O-Nitrosobis(trifluoromethyl)hydroxylamine: Unexpected Conformational Properties and an Unusually Long (CF₃)₂NO–NO Bond. A Combined Study of the Gaseous and Solid States

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Abstract: The conformational properties and the geometric structure of gaseous *O*-nitrosobis(trifluoromethyl)-hydroxylamine, $(CF_3)_2N$—O—N=O, have been studied by infrared spectroscopy, electron diffraction, and ab initio calculations. From the relative intensities and band contours of the two N=O vibrations, a mixture of 80(10)% trans–syn and 20(10)% trans–anti conformers ($\Delta G = G(\text{syn}) - G(\text{anti}) = -0.8(3)$ kcal/mol) is derived (trans describes the orientation of the O—N bond relative to the CNC bisector and syn/anti refers to the orientation of N=O relative to N—O). Such a mixture of conformers with planar NONO groups is consistent with the electron diffraction intensities. In addition, the compound has been subjected to X-ray crystal structure analysis. In the solid state, only the trans–syn conformer is present. The O—N single bond is unusually long and differs strongly in the two phases: 1.572(21) Å in the gaseous state and 1.669(3) Å in the solid state. The results of ab initio calculations depend strongly on the calculational method, especially for the relative energy of the two conformers and for the O—N bond length: $\Delta E = E(\text{syn}) - E(\text{anti}) = -1.8, +0.6,$ and -3.3 kcal/mol and O—N $= 1.527, 1.401,$ and 1.717 Å with HF/3-21G, HF/6-31G*, and MP2/6-31G*, respectively. None of these predictions agrees very well with the experimental results for the gas phase.

Introduction

For many compounds the conformational properties are a delicate balance between various interactions involving atoms, bonds, and lone pairs. The latter play a crucial role for the conformations of compounds which contain two adjacent atoms with lone pairs. In the discussion of stereochemical effects, the directionality of lone pairs is of essential importance. Whereas this is quite obvious in the case of nitrogen, different pictures can be used for oxygen. As pointed out by Kirby,[2] the nonbonding orbitals can be represented either by a pair of canonical orbitals of π and σ symmetry (a) or by two sp³-hybridized orbitals (b).
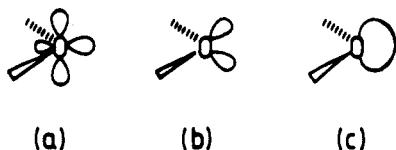
In both cases, the electron density distribution (c) which is responsible for the stereochemical interactions is equivalent. Peroxides (RO—OR)[3] or hydrazines (R₂N—NR₂)[4] possess skewed structures, i.e., the electron densities corresponding to the lone pairs are in gauche positions. On the other hand, compounds containing N—O bonds, such as hydroxylamines (R₂N—OR, R = H[5] or Me)[6] and nitrites (RO—N=O, R = H[7]

or Me),[8] adopt planar anti or syn conformations. *O*-Nitrosobis-(trifluoromethyl)hydroxylamine, $(CF_3)_2NONO$ (from now on called NONO), possesses three adjacent atoms with stereochemically active lone pairs. Assuming planarity of the NONO skeleton, as suggested by the structures of hydroxylamines and nitrites, four conformations are conceivable: trans–anti, trans–syn, cis–anti, and cis–syn. Trans/cis refers to the orientation of
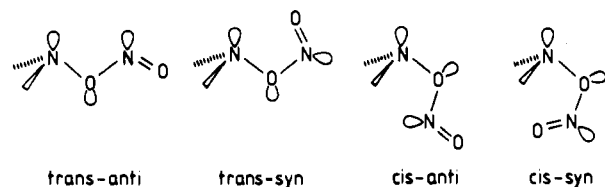
the O—N bond relative to the CNC bisector and anti/syn describes the position of the N=O double bond relative to the N—O single bond. Trans/cis and anti/syn also apply to the relative orientations of the lone pairs in the N—O—N chain. Since very little is known about the relative magnitudes of the different interactions between atoms, bonds, and lone pairs, a reliable prediction of the relative stabilities of these four conformations is impossible. In this publication, we report an experimental investigation of the conformational properties and geometric structure of NONO applying infrared spectroscopy, gas electron diffraction (GED), and X-ray diffraction. The experimental studies are supplemented by ab initio calculations at various levels of theory with the aim to test "standard" calculational methods for this type of compound.

Ab Initio Calculations

The theoretical calculation of conformational compositions is a difficult task, since it requires the prediction of relative energies

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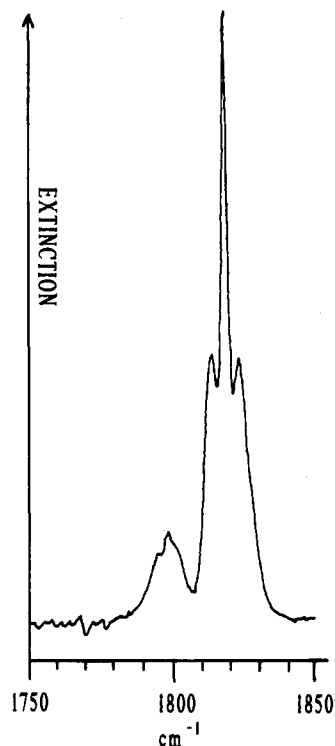
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Table I. Geometric Parameters for $(CF_3)_2NONO$ and Relative Stabilities of Syn vs Anti Conformers from Experiment and from Ab Initio Calculations

	GED[a]	X-ray[b,c]	HF/3-21G[b] syn	HF/6-31G*[b] syn	HF/6-31G*[b] anti	MP2/6-31G*[b] syn	MP2/6-31G*[b] anti
C—F	1.321(3) (p_1)	1.314(4)	1.337	1.309	1.310	1.338	1.338
N—C	1.426(10) (p_2)	1.431(4)	1.412	1.431	1.432	1.437	1.439
N1—O1	1.410(15) (p_3)	1.376(3)	1.417	1.371	1.371	1.382	1.408
O1—N2	1.572(21) (p_4)	1.669(3)	1.527	1.401	1.402	1.717	1.598
N2=O2	1.156(8) (p_5)	1.120(4)	1.150	1.136	1.139	1.156	1.164
F—C—F	108.7(3) (p_6)	108.0(2)	108.5	108.6	108.7	108.6	108.6
C—N—C	121.5(14) (p_7)	118.2(2)	122.1	119.6	119.2	118.4	117.5
C—N1—O1	112.1(11) (p_8)	109.6(2)	111.4	108.6	108.4	108.9	107.2
N1—O1—N2	107.6(19) (p_9)	106.9(2)	111.2	114.4	108.4	103.1	103.7
O1—N2=O2	115.7(43) (p_{10})	110.9(2)	113.0	115.0	109.2	110.1	108.9
ΔE (kcal/mol)[d]	−0.8(3)		−1.8	+0.6		−3.3	

[a] r_a distances in Å and $\angle_\alpha$ angles in degrees. Error limits are 3σ values and include possible systematic errors (see text). For atom numbering, see Figure 2 or 3. [b] For parameters which are not unique, average values are given. [c] Error limits are σ values. [d] $\Delta E = E(\text{syn}) - E(\text{anti})$ from vibrational analysis and ab initio calculations, respectively.

of at least better than 0.5 kcal/mol. In many cases the predicted energy differences depend strongly on the calculational procedure, such as the size of basis sets or inclusion of electron correlation effects. Therefore, we have applied three different "standard" methods in the present study for NONO, HF/3-21G, HF/6-31G*, and MP2/6-31G*, using the GAUSSIAN 90 program system.[9] The calculations were performed on a Convex C220 (University of Tübingen) and Cray 2 (University of Stuttgart). Only three conformations were considered in these calculations. The cis–syn structure possesses unreasonably short contacts between the nitrite oxygen and fluorine atoms (1.8 Å for standard bond lengths and bond angles) and is not expected to correspond to a stable structure, but to converge via inversion at the nitrogen or via rotation around N—O to the trans–syn form. The cis–anti form does not represent a minimum in the HF/3-21G calculations. Geometry optimization leads to inversion at the nitrogen and results finally in a trans–anti structure. The HF/6-31G* method predicts an energy minimum for the cis–anti conformation which lies, however, considerably higher than that for the trans–anti form (5.6 kcal/mol). No MP2 calculations were performed for this conformer, and only the trans–anti and trans–syn conformations (from now on called anti and syn) were considered in the further analysis. The predicted energy difference of these two forms, $\Delta E = E(\text{syn}) - E(\text{anti})$, depends strongly on the calculational procedure. The HF method with the small basis set and the MP2 method with the large basis set lead to a strong preference of the syn conformer ($\Delta E = -1.8$ and -3.3 kcal/mol, respectively). The intermediate level of theory (HF/6-31G*) reverses the relative stability to $\Delta E = +0.6$ kcal/mol. From these results we conclude, that "standard" ab initio methods do not provide a reliable prediction of the conformational properties of NONO. The size of the basis sets also affects the predicted symmetries of the two conformations. The 6/31G* structures possess C_s symmetry with exactly planar NONO skeletons and with the CF_3 groups nearly staggering the opposite N—C bonds. The small basis set predicts structures with C_1 symmetry, i.e., both CF_3 groups are rotated in opposite directions by about 10°. Consequently, the NONO skeleton deviates slightly from planarity ($\delta(\text{NONO}) = 179.9°$ for anti and 3.0° for syn). The energy difference between syn and anti conformers, which is the primary interest in these calculations, changes by less than 0.1 kcal/mol if the symmetry of both conformers is constrained to C_s. The MP2 optimizations were performed for C_s symmetry, and because of the high expense of these calculations, structures with C_1 symmetry were not considered. Single-point calculations at the HF/3-21G level for nonplanar gauche forms lead to much higher

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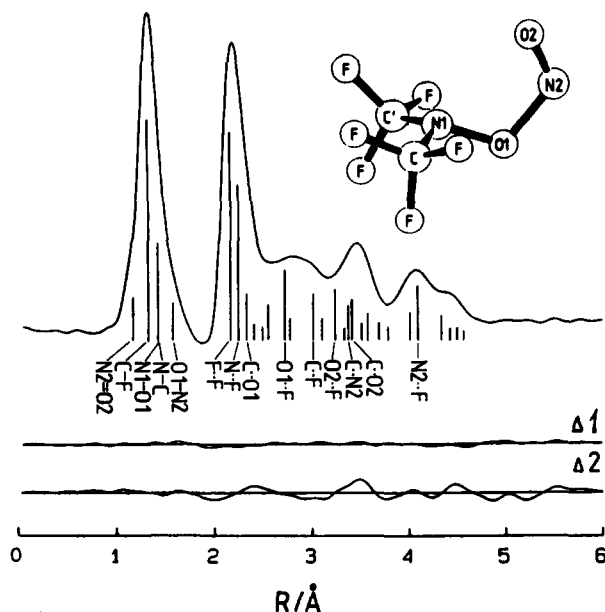

Figure 1. Experimental infrared N=O vibrations in $(CF_3)_2NONO$.

energies, and further energy minima can be excluded. The calculated geometric parameters (Table I) and vibrational frequencies are discussed in context with the experimental investigations.

Infrared Spectra

In the region of the N=O vibration, two bands are observed at 1820 and 1800 cm^{-1} (Figure 1), demonstrating the presence of two conformers. The possibility that the weaker band is an overtone or combination band can be excluded when all possible combinations of intensive IR bands (see the Experimental Section) are considered. The intensity ratio of the two bands is 4:1. The stronger band at higher wavenumber possesses a PQR contour with a strong Q branch typical for a C-type vibration. For all molecular structures (ab initio and GED, see below), the N=O bond of the syn conformer lies almost exactly parrellel to the c rotational axis. In the anti form, the N=O bond lies between the a and c axes and the expected hybrid is consistent with the contour of the weaker band in Figure 1.[10] Thus, according to the infrared spectrum, the syn conformer is predominant. If equal absorbances (squared dipole moment derivatives) for the N=O

Figure 2. Experimental radial distribution function: Δ_1 = difference curve for the mixture of 80% syn and 20% anti; Δ_2 = difference curve for the mixture of 20% syn and 80% anti. The positions of important interatomic distances and their contributions are indicated by vertical bars.

vibrations in the two conformers are assumed, a contribution of 80(10)% syn form is obtained from the relative intensities. The estimated error accounts for differences in the absorbances of the two conformers. The ab initio calculations predict the ratio of the absorbances in the syn and anti structures to be 0.90 (HF/3-21G) and 0.83 (HF/6-31G*). The conformational composition corresponds to a free energy difference $\Delta G = G(\text{syn}) - G(\text{anti}) = -0.8(3)$ kcal/mol. The HF/6-31G* calculations predict the difference between ΔG and ΔE (differences in entropy, thermal contributions, and zero point vibrational energies) to be ca. 0.01 kcal/mol. Thus, the experimental ΔG can directly be compared with the calculated ΔE values. The experimental splitting of the two N=O vibrations, $\Delta\nu = \nu(\text{syn}) - \nu(\text{anti}) = 20$ cm^{-1}, is not well reproduced by the HF calculations. The small basis set results in a difference of 7 cm^{-1} ($\nu(\text{syn}) = 1772$ and $\nu(\text{anti}) = 1765$ cm^{-1}), and the large basis set leads to a reversed sequence of these vibrational frequencies ($\nu(\text{syn}) = 2080$ and $\nu(\text{anti}) = 2086$ cm^{-1}). The vibrational frequencies were not calculated at the MP2 level.

Electron Diffraction Analysis

(CF₃)₂NONO is not a well-suited molecule for a structure investigation by GED. All bonds (except N2=O2 and O1—N2) have rather similar lengths, and all bond angles are close to tetrahedral. This causes high correlations between several parameters and prevents their determination with the desired accuracy. This is especially true for the more interesting parameters of the NONO group. Calculated radial distribution functions (RDF) for the syn and anti structures are not very different. Although the anti conformer possesses F···O2 distances around 5 Å, where no peak occurs in the experimental RDF (Figure 2), reasonable agreement in this r-range can still be obtained with very large vibrational amplitudes for these distances. The only serious discrepancy for the anti model remains near 3.5

(10) The N=O band contours have been simulated with the program KILOTRA. Rotational constants were calculated for the experimental structures; centrifugal distortion constants were derived from a diagonal force field and α values were estimated. The simulated band contours agree very well with the experimental bands (Figure 1) except for their overall width. Because of computational limitations the maximum J and K_a values had to be set to 30 and 31, respectively, causing the simulated bands to be too narrow. We are very grateful to Prof. H. Bürger and Dipl. Chem. M. Paplewski, Universität Wuppertal, Germany, for performing these simulations.

Table II. Interatomic Distances and Vibrational Amplitudes for the Syn Conformer of (CF₃)₂NONO[a]

	d	amplitude		d	amplitude
N=O	1.16	0.035[b]	A···F[c]	2.53–3.11	0.14(3) (a_3)
C—F	1.32	0.045[5][d]	N···O2	2.52	
N—O	1.41		C···N2	3.34	0.09(2) (a_4)
N—C	1.43		C···O2	3.39	
O—N	1.57		B···F[e]	3.43–3.59	0.08[b]
F···F	2.15	0.058(6) (a_1)	D···F[f]	3.22–3.78	0.22(3) (a_5)
N1···F	2.26		D···F[f]	4.02–4.35	0.13(2) (a_6)
O1···O2	2.32	0.059(14) (a_2)	E···F[g]	4.42–4.58	0.10[b]
C···O1	2.35				
C···C'	2.48				

[a] Values in Å. Error limits are 3σ values. For atom numbering, see Figure 2. [b] Not refined. [c] A = C, O1, or F. [d] Not refined, but varied in the range given in square brackets (see text). [e] B = C or O1. [f] D = N2, O2, or F. [g] E = O2 or F.

Å, where the area of the calculated function is smaller than that of the experimental curve. Thus, the experimental RDF is consistent only with the syn conformer being the predominant component, in agreement with the interpretation of the infrared spectrum. The GED intensities (and RDF) are not very sensitive toward the ratio of the two conformers, and the composition derived from the infrared spectra was used in the further analysis. If the ratio of the two forms is reversed, i.e. 20% syn and 80% anti, the agreement between calculated and experimental RDF's becomes considerably worse, as shown by the difference curve Δ_2 in Figure 2.

The right-hand slope of the first peak in the RDF demonstrates the presence of a long bond distance at ca. 1.57 Å. The other peaks of the curve are consistent only with O1—N2 being this long bond. Model calculations with a long N1—O1 bond lead to a bad fit of the experimental RDF in the range 2.5–3.0 Å, which contains O1···F distances. Models with both N1—O1 and O1—N2 distances being short (1.40–1.45 Å) do not fit the peaks of the RDF in the range ≥3 Å, which contains the nonbonded distances from the CF₃ groups to N2 and O2. In the least-squares refinements, the molecular intensities were modified with a diagonal weight matrix and known scattering amplitudes and phases were used.[11] The C₂NONO skeleton was constrained to C_s symmetry, and local C_{3v} symmetry was assumed for the CF₃ groups. Attempts to refine a tilt angle between the C_3 axis of the CF₃ groups and the N—C bond direction resulted in error limits which are larger than the refined value (2.2(31)°), and the tilt was set to zero in further refinements. The CF₃ groups were allowed to rotate around the N—C bonds in the same direction (C_s symmetry for the (CF₃)₂N group) or in opposite directions (C_2 symmetry for (CF₃)₂N). The latter model leads to a slightly better fit of the experimental intensities. The adjusted torsional angle of 10° is an "effective" angle due to large amplitude torsional vibrations. The vibrational amplitudes were grouped together according to their distances, and further constraints are evident from Table II. The amplitudes for all single bonds were set equal and were not refined. Possible systematic errors introduced by this constraint were estimated by varying this amplitude by ±0.005 Å and are included in the uncertainties for the geometric parameters. Bond lengths, angles, and vibrational amplitudes for the anti and syn structures were set equal. If the differences for geometric parameters in the two conformers which are predicted by the MP2 calculations (Table II) are introduced as constraints in the least-squares refinement, the agreement factors remain unchanged. With these assumptions, ten geometric parameters and six vibrational amplitudes were refined simultaneously. The following correlation coefficients had values larger than $|0.7|$: $p_2/p_3 = -0.82$, $p_2/p_9 = 0.72$, $p_2/p_{10} = -0.77$, $p_3/p_9 = -0.76$, $p_7/p_{10} = 0.71$, $p_9/p_{10} = -0.78$, $p_{10}/a_2 = -0.70$, $a_1/a_2 = 0.78$, $a_3/a_5 = 0.79$. The full correlation matrix is available as

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Table III. Atomic Parameters, Bond Lengths (Å) Bond Angles (deg) and Selected Torsional Angles (deg) of the Molecule in the Crystal Structure with Estimated Standard Deviations in Parentheses

atom	x	y	z	U^a
F11	0.2810(4)	0.2117(2)	0.6440(1)	5.22(6)
F12	0.3666(4)	0.1574(2)	0.4795(1)	6.06(7)
F13	0.5677(4)	0.0661(3)	0.6102(2)	7.30(8)
F21	0.0231(4)	0.0259(2)	0.7478(1)	5.03(5)
F22	−0.0545(5)	−0.1715(2)	0.6638(1)	6.67(7)
F23	0.2943(5)	−0.1360(2)	0.7327(1)	6.73(7)
O1	0.2484(4)	−0.1157(2)	0.5083(1)	4.18(5)
O2	−0.1050(5)	−0.0397(3)	0.4237(2)	5.31(7)
N1	0.1763(4)	−0.0088(2)	0.5796(1)	2.89(5)
N2	0.0419(6)	−0.1216(3)	0.4093(2)	4.73(7)
C1	0.3506(5)	0.1059(3)	0.5794(2)	3.98(7)
C2	0.1111(6)	−0.0726(3)	0.6820(2)	3.94(7)

N1–O1	1.376(3)	C1–N1	1.427(4)
O1–N2	1.669(3)	C2–N1	1.435(3)
N2–O2	1.120(4)		

N1–O1–N2	106.9(2)	C1–N1–O1	109.4(2)
O1–N2–O2	110.9(2)	C2–N1–O1	109.8(2)
N1–O1–N2–O2	−0.4(3)	C1–N1–C2	118.2(2)
C1–N1–O1–N2	−115.4(2)	F11–C1–N1–O1	177.7(2)
C2–N1–O1–N2	113.4(2)	F21–C2–N1–O1	−174.7(2)

F11–C1	1.313(3)	F21–C2	1.308(3)
F12–C1	1.319(3)	F22–C2	1.309(4)
F13–C1	1.309(4)	F23–C2	1.323(4)

F11–C1–N1	110.5(2)	F21–C2–N1	110.6(2)
F12–C1–N1	108.2(2)	F22–C2–N1	108.0(2)
F13–C1–N1	114.2(2)	F23–C2–N1	113.7(2)
F11–C1–F12	108.4(2)	F21–C2–F22	109.1(3)
F11–C1–F13	107.5(2)	F21–C2–F23	107.3(2)
F12–C1–F13	107.9(2)	F22–C2–F23	107.9(2)

^{a} The isotropic displacement parameters U are listed as multiples of 0.01 Å^2 and derived from the anisotropic U_{ij} values by $U = \frac{1}{3}(U_{11}a^2a^{*2} + U_{23}bcb^*c^* \cos \alpha + ...)$.
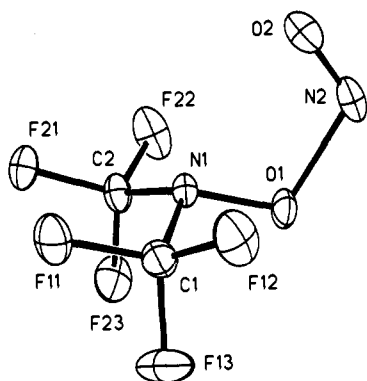
Figure 3. The molecule in the crystal structure with 25% probability ellipsoids.

supplementary data. Numbering of geometric parameters p_i and vibrational amplitudes a_k and their final values are listed in Tables I and II.

X-ray Diffraction Analysis

The crystal structure of NONO is orthorhombic with space group $P2_12_12_1$ and $Z = 4$ molecules per unit cell, i.e., one molecule in the general position of the space group as the asymmetric unit. The lattice constants are $a = 5.519(4)$, $b = 9.198(5)$, and $c = 12.291(9)$ Å. The atomic parameters as well as bond lengths, bond angles, and selected torsional angles are listed in Table III. Averaged geometric parameters are included in Table I. Corrections for some models of correlated thermal motions are not applied. The molecule is shown in Figure 3. It adopts the trans–syn conformation and approximate (noncrystallographic) C_s symmetry. A larger part of the crystal structure is shown in Figure 4.
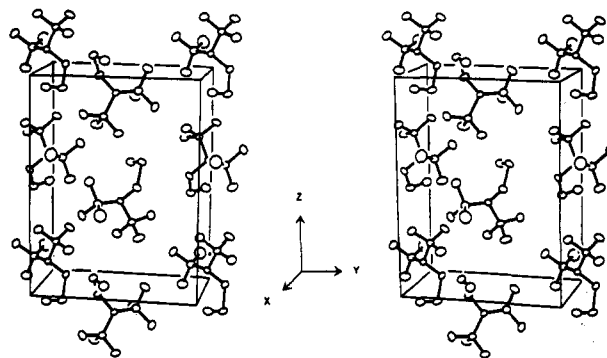
Figure 4. Stereoscopic drawing of the unit cell with several molecules.

Discussion

Two results of this study are remarkable, i.e., the unexpected conformational properties of this compound and the unusually long O1—N2 bond. In both cases, the predictions of the theoretical calculations are not unambiguous. According to experimental studies, NONO exists in the gas phase as a mixture of trans–syn and trans–anti conformers, with the syn form energetically favored by $\Delta E = -0.8(3)$ kcal/mol. In the solid state, only the syn conformer is present. In this structure, the lone pairs at the amine nitrogen N1 and at the central oxygen O1 are trans to each other, whereas the lone pairs at O1 and at the nitrite nitrogen N2 are cis to each other. This result is unexpected, since it leads to a very short contact between the terminal oxygen O2 and the amine nitrogen of 2.52 Å in the gas phase and 2.48 Å in the crystal. This distance is much shorter than the sum of the van der Waals radii (2.90 Å). We are unable to give a straightforward explanation for the preference of this structure. Ab initio calculations result in contradicting predictions for the relative stabilities of the two conformers. Whereas the HF/3-21G and MP2/6-31G* methods lead to a strong preference of the syn form ($\Delta E = -1.8$ and -3.2 kcal/mol, respectively), the HF/6-31G* method predicts a predominance of the anti conformer ($\Delta E = +0.6$ kcal/mol).

In the comparison of crystal and gas-phase structures, systematic differences due to vibrational effects and intermolecular interactions in the solid phase have to be considered. Vibrational effects may lead to differences in bond lengths up to ca. 0.03 Å. Intermolecular interactions (packing effects) usually have a small effect on bond lengths, but can distort bond angles or dihedral angles by several degrees. Considering these systematic differences and the experimental error limits, the geometric parameters of the $(CF_3)_2N$ group are very similar in both phases and correspond closely to those observed for analogous compounds, e.g., $(CF_3)_3N$[12] or $(CF_3)_2NF$.[13] The N1—O1 distance (1.410(15) Å in the gas phase and 1.376(3) Å in the crystal) is shorter than the analogous bond in hydroxylamine (1.453(3) Å),[5] and this trend can be rationalized by the stronger electron-withdrawing substituents in NONO. The O1—N2 bond in the gas phase (1.572(21) Å) is much longer than O—N single bonds in nitrites RO—NO: 1.392(10) Å in cis HO—N=O[7] and 1.398(5) Å in cis MeO—N=O.[8] This unusually long N—O bond in NONO is consistent with the chemical reactivity of this compound, which is characterized by the ease of cleavage of the $(CF_3)_2NO$—NO bond.[14] In the crystal, this bond (1.669(3) Å) is still longer by about 0.1 Å. To our best knowledge, no such strong variation of a covalent bond between the gas and solid phases has been reported so far. Large differences have been observed for dative bonds, e.g., in F_3B·$NCCH_3$ where the B·N

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Conformational Properties and Structure of (CF₃)₂NONO

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bond is much shorter in the crystal (1.630(4) Å)[15] than in the gas phase (2.011(7) Å).[16] At present we have no convincing explanation for this strong variation of the N—O bond length between the gaseous and solid states. There are no unusually short intermolecular contacts in the crystal. The shortest intermolecular distance involving an atom of the NONO moiety amounts to 3.07 Å and extends from N2 to an F atom (F22 in $^1/_2 + x$, $-^1/_2 - y$, $1 - z$) of the neighboring molecule.

The ab initio calculations demonstrate that the O1—N2 bond length depends drastically on the calculational method: 1.527 Å with HF/3-21G, 1.401 Å with HF/6-31G*, and 1.717 Å with MP2/6-31G* for the syn conformer. The experimental gas-phase value (1.572(21) Å) is intermediate between the values obtained with the large basis set with and without correlation effects. The HF methods predict very similar values for this bond length in the syn and anti forms (for the small basis set, only the former value is given in Table I), but the MP2 calculations result in a difference of more than 0.1 Å between the two conformers (1.717 Å for syn vs 1.598 Å for anti). Such a high sensitivity of geometric parameters toward the size of basis sets or inclusion of electron correlation, which has previously been observed, e.g., for O_2F_2[17] or FONO,[18] implies that small variations of the electronic structure have a strong effect on this bond length. Thus, even weak intermolecular interactions in the crystal may be responsible for the large difference between the gas phase and the crystal.

Conclusion

The relative intensities and band contours of the two N=O vibrations in the IR spectrum demonstrate that O-nitrosobis-(trifluoromethyl)hydroxylamine exists in the gas phase as a mixture of 80(10)% trans–syn and 20(10)% trans–anti conformers. This conformational composition is confirmed by the GED analysis. In the crystal, only the trans–syn form is present. The GED intensities can be fitted only with an unusually long O1—N2 bond of 1.57(2) Å. This result is independent of geometric assumptions and constraints for vibrational amplitudes which were applied in the least-squares analyses. An even larger value of 1.669(3) Å is determined for this bond distance in the crystal. "Standard" ab initio methods (HF/3-21G, HF/6-31G*, and MP2/6-31G*) give rather different results for the conformational properties and for the O1—N2 bond length, and none of these predictions agree with the experiments.

Experimental Section

A pure sample of NONO, first reported by Jander and Haszeldine,[19] was prepared by the reaction of nitrosyl chloride with di[bis(trifluo-romethyl)nitroxyl]mercury.[20] Mercury (0.8184 g, 4.08 mmol) was evaluated in a pyrex glass Schlenk tube for 2 h so that it was free of moisture. Bis(trifluoromethyl)nitroxyl radical (4.5254 g, 26.93 mmol) was introduced into the Schlenk tube such that it condensed into a liquid under its own vapor pressure. The reaction vessel was left at room temperature for 1 day with occasional shaking. Gradual formation of white powdery mercurial was observed. After 24 h, excess radical was removed by vacuum suction. The di[bis(trifluoromethyl)nitroxy]mercury obtained was stored in vacuum. Hydrolysis by atmospheric moisture rapidly yielded a yellow mass. In a typical preparation, quantitative yield of mercurial was obtained.

Nitrosyl chloride (0.5178 g, 7.91 mmol) was condensed in vacuo into a pyrex glass ampule containing di[bis(trifluoromethyl)nitroxy]mercury
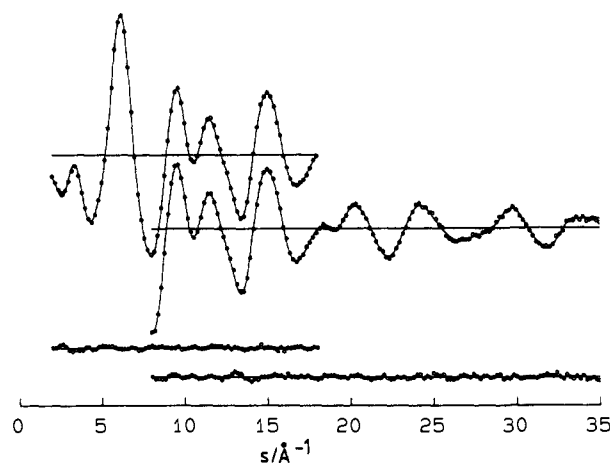

Figure 5. Experimental (dots) and calculated (full line) molecular intensities and differences.

(2.1304 g, 3.97 mmol). The sealed ampule was left at room temperature for 2 days, with occasional shaking. Trap-to-trap vacuum fractionation of the products gave O-nitrosobis(trifluoromethyl)hydroxylamine which passed the -96 °C trap slowly and was trapped in the -126 °C trap as an orange brown liquid in 92% yield (1.408 g, 7.28 mmol). Its infrared spectral data (cm⁻¹) in the gas phase are as follows: 1820 (vs), 1800 (s), 1317 (vs), 1280 (vs), 1255 (s), 1225 (vs), 1072 (m), 982 (s), 850 (w), 775 (w), 720 (m), 652 (w), 530 (w), 495 (w), 420 (m).

The GED intensities were recorded with a gas diffractograph KD-G2[21] at two camera distances (25 and 50 cm) using Kodak Electron Image plates (18 × 13 cm). The accelerating voltage was approximately 60 kV, and the electron wavelength was calibrated with ZnO powder diffraction. The sample reservoir was cooled to -65 °C, and the inlet system and nozzle were maintained at room temperature. Two plates for each camera distance were analyzed by the usual procedures.[22] Numerical values for the total scattering intensities in the s ranges 2–18 and 8–35 Å⁻¹ in steps of $\Delta s = 0.2$ Å⁻¹ are available as supplementary material, and averaged molecular intensities are presented in Figure 5.

A single crystal of NONO, which is gaseous at ambient conditions, was grown in a thin-walled quartz-glass capillary of ca. 0.35 mm in diameter. A miniature zone-melting technique[23] using focused heat radiation was applied on a Siemens AED2 diffractometer equipped with a low-temperature device. The X-ray measurements were done at -140 °C with a graphite-monochromatized Mo Kα radiation (λ = 0.710 73 Å, ω–Θ scan for intensities). Of 1255 independent reflections measured (3 ≤ 2Θ ≤ 65°), 1002 were observed ($|F_o| \geq 4\sigma_F$). Absorption was considered negligible ($\mu = 0.28$ mm⁻¹) and a correction not applied. The structure was solved and refined in the usual way (final $R = 0.044$, residual electron density between -0.25 and +0.30 eÅ⁻³). The program system SHELXTL PLUS[24] was used on a VAXstation 3200 (Digital) computer.

Supplementary Material Available: The correlation matrix of the GED analysis and tables of total GED intensities and anisotropic displacement parameters of the crystal structure (4 pages); a listing of observed and calculated structure factors (5 pages).

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