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Structure of a Fluorinated Azoxy Compound: Fluoro(trifluoromethyl)-diazene-2-oxide, $CF_3N(O)NF$[§]

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A gas-phase electron diffraction study of the azoxy compound which was synthesized by the reaction of CF_3NO with N_2F_4 in a Pyrex glass vessel results in a trans $CF_3N(O)NF$ structure (F trans to CF_3), although quantum chemical calculations (MP2 and B3LYP) predict a greater stability of the cis $CF_3NN(O)F$ isomer by about 12 kcal/mol. The CF_3 group eclipses the N═N double bond. The following skeletal geometric parameters (r_a values with 3σ uncertainties) were obtained: N═N 1.287(15) Å; N═O 1.231(6) Å; N—F 1.380(6) Å; N—C 1.498(6) Å; N═N═O 131.2(13)°; N═N—F 103.5(13)°; N═N—C 114.0(12)°. The bond lengths in $CF_3N(O)NF$ are compared to those in azo, nitryl, and nitrosyl compounds with fluorine and/or CF_3 substituents.

Introduction

Azoxy compounds of the type XN(O)NY (diazene *N*-oxides) with organic substituents X and Y have attracted considerable interest, because of their possible biological activities.[1] Azoxymethane, $CH_3N(O)NCH_3$, has been found to induce colon carcinogenesis.[2] Several antibiotics possessing azoxy groups exhibit antibacterial, antifungal, and antitumor activities.[3,4] A great number of azoxy compounds with organic substituents X and Y (alkyl and/or aryl groups) have been synthesized and characterized.[5] However, very few azoxy compounds with halogen or halogenated groups as substituents have been reported, such as hexafluoroazoxymethane $CF_3N(O)NCF_3$.[6] $CF_3N(O)NF$ is, besides *c*-C_4F_7N-(O)NF,[7] the only azoxy compound known in which a halogen atom is bonded directly to one of the nitrogen atoms. Its first synthesis and a short characterization by vibrational and ^{19}F NMR spectroscopy and mass spectrometry have been reported in 1962.[8] Several resonance structures have been proposed to describe the bonding in azoxy compounds (Chart 1), ionic structures Ia and Ib, a diradical structure II, and a hypervalent structure III.[9,10] According to a quantitative valence bond (VB) analysis of the parent compound HN(O)-NH, the hypervalent structure III possesses the strongest contribution (50%), and the two ionic structures contribute about 20% each.[10] In the present communication, we report the gas-phase structure of $CF_3N(O)NF$ as determined by gas electron diffraction (GED) and quantum chemical calculations.

Quantum Chemical Calculations

Azoxy compounds with different substituents X and Y can exist in two isomeric forms, XN(O)NY and XNN(O)Y, each of which can possess trans (E) or cis (Z) conformation. Trans

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§ Dedicated to Professor Rüdiger Mews on the occasion of his 60th birthday.

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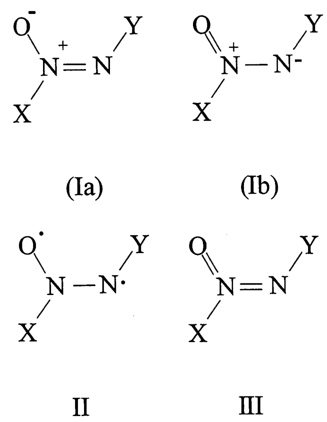
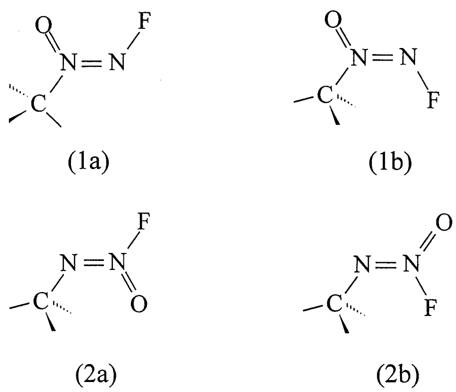
Chart 1



(Ia) (Ib)

II III

Chart 2



(1a) (1b)

(2a) (2b)

Table 1. Relative Energies (kcal/mol) of Cis and Trans Conformers of $CF_3N(O)NF$ and $CF_3NN(O)F$ Isomers Predicted by B3LYP/6-31G* and MP2/6-31G* Methods and Geometric Parameters (B3LYP/6-31G*)

	$CF_3N(O)NF$ trans (**1a**)	$CF_3N(O)NF$ cis (**1b**)	$CF_3NN(O)F$ trans (**2a**)	$CF_3NN(O)F$ cis (**2b**)
E_{rel} (B3LYP)	12.4[a]	17.3	1.0	0.0
E_{rel} (MP2)	12.0[b]	17.9	1.1	0.0
N═N	1.285	1.286	1.252	1.246
N═O	1.234	1.235	1.196	1.187
N—F	1.375	1.399	1.423	1.479
N—C	1.522	1.558	1.452	1.448
C—F	1.322	1.321	1.337	1.336
N═N═O	130.2	121.6	136.5	131.6
N═N—F	106.2	107.4	109.2	115.6
N═N—C	113.2	121.6	112.8	118.6
F—C—F	110.4	110.6	108.8	108.7
tilt (CF_3) [c]	2.8	2.0	3.4	4.3

[a] $E = -622.020141$ au. [b] $E = -620.516802$ au. [c] Tilt angle between C_3 axis of CF_3 group and N—C bond.

and cis describe the relative orientation of the substituents X and Y. Geometry optimizations for all four structures of this azoxy compound have been performed (Chart 2), using the MP2 approximation and the hybrid method B3LYP with 6-31G* basis sets. The relative energies and geometric parameters are listed in Table 1. Both methods predict the cis conformation of the $CF_3NN(O)F$ isomer to be lowest in energy and about 12 kcal/mol lower than the trans form of the $CF_3N(O)NF$ isomer. In the $CF_3N(O)NF$ isomer, the trans conformer is about 5−6 kcal/mol lower than the cis form, whereas in the $CF_3NN(O)F$ isomer the cis form is lower than the trans form by about 1 kcal/mol. One C—F bond of the CF_3 group eclipses the N═N double bond in the trans conformer of the $CF_3N(O)NF$ isomer, and the CF_3 group staggers the N═N bond in the other three structures. None of these structures possess an imaginary vibrational frequency. The skeletal bond lengths differ appreciably between the $CF_3N(O)NF$ and $CF_3NN(O)F$ isomers. Whereas the N═N and N═O double bonds lengthen only slightly, the N—F bond lengthens by up to about 0.1 Å, and the N—C bond shortens by about this amount when going from $CF_3N(O)NF$ to $CF_3NN(O)F$. Bond angles vary by up to 15° among the four possible structures. The geometry of the experimentally observed trans $CF_3N(O)NF$ isomer was optimized also with a QCISD/cc-pVTZ calculation (see Table 2). The unscaled Cartesian force constants (MP2) of the four structures were used to derive vibrational amplitudes with the program ASYM40.[11] Although the MP2 method is known to predict stretching force constants that are slightly too large, calculated values for bending, torsional, and out-of-plane vibrations, for which no experimental values are known, may be too large or too small. Because most vibrational amplitudes depend much more strongly on these low-frequency vibrations, no scaling factors were used for the force constants. All quantum chemical calculations were performed with the GAUSSIAN98 program suite.[12]

Table 2. Experimental and Calculated Geometric Parameters for Trans $CF_3N(O)NF$ (**1a**)[a]

	GED	B3LYP/ 6-31G*	MP2/ 6-31G*	QCISD/ cc-pVTZ [b]
N1═N2	1.287(15)	1.285	1.318	1.286
N1═O	1.231(6)	1.234	1.242	1.233
N2—F4	1.380(6)	1.375	1.385	1.373
N1—C	1.498(6)	1.522	1.497	1.509
C—F	1.312(3)	1.322[c]	1.327[c]	1.319[c]
N1═N2═O	131.2(13)	130.2	129.7	130.4
N1═N2—F	103.5(13)	106.2	104.6	106.0
N2═N1—C	114.0(12)	113.2	113.4	113.3
F—C—F	110.4(6)	110.4[c]	110.2[c]	110.3[c]
tilt(CF_3) [d]	2.8[e]	2.8	2.3	2.7

[a] Values in angstroms and degrees. Error limits are 3σ values. For atom numbering, see Figure 1. [b] Energy $E = -620.626818$ au. [c] Mean value. [d] Tilt angle between the C_3 axis of the CF_3 group and the N1—C bond direction, away from the N═N bond. One C—F bond of the CF_3 group eclipses the N═N bond. [e] Not refined.

Structure Analysis

The experimental radial distribution function (RDF), which was derived by Fourier transformation of the molecular intensities, is shown in Figure 1. Comparison of calculated RDFs for the four theoretical structures (Table 1) with the experimental curve demonstrates that it is reproduced

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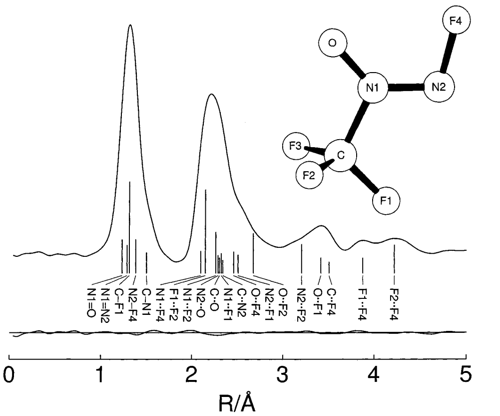

Figure 1. Experimental radial distribution function and difference curve. The positions of interatomic distances are indicated by vertical bars.

Table 3. Interatomic Distances and Experimental and Calculated Vibrational Amplitudes for Trans $CF_3N(O)NF$ (**1a**)[a]

	distance	amplitude[a]		
		GED		MP2
N=O	1.23	0.039[b]		0.039
N=N	1.29	0.041[b]		0.041
C−F	1.31	0.043[b]		0.043
N−F	1.38	0.045[b]		0.045
N−C	1.50	0.053[b]		0.053
N1···F4	2.10	0.153[b]		0.053
F1···F2	2.15	0.055[b]		0.055
N1···F	2.26−2.32	0.064[b]		0.064
N2···O	2.29	0.050[b]		0.050
C···O	2.30	0.063[b]		0.063
N2···C	2.34	0.062[b]		0.062
O···F4	2.46	0.085[b]		0.085
N2···F1	2.50	0.091[b]		0.091
O···F2	2.67	0.152(23)	l_1	0.172
N2···F2	3.20	0.159(33)	l_2	0.161
O···F1	3.42	0.081(20)	l_3	0.061
C···F4	3.50	0.081(20)	l_3	0.062
F1···F4	3.87	0.080(21)	l_4	0.092
F2···F4	4.22	0.149(25)	l_5	0.145

[a] Values in angstroms, error limits are 3σ values. For atom numbering, see Figure 1. [b] Not refined

satisfactorily only with the trans $CF_3N(O)NF$ isomer and the three other structures can be excluded (see later). In the least-squares fitting of the molecular intensities, C_{3v} symmetry of the CF_3 group with a possible tilt angle between the C_3 axis and the N−C bond direction were assumed. This assumption is justified by the theoretical calculations, which predict differences in C−F bond lengths and F−C−F bond angles to be less than 0.003 Å and 0.5°, respectively. Vibrational amplitudes, which either caused large correlations between geometric parameters or which were poorly determined by the GED experiment, were set to the calculated values. Attempts to refine amplitudes for bonded or geminal distances in groups resulted in correlation coefficients larger than 0.95. If individual amplitudes were varied by ± 0.002 Å, refined geometric parameters changed by less than the error limits given in Table 3, which are 3-fold standard deviations. With these constraints, nine geometric parameters and five vibrational amplitudes for long nonbonded distances (l_1−l_5, see Table 2) were refined simultaneously. The following correlation coefficients had values larger than |0.7|: NN/CF = −0.88, NN/NNF = −0.70, NN/FCF = −00.78, CF/FCF = 0.89, NN/FCF = 0.78. The final results are summarized together with the calculated values in Table 2 (geometric parameters) and Table 3 (vibrational amplitudes), and the molecular model is shown in Figure 1. Least squares refinements were performed also for the cis conformer of $CF_3N(O)NF$ (**1b**) and for the two conformers of the $CF_3NN(O)F$ isomer (**2a** and **2b**). Because some vibrational amplitudes converged toward highly unreasonable values in these refinements, all amplitudes were fixed at their calculated (MP2) values. The agreement factor for the intensities of the long nozzle-to-plate distance (R_{50}), which is more sensitive toward changes in the region of long nonbonded distances, increased from 3.6% for trans CF_3N-(O)NF to 12.8−14.9% for the three other structures. Thus, in the unlikely case that one of these structures should be present at all, its contribution must be less 10%.

Table 4. Skeletal Bond Lengths (Å) in $CF_3N(O)NF$ and in Fluorine and Trifluoromethyl Substituted Azo, Nitrosyl, and Nitryl Derivatives

	N=N	N=O	N−F	N−C
$CF_3N(O)NF$[a]	1.287(15)	1.231(6)	1.380(6)	1.498(6)
FN=NF (trans)[b]	1.231(20)		1.396(20)	
$CF_3N{=}NCF_3$ (trans)[c]	1.235(10)			1.460(6)
FN=O[d]		1.1316(3)	1.5166(3)	
$F_3N{=}O$[e]		1.158(4)	1.431(3)	
$CF_3N{=}O$[f]		1.198(4)		1.512(16)
FNO_2[g]		1.180(5)	1.467(15)	
CF_3NO_2[h]		1.217(4)		1.534(5)

[a] This work. [b] Reference 13. [c] Reference 14. [d] Reference 15. [e] Reference 16. [f] Reference 17. [g] Reference 18. [h] Reference 19.

Discussion

The azoxy compound investigated in this study exists as the $CF_3N(O)NF$ isomer, although quantum chemical calculations predict the $CF_3NN(O)F$ isomer to be lower in energy by about 12 kcal/mol. This result which is supported by various spectral observations, including mass, infrared, and nuclear magnetic resonance spectra,[8] can be rationalized by the synthetic route by which it was prepared (see Experimental Section). The use of the reactant CF_3NO, in which NO is already bonded to the CF_3 group, leads to the formation of the $CF_3N(O)NF$ isomer in the first step. Apparently, the activation energy for rearrangement to the energetically favored $CF_3NN(O)F$ isomer via a cyclic oxadiaziridine intermediate is too high to occur at temperatures even as high as 120 °C that were used in the synthesis of this compound (see later). Such activation energies for substituents (X, Y = H, CH_3, C_6H_5, F, and Cl) have been calculated to be about 70−80 kcal/mol.[10]

Considering experimental uncertainties and systematic differences between experimental geometric parameters, which are vibrationally averaged r_a values, and calculated equilibrium parameters (r_e values), all three quantum chemical methods reproduce the experimental structure satisfactorily, that is, within ±0.03 Å and ±3° (see Table 2). Table 4 compares skeletal bond lengths of $CF_3N(O)NF$ with those of azo, nitrosyl, and nitryl compounds, which possess fluorine and/or trifluoromethyl substituents. These bond lengths depend on the kind of substituents (F or CF_3) and on the type of nitrogen atom, that is, whether it forms three normal covalent bonds or whether it forms an additional dative bond to oxygen. However, no systematic trends between these bond lengths are observed. The N═N bond in the azoxy compound (1.287(15) Å) is longer by about 0.05 Å than that in the azo derivatives. The N═O bond (1.231(6) Å) is longer than those in nitrosyl and nitryl fluorides, and it is close to those in CF_3 substituted derivatives. The N—F bond in the azoxy compound (1.380(6) Å) is within experimental uncertainties equal to that in trans FN═NF, and it is considerably shorter than those in nitrosyl and nitryl fluorides. The N—C bond in $CF_3N(O)NF$ (1.498(6) Å) is intermediate between those in CF_3 substituted azo, nitrosyl, and nitryl compounds.

No structural parameters are known for other halogen or CF_3 substituted azoxy compounds. X-ray diffraction studies of some azoxyarenes, however, have been reported in the literature.[20] The mean N═N bond length in these compounds (1.268 ± 0.013 Å) is within uncertainties equal to that in $CF_3N(O)NF$ (1.287(15) Å), and the mean N═O bond length (1.265 ± 0.010 Å) is slightly longer than that in $CF_3N(O)$-NF (1.231(6) Å).

Experimental Section

$CF_3N(O)NF$ was synthesized by reacting CF_3NO with excess N_2F_4 in a Pyrex glass vessel at 120 °C for 12 h. It was initially separated by trap-to-trap distillation. The compound passes a trap at −78 °C and stops in a trap at −95 °C. Final purification was obtained by gas chromatography. The compound obtained with this method, which is a slight modification of that reported in ref 8, was identified as the $CF_3N(O)NF$ isomer on the basis of IR, ^{19}F NMR, and mass spectrometric data.[8]

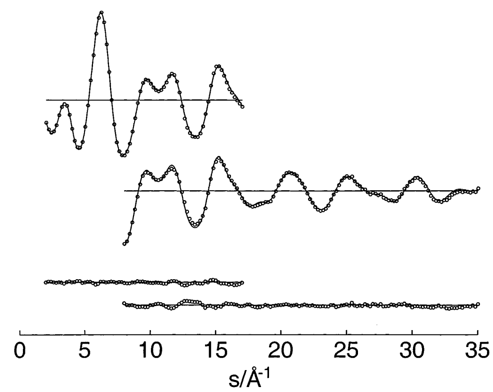

Figure 2. Averaged experimental (○) and calculated (—) molecular intensities for long (above) and short (below) nozzle-to-plate distances and residuals.

Electron diffraction intensities were recorded with a Gasdiffraktograph KD-G2[21] at 25 and 50 cm nozzle-to-plate distances and with an accelerating voltage of about 60 kV. The sample was cooled to −55 °C, and the inlet system and nozzle were at room temperature. The photographic plates were analyzed with the usual methods,[22] and averaged molecular intensities in the s-ranges 2−18 and 8−35 $Å^{-1}$ ($s = (4\pi/\lambda)\sin\vartheta/2$, λ = electron wavelength, ϑ = scattering angle) are shown in Figure 2.

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