Inorg. Chem. **2002**, *41*, 7049–7052

Inorganic Chemistry
Article

# Gas Phase Structure of *O*-Nitrobis(trifluoromethyl)hydroxylamine, $(CF_3)_2NONO_2$: An Extremely Long O−N Bond

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Received June 20, 2002

The gas phase structure of *O*-nitrobis(trifluoromethyl)hydroxylamine, $(CF_3)_2NONO_2$, has been determined with gas electron diffraction and quantum chemical calculations (HF, MP2, and B3LYP with 6-31G* basis sets). The calculations predict a structure with $C_s$ overall symmetry, a planar $NONO_2$ skeleton, and the $NO_2$ group oriented anti with respect to the CNC plane. The electron diffraction intensities are reproduced very well with such a model. The molecule possesses pyramidal configuration at the amino nitrogen atom, and the following geometric parameters ($r_a$ values with $3\sigma$ uncertainties) were obtained for the $NONO_2$ skeleton: N−O = 1.392(18) Å, O−N = 1.597(16) Å, $(N{=}O)_{mean}$ = 1.192(4) Å, N−O−N = 106.9(25)°, O=N=O = 138.4(24)°. The extremely long O−N distance is rationalized by very weak bonding between the two stable radicals $(CF_3)_2NO$ and $NO_2$. Whereas the ab initio methods HF (O−N = 1.395 Å) and MP2 (O−N = 1.664 Å) fail to reproduce this bond length correctly, the hybrid method B3LYP (O–N = 1.584 Å) results in good agreement.

## Introduction

The O−N single bond length in covalent nitrates $MO-NO_2$ depends strongly on the substituent M. In "simple" nitrates with M = $SiMe_3$,[1] $CH_3$,[2] H,[3] Br,[4] Cl,[4] $CF_3$,[5] or F,[6] this bond lengthens steadily with increasing electronegativity of M from 1.383(5) Å in $Me_3SiONO_2$ to 1.507(4) Å in $FONO_2$. Such a strict correlation between bond length and electronegativity does not hold for peroxynitrates $ROO-NO_2$. In these compounds, the O−N bond length varies between 1.492(7) Å in $CH_3C(O)OONO_2$[7] to 1.526(10) Å in $CF_3C(O)OONO_2$.[7] Intermediate O−N bond lengths occur in $FC(O)OONO_2$ (1.514(6) Å)[8] and $CF_3OONO_2$ (1.523(7) Å).[9] Because of the chemical instability of covalent nitrites MO−NO, only a very limited number of gas phase structures for such compounds have been reported. The O−N bond lengths in HONO (1.397(6) Å)[10] and $CH_3ONO$ (1.398(5) Å)[11] are very similar to those in the corresponding nitrates (1.410(2) and 1.402(5) Å, respectively). Rotational constants derived from microwave spectra of ClONO are not sufficient for a complete structure determination.[12] High level ab initio calculations predict an O−N length for chlorine nitrite of 1.489 Å,[13] again very close to the experimental value for chlorine nitrate (1.496(3) Å). Thus, a similar correlation between electronegativity of M and O−N bond lengths, which occurs in simple nitrates, may also exist for nitrites. On the other hand, an extremely long O−N bond occurs in the nitrite *O*-nitrosobis(trifluoromethyl)hydroxylamine, $(CF_3)_2NO-NO$ (**1**) (1.572(21) Å).[14] This observation made it of

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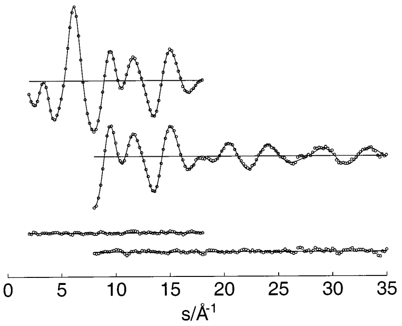

**Figure 1.** Averaged molecular intensities for 50 cm (top) and 25 cm (bottom) nozzle-to-plate distances and residuals.

great interest to study the molecular structure of the analogous nitrate $(CF_3)_2NO-NO_2$ (**2**). *O*-Nitrobis(trifluoromethyl)hydroxylamine (bis(trifluoromethyl)aminonitrate) has been synthesized for the first time by Blackley and Reinhard by reacting the stable bis(trifluoromethyl)nitroxide radical with nitrogen dioxide.[15] In the present study, we report the structure determination by gas electron diffraction (GED), which is supported by quantum chemical calculations.

## Experimental Section

$(CF_3)_2NONO_2$ was synthesized according to ref 15 by reacting bis(trifluoromethyl)nitroxide with nitrogen dioxide. The product was purified by repeated trap-to-trap distillation. It was stored and transported at liquid nitrogen temperature. Electron diffraction intensities were recorded with a Gasdiffraktograph KD-G2[16] at 25 and 50 cm nozzle-to-plate distances and with an accelerating voltage of about 60 kV. The sample reservoir was kept at −51 °C, and inlet system and nozzle were at room temperature. Two photographic plates (Kodak Electron Image Plates 18 × 13 cm) for each nozzle-to-plate distance were analyzed with the usual methods.[17] Averaged molecular intensities in the s-ranges 2−18 and 8−35 $Å^{-1}$ in steps of $\Delta s = 0.2$ $Å^{-1}$ are shown in Figure 1 ($s = (4\pi/\lambda)\sin \theta/2$; $\lambda$ is the electron wavelength, and $\theta$ is the scattering angle).

## Quantum Chemical Calculations

The geometry of **2** was fully optimized with the ab initio methods HF and MP2 and with the hybrid method B3LYP. 6-31G* basis sets were used for all methods. All three approximations predict only one stable structure with $C_s$ symmetry, a planar $NONO_2$ skeleton, and the $NO_2$ group oriented anti with respect to the CNC plane. Vibrational frequencies were derived with the B3LYP method. Vibrational amplitudes were calculated from the Cartesian force constants. All quantum chemical calculations were performed with the GAUSSIAN 98 program system,[18] and vibrational amplitudes were derived with the program ASYM40.[19]

## Structure Analysis

The radial distribution function (RDF) of **2** was calculated by Fourier transformation of the molecular intensities (Figure 2). A preliminary molecular model, which was derived from the RDF, was then refined by least-squares fitting of the molecular intensities. The B3LYP method predicts for this molecule some very low-frequency vibrations: 34 and 54 $cm^{-1}$ for the symmetric and asymmetric $CF_3$ torsions, respectively, and 58 and 71 $cm^{-1}$ for the torsional vibrations around the N1−O1 and O1−N2 bonds, respectively. In such cases, the concept of rectilinear vibrations that is used in the program ASYM40 leads to unreasonably large values for some perpendicular vibrations. The use of curvilinear displacements as suggested by Sipachev[20] is also highly problematic in this case, because the predicted vibrational frequencies cannot be considered to be very reliable. Therefore, the refinement was based on an $r_a$ structure, without any vibrational corrections. Because only the B3LYP method reproduces the experimental O1−N2 bond length satisfactorily (see later), the following constraints applied in the least-squares analysis were based on the results of this calculation: (1) $C_s$ overall symmetry for the molecule and local $C_{3v}$ symmetry for the $CF_3$ groups were used, along with equal C−F bond lengths and F−C−F bond angles. According to the quantum chemical calculations, the individual C−F bond lengths deviate by less than ±0.005 Å and the FCF bond angles by less than ±0.5° from the mean values. (2) The tilt angle between the $C_3$ axis of the $CF_3$ group and the N−C bond direction was set to the calculated angle (2.8°). The tilt occurs in the CNC plane and is away from the opposite N−C bond. (3) The two N=O bonds were set as equal. The calculated bond lengths differ by 0.002 Å. (4) The difference between the O−N=O angles, (O1−N=O2)−(O1−N=O3), was constrained to the calculated value (6.7°). (5) Vibrational amplitudes were collected in groups,

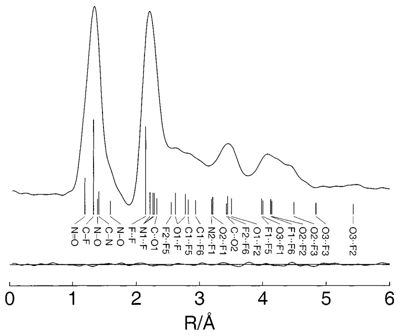

**Figure 2.** Experimental radial distribution function and difference curve. The positions of important interatomic distances are indicated by vertical bars.

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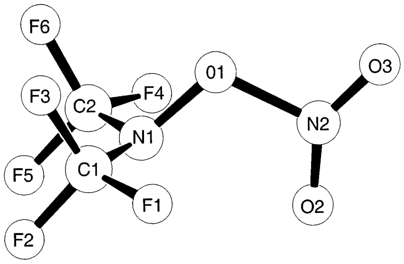

**Figure 3.** Molecular model of $(CF_3)_2NONO_2$.

**Table 1.** Experimental and Calculated Geometric Parameters for $(CF_3)_2NONO_2$

| | GED[a] | | HF[b] | MP2[b] | B3LYP[b] |
|---|---|---|---|---|---|
| $(C-F)_{mean}$ | 1.327 (1) | *p*1 | 1.307 | 1.339 | 1.336 |
| C−N1 | 1.408 (8) | *p*2 | 1.434 | 1.440 | 1.449 |
| N1−O1 | 1.392(18) | *p*3 | 1.360 | 1.371 | 1.367 |
| O1−N2 | 1.597 (16) | *p*4 | 1.395 | 1.664 | 1.584 |
| $(N=O)_{mean}$ | 1.192 (4) | *p*5 | 1.168 | 1.197 | 1.191 |
| C−N−C | 118.9 (8) | *p*6 | 120.3 | 119.4 | 119.6 |
| C−N1−O1 | 110.6 (19) | *p*7 | 108.7 | 109.5 | 110.4 |
| N1−O1−N2 | 106.9 (25) | *p*8 | 112.7 | 105.8 | 109.1 |
| $\sum\alpha(N1)^c$ | 340.1(21) | | 337.7 | 338.4 | 340.4 |
| $(O1-N2=O)_{mean}$ | 110.8 (17) | *p*9 | 114.3 | 111.2 | 112.5 |
| $\Delta(O1-N2=O)^d$ | 6.7 [20]$^e$ | | 7.9 | 5.1 | 6.7 |
| O1−N2═O2 | 114.2 (21) | | 118.2 | 113.8 | 115.8 |
| O1−N2═O3 | 107.5 (21) | | 110.3 | 108.7 | 109.1 |
| O2═N2═O3 | 138.4 (24) | | 131.4 | 137.6 | 135.0 |
| $(F-C-F)_{mean}$ | 108.1 (18) | *p*10 | 109.1 | 108.7 | 109.0 |
| $tilt(CF_3)^f$ | 2.8$^g$ | | 2.4 | 2.7 | 2.8 |
| C2−N1−C1−F1 | 172.4 (24) | *p*11 | 176.5 | 175.3 | 175.6 |

[a] $r_a$ values in angstroms and degrees. Uncertainties are $3\sigma$ values from least-squares procedure. For atom numbering, see Figure 3. [b] 6-31G* basis sets. [c] Sum of bond angles around amino nitrogen N1. [d] Δ(O1−N2═O) = (O1−N2═O2) − (O1−N2═O3). [e] Not refined, but varied within the estimated uncertainty. [f] Tilt angle of $CF_3$ group in the CNC plane and away from the opposite N−C bond. [g] Not refined.

and amplitudes which caused either high correlations between geometric parameters or which were badly determined in the GED experiment were set to the calculated values. With these assumptions, 11 geometric parameters (*p*1 to *p*11) and 7 vibrational amplitudes (*l*1 to *l*7) were refined simultaneously. The following correlation coefficients had values larger than |0.5|: $p2/p3 = -0.81$, $p7/p8 = 0.75$, and $p8/p10 = -0.51$. The final results are listed together with the calculated values in Table 1 (geometric parameters) and in Table 2 (vibrational amplitudes). A molecular model is shown in Figure 3.

## Discussion

According to all quantum chemical methods, $(CF_3)_2NONO_2$ possesses a structure with a planar $NONO_2$ skeleton and $C_s$ overall symmetry. The planarity of the $NONO_2$ skeleton is in agreement with the planar configuration of all covalent nitrates $MONO_2$, whose structures have been determined in the gas phase.[21] The $NO_2$ group is oriented anti with respect to the CNC plane of the $(CF_3)_2N$ group. The electron diffraction intensities are reproduced very well with such a structural model. The configuration around the amino nitrogen atom is pyramidal with the sum of the nitrogen bond angles $\sum\alpha_{N1} = 340(2)°$. The most striking structural feature of this nitrate is the extremely long O−N bond of 1.597(16) Å. In principle, this experimental value depends on the vibrational amplitudes and asymmetries of all bonded distances, but these effects are estimated to be considerably smaller than the large experimental uncertainty ($3\sigma$ value). As pointed out in the Introduction, such bonds are much shorter in all other covalent nitrates where they vary from 1.383(5) Å in $SiMe_3ONO_2$ to 1.526(19) Å in the peroxynitrate $CF_3C(O)OONO_2$. A similarly long O−N single bond as observed for **2** has been determined for the analogous nitrite **1** (1.572(21) Å).[14] A possible explanation for the long O−N bonds in compounds **1** and **2** is easy dissociation into thermodynamically stable radicals.

$$(CF_3)_2NONO \leftrightarrow (CF_3)_2NO^{\bullet} + {}^{\bullet}NO \qquad (1)$$

$$(CF_3)_2NONO_2 \leftrightarrow (CF_3)_2NO^{\bullet} + {}^{\bullet}NO_2 \qquad (2)$$

Such dissociation has been observed in the case of nitrite **1**,[22] but it has not been investigated for nitrate **2**. The N−O bond lengths (1.392(18) Å in **1** and 1.410(15) Å in **2**), which are appreciably shorter than the analogous bond in hydroxylamine (1.453(3) Å)[23] or the Schomaker−Stevenson value for such a single bond (1.44 Å),[24] support this bonding model. The N═O bond lengths in **1** and **2** (1.156(8) and 1.192(4) Å, respectively) are indistinguishable from or slightly shorter than those in NO (1.1540(1) Å)[25] and in $NO_2$ (1.202(3) Å).[26] These trends are reproduced by the B3LYP method, which predicts N═O bond lengths of 1.151 and 1.158 Å for the bonded and free NO group and 1.196 and 1.203 Å for the bonded and free $NO_2$ group, respectively. The calculated (B3LYP) dissociation enthalpies for **1** and **2** which correspond to the O−N bond energies in the nitrite and nitrate are $\Delta H° = 15.9$ and 11.9 kcal/mol, respectively. These bond enthalpies are much lower than usual single bond enthalpies, which typically range between 40 and 100 kcal/mol. The calculated Gibbs free energies $\Delta G°$ for the dissociation equilibria 1 and 2 are still lower, 7.9 and 2.6 kcal/mol. Thus, nitrite **1** and nitrate **2** can be considered to be weak adducts of the $(CF_3)_2NO$ radical with NO and $NO_2$ radicals, respectively. The strength of the interaction between the two radicals depends primarily on the spin densities at the two bonding atoms. According to B3LYP calculations, these are only some 40% at the $NO_2$ nitrogen atom and 65% at the nitroxide oxygen atom. A similarly weak interaction between two radicals occurs in the $NO_2$ dimer with an N−N distance of 1.777(6) Å.[27]

A further unexpected structural feature of **2** is the short nonbonded contact between the amino nitrogen atom and the cis-standing oxygen atom of the $NO_2$ group, N1···O2, of 2.50(2) Å. This distance is much shorter than the van der Waals distance of 2.90 Å.[24] Similarly, in **1**, the syn

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**Table 2.** Interatomic Distances and Experimental and Calculated Vibrational Amplitudes[a]

| | distance | amp GED | | amp B3LYP |
|---|---|---|---|---|
| N═O | 1.19 | 0.037 | | 0.037 |
| C−F | 1.33 | 0.044 | | 0.044 |
| N1−O1 | 1.39 | 0.049 | | 0.049 |
| N1−C | 1.41 | 0.049 | | 0.049 |
| N2−O1 | 1.59 | 0.070 | | 0.070 |
| F···F | 2.15 | 0.056 | | 0.056 |
| N1···F1 | 2.21 | 0.059 | | 0.059 |
| O2···O3 | 2.23 | 0.045 | | 0.045 |
| O1···O3 | 2.25 | 0.074 | | 0.074 |
| N1···F2 | 2.27 | 0.067 | | 0.067 |
| N1···F3 | 2.28 | 0.077 | | 0.077 |
| C···O1 | 2.32 | 0.068 | | 0.068 |
| O1···O2 | 2.34 | 0.064 | | 0.064 |
| C1···C2 | 2.43 | 0.065 | | 0.065 |
| N1···N2 | 2.43 | 0.067 | | 0.067 |
| N1···O2 | 2.53 | 0.093 | | 0.093 |
| F2···F5 | 2.55 | 0.114 (20) | *l*1 | 0.132 |
| O1···F1 | 2.62 | 0.114 (20) | *l*1 | 0.118 |
| O1···F3 | 2.77 | 0.194 (36) | *l*2 | 0.184 |
| C1···F5 | 2.82 | 0.114 (20) | *l*1 | 0.124 |
| F3···F6 | 2.83 | 0.194 (36) | *l*2 | 0.214 |
| C1···F6 | 2.94 | 0.194 (36) | *l*2 | 0.199 |
| N2···F1 | 3.19 | 0.145 (45) | *l*3 | 0.118 |
| O2···F1 | 3.21 | 0.331 | | 0.331 |
| C···N2 | 3.37 | 0.145 (45) | *l*3 | 0.121 |
| N1···O3 | 3.42 | 0.108 (13) | *l*4 | 0.062 |
| C···O2 | 3.43 | 0.188 | | 0.188 |
| F2···F6 | 3.44 | 0.327 | | 0.327 |
| O1···F2 | 3.50 | 0.108 (13) | *l*4 | 0.062 |
| C1···F4 | 3.53 | 0.108 (13) | *l*4 | 0.063 |
| F1···F5 | 3.98 | 0.103 (23) | *l*5 | 0.098 |
| O3···F1 | 4.00 | 0.260 (67) | *l*6 | 0.234 |
| F1···F6 | 4.13 | 0.121 | | 0.121 |
| O2···F2 | 4.14 | 0.248 | | 0.248 |
| N2···F3 | 4.15 | 0.260 (67) | *l*6 | 0.220 |
| C···O3 | 4.29 | 0.166 (26) | *l*7 | 0.137 |
| N2···F2 | 4.39 | 0.166 (26) | *l*7 | 0.141 |
| F1···F4 | 4.41 | 0.081 | | 0.081 |
| O2···F3 | 4.49 | 0.200 | | 0.200 |
| O3···F3 | 4.84 | 0.289 | | 0.289 |
| O3···F2 | 5.43 | 0.166 (26) | *l*7 | 0.130 |

[a] Values in angstroms. Uncertainties are $3\sigma$ values. amp = amplitude. For atom numbering, see Figure 3.

conformation (N═O bond synperiplanar relative to the N−O bond), which also results in a short N···O contact of 2.52(2) Å, is preferred. Intuitively, one would expect strong repulsion between the electron lone pairs of the amino nitrogen and the nitroso or nitro oxygen atoms. Quantum chemical calculations, however, result in a very weak attractive interaction between these two atoms with positive Mulliken overlap populations of 0.010 and 0.012 au in **1** and **2**, respectively, which apparently reduces the expected strong repulsion. This attraction results from a HOMO−LUMO interaction. The HOMO corresponds mainly to the nitrogen lone pair and the LUMO to the (N═O)$\pi^*$ orbital.

Table 1 compares the experimental geometric parameters with calculated values. According to a simple diatomic model and estimated anharmonic constants, vibrationally averaged $r_a$ bond distances derived from the experiment are systematically longer by about 0.004−0.008 Å than calculated equilibrium values $r_e$.[28] For most bond lengths in **2**, the experimental uncertainties ($3\sigma$ values) are larger than these systematic differences. All three methods, HF, MP2, and B3LYP with 6-31G* basis sets, predict similar values for bond lengths and angles except for the O−N single bond length and the N−O−N bond angle. Whereas the HF approximation (1.395 Å) predicts the O−N bond to be much too short, the MP2 method results in a value that is too long (1.664 Å). Only the hybrid method B3LYP (1.584 Å) reproduces the experimental bond length (1.597(16) Å) correctly. A similar failure of the HF and MP2 approximations exists for other nitrates $MO{-}NO_2$ with electronegative substituents M, such as F, Cl, or RO,[21] and for nitrite **1**. In these compounds, the HF method results in O−N bond distances which are too short by up to 0.19 Å, and the MP2 values are too long by up to 0.08 Å. Increasing the basis sets for MP2 calculations to cc-pVTZ does not improve the result for $FONO_2$ substantially.[21] In the case of **2**, the predicted N−O bond lengthens further to 1.679 Å, if the basis set is increased to cc-pVDZ. On the other hand, the hybrid method B3LYP/6-31G* reproduces the O−N bond distances in all nitrates and in **1** very closely.

**Acknowledgment.** We thank one of the reviewers, who pointed out the importance of spin densities for the interaction between radicals and who reported also calculated values for the $NO_2$ and nitroxide radicals. Financial support by the Deutsche Forschungsgemeinschaft is gratefully acknowledged.

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