Structure of *O*-Methyl-*N*,*N*-bis(trifluoromethyl)hydroxylamine, $(CF_3)_2NOCH_3$

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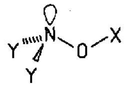
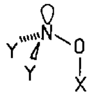
The molecular structure of $(CF_3)_2NOCH_3$ was determined by gas electron diffraction. The molecular intensities were reproduced by use of a single conformation with *syn* orientation of the $O-CH_3$ group relative to the nitrogen lone pair. This was confirmed by ab initio calculations (HF/3-21G$^{(*)}$, polarization functions only on nitrogen, and MP2/6-31G*). The observed structure demonstrates that the generalized anomeric effect is of minor importance to this compound. The following skeletal geometric parameters (bond lengths [pm] and angles [°] with 3-σ uncertainties) were derived: N−C 142.9(7), N−O 142(3), O−C 145(3), CNC 118.0(9), CNO 108.1(17), and NOC 109.4(17). The experimental structure is well reproduced by the ab initio calculations.

The conformational properties of hydroxylamine, NH_2OH, and substituted derivatives thereof have been the subject of several experimental[1−4] and theoretical studies[5−12]. The most interesting feature is the orientation of the O−X bond. Two different orientations are most likely, *syn* (synperiplanar) or *anti* (antiplanar) with respect to the nitrogen lone pair, lp(N). Weaker steric interactions between the substituents X and Y and reduced repulsion between the nitrogen and oxygen lone pairs favor the *syn* form. On the other hand, the generalized anomeric effect[11,13] which corresponds to an interaction between a lone pair and a vicinal antibonding orbital, lp→σ*, stabilizes the *anti* form. Reed and Schleyer[11] consider in their theoretical investigation only the lp(N)→σ*(O−X) interaction, but lp(O)→σ*(N−Y) interactions have to be taken into account as well.



syn



anti

Microwave spectroscopic studies of the parent compound NH_2OH[1] and of its *O*-methyl[2] and *N*-methyl[3] derivatives, NH_2OMe and MeNHOH, have demonstrated that the *syn* form predominates, but the presence of small amounts of another form cannot be excluded. The preference of the methyl-substituted hydroxylamines NH_2OMe, MeNHOH, MeNHOMe, and Me_2NOMe to adopt the *syn* conformation was confirmed by gas electron diffraction (GED) investigations[4]. According to these analyses ca. 30 and 20% of a second conformer, probably with *anti* orientation of the O−Me bond, are present in MeNHOMe and Me_2NOMe, respectively.

Ab initio calculations at various levels on hydroxylamine and substituted derivatives confirmed the existence of two minima of the torsional potential curve around the N−O bond for the *syn* [ϕ(lpNOX) = 0°] and *anti* [ϕ(lpNOX] = 180°) conformation[5−12]. In the parent compound the *syn* form was predicted to be more stable by 5.5 to 9.4 kcal mol^{-1} than the *anti* structure, depending on the basis set used in these calculations. The high-quality calculations (MP2/6-311G**) of Tyrrell et al.[12] cannot be used in this discussion. The orientation of the O−H bond is described by the dihedral angle Θ(HNOH), and the range considered in these calculations [0° ≤ Θ(HNOH) ≤ 180°] does not cover the entire conformational space. The *anti* form with Θ(HNOH) ca. −60 or 300° was omitted and only one minimum in the potential curve was observed. Ab initio calculations predict the *syn* form to be preferred also for the methyl-substituted derivatives NH_2OMe and MeNHOH by 7.0 and 6.7 kcal mol^{-1}, respectively[7], in accordance with the microwave spectroscopic results.

On the other hand, ab initio calculations suggest that fluorination at oxygen and/or nitrogen leads to a reversed conformational stability of *syn* and *anti* forms[9,11]. For NH_2OF, NF_2OH, and NF_2OF the *anti* forms were predicted to be lower in energy by 4.5, 2.0, and 5.6 kcal mol^{-1}, respectively, than the *syn* structures. This reversal of conformational stabilities can be explained by the anomeric effect, since fluorination leads to a strong increase of the lp(N)→σ*(O−X) and lp(O)→σ*(N−Y) interactions.

In the present study we report on a structural and conformational analysis of $(CF_3)_2NOCH_3$ using GED and ab initio calculations. Since the strength of the lp(N)→σ* ($O-CH_3$) and lp(O)→σ*($N-CF_3$) interactions is unknown, it is impossible to predict the conformational

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properties of this compound on the basis of the anomeric effect. Some spectroscopic data suggest the presence of a mixture of two conformations. In the IR (gas) and Raman (liquid) spectra four bands are observed in the region of the CH_3 stretching vibrations. Furthermore, the ^{1}H-NMR signal of the neat liquid at room temperature is split into two lines with an intensity ratio of 1:1.5. However, no splitting was observed for the ^{19}F, $^{13}CH_3$, or ^{14}N signals.

Ab initio Calculations

The geometric structure of the *syn* form was fully optimized with the HF/3-21G$^{(*)}$ [G$^{(*)}$ implies polarization functions on nitrogen only] and MP2/6-31G* methods. The structure of the *anti* conformer was optimized by means of the HF/3-21G$^{(*)}$ method only. Its energy was predicted to be 7.6 kcal mol^{-1} higher than that of the *syn* form. Due to close contacts between the CH_3 and CF_3 groups, the CNO and NOC bond angles increase by 7.2 and 6.8°, respectively, relative to those for the *syn* structure, whereas all other structural parameters are very similar for both conformations. The calculations were performed with the GAUSSIAN 92 program system[14]. The results of the *syn* structure are included in Table 1.

Table 1. Experimental and calculated geometric parameters for $(CF_3)_2NOCH_3$

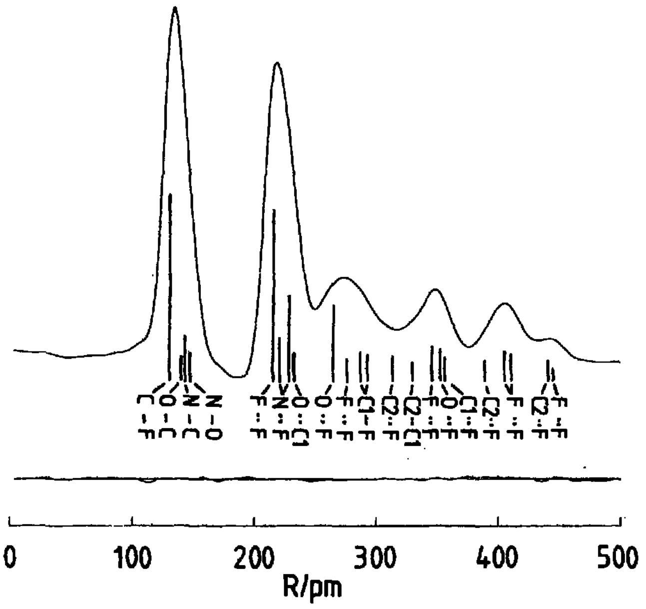
	GED [a]		HF/3-21G$^{(*)}$	MP2/6-31G*
C–F	132.4 (2)	p_1	133.8	134.1
N–C	142.9 (7)	p_2	141.2	144.0
N–O	142.4 (28)	p_3	143.1	142.2
O–C	145.0 (26)	p_4	146.7	143.9
C–H	110.0 [b]		107.7	109.1
C–N–C	118.0 (9)	p_5	117.6	116.7
C–N–O	108.1 (17)	p_6	106.9	106.5
N–O–C	109.4 (17)	p_7	109.5	107.9
F–C–F	108.3 (3)	p_8	108.3	108.5
H–C–H	110.0 [b]		111.2	110.5
tilt (CF_3)[c]	3.7 (8)	p_9	1.9	2.3
τ (CF_3) [d]	3.1 (34)	p_{10}	5.4	1.4

[a] Distances [pm] and angles [°], uncertainties are 3-σ values. – [b] Not refined. – [c] Tilt angle in the CNC plane between the C_3 axis of the CF_3 group and the N–C bond direction. The positive value corresponds to a tilt away from each other. – [d] Torsional angle of the CF_3 groups; for $\tau = 0$ the CF_3 groups stagger exactly the opposite N–C bond.

Structure Analysis

The radial distribution function (RDF) was calculated by a Fourier transformation of the molecular scattering intensities by using an artificial damping function $\exp(-\gamma s^2)$ with $\gamma = 19$ nm^2. The experimental curve (Figure 1) in the range $r > 250$ pm can be reproduced only with a molecular model with *syn* structure. Preliminary geometric parameters derived from the RDF were refined by least-squares fitting of the molecular intensities. The intensities were multiplied by a diagonal weight matrix, and known scattering amplitudes and phases were used[15]. Local C_{3v} symmetry was assumed for the CF_3 and CH_3 groups in accordance with the ab initio calculations which predict very small deviations (<1°) for the bond angles. The C–H bond length and HCH bond angle were not refined. For the CF_3 groups a tilt angle in the CNC plane between the C_3 axis and the N–C bond was introduced, and torsion around the N–C bonds in equal directions was allowed. Thus, C_s overall symmetry was assumed for this molecule, in agreement with the ab initio results. Vibrational amplitudes for closely spaced interatomic distances were refined in groups. Further constraints are evident from Table 2. As can be seen in Figure 1, the skeletal bond lengths N–C, N–O, and O–C are closely spaced. Whereas the N–C bond distance was reasonably well determined indirectly by the strong contributions of the C–F, F···F and N···F distances, the N–O and O–C bond lengths were badly determined by the GED experiment. These two bond distances are highly correlated with each other (–0.85, see Table 3) and with the respective vibrational amplitude a_2. Independent of the starting values for these two distances (N–O = O–C, N–O < O–C or N–O > O–C), least-squares refinements converged to the same result with the O–C bond longer than the N–O bond. The results of the least squares analysis are collected in Table 1 (geometric parameters p_i) and Table 2 (vibrational amplitudes a_k). Refinements of mixtures of *syn* and *anti* forms led to a significant increase of the agreement factors for *anti* contributions larger than 5%. Thereby the geometric parameters of the *anti* form were set equal to those of the *syn* structure, except for the CNO and NOC angles, for which the ab initio values were used.

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



Discussion

According to the GED analysis $(CF_3)_2NOCH_3$ occurs only in the *syn* conformation. This result is in agreement with the ab initio calculations which predict that the *anti*

Table 2. Interatomic distances and vibrational amplitudes (without distances involving hydrogen)[a]

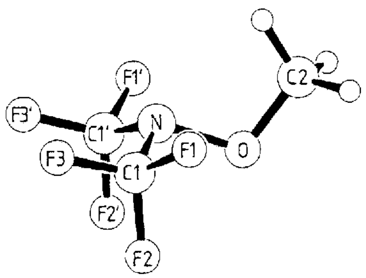
	distance	amplitude		distance	amplitude
C−F	132	4.2 (3) a_1	C1···F1'	287	11 (2) a_5
N−O	142	4.1 (13) a_2	C1···F3'	291	
N−C	143		C2···F1	314	12 (4) a_6
O−C	145		C1···C2	328	
F···F	215	5.4 (5) a_3	F2···F3'	3.45	11 (1) a_7
N···F	221-229		O···F3	3.52	
O···C1	231	6.0 [b]	C1···F1'	3.54	
N···C2	234		C2···F	3.89-4.39	9 (2) a_8
C1···C1'	244		F···F	4.04-4.09	
O···F1	263	13.2 (15) a_4	C2···F	4.39	15^b
O···F2	265		F1···F1'	4.41	
F···F	265-276				

[a] Values in pm, uncertainties are 3-σ values. For atom numbering see Figure 2. – [b] Not refined.

Table 3. Correlation coefficients (· 100) of least-squares analysis

p1	100																	
p2	-47	100																
p3	45	-12	100															
p4	-27	-29	-85	100														
p5	2	-40	34	-17	100													
p6	12	2	71	-74	52	100												
p7	-6	20	8	-31	43	21	100											
p8	63	-68	31	-3	32	9	-8	100										
p9	26	28	15	-29	-66	-18	-18	-35	100									
p10	-18	5	-68	65	-52	-91	-6	-18	18	100								
a1	38	-7	12	-33	2	21	28	18	16	-16	100							
a2	50	7	83	-92	19	69	26	22	28	-61	54	100						
a3	16	-5	12	-12	-25	-10	-17	-31	58	11	8	14	100					
a4	-23	-26	-52	63	-16	-52	-17	9	-30	60	-20	-58	-22	100				
a5	-6	-28	0	11	26	14	1	23	-38	-3	-4	-9	-26	57	100			
a6	4	-17	21	-15	28	32	3	22	-26	-28	3	15	-17	17	73	100		
a7	25	-3	58	-57	25	48	22	12	15	-35	19	56	10	-22	33	57	100	
a8	-9	2	-37	36	-38	-61	13	-16	20	79	-9	-34	13	44	-3	-24	-20	100

Figure 2. Molecular model for the *syn* conformer of $(CF_3)_2NOCH_3$ with atom numbering



form is higher in energy by 7.6 kcal mol^{-1}. This implies that steric interactions between the CF_3 and CH_3 groups and repulsion between the nitrogen and oxygen lone pairs which favor the *syn* form are much stronger than the anomeric effect due to $lp(N) \rightarrow \sigma^*(O-CH_3)$ and $lp(O) \rightarrow \sigma^*(N-CF_3)$ orbital interactions, which would stabilize the *anti* structure. As pointed out in the introduction, some spectroscopic data suggest the presence of a mixture of two conformers. The observation of four bands in the CH_3 stretching region of the IR (gas) spectrum, however, is perfectly compatible with the presence of a single conformer. Reduction of the local symmetry from C_{3v} to C_s leads to a splitting of the degenerate ν_{as} stretching vibrations (e) into a symmetric a' and an asymmetric a'' stretch. The two high-frequency bands [3022 (m) and 3005 (m) cm^{-1}] are assigned to these two stretching vibrations. A similar splitting of the asymmetric stretching vibrations was observed for other methoxy compounds. The band at 2961 (w) cm^{-1} which has a very strong analog in the Raman (liquid) spectrum [2969 (100%) cm^{-1}] corresponds to $\nu_s(a')$. The fourth band at 2838 (w) cm^{-1} is assigned to the overtone of the deformation $\delta(CH_3)$ at 1450 cm^{-1}. The splitting of the ^1H signal in the NMR spectrum of the neat liquid at room temperature with a ratio of 1:1.5 (the more intens line being rather broad) is not due to the presence of two conformers since a sharp singlet is observed for dilute solutions with CCl_4 or $(C_2H_5)_2O$ at room temperature and at −50°C. Thus, we suggest that the splitting of the ^1H signal of the neat liquid is due to intermolecular interactions in the liquid phase.

Because of large experimental uncertainties in the N−O [142(3) pm] and O−C [145(3) pm] distances, the GED analysis is not conclusive concerning the relative lengths of these bonds. Previous GED studies of methyl-substituted hydroxylamines reported N−O bond lengths between 146.3(3) pm in NH_2OMe and 151.1(9) pm in Me_2NOMe and O−C bond lengths between 135.0(6) pm in Me_2NOMe and 138.8(4) pm in NH_2OMe, i.e. in all cases N−O bonds are considerably longer than O−C bonds[4]. These two bond lengths in $(CH_3)_2NOCH_3$ differ drastically from those in $(CF_3)_2NOCH_3$. The N−O bond shortens from 151.3(9) to 142(3) pm and the O−C bond lengthens from 135.0(6) to 145(3) pm upon CH_3/CF_3 substitution. Short N−O bonds were reported also for two other $(CF_3)_2N$ derivatives, $(CF_3)_2NOH$ [140(3) pm[16]] and $(CF_3)_2NONO$ [141.0(15) pm[17]]. Unfortunately, the conformational properties of the former compound, i.e. the orientation of the O−H bond relative to the nitrogen lone pair, could not be determined in the GED study, because of the very weak contribution of hydrogen to the scattering intensities. In NONO the O−N bond is *syn* to the nitrogen lone pair. The ab initio calculations reproduce the experimental bond lengths and bond angles of $(CF_3)_2NOCH_3$ very well, i.e. within ±2 pm and ±2°, respectively. Both methods, HF/3-21G(*) and MP2/6-31G*, predict the N−O bond to be shorter than the O−C bond as suggested by the GED experiment. The geometric parameters obtained at the very different calculational levels do not differ strongly.

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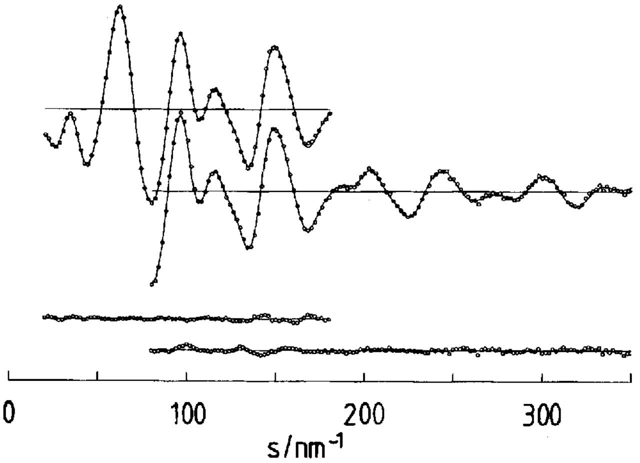
Experimental

O-Methyl-N,N-bis(trifluoromethyl)hydroxylamine, $(CF_3)_2NOCH_3$: *N,N*-Bis(trifluoromethyl)hydroxylamine, $(CF_3)_2NOH$, was synthesized by the reaction of trifluoronitrosomethane with ammonia[18]. The sodium salt was prepared by stirring 10 mmol of $(CF_3)_2NOH$, 10 mmol of NaOH, and 5 ml of THF in a 50-ml reaction vessel for 8 h. After THF had been pumped off and the sodium salt dried for 24 h in vacuo, a colorless, hygroscopic powder was obtained[19]. 10 mmol of $(CH_3O)_2SO_2$ was added, and the reaction mixture was stirred for 12 h at 50°C. At −50°C $(CF_3)_2NOCH_3$ was condensed into a trap at −196°C. The yield was 70%, and no further purification was needed. $(CF_3)_2NOCH_3$ is a colorless liquid with m.p. −120°C and b.p. 19°C.

Measurement of Molecular Intensities: A sample was transported at liquid nitrogen temp. to Tübingen. The GED intensities were recorded with a Gasdiffractograph[20] at 25- and 50-cm nozzle-to-plate distances and at an accelerating voltage of ca. 60 kV. The electron wavelength was calibrated with ZnO powder. The sample reservoir was cooled to −55 °C, and the inlet nozzle was at room temp. The photographic plates (Kodak Electron Image, 18 × 13 cm) were analyzed by the usual procedures[21] and averaged molecular intensities in the s ranges [$s = (4\pi/\lambda)\sin\Theta/2$, λ = electron wavelength, Θ = scattering angle] 20–180 and 40–350 nm^{-1} are shown in steps of $\Delta s = 2\ nm^{-1}$ in Figure 3.

Figure 3. Experimental (dots) and calculated (full line) molecular scattering intensities for long (above) and short (below) nozzle-to-plate distances, and differences



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