was calibrated with the Ar $^2P_{3/2,1/2}$ spin−orbit doublet, with a fwhm of 25 meV.

Computational Methods

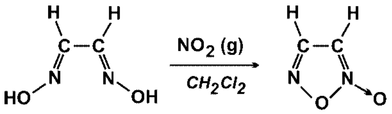
In order to test the effects of nondynamical and dynamical electron correlation as well as basis set size, the structure of **1** was investigated at various computational levels and basis sets, including B3LYP, MP*n* ($n = 2-4$), CISD, QCISD, CCSD, CCSD(T), RSPT*n* ($n = 2, 3$), MRCI, and MR-AQCC levels and 6-311++G(2d,2p), cc-pVTZ, aug-cc-pVTZ, cc-pCVTZ, and cc-pVQZ basis sets. Equilibrium molecular geometries were fully optimized and harmonic vibrational frequencies were calculated to confirm them as minima on the potential energy surface (zero imaginary frequencies). Stability checks of wave functions were performed for all calculated structures.

Relative Raman intensities were calculated using the computed Raman activities (S_i) and the expression provided in ref 19, *viz*: $I_i = f(\nu_0 - \nu_i)^4 S_i/(\nu_i[1 - \exp(- hc\nu_i/kT)])$, where ν_0 is the exciting frequency, ν_i is the vibrational wavenumber of the *i*th normal mode, *h*, *c*, and *k* are fundamental constants, and *f* is a chosen normalization factor for all peak intensities (Raman intensity of the ν_9 vibrational mode is assumed to be 100). For characterization of the normal modes of **1**, the total energy distribution (TED), which provides a measure of the internal coordinate contributions, was determined.[20] Ionization potentials (IPs) for **1** were calculated using the outer valence Green's function (OVGF) method. All calculations were performed with the Gaussian-98, MOLPRO, COLUMBUS, and MOLCAS quantum chemistry packages.[21−24]

Results and Discussion

Synthesis and Identification of 1. Godovikova et al. published the first, and hitherto only, synthetic route to **1**, stating that N_2O_4 (1 mol) oxidized glyoxime in dichloromethane at 35−38 °C producing **1** (1 h, 45% yield). Purification of **1** was achieved by column chromatography (silica gel, CH_2Cl_2) with subsequent distillation.[10] No other details of the synthesis were provided, but the selection of solvent and oxidizing agent seemed to be essential. We slightly modified this procedure using NO_2 gas (see Scheme 1 and Experimental Section) and the usual workup of the reaction mixture produced **1** with a purity of higher than 95% according to the NMR. Attempted purification of the raw product on a silica gel column led to decomposition of **1**, and so the raw product was purified by distillation.

SCHEME 1



Calculated Structure and Aromaticity of 1. Structural studies of simple furoxans are limited. A comparison of the calculated equilibrium structure and the experimental crystallographic data for the dicyano-,[17] dibromo-[25] and parent-furoxan[15] indicates that both HF and MP2 methods perform poorly. On the other hand, structures calculated with B3LYP DFT showed good agreement with experiment, suggesting that B3LYP is a possible alternative to *ab initio* methods. In order to understand the computational difficulties and to calculate the equilibrium structure of **1**, *ab initio* and DFT calculations were performed at various levels of theory including single and multireference methods. The results are included in Table 1 and in the Supporting Information (Table S1 and S2). The structure and numbering of atoms are shown in Figure 1. The experimental X-ray structure of **1** is also listed in Table 1 for comparison, and although the theoretical equilibrium structure cannot be compared directly with the crystallographic structure due to vibrational averaging and solid-state effects, we expect the differences for rigid molecules like **1** to be small. All quantum chemical methods give a planar ring structure for **1**, which extends to the exocyclic atoms. The description of the bond lengths however, especially the key endocyclic O_1-N_2 bond, is varied. This variation demonstrates a strong effect of triple excitations on geometry, with triples markedly increasing the O_1-N_2 bond (compare e.g. CCSD vs CCSD(T)). Tracking the MP*n* expansion series (MP1 = HF, MP2, MP3, MP4; Table S2, Supporting Information), an oscillatory behavior can be seen not only in the calculated geometry (especially the O_1-N_2 bond) but also in the total energy. The possibility of oscillatory behavior of the MP*n* series is known, however, these pronounced oscillations suggest an unusual effect. Indeed, the stability check of HF wave function indicated a RHF-UHF instability, therefore the result of MP*n* calculations must be regarded as artifacts. To test the reliability of the single reference approximation, CASSCF(16,16)/cc-pVTZ calculations were done,[26] indicating that, apart from the main HF configuration (weight 85%), there was no other important configuration and thus single reference post-HF methods seemed to be sufficient for describing the structure (calculated weight of the second most important configuration was only 1.7%, corresponding to excitation from HOMO to LUMO). The natural occupancies of HOMO and LUMO were 1.913 and 0.116 e, respectively, and higher than 1.95 for all occupied and lower than 0.06 for all unoccupied MOs. The CCSD *T1* diagnostics for **1** were 0.020. Although close to the usual 0.02 threshold, this suggests that nondynamical electron correlation has minor importance and confirms the adequacy of single reference post-HF methods. Multireference

TABLE 1: Calculated[a] Structure of Furoxan at Various Levels of Theory

	B3LYP	RSPT2	RSPT3	CISD	MRCISD	MR-AQCC	CCSD	CCSD(T)	expt[d]
N_2-O_6	1.210	1.207	1.210	1.206	1.205	1.214	1.216	1.216	1.240
O_1-N_2	1.464	1.463	1.388	1.356	1.362	1.417	1.406	1.449	1.441
N_2-C_3	1.325	1.351	1.324	1.307	1.304	1.324	1.321	1.332	1.302
C_3-C_4	1.408	1.389	1.411	1.406	1.409	1.414	1.414	1.412	1.401
C_4-N_5	1.302	1.322	1.302	1.283	1.291	1.302	1.300	1.312	1.292
N_5-O_1	1.360	1.351	1.368	1.350	1.352	1.369	1.368	1.370	1.379
C_3-H_7	1.073	1.072	1.069	1.063	1.063	1.070	1.071	1.073	0.92
C_4-H_8	1.077	1.075	1.073	1.067	1.067	1.074	1.075	1.077	0.97
$O_1N_2O_6$	118.4	118.8	117.8	118.0	117.7	117.9	117.9	118.2	116.4
$O_1N_2C_3$	105.6	104.9	108.0	108.3	108.4	107.3	107.5	106.3	107.2
$N_2C_3C_4$	107.4	107.4	105.7	105.4	105.6	106.2	106.2	106.9	107.2
$C_3C_4N_5$	111.7	112.0	111.2	110.7	110.5	111.5	111.3	111.8	111.9
$C_4N_5O_1$	107.1	106.8	106.2	106.3	106.2	106.4	106.4	106.6	106.6
$C_4C_3H_7$	132.3	133.5	133.6	133.6	133.5	133.1	133.2	132.9	130
$C_3C_4H_8$	127.9	128.3	128.5	128.6	128.7	128.2	128.4	128.1	128
tot. energy	−337.333465	−336.647956	−336.629088	−336.410388	−336.423445	−336.632174	−336.634732	−336.702293	
μ^b	3.79	4.60	*e*	4.29	4.46	4.03	4.06	3.81	
A^c	9.791	9.675	10.001	10.316	10.250	9.900	9.968	9.738	
B	4.039	4.040	4.135	4.215	4.208	4.085	4.097	4.029	
C	2.860	2.850	2.925	2.992	2.983	2.892	2.904	2.850	

[a] Calculated using cc-pVTZ basis set. RSPT2(2,2), RSPT3(2,2), MRCISD+Q(2,2), and MR-AQCC(2,2) calculations (HOMO and LUMO included in the active space; see also Table S2, Supporting Information). Valence electrons were correlated in electron correlation calculations (i.e., frozen-core). Bond lengths are in Å and bond angles in deg. Total energy is given in atomic units. See Figure 1. [b] Dipole moment in Debye. [c] Rotational constants in GHz. [d] Crystal structure from ref 10. [e] Not calculated.

TABLE 2: Aromaticity Measures of Furoxan, Furazan, and Furan[a]

	magnetic		geometric		energetic	
	NICS(0)	NICS(1)	Bird	BDSHRT	ASE	ISOD
furoxan	−10.7	−7.2	42.6	44.0	23.0	53.5
furazan	−13.5	−11.7	54.3	51.2	78.5	86.2
furan	−11.5	−9.1	48.5	50.8	64.6	32.4

[a] Calculated at the B3LYP/6-311++G(2d,2p) level.

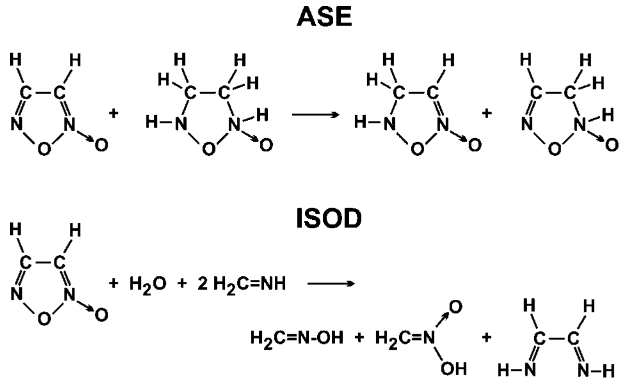
methods were also used to calculate the structure (Table 1 and S2 (Supporting Information). The selection of active space was tested, and calculations using (2,2), (4,4), and (6,6) active space indicated minor differences in calculated structures. Comparing single and multi reference methods, viz. CISD to MRCI+Q and CCSD to MR-AQCC, only minor differences are found between calculated structures, confirming again the adequacy of single reference methods. The best structural description of **1**, compared to the X-ray structure, is obtained by the CCSD(T) method. B3LYP also performs well. The difficulties of HF and low-level post-HF methods in calculating the structure of furoxans thus arise due to the unstable HF wave function and importance of proper description of dynamical electron correlation. Stable wave functions were obtained for the B3LYP, CISD, QCISD, CCSD, and CCSD(T) methods. The effect of basis set size and inclusion of core electrons into the electron correlation calculations were also tested and found to have minor importance, at least among the tested basis sets (see Table S1, Supporting Information).

The calculated structure of **1** is shown in Figure 1 along with calculated NPA charges and bond orders obtained using Gordy's rule.[27,28] The molecule is planar, the C−N bond lengths and bond orders implying imine-like partial double-bond character, and the C−C and N_5-O_1 bonds, nominally single bonds, are slightly shorter than a C−C or N−O single bond. This tendency to bond order equalization is in agreement with the expected aromaticity of furoxans. The longest bond in the ring frame, with small bond order (0.96), is O_1-N_2, a possible point of cleavage and ring opening, as demonstrated in some substituted furoxans.[29−31] The exocyclic N_2-O_6 bond is short (bond order 1.93) and may be regarded as a double bond. The electron richness of the furoxan moiety is indicated by a large negative charge on the constituent atoms (−0.46 e). There is a large negative charge on the exocyclic oxygen (−0.39 e) and a large positive charge on the connected nitrogen (+0.36 e), which makes the exocyclic N_2-O_6 bond very polar. A negative charge is found on all other ring atoms, decreasing in the order of $O_1 > C_3 > N_5 > C_4$. The structure and charge distribution of **1** is clearly complicated and cannot be described simply by one or two mesomeric structures. The same conclusion was pointed out earlier on the basis of dipole moment measurements of substituted furoxans.[32]

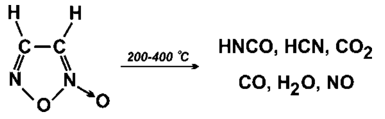
Furoxans are expected to be aromatic. However possible aromatic character has not been examined thus far. Aromaticity is a major issue in chemistry and an extensive set of aromaticity indexes have been developed.[33] These can be grouped into structural, energetic, and magnetic criteria. We selected aromaticity indexes from each group to provide a combined description of aromaticity and compared these indexes to those of furazan and furan, well-known similar aromatic molecules, also calculated in this work. The aromaticity indexes are presented in Table 2. Nucleus independent chemical shift (NICS) values are useful quantities for description of aromaticity. A negative value indicates aromaticity whereas a positive value demonstrates antiaromaticity. NICS(0) as well as NICS(1) values of **1** are negative, with similar extent to those of furazan and furan, and indicate that the aromaticity of these molecules is comparable. The same conclusion can be drawn on the basis of Bird[34] and BDSHRT (bond shortening)[35] indexes. Energetic measures, ASE (aromatic stabilization energy) and ISOD (isodesmic reaction energy), are calculated using equations in Scheme 2. They are more varied than magnetic and geometric measures, but support again the aromaticity of **1**. In short, **1** is nearly as aromatic as furan and furazan.

Gas-Phase Thermolysis of 1. Thermal decomposition of furoxans is interesting not only from the viewpoint of high energy materials, but the generation of nitrile oxides or other small reactive species. Given that **1** is the dimer of HCNO, a

SCHEME 2



SCHEME 3



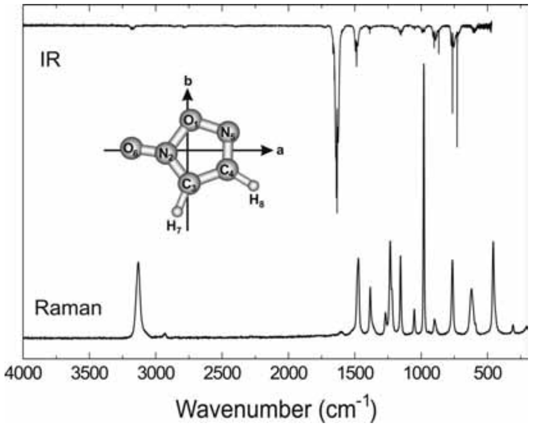


Figure 2. Gas-phase IR and liquid-phase Raman spectra of furoxan. (The molecule in the main principal axis system is shown in the inset.)

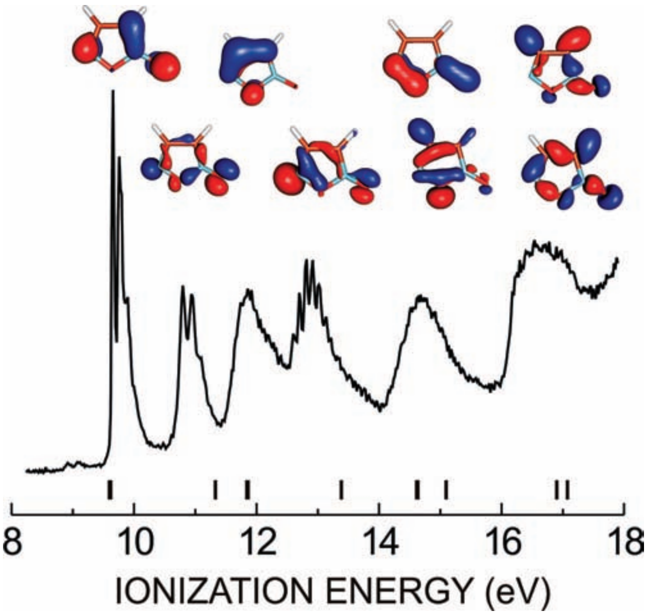


Figure 3. He I photoelectron spectrum of gaseous furoxan and schematics of the corresponding molecular orbitals. The positions of the calculated OVGF/6-311++G(2d,2p) ionization potentials are marked.

potential route to this molecule is the thermal decomposition of **1**. For the generation of NCCNO,[29] CH_3CNO[30] and CF_3CNO[31] from their stable dimers, this is the method of choice. Thermolysis of **1** in the gas phase at 1 Torr was carried out in a quartz tube (8 mm i.d.) heated along 15 cm, packed with quartz chips to improve efficiency. The formation of HCNO, however, was not found upon pyrolysis of **1** (Scheme 3). The products of this reaction between 200 and 400 °C are HNCO, HCN, CO_2, CO, H_2O, and NO, with relative amounts depending on temperature.

Infrared and Raman Spectra. The IR (gas) and Raman (liquid) spectra are shown in Figure 2, with the experimental and calculated frequencies (including calculated IR and Raman intensities and the TED) listed in Table 3. Theoretical frequencies are scaled by general scale factors of 0.9692 for B3LYP and 0.9639 for CCSD(T).[36] Figure 2 also shows the molecule in its principal axis system. The IR of liquid has been noted before[11] and is in general accord with the gas and liquid data given here. The complementary character of IR and Raman spectroscopy (albeit gas versus liquid) is demonstrated in Figure 2 where, in general, weak bands in the IR spectrum correspond to strong ones in the Raman and *vice versa*.

For this planar structure of C_s symmetry and using the CCSD(T)/cc-pVTZ rotational constants, the asymmetry parameter κ is -0.66 and thus the molecule is a prolate asymmetric rotor ($\rho^*= 1.71$ and $\beta= 1.42$). The 18 normal modes transform into $13a' + 5a''$ vibrational species, all being IR and Raman active. All but 6 of these fundamentals are identified in the gas-phase IR. In general, type-A, type-B, and type-C IR bands are expected for this prolate rotor with PQR, PQQR, and PQR band structures, respectively, for pure A, B, and C bands. Using the equations of Seth-Paul[37] and the CCSD(T) rotational constants, the calculated PR separations for pure A, B, and C-type bands are 17, 14, and 25 cm^{-1}, respectively.

The experimental fundamentals of a′ symmetry are of A/B-hybrid type, while those of a″ symmetry modes are C-type bands with pronounced Q-branches. In the gas-phase IR spectrum the PQR structure is clearly observed on many bands (see details in the Supporting Information). The experimental PR separations for all A/B type bands are in the range of 14−17 cm^{-1}, in good agreement with the predicted separations, and C-type bands are easily identified by their strong Q branch, notably at 867 and 729 cm^{-1}. The other three fundamentals of a″ symmetry are not observed due to low IR intensity (see Table 3). The calculated frequencies and relative IR and Raman intensities are in good agreement with experiment and support the band assignments. It is important to note that Rauhut and Werner calculated recently the IR spectrum of **1** using density functional and local electron correlation methods, including scaling the force constants with empirical factors.[14] These calculations are in excellent agreement with experiment, providing further support for the assignment.

Most substituted furoxans lacking CH groups (see, e.g., dibromo-,[38] dichloro-,[39] and bis(trifluoromethyl)furoxan[31]) exhibit no IR bands above 1700 cm^{-1}, and the same is true here except for the two weak stretches in the C−H region (ca. 3170 cm^{-1}). Only the higher frequency band has sufficient intensity to be observed in the IR and an overlapping band is detected in Raman. The two prominent CH wags (a″), only seen in the gas-phase IR at 867 and 729 cm^{-1}, have archetypal C-type Q-branch structure. The band assignment for the two in-plane CH deformations is less straightforward because these modes are strongly mixed with ring vibrations (see TED in Table 3). A

TABLE 3: Experimental and Calculated (Scaled Harmonic) Vibrational Frequencies (cm^{-1}) of Furoxan

experimental[a]			calculated					
			B3LYP/6-311++G(2d,2p)			CCSD(T)/ cc-pVDZ		
IR gas phase[b]	IR liquid	Raman liquid	freq.[c]	IR int.[d]	Raman int.[e]	freq.[f]	IR int.[d]	assignment and TED (%)[g]
3183 R	3139 m	3136[h] m	3198	11	41 (79)	3197 (3196)	10	ν_1 97% C_3H_7 st
3169 P								
N.O.	N.O.	3136[h] m	3156	0.01	50 (92)	3160 (3156)	0.2	ν_2 98% C_4H_8 st
1642[i]								
1639 Q	1602 vs	1603 vw	1620	477	8 (3)	1657 (1624)	403	ν_3 52% N_2O_6 st, 34% N_2C_3 st
1633 Q								
1626								
1495								
1495 Q	1474 s	1474 m	1487	63	67 (22)	1474 (1473)	26	ν_4 59% C_4N_5 st, 21% C_4H_8 b
1487 Q								
1479								
1395 R								
1388 Q	1383 w	1384 w	1373	5	40 (11)	1357 (1361)	6	ν_5 43% C_3C_4 st, 34% C_3H_7 b
1378 P								
N.O.	N.O.	1233 m	1231	2	82 (19)	1217 (1218)	1	ν_6 33% C_4H_8 b, 26% C_4N_5 st, 15% N_2C_3 st, 12% N_2O_6 st
1160 R								
1158 Q	1155 m	1156 m	1149	27	33 (7)	1127 (1137)	19	ν_7 30% N_2C_3 st, 20% C_4H_8 b, 17% rb, 14% C_3H_7 b, 12% N_2O_6 st
1152 Q								
1145 P								
1058 R								
1050 Q	1051 w	1051 w	1037	4	14 (2)	1019 (1028)	4	ν_8 44% C_3C_4 st, 37% C_3H_7 b, 16% C_4H_8 b
1041 P								
993 R								
986 Q	979 m	980 vs	987	21	100 (16)	964 (969)	16	ν_9 49% O_1N_5 st, 28% rb, 13% N_2C_3 st
978 P								
909 R								
902 Q	898 m	897 w	890	43	16 (2)	868 (875)	27	ν_{10} 70% rb, 19% O_1N_5 st
892 P								
867 Q	N.O.	N.O.	863[j]	9	2 (0.3)	822 (846)[j]	13	ν_{14} 96% C_4H_8 w
772 R								
764 Q	762 s	763 m	756	44	79 (9)	736 (755)	36	ν_{11} 55% rb, 20% O_1N_5 st, 13% N_2O_6 st
755 P								
729 Q	N.O.	N.O.	733[j]	46	11 (1)	668 (705)[j]	41	ν_{15} 89% C_3H_7 w, 10% N_2O_6 w
N.O.	N.O.	N.O.	639[j]	0.3	2 (0.1)	607 (628)[j]	2	ν_{16} 57% rt, 37% N_2O_6 w
(601)	617 w	620 m	594	11	81 (6)	566 (607)	14	ν_{12} 38% O_1N_2 st, 36% N_2O_6 b, 10% rb
N.O.	N.O.	N.O.	592[j]	0.1	3 (0.2)	560 (578)[j]	0.5	ν_{17} 78% rt, 21% N_2O_6 w
N.O.	N.O.	455 m	441	8	111 (6)	405 (448)	11	ν_{13} 52% O_1N_2 st, 44% N_2O_6 b
N.O.	N.O.	306 vw	291[j]	0.7	10 (0.3)	280 (282)[j]	0.1	ν_{18} 72% rt, 30% N_2O_6 w

[a] This work; N.O. = not observed. [b] Additional very weak bands at 2862, 2783, 1727, 1595 (Q), 1450, 1200, 881 (Q). [c] Scale factor: 0.9692. [d] IR intensities in km/mol. [e] Relative Raman intensities (Raman activities in A^4/AMU are in parenthesis). [f] Frequencies in parenthesis are calculated at the CCSD(T)/cc-pVTZ level. Scale factor: 0.9639. [g] Characterization of the fundamentals; TED (total energy distribution). Only contributions above 10% are given. Abbreviations: stretching (st), bend (b), ring bend (rb), wagging (w), ring torsion (rt). [h] broadband, overlapping fundamentals. [i] Q subbands at 1664, 1654, (1644), 1637 and 1636. [j] Out-of-plane deformations (a″).

careful comparison of the available experimental data[17,31,38,39] of substituted furoxans with that of **1**, however, have indicated that IR bands of **1** at 1050 and 1155 cm^{-1} must have significant CH deformation character. All other fundamentals in the IR or Raman spectra originate from vibrations of the furoxan moiety. The most characteristic IR absorption in the substituted derivatives[17,31,38−40] usually appears in the 1700−1600 cm^{-1} region. This band occurs in the spectrum of **1** at 1636 cm^{-1} and is assigned to the exocyclic N→O bond according to the TED. The highest frequency and largest IR intensity of this mode out of all the furoxan vibrational modes concurs with the largest bond order and the very polar N−O bond (see above). This normal mode also possesses some *C*═N character and may be described as the antisymmetric *C*═N→O stretch. The symmetric counterpart is not observed in the IR due to low intensity, but gives rise to a medium band in the Raman at 1233 cm^{-1} (comparable to that at 1244 cm^{-1} in dichlorofuroxan[39]). Most aryl-, acyl-, and alkyl-susbstituted furoxans also show a second *C*═N based stretch, anywhere between weak and strong, between 1500 and 1600 cm^{-1}. In **1**, this mode is observed as relatively strong IR band at 1491 cm^{-1} (1521 cm^{-1} in bis(trifluoromethyl)furoxan[31]). Bands in the gas-phase IR spectrum at 1388 and 986 cm^{-1} having significant C−C and endocyclic N−O character, respectively, can be unambiguously assigned to furoxan ring stretches and bands at 902 and 764 cm^{-1} to ring deformations. These four bands have been observed in the spectra of all furoxan derivatives investigated so far.[17,31,38−40] Three bands are observed below 700 cm^{-1} in the Raman spectrum of **1** at 620, 455, and 306 cm^{-1}. According to the calculations bands at 620 and 455 cm^{-1} may be assigned to the endocyclic N−O stretch and exocyclic N−O in-plane bend (these modes are strongly mixed), and the band at 306 cm^{-1} to the furoxan ring torsion.

The most advanced and comparative theoretical study of the vibrational spectrum of **1** was published by Rauhut and Werner,[14] and now, a comparison between theory and experiment can be done. There is a very nice agreement between our experimental results and theoretical data calculated with methods including anharmonicity effects at the SQM/B97r/cc-pVTZ and cc-VSCF/B3LYP/cc-pVTZ levels. The comparison and calcula-

TABLE 4: Experimental and Calculated Ionization Potentials (eV) of Furoxan

Experimental		Calculated		
E_i[a]	ν^+	OVGF/cc-pVTZ[b]	OVGF/6-311++G(2d,2p)[c]	orbital character
9.66	(1130, 810)[d]	9.48 (a″)	9.58 (a″)	π (n_O)
10.80	(1210)[d]	11.21 (a′)	11.30 (a′)	σ (n_O)
11.85		11.78 (a″)	11.84 (a″)	π
12.91	(810)[d]	13.22 (a′)	13.35 (a′)	σ (n_N)
14.68		14.38 (a″)	14.54 (a″)	π
		14.98 (a′)	15.08 (a′)	σ ($n_{O, \text{ring oxigen}}$)
16.7		16.78 (a′)	16.93 (a′)	σ ($n_{N\rightarrow O}$)
		17.02 (a′)	17.09 (a′)	σ (C−H)

[a] Vertical ionization potentials. [b] CCSD(T)/cc-pVTZ geometry was used. [c] B3LYP/6-311++G(2d,2p) geometry was used. [d] Cationic frequencies, ± 100 cm^{-1}.

tions clearly indicate that anharmonic corrections are most important for C−H and N−O vibrational modes.

He I Photoelectron Spectrum. The He I photoelectron spectrum of the furoxan is shown in Figure 3 and experimental and calculated ionization potentials are listed in Table 4. OVGF calculations for IPs give very good agreement with experiment (within 0.5 eV), especially for a″ orbitals (within 0.3 eV). The sequence of molecular orbitals (MOs) deduced for this molecule (see below) is...$(7a')^2(1a'')^2(8a')^2$ $(9a')^2(10a')^2$ $(2a'')^2(11a')^2$ $(3a'')^2(12a')^2$ $(4a'')^2$.

The observed photoelectron spectrum corresponds to eight ionic states with the sequence X($^2A''$), A($^2A'$), B($^2A''$), C($^2A'$), D($^2A''$) ≈ E($^2A'$), F($^2A'$) ≈ G($^2A''$). From the calculated IPs and from a comparison with the known PE spectra of the dichloro,[39] dibromo,[38] and dicyano[17] derivatives, the assignment is relatively straightforward.

A possible starting point to describe the electronic structure of furoxan is to consider the MOs of a furazan ring, modified with an exocyclic oxygen atom. Five PE bands corresponding to ionization of eight MOs are observed in the spectrum of furazan below 18 eV.[41] These bands are expected to shift toward higher IPs due to the electronegative oxygen atom, and one of the nitrogen lone pairs will form the exocyclic N → O bond. Furazan has three π orbitals, two high lying at 11.79 eV and one deeper at 16.33 eV. The two high energy π orbitals will mix strongly with the exocyclic oxygen lone pair orbital, O_6 pπ and the O_6 pσ orbitals will mix with the ring σ framework. These five orbitals together with another five σ orbitals from the furazan ring or CH bonds are thus expected in the investigated region. Six PE bands are observed in the spectrum of **1** (see Figure 3). According to OVGF calculations one of the expected π and one of the expected σ orbitals are below our 18 eV detection limit, thus the six PE bands originate from ionization of eight MOs. The oxygen pπ and pσ orbitals in relatively simple *N*-oxides, e.g. pyridine *N*-oxides,[42] are high lying (8−10 eV) and are separated by *ca.* 1 eV. The first band in the spectrum of **1** at 9.66 eV can thus be assigned, in agreement with calculations, to the O_6 oxygen π lone pair with some contribution from the ring. The PE band shows vibrational fine structure, not entirely resolved, but our best estimates indicate ionic vibrational frequencies of 1130 ± 100 and 810 ± 100 cm^{-1}. The next band at 10.80 eV is assigned to the in-plane O_6 pσ orbital, mixed with the ring σ orbitals. Further justification for the assignment is provided by a comparison with the corresponding pσ orbital in nitrosyl or carbonyl groups which appears in the 10 and 12 eV IP regions.[43,44] From the vibrational fine structure a vibrational frequency of 1210 ± 100 cm^{-1} is deduced for the corresponding ionic state. The third band at 11.85 eV is assigned to one of the high lying furazan-like π orbital (in furazan itself at 11.79 eV[40]). This band is observed at 10.72, 11.10, and 12.09 eV in dibromo-,[38] dichloro-,[39] and dicyanofuroxan,[17] respectively. The shift of these bands compared to that of **1** is in agreement with the expected mesomeric and inductive effects of substituents attached to the furoxan moiety. The fourth band at 12.91 eV has an elegant vibrational fine structure indicative of ionization from a bonding orbital. The vibrational frequency of the corresponding ionic state is 810 ± 100 cm^{-1}. Calculations indicate that the MO corresponding to the band is delocalized, although has a predominant nitrogen lone pair character. Nitrogen lone pairs in furazan are observed at 12.0 and 12.75 eV.[40] The next band at 14.68 eV is assigned to two MOs, the first the second furazan-like π orbital, mixed with the exocyclic oxygen pπ orbital, and the second a ring σ orbital, with strong contribution from endocyclic oxygen (in furazan at 14.4 eV[40]). The last broadband in the spectrum at 16.7 eV is assigned again to two MOs. An unambiguous assignment is not possible due to the delocalization over the entire σ framework; calculations indicate that one of the MOs has some exocyclic oxygen terminal lone pair character and the other corresponding to the band has C−H character.

Conclusion

The parent furoxan molecule can be synthesized from glyoxime by chemical reaction with NO_2 gas. On the basis of DFT and single- and multireference *ab initio* calculations which include correlation through perturbation, configuration interaction, or coupled cluster theory, the molecule is planar with a short exocyclic N−O bond and a long endocyclic N−O bond. A computational difficulty for furoxan emerges due to the unstable HF wave function, and the proper description of the structure requires the possible best description of dynamic electron correlation. According to various aromaticity indices, furoxan is nearly as aromatic as furan and furazan. The electron richness of the furoxan moiety is indicated by a large negative NPA charge (−0.46 e), which may be released toward electronegative substituents. Although alkyl- and dicyanofuroxan are sources of nitrile oxides, pyrolysis of the parent furoxan leads not to HCNO, but to the generation of HNCO, HCN, CO_2, CO, NO, and H_2O. The vibrational and photoelectron spectroscopy applied to furoxan has provided information on the valence occupied levels and on the fundamental vibrations. In both cases considerable mixing occurs, commensurate with the delocalized electronic structure and the heavy atom framework based on only C, N, and O atoms.

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Supporting Information Available: Calculated equilibrium geometry data of the parent furoxan at the B3LYP, QCISD, HF, MP*n* (n = 2−4), RSPT2, and MR-AQCC levels using various basis sets listed in Tables S1 and S2 and details of gas-phase IR bands shown in Figure S1. This material is available free of charge via the Internet at http://pubs.acs.org.

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