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N,*N*-Dimethylhydroxylamine: structural studies of the free molecule and of hydrogen-bonding in the solid state

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The structure of *N*,*N*-dimethylhydroxylamine 1 has been studied in the gas phase by electron diffraction, in the solid state by low-temperature X-ray crystallography and by *ab initio* methods. The analysis of the gas-phase data was carried out by the recently established method of applying flexible restraints (based on the results of *ab initio* calculations) to otherwise unrefinable parameters and shows the advantage of this method in comparison with conventional gas-phase structure analysis. The structural parameters of the free molecule (gas phase) are compared with those of the chain aggregates, which 1 forms in the crystal by N · · · H–O hydrogen bonding [the intermolecular NO distance is 2.777(4) Å]. The core of 1 has been found to be affected little by the formation of hydrogen bonds. Important structural parameter values were found to be [gas phase (r_α, $<_\alpha$), crystal structure (values for one of the two independent molecules)]: *r*(NO) 1.448(11), 1.452(2) Å; *r*(NC) 1.463(7), 1.446(4) and 1.448(4) Å; <(CNO) 106.4(4), 106.5(2) and 104.8(2)°; <(CNC) 110.4(15), 110.5(2)°.

Introduction

In contrast to the well established preparative organic chemistry of hydroxylamines[1] and their industrial importance (*e.g.* in the caprolactam process[2]), the structural chemistry of simple hydroxylamines is only sparingly developed. In early work of Meyers and Lipscomb,[3] the crystal structure of hydroxylamine, H_2NOH, was elucidated, but the hydrogen positions could not be resolved at this time. The determination of the structures of methylated hydroxylamines in the gas phase was undertaken some years ago in our laboratories, but some doubt remained about the precise values of the NO and NC bond lengths in these molecules.[3,4] With increasing applicability of sophisticated theoretical methods in the last decade, it became possible to obtain highly reliable predictions for the geometries of most small molecules and in a contribution published in 1992 by Gange and Kallel[5] substantial deviations of the calculated values from those obtained experimentally were reported. The only methylated hydroxylamine which has not been studied experimentally so far is *N*,*N*-dimethylhydroxylamine **1**. Our recent interest in metal and metalloid hydroxylamides[6] led us to study the free molecules in the gas phase and the solid state for comparison and allows us now to shed new light on the structural chemistry of these fundamentally important compounds.

Experimental

A sample of *N*,*N*-dimethylhydroxylamine was prepared by condensing an excess of dry ammonia onto *N*,*N*-dimethylhydroxylamine hydrochloride, stirring the mixture at the boiling temperature for 2 h, evaporating the ammonia and extracting the residue with diethyl ether. The solution was then distilled to yield ether and free *N*,*N*-dimethylhydroxylamine.

Electron diffraction

Electron scattering intensity data for **1** were recorded on Kodak Electron Image plates using the Edinburgh gas diffraction apparatus.[7] The sample of **1** and the inlet nozzle were held at ambient temperature (293 K) during the experiments. Scattering data for benzene were recorded concurrently and used to calibrate the camera distance and electron wavelength, which were 285.96 mm and 0.056 71 Å for the long camera distance and 128.21 mm and 0.056 71 Å for the short camera distance, respectively. Three plates were taken at each camera distance. Data were obtained in digital form using the Joyce Loebl MDM6 microdensitometer[8] at the EPSRC Daresbury Laboratory. The data analysis followed standard procedures, using established data reduction[8] and least-squares refinement programs[9] and the scattering factors established by Fink and co-workers.[10] The following data ranges, intervals and weighting points (trapezoidal weighting function) were used in the refinement: $s_{min} = 2.0$, $s_{max} = 14.4$, $\Delta s = 0.2$, $sw_1 = 4.0$, $sw_2 = 12.2$ Å^{-1} for the long camera data; $s_{min} = 6.0$, $s_{max} = 34.0$, $\Delta s = 0.4$, $sw_2 = 8.0$, $sw_2 = 29.2$ Å^{-1} for the short camera data. The scale factors refined to 0.765(4) and 0.832(11) and the correlation parameters were 0.4227 and 0.2667 for long and short camera data, respectively.

Crystal structure determination

A cylindrical crystal (>0.8 mm long, 0.5 mm diameter) was grown from the pure liquid in a capillary mounted on a Stoe Stadi-4 diffractometer with an Oxford Cryosystems low-temperature device.[11] After growing a seed crystal, the sample was cooled from 286.0 to 280.0 K at a rate of 10 K h^{-1}. C_2H_7NO: $M_r = 61.09$, orthorhombic, space group *Pbca*, $a = 9.924(2)$, $b = 14.399(3)$, $c = 10.422(3)$ Å, $V = 1489.3(6)$ Å, $Z = 16$, $\rho_{calc} = 1.090$ Mg m^{-3}, $2\theta_{max} = 50.0°$; Mo-Kα radiation, $\lambda = 0.710\,73$ Å, $T = 140.0$ K; 2325 reflections, 1317 independent, $R_{int} = 0.064$; no absorption correction. The structure was solved for all non-H atoms by direct methods[12] and refined against F^2.[13] Hydrogen atoms were located in difference Fourier maps and refined freely with isotropic thermal parameters, while non-H atoms were refined with anisotropic displacement parameters. The refinement converged to a conventional *R* of 5.0% [based on *F* and 1305 data with $F > 4\sigma(F)$] and wR_2 of 12.2% (based on F^2 and 1305 unique data) for 130 parameters. The extrema of electron density in the final difference Fourier maps were +0.25 and −0.20 e Å^{-3}, final weighting scheme: $w = [\sigma^2(F_o^2) + (0.0224\,P)^2 + 1.2397\,P]^{-1}$, where $P = (F_o^2 + 2\,F_c^2)/3$.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). For details of the deposition scheme, see 'Instructions for Authors', *J. Chem. Soc., Perkin Trans. 2*, 1996, Issue 1. Any request to the CCDC for this

Table 1 Calculated molecular geometries of **1** (in Å and °)

	SCF			MP2			QCISD
	3-21G*	6-31G*	6-311G**	6-31G*	6-31+G*	6-311G**	6-31G*
NO	1.467	1.406	1.400	1.458	1.461	1.442	1.454
NC	1.472	1.447	1.447	1.459	1.461	1.458	1.463
OH	0.968	0.947	0.940	0.994	0.976	0.960	0.972
CH[a]	1.082	1.085	1.086	1.086	1.095	1.095	1.097
CNO	105.0	106.6	106.9	104.8	105.1	105.4	105.0
CNC	112.9	112.5	112.4	110.8	111.0	110.3	110.9
NCH[a]	109.5	110.0	110.0	109.7	109.2	110.0	109.7
NOH	104.0	104.5	104.9	101.3	102.1	101.5	102.0
Δ(NO–NC)	−0.005	−0.041	−0.047	−0.001	0.000	−0.016	−0.009

[a] Average value.

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***Ab initio* calculations**

All *ab initio* molecular orbital calculations were performed on a DEC Alpha APX 1000 computer using the GAUSSIAN92 program.[14] Geometry optimisations on *N*,*N*-dimethylhydroxylamine were performed at the SCF level of theory using the standard 3-21G*,[15–17] 6-31G*[18–20] and 6-311G**[21–22] basis sets, while the two larger basis sets were used for optimisations at the MP2 level of theory. Estimates of the effects of a more sophisticated treatment of electron correlation on the molecular geometry were obtained by performing a geometry optimisation at the 6-31G*/QCISD level, while the addition of diffuse functions was investigated at the 6-31+G*/MP2 level.

Force fields were obtained from analytic second derivatives using the 3-21G* (SCF) and 6-31G* (SCF and MP2) basis sets and were used to obtain estimates of vibrational amplitudes to be used in the GED refinement.

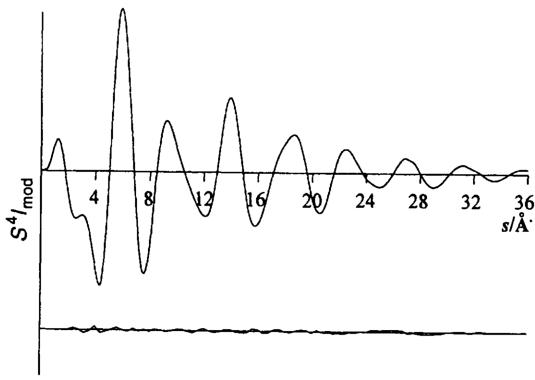

Fig. 1 Observed and final weighted difference combined molecular-scattering intensity curves for the GED study of **1**. Theoretical data are shown for the region 0–2 Å^{-1}, for which no experimental data are available.

Results

Two possible structures based on C_s symmetry can be envisaged for *N*,*N*-dimethylhydroxylamine, with the hydroxy hydrogen atom being either *cis* or *trans* with respect to the nitrogen lone pair of electrons. Since earlier *ab initio* calculations[5] performed at the 6-31G*/MP2 level predicted that the *cis* isomer lies 11.8 kJ mol^{-1} above the *trans* isomer, only the *trans* arrangement was considered for further theoretical investigations. Vibrational frequency calculations show that the *trans* structure is a local minimum on the potential energy surface.

A carefully graded series of calculations (see Table 1) was performed to obtain reliable structural information for comparison with experiment and to supplement the electron diffraction data in the refinement.[23,24] In general, both bond lengths and angles proved to be rather insensitive to improvements in either the basis set or theoretical method, the N–O and O–H bond lengths being notable exceptions. SCF estimates of the N–O distances were close to 1.40 Å, except when the smallest of the basis sets (3-21G*) was used, while the inclusion of electron correlation led to substantially longer bonds. Substantial reported differences between calculated and experimentally obtained data led us to perform calculations with the level of correlation improved from MP2 to QCISD and to explore the effect of diffuse functions. Both these improvements resulted in only minor changes in bond lengths and angles, which were always found to be less than 0.005 Å or 0.7°, and so contribute to the confidence in these data (see Table 1).

Gas phase structure

Refinements based on electron diffraction data alone. *N*,*N*-Dimethylhydroxylamine was assumed to have C_s symmetry. Ten independent geometrical parameters were used to define the structure. These were: the weighted average *r*(NC/NO) distance, the difference between *r*(NC) and *r*(NO), *r*(CH), the difference between *r*(CH) and *r*(OH), the angles <(CNC), <(CNO), <(NOH), the average of the three non-symmetry-equivalent <(NCH), the twist angle $\tau(CH_3)$ (defining a twist about the CN bond) and the angle $\delta(CH_3)$, which allowed tilting of both CH_3 groups. This parameter was introduced to break the local C_{3v} symmetry of the NCH_3 groups and was defined as the angle between the local C_3 axis of a CH_3 group and the adjacent N–C bond, with the C_3 axis remaining in the CNC plane. A positive tilt angle represented displacement of the CH_3 groups away from one another.

An additional parameter was used to define the orientation of the OH group relative to the bisector of the CNC angle, giving the *cis* and *trans* conformers of the hydroxylamine skeleton. It could be shown in subsequent refinements that the *trans* conformer is undoubtedly predominant, which is also consistent with the results of earlier *ab initio* calculations. The calculated energy difference[5] between *cis* and the more stable *trans* conformer of 11.8 kJ mol^{-1} corresponds to less than 0.8% *cis* conformer at ambient temperature, at which the diffraction experiment was performed. Consequently the refinements were carried out neglecting the influence of this conformer.

Cartesian force constants were derived from force field calculations at the 6-31G*/MP2 level and converted to internal coordinates and scaled by common factors using the program ASYM40.[25] These calculated vibrational amplitudes and perpendicular amplitude corrections (*K*) were used throughout unless refinement of amplitudes was possible, and were also used to derive ratios for tying amplitudes as indicated in Table 2.

Fig. 1 shows the combined molecular intensity curve obtained by merging the two experimental data sets. This was Fourier transformed to give the radial distribution curve given in Fig. 2, which shows three prominent resolved peaks originat-

Table 2 Interatomic distances (r_a) and amplitudes of vibration (u) (restrained refinement)

Atoms	Distance/Å	Amplitude/Å	
d_1 N(1)–C(2)	1.452(7)	0.057(1)	
d_2 N(1)–O(10)	1.448(11)	0.059	tied to u_1
d_3 C(2)···O(10)	2.333(6)	0.081(6)	
d_4 C(2)···C(6)	2.401(24)	0.065	tied to u_3
d_5 C(2)···H(3)	1.135(6)	0.090(4)	
d_6 O(10)···H(11)	1.065(26)	0.082	tied to u_5
d_7 N(1)···H(3)	2.127(10)	0.099(6)	
d_8 N(1)···H(4)	2.082(15)	0.097	tied to u_7
d_9 N(1)···H(11)	1.946(23)	0.101	fixed
d_{10} C(2)···H(11)	2.948(21)	0.156	fixed
d_{11} O(10)···H(3)	2.704(16)	0.112(13)	
d_{12} O(10)···H(4)	2.413(21)	0.169	fixed
d_{13} O(10)···H(5)	3.241(15)	0.389(49)	
d_{14} C(2)···H(7)	3.329(22)	0.394	tied to u_{13}
d_{15} C(2)···H(8)	2.684(15)	0.108	tied to u_{11}
d_{16} C(2)···H(9)	2.527(27)	0.107	tied to u_{11}
d_{17} H(3)···H(4)	1.877(13)	0.103	fixed
d_{18} H(3)···H(7)	4.211(23)	0.134	fixed
d_{19} H(3)···H(8)	3.720(13)	0.138	fixed
d_{20} H(3)···H(9)	3.522(29)	0.138	fixed
d_{21} H(4)···H(7)	3.717(13)	0.166	fixed
d_{22} H(4)···H(8)	2.452(31)	0.267	fixed
d_{23} H(4)···H(9)	2.958(21)	0.134	fixed
d_{24} H(5)···H(7)	3.508(29)	0.261	fixed
d_{25} H(5)···H(8)	2.947(21)	0.219	fixed
d_{26} H(5)···H(9)	2.010(47)	0.530	fixed
d_{27} H(11)···H(3)	3.026(26)	0.236	fixed
d_{28} H(11)···H(4)	3.361(28)	0.198	fixed
d_{29} H(11)···H(5)	3.862(27)	0.167	fixed

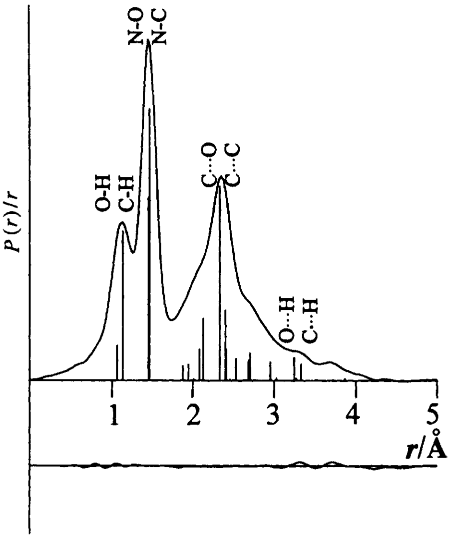

Fig. 2 Observed and final weighted difference radial distribution curves for **1**. Before Fourier inversion the data were multiplied by $s \cdot \exp[(-0.002\,s^2)/(Z_N-f_N)/(Z_C-f_C)]$.

ing from the contributions of O–H and C–H bonded distances, N–O and N–C bonded distances and a broad feature covering many smaller contributions and the C···O and C···C non-bonded distances.

Table 3 shows the structural parameter values of **1** for two types of refinement. The first set was obtained by refining as many parameters as possible, while keeping other parameters, which led to unstable refinements, fixed at values calculated at the highest level employed (6-31G**/MP2). Fixed parameters are p_4, p_7, p_8 and p_{10}, which all define hydrogen positions. All refined amplitudes gave reasonable values apart from those associated with the three-bond C···O and C···C distances appearing in the radial distribution curve as contributions at 3.31 and 3.34 Å. These refined (as a single parameter) to about four times the calculated value, but were nevertheless finally allowed to refine freely, as they give rise to a too high angle <(CNC) and a poor fit to the experimental intensities if fixed at their calculated value.

The difference between r(NO) and r(NC) refined to a value of 0.058(11) Å, and led to values of the dependent parameters r(NO) and r(NC) of 1.492(8) and 1.434(4) Å, respectively. These values differ substantially from the calculated ones (1.442 and 1.458 Å), but are close to those determined by electron diffraction for trimethylhydroxylamine in the gas phase, which are 1.513(9) and 1.442(5) Å, respectively. Since calculated values were shown to be almost converged with respect to improving both basis set and level of theory, a discrepancy of 0.05 Å is unsatisfactory. We therefore wished to improve the quality of our refinement further by reducing the number of assumptions.

Refinements based on electron diffraction data with restraints derived from *ab initio* calculations

We have recently shown that gas-phase electron-diffraction results can be improved in quality by the SARACEN procedure,[23,24] in which all important geometrical parameters are refined and flexible restraints based on the results of *ab initio* calculations are used to make this possible. In addition to the refinement described above, we carried out such a flexibly restrained refinement. The results are shown in Table 3 together with the restraints which were applied and their assigned uncertainties. The most important restraint in the refinement is that on the difference between the NO and NC distances, which was restrained to the *ab initio* calculated difference of −0.016 Å with an uncertainty of 0.020 Å. The value −0.016 Å is derived from our highest level calculation. Taking only electron correlated calculations into account, Table 1 shows that both improvements of the basis set and the treatment of electron correlation leads to an increase of the difference between the NO and NC distances and explains why we have chosen the MP2/6-311G** value despite it being an extreme among these predictions. The assigned uncertainty of 0.020 Å (which determines the weight given to this observation in the refinement) corresponds to our estimate of the reliability of the calculated value; it has deliberately been chosen to be rather large in order to avoid too pronounced an influence of non-GED data and to reflect the fact that the calculations have still not completely converged with respect to the level of theory. The difference between the values obtained at the MP2/6-31G* and MP2/6-311G** levels of theory, which is 0.016 Å, provides us with a rough guess of what differences further improvements in the level of theory might cause and thus 0.020 Å seems to be a realistic uncertainty.

For the other restraints the uncertainties were chosen to allow for the fact that these restrained parameters are absolute distances and angles (except p_4) and therefore less reliably predicted than differences of values. The angle NOH was assigned the highest uncertainty, as its calculated values are probably the most uncertain because of the important contribution of electron correlation on the NO skeleton.

This restrained refinement converged at a lower R_g value of 4.88% than the rigidly constrained refinement (5.62%), corresponding to a better fit to the experimental data. The dependent distances r(NO) and r(NC) refined to 1.448(11) and 1.463(7) Å, which is in excellent agreement with the other experimental and theoretical data (Table 4). Note that the order of the distances has been inverted by this procedure; this shows how even a gentle restraint can have an important and beneficial influence on the outcome of the refinement. The higher esds reflect the real uncertainties of these highly correlated parameters much better than in the first refinement.

Other parameters for which there is sufficient information contained in the experimental data have improved esds, *e.g.* the CNO angle or the twist angle of the CH_3 groups. The esds of the distances CH and OH, which were unreliably low in the first

Table 3 Geometrical parameters $r_a/\angle_a$(Å/°) and flexible restraints

Parameter		Without restraint	With restraint	Restraint (uncertainty)
Independent				
p_1	r(NC/NO-mean)	1.453(1)	1.458(1)	
p_2	Δr(NO/NC)	0.058(11)	0.014(17)	−0.016(20)
p_3	r(CH)	1.122(2)	1.116(6)	
p_4	Δr(CH/OH)	−0.135 fixed	−0.105(31)	−0.135(40)
p_5	$\angle$(CNC)	112.2(17)	110.4(15)	
p_6	$\angle$(CNO)	106.4(7)	106.7(3)	
p_7	$\angle$(NOH)	101.5 fixed	101.4(15)	101.5(20)
p_8	$\angle$(NCH)	110.0 fixed	107.4(7)	110.0(15)
p_9	τ(CH_3)	1.4(98)	9.3(13)	
p_{10}	δ(CH_3)	−2.2 fixed	−2.3(12)	−2.2(15)
Dependent				
p_{11}	r(NO)	1.492(8)	1.448(11)	
p_{12}	r(NC)	1.434(4)	1.463(7)	
p_{13}	r(OH)	0.987(2)	1.011(25)	
R_g-values		5.62%	4.88%	

Table 4 Structural parameters of **1** obtained by gas phase electron diffraction (ED, restrained refinement), single-crystal X-ray diffraction (XRD) and *ab initio* calculations (distances in Å, angles in °, estimated standard deviations in parentheses)

	GED	XRD		MP2/6-311G**
	$r_a/\angle_a$	$r_{\mathrm{Mol.1}}$	$r_{\mathrm{Mol.2}}$	r_e
r(NO)	1.448(11)	1.452(2)	1.451(2)	1.442
r(NC)	1.463(7)	1.446(4) 1.448(4)	1.452(3) 1.455(3)	1.458
r(CH)	1.116(6)	0.96–1.02(3)[a]	0.95–1.05(3)[a]	1.091–1.101[b]
r(OH)	1.011(25)	0.86(3)	0.81(3)	0.960
$\angle$(CNC)	110.4(15)	110.5(2)	110.6(2)	110.3
$\angle$(CNO)	106.7(4)	106.5(2) 104.8(2)	105.7(2) 104.1(2)	105.4
$\angle$(NCH)	107.4(7)	107–112(2)[a]	107–112(2)[a]	108.3–111.8[b]
$\angle$(NOH)	101.1(15)	101(2)	103(2)	101.5

[a] Range of values with highest esd of one single parameter. [b] Range of values.

Table 5 Correlation matrix (×100) for the restrained GED refinement of **1**. Only elements with absolute values greater than 50 are shown

	p_2	p_4	p_6	p_9	p_{10}	u_1	u_3	u_5	u_7	u_{11}
p_1	−90					−69				
p_2						−77				
p_3		−96						−90		
p_4								−93		
p_5			−92	−56	−77		−85			
p_6				62	68		80			
p_8					62		64		54	
p_9								53		−78
p_{10}							58			
u_3									60	

refinement, are also more realistic and reflect the strong correlation between these parameters (see correlation matrix in Table 5). The amplitudes of vibration for the three-bond O⋯H and C⋯H distances at 3.241 and 3.329 Å are again unexpectedly large in this refinement. The values of these amplitudes [0.39(5) Å] differ markedly from their calculated magnitudes (0.097 and 0.098 Å), although there is a large esd associated with the experimental value.

In order to gauge the effect of different uncertainties assigned to the restraint on the difference between the distances r(NO) and r(NC), we carried out further refinements, two of which must be mentioned. In the first of these, the uncertainty was set to half the original value (0.010 Å); this led to virtually no changes in the parameter values, but to a decrease of the uncertainties of the distances r(NO) and r(NC), which then seemed to be unrealistically small [r(NO) 1.448(6) Å and r(NC) 1.463(4) Å]. In the second refinement we removed the restraint; this led to only slight changes in the parameter values, but to uncertainties more than twice as large as if the restraint was −0.016(20) Å [r(NO) 1.454(25) Å and r(NC) 1.459(16) Å]. The weight given to this restraint is, of course, critical in determining the final esds of parameters which depend on it. Although this weight is necessarily to some extent subjective, with care a realistic value can be assigned. The outcome is then standard deviations which reflect our total knowledge, experimental and theoretical, about the structure. The alternative to the SARACEN method is to fix the parameter at the calculated value, in which case the esds are much too small.

Crystal structure

After numerous attempts to transfer long needle-shaped crystals of **1**, which grow by sublimation in closed vessels at temperatures between 0 and 15 °C, we were finally successful in acquiring a crystallographic data set after growing a crystal by

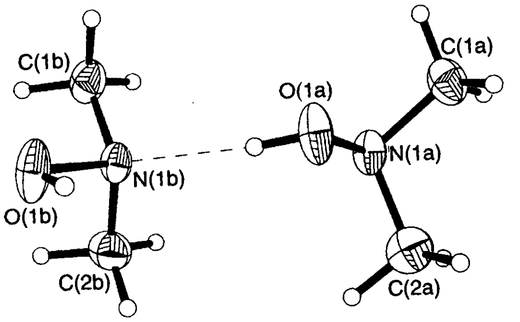

Fig. 3 The two independent molecules of **1** in the asymmetric unit of the crystal showing the intermolecular OH · · · N hydrogen bond. Non-hydrogen atoms are plotted as thermal ellipsoids at the 50% probability level and the hydrogen atoms are shown as circles of arbitrary size.

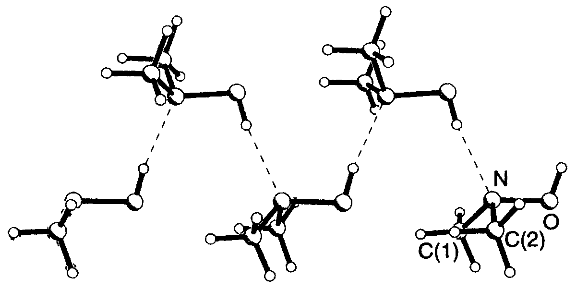

Fig. 4 The packing of molecules of **1** in the crystal showing the chain-like aggregation by hydrogen bonding

using *in situ* methods with the compound sealed in a capillary. The structure solution showed two independent molecules of **1** to be present in the asymmetric unit (see Fig. 3). They form infinite zig-zag chains by hydrogen bonding between the OH function of one molecule and the N atom of another (see Fig. 4). This simple head-to-tail linkage is analogous to the hydrogen bonding which was found in crystals of 1-[3-(*N*-*tert*-butylhydroxyamino)-4-chlorophenyl]buta-1,3-diyne.[26] In *N*,*N*-dibenzylhydroxylamine,[27] a diphenyl derivative of **1**, the molecules are arranged as dimers with $N_2O_2H_2$ rings. As there are no other prominent intermolecular interactions we cannot offer a simple explanation for the differences in hydrogen bonding behaviour, which probably depend on the multitude of interactions which determine crystal packing.

The intermolecular NO distances in the NHO units are 2.777(4) Å, a value which is typical for this type of hydrogen bond.[26,27] The angles N(1a)–O(1a) · · · N(1b) and N(1b)–O(1b) · · · N(1a) are 106.9(2) and 109.0(2)°, respectively, showing the geometry at the oxygen atoms to be nearly undistorted. The angles O(1a)–N(1a) · · · O(1b) and O(1b)–N(1b) · · · O(1a) are 114.2(2) and 115.5(2)°.

The CNO and CNC angles have very similar values in the gas phase and crystal structures. This indicates that the nitrogen lone pair, which is involved in hydrogen bonding, is as sterically demanding as in the free molecule. However, because X-ray diffraction detects the centres of electron density rather than the nuclear positions (as electron diffraction does), the oxygen and nitrogen position determined in the crystal are displaced away from the nucleus towards the lone pairs of electrons. This could lead to an overestimation of the steepness of the ONC_2 pyramid in the solid state, but is probably not significant: the magnitude of this nitrogen displacement for trimethylamine is very small as has been shown by the determination of its structure by X-ray diffraction in the crystal [CNC angle 110.40(7)°] and electron diffraction in the gas phase [110.6(6)°].[28]

The differences between the values of the two angles CNO in one molecule of **1** in the crystal is similar in both independent molecules (1.7 and 1.6°), and the average of all four values is 105.3°, which is close to the gas phase value of 106.7(4)°. The calculated CNO angle (105.4°) is in excellent agreement with the experimental data. The CNC angles determined in the crystal (average 110.6°), the gas phase [110.4(15)°] and calculated (110.3°) fall within a narrow range, although the gas phase value has a relatively large esd.

The bond distances in the non-hydrogen atom skeletons of both independent molecules of **1** show the complexity of the question: which are longer, the NO or the NC bonds? Within the experimental errors, the parameter values are indistinguishable. The distances NO and NC are very similar to those determined in the gas phase, although the latter were restrained by the computed difference. This also shows that these values are not detectably affected by involving the nitrogen atom in hydrogen bonding.

Conclusions

We have shown that the elucidation of the structure of such a simple molecule as *N*,*N*-dimethylhydroxylamine **1** can be a problem if great care is not taken in the interpretation of experimental results. Combining the advantages of theoretical calculations, crystallographic and gas phase electron-diffraction data leads to the most reliable structural parameter values in this case. The new SARACEN method of flexibly restraining the analysis of gas phase data turned out to be essential in this case to get an accurate structure for the free molecule. The structural results show that the N–O and N–C bonds in **1** have comparable lengths in the solid state and in the gas phase. Aggregation with the formation of OH · · · N hydrogen bonds does not lead to substantial changes in the structure of the C_2NO core in **1**.

Comparison with earlier gas phase structure elucidations of related methylated hydroxylamines suggests that these structures need reinvestigation.

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References

1 B. Zeeh and H. Metzger, *Hydroxylamine* in *Methoden der organischen Chemie* (*Houben-Weyl*), Thieme-Verlag, Stuttgart, 1971, Bd. X/1.
2 G. Zinner, *Chemiker-Ztg.*, 1990, **114**, 197.
3 E. A. Meyers and W. N. Lipscomb, *Acta Crystallogr.*, 1955, **8**, 583.
4 (*a*) F. G. Riddell, E. S. Turner, D. W. H. Rankin and M. R. Todd, *J. Chem. Soc., Chem. Commun.*, 1979, 72; (*b*) D. W. H. Rankin, M. R. Todd, F. G. Riddell and E. S. Turner, *J. Mol. Struct.*, 1981, **71**, 171.
5 D. M. Gange and E. A. Kallel, *J. Chem. Soc., Chem. Commun.*, 1992, 824.
6 (*a*) N. W. Mitzel, S. Parsons, A. J. Blake and D. W. H. Rankin, *J. Chem. Soc., Dalton. Trans.*, 1996, 2089; (*b*) N. W. Mitzel, M. Hofmann, E. Waterstradt, P. v. R. Schleyer and H. Schmidbaur, *J. Chem. Soc., Dalton Trans.*, 1994, 2503.
7 C. M. Huntley, G. S. Laurenson and D. W. H. Rankin, *J. Chem. Soc., Dalton Trans.*, 1980, 954.
8 S. Cradock, J. Koprowski and D. W. H. Rankin, *J. Mol. Struct.*, 1981, **77**, 113.
9 A. S. F. Boyd, G. S. Laurenson and D. W. H. Rankin, *J. Mol. Struct.*, 1981, **71**, 217.
10 A. W. Ross, M. Fink and R. Hilderbrandt, *International Tables for X-Ray Crystallography*, ed. A. J. C. Wilson, Kluwer Academic Publishers, Dodrecht, Boston, 1992, vol. C., p. 245.
11 J. Cosier and A. M. Glazer, *J. Appl. Cryst.*, 1986, **19**, 105.
12 A. Altomare, G. Cascarano, C. Giacovazzo and A. Guagliardi, *J. Appl. Cryst.*, 1993, **26**, 343.

13 G. M. Sheldrick, SHELXL-93, Universität Göttingen, 1993.
14 GAUSSIAN 92, Revision F.4; M. J. Frisch, G. W. Trucks. M. Head-Gordon, P. M. W. Gill, M. W. Wong, J. B. Foresman, B. G. Johnson, H. B. Schlegel, M. A. Robb, E. S. Replogle, R. Gomperts, J. L. Andres, K. Raghavachari, J. S. Binkley, C. Gonzalez. R. L. Martin, D. J. Fox, D. J. Defrees, J. Baker, J. J. P. Stewart and J. A. Pople, Gaussian, Inc., Pitsburgh. PA, 1992.
15 J. S. Binkley, J. A. Pople and W. J. Hehre, *J. Am. Chem. Soc.*, 1980, **102**, 939.
16 M. S. Gordon, J. S. Binkley, J. A. Pople, W. J. Pietro and W. J. Hehre, *J. Am. Chem. Soc.*, 1982, **104**, 2797.
17 W. J. Pietro, M. M. Francl, W. J. Hehre, D. J. Defrees, J. A. Pople and J. S. Binkley, *J. Am. Chem. Soc.*, 1982, **104**, 5039.
18 W. J. Hehre, R. Ditchfield and J. A. Pople, *J. Chem. Phys.*, 1972, **56** 2257.
19 P. C. Hariharan and J. A. Pople, *Theor. Chim. Acta*, 1973, **28**, 213.
20 M. S. Gordon, *Chem. Phys. Lett.*, 1980, **76**, 163.
21 R. Krishnan, J. S. Binkley, R. Seeger and J. A. Pople, *J. Chem. Phys.*, 1980, **72**, 650.
22 A. D. McLean and G. S. Chandler, *J. Chem. Phys.*, 1980, **72**, 5639.
23 A. J. Blake, P. T. Brain, H. McNab, J. Miller, C. A. Morrison, S. Parsons, D. W. H. Rankin, H. E. Robertson and B. A. Smart, *J. Phys. Chem.*, 1996, **100**, 9339.
24 N. W. Mitzel, B. A. Smart, A. J. Blake, H. E. Robertson and D. W. H. Rankin, *J. Phys. Chem.*, 1996, **100**, 12 280.
25 L. Hedberg and I. M. Mills, *ASYM20*, *ASYM40*, *Programs for Force Constants and Normal Coordinate Analysis*, Version 3.0, June 1994; see also L. Hedberg and I. M. Mills, *J. Mol. Spectrosc.*, 1993, **160**, 117.
26 K. Inoue, N. Koga and H. Iwamura, *J. Am. Chem. Soc.*, 1991, **113**, 9803.
27 N. W. Mitzel, K. Angermaier and H. Schmidbaur, *Z. Naturforsch.*, *Teil B*, 1995, **50**, 699.
28 A. J. Blake, E. A. V. Ebsworth and A. J. Welch, *Acta Crystallogr.*, *Sect. C*, 1984, **40**, 413.

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