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The crystal and liquid structures of *N*,*N*-dimethylthioformamide and *N*,*N*-dimethylformamide showing a stronger hydrogen bonding effect for C–H · · · S than for C–H · · · O†

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The crystal structures of *N*,*N*-dimethylthioformamide and *N*,*N*-dimethylformamide were determined at 90 ± 2 K from single crystal X-ray diffraction data. Both compounds comprise planar molecules, a consequence of the π-electron delocalization over the N–C–S and N–C–O entities, respectively. In *N*,*N*-dimethylthioformamide, almost linear, 175.4(7)°, C–H · · · S cooperative hydrogen bonding between the thioformyl groups connects the molecules in helix-shaped chains with an intermolecular C · · · S distance of 378.10(7) pm. The two crystallographically independent molecules in *N*,*N*-dimethylformamide form four-membered centrosymmetric rings held together by C–H · · · O intermolecular interactions, two *via* the formyl protons, C · · · O 329.41(9) pm, and two involving methyl protons, C · · · O 341.41(9) pm. The structures of both liquids were studied at room temperature by large angle X-ray scattering in transmission mode and for *N*,*N*-dimethylthioformamide also in reflection geometry. The structure of liquid *N*,*N*-dimethylformamide can, despite the stronger hydrogen bond *acceptor* properties of the oxygen atom, be described without hydrogen bonding. This apparent anomaly with more significant effect of hydrogen bonding in both crystal and liquid forms of *N*,*N*-dimethylthioformamide than *N*,*N*-dimethylformamide is discussed using results from theoretical calculations on single molecules. Mulliken population analyses indicate a lower positive charge and thus weaker hydrogen-bond *donor* properties of the formyl than of the thioformyl hydrogen atom. Raman and infrared spectra of the solids and the liquids are used for discussions of the hydrogen bonding effects.

Introduction

The similarity between the molecular structures of *N*,*N*-dimethylthioformamide and its oxygen analogue *N*,*N*-dimethylformamide leads to many related properties of the liquids. The high dipole moments, $\mu = 4.44$ and 3.91 D, permittivities, $\varepsilon = 47.4$ and 36.7,[1] and wide and convenient liquid ranges, −18 to approximately 220 °C (about 60 °C at 1 torr) and −60 to 150 °C, respectively, make both liquids efficient solvents for ionic compounds. This property, which is unusual for aprotic sulfur donor solvents, allows preparation of electrolyte solutions with high concentration and makes structural and thermochemical studies of solvated metal ions possible in solution. Structure studies in solution are of special value for investigating the bonding and coordination of metal ions without perturbations by the packing and symmetry restrictions of a crystal lattice. *N*,*N*-Dimethylthioformamide has a much softer Lewis base character than *N*,*N*-dimethylformamide (the D_S values are 52 and 24, respectively[2]) which results in strong solvation of soft acceptors, such as mercury(II), copper(I), silver(I) and gold(I), and brings out the characteristic bonding properties of these ions.[3–6]

A number of metal ions solvated by *N*,*N*-dimethylthioformamide have been studied in solution using large angle X-ray scattering, LAXS,[4–6] transfer thermodynamic,[6,7] and vibrational spectroscopic methods.[4–6,8] Significant bulk order of the *N*,*N*-dimethylthioformamide solvent has been indicated by all the methods used. The radial distribution functions from LAXS studies of *N*,*N*-dimethylthioformamide solutions of zinc, cadmium, mercury(II), copper(I) and silver(I) ions are all consistent with fairly well-defined intermolecular interactions within the solvent.[4,5] Transfer thermodynamic studies showed much stronger solvation of silver(I), zinc, cadmium and mercury(II) ions in *N*,*N*-dimethylthioformamide than in water.[7] The entropies of transfer are close to zero, consistent with a high degree of bulk order in *N*,*N*-dimethylthioformamide. The lower heats of solvation for HgX_2 molecules, X = I or Br, in liquid *N*,*N*-dimethylthioformamide than in a dilute benzene solution of *N*,*N*-dimethylthioformamide are consistent with a hydrogen bonding enthalpy in the neat solvent of about 12 kJ mol^{-1}.[6]

The liquid structure of *N*,*N*-dimethylformamide has been investigated previously. An *ab initio* MO–SCF calculation suggested that weak hydrogen bonds could be formed between pairs of *N*,*N*-dimethylformamide molecules with a C–(H) · · · O distance of 320 ± 15 pm,[9] but no such intermolecular interactions or bulk ordering were observed in a LAXS study.[9]

Even weak intermolecular hydrogen bond interactions in a liquid have important implications for the liquid structure and for the properties as a solvent. Relative hydrogen-bond basicity scales for many different solvent molecules have been generated by means of linear free energy relationships with thermodynamic or spectroscopic data related to a hydrogen-bond association.[2] Generally, comparable molecular compounds with oxygen or sulfur electron-pair donor atoms show consistently that the oxygen atom is a better acceptor of hydrogen bonds than the sulfur atom of the corresponding thiocompound.[10–12] Direct comparisons of such hydrogen-bond

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† Vibrational spectra of the solids and liquids, and for *N*,*N*-dimethylthioformamide the IR gas phase spectrum, are available as supplementary data from BLDSC (SUPPL. NO. 57682, 17 pp.) or the RSC Library. See Instructions for Authors available *via* the RSC web page (http://www.rsc.org/authors).

basicity values for the present single *N*,*N*-dimethylformamide and *N*,*N*-dimethylthioformamide molecules are given in the pK_{HB} scale based on 1 : 1 hydrogen bonded complexes formed with 4-fluorophenol, 2.06 and 1.05,[11,13] in the averaged hydrogen-bonding basicity β-scale by Taft *et al.*, 0.69 and 0.35,[12,14] and the β_2^H parameters of Abraham *et al.*, 0.66 and 0.46,[12,14] respectively. This confirms that the oxygen atom in *N*,*N*-dimethylformamide is a better hydrogen-bond acceptor than the sulfur atom in *N*,*N*-dimethylthioformamide. Thus, this pair of related molecules provides a clear-cut example of the hard–soft acid–base principle.[15,16] The softer sulfur atom is the stronger Lewis base towards soft electron-pair acceptors such as the mercury atom of $HgBr_2$ as is shown by the D_S scale, and the harder oxygen atom is the stronger Lewis base in the harder hydrogen-bond interactions, as discussed above.

A recent review of crystal structures in the Cambridge Structural Database analyzing (N,O)-H · · · S=C hydrogen bonds also showed stronger hydrogen bonding to terminal oxygen atoms than to sulfur.[17] C–H · · · S hydrogen bonding has very rarely been discussed in the literature,[18–24] probably because other stronger interactions frequently dominate, but also because of the rather restrictive criteria based on van der Waals radii, which often are applied for the recognition of a hydrogen bond. As discussed elsewhere, for weak hydrogen bonds the long-range electrostatic attraction predominates and the phenomenological definition as given by Pimentel and McClellan should be used: a hydrogen bond (HB) is considered formed (1) when evidenced by the molecular association, and (2) when there is structural evidence that the bond involves the hydrogen atom;[21–25] or in short: if it looks like a HB and if it acts like a HB, then it is a HB.

We have found reports of C–H · · · S hydrogen bonding in five crystal structures.[19–21,26,27] In solid 1,3-diethyl-2-thiobarbituric acid there are two intramolecular but no intermolecular C–H · · · S hydrogen bonds.[26] 3-Mercapto-1,3-diphenylprop-2-en-1-one (the enol form) has one intramolecular and one intermolecular C–H · · · S interaction, the latter between a double bonded sulfur and a phenyl hydrogen.[27] However, the strongest hydrogen bond in this structure is O–H · · · S. None of the three structures discussed by Novoa *et al.* contain intermolecular C–H · · · S hydrogen bonds,[20] and other stronger interactions are responsible for the molecular packing. A search in the Cambridge Structural Database revealed another two molecular compounds with probable intermolecular C–H · · · S hydrogen bonding according to the criteria given above. In *N*,*N*-dithioformylaniline the C–(H) · · · S distances are 3.64 and 3.66 Å, and the C–H · · · S angles 139.1 and 140.7°, respectively.[28] In ethylene trithiocarbonate the corresponding values are 3.71 Å and 139.2°,[29] as calculated from the given atomic parameters.

A study of the structure of liquid *N*,*N*-dimethylthioformamide became necessary in order to satisfactorily interpret the solution structure for the LAXS structure determinations of the solvated metal ions in solution.[4–6] In order to provide a model for the intermolecular interactions in the liquid the crystal structure of *N*,*N*-dimethylthioformamide was solved in the present work. Because of the apparent anomaly with less well-defined hydrogen bonding for the oxygen analogue, the crystal and liquid structures of *N*,*N*-dimethylformamide were also studied.

Experimental

Chemicals

N,*N*-Dimethylthioformamide was prepared by reacting *N*,*N*-dimethylformamide (Merck) and phosphorus pentasulfide (Merck), as described by Gutmann *et al.*,[30] or purchased (Aldrich) and distilled. For vibrational spectroscopy 5% solutions of *N*,*N*-dimethylformamide and *N*,*N*-dimethylthioformamide in d_6-benzene (Merck, analytical grade) were prepared.

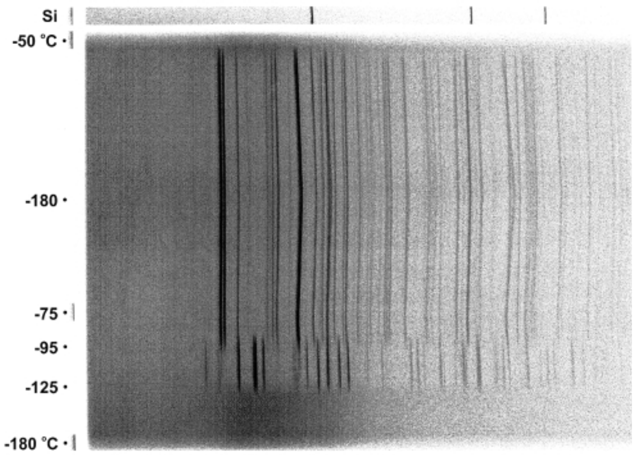

Fig. 1 Temperature dependence of Guinier X-ray diffraction (Cu-Kα1) pattern of solid *N*,*N*-dimethylformamide. After initial quenching to −180 °C (bottom) the sample was heated to −75 °C, recooled to −180 °C, and finally warmed up to −50 °C (top), with the rate 18 °C h^{-1} for all temperature variations. At the top of the figure the powder diagram of silicon at ambient temperature is given for calibration of the 2θ scale.

Single crystal preparation and data collection

Samples of both compounds were condensed in high vacuum into carefully cleaned Pyrex capillaries, which subsequently were sealed by burning. Powder X-ray diffraction experiments using a modified Guinier technique,[31] were performed to study the crystallization behavior. A typical temperature dependence of the powder diagram for *N*,*N*-dimethylformamide is shown in Fig. 1. After quenching the sample to −180 °C an amorphous solid phase was formed. During warm-up, crystallization occurred at about −125 °C, and at about −95 °C a solid–solid phase transition was observed. The respective changes of the powder lines are a clear indication that the transition is of first order type. The temperature of the sample was further increased up to −75 °C, but before the melting point was reached a new temperature cycle was made down to −180 °C followed by an increase to −50 °C. Clearly, the phase transition observed during the first temperature rise did not occur again, only the melting of *N*,*N*-dimethylformamide at −60 °C is visible. The crystallization and transition temperatures varied only slightly with heating rates and different samples. Interestingly, a similar behavior was observed for *N*,*N*-dimethylthioformamide. As this characteristic behavior occurred with every sample investigated, it seems likely that the crystalline phase first formed from the amorphous solid is metastable.

Single crystals for the data collection of both compounds were grown *in situ* in the four-circle diffractometer by cooling the liquids slowly below the melting point. Annealing at −18 °C resulted for *N*,*N*-dimethylthioformamide in a needle-like crystal of excellent quality. Crystallization of *N*,*N*-dimethylformamide was more difficult and was hampered by twinning. However, after several attempts at partial remelting and annealing at −64 °C a single crystal of good quality had grown. The structures of both compounds were solved from preliminary data sets collected at about 20 °C below the melting point. For the final data sets the crystals were cooled at a rate of 5 °C h^{-1} to −183 °C. Further details of the crystallographic experiments and structure determination are given in Table 1.‡

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‡ CCDC reference number 188/197. See http://www.rsc.org/suppdata/p2/a9/a904531g for crystallographic files in .cif format.

Table 1 Crystal data and structure refinement conditions for *N*,*N*-dimethylthioformamide (DMTF) and *N*,*N*-dimethylformamide (DMF)

	DMTF	DMF
Chemical formula	$(CH_3)_2NC(S)H$	$(CH_3)_2NC(O)H$
Formula weight/g mol^{-1}	89.159	73.095
T/K	90 ± 2	90 ± 2
Crystal system	Orthorhombic	Triclinic
Space group	$P2_12_12_1$ (No. 19)	$P\bar{1}$ (No. 2)
Unit cell dimensions		
a/pm	474.87(7)	594.55(9)
b/pm	597.11(9)	700.42(10)
c/pm	1701.7(3)	1040.41(19)
α/°	90	77.238(13)
β/°	90	88.132(14)
γ/°	90	75.280(12)
Unit cell volume/nm^3	0.48251(12)	0.40856(11)
Formula cell units *Z*	4	4
Abs. coeff. μ/mm^{-1}	0.253	0.055
Reflections collected	5764	9920
Independent reflections	2885	4902
R_{int}	0.0164	0.0354
R indices R_1, wR_2 [$I > 2\sigma(I)$]	0.0195, 0.0461	0.0331, 0.0868
R indices R_1, wR_2 [all data]	0.0223, 0.0467	0.0515, 0.0912

Large angle X-ray scattering

The scattered intensity of Mo-Kα radiation, $\lambda = 0.7107$ Å, was measured in reflection geometry from the free surface of liquid *N*,*N*-dimethylthioformamide by means of a previously described θ–θ goniometer equipped with a scintillation counter.[32] The 2θ range was covered twice in step scan mode collecting 10^5 counts in each scan at 430 preset θ-values, corresponding to a statistical error of about 0.3%. The step was 0.1° in the range $1 < \theta < 30°$ and 0.25° in the range $30 < \theta < 65°$. The data treatment, including corrections for absorption, polarization and multiple scattering, was performed in the same way as before.[4,33] A focusing LiF-monochromator in the scattered beam removed most (>90%) of the Compton scattering at high scattering angles. The corrected intensity values were normalized by comparison to the structure-independent scattering calculated for a stoichiometric unit volume chosen to contain one sulfur atom, followed by a subtraction of the remaining Compton scattering calculated by means of a pre-determined apparatus function.

The semi-focusing Bragg–Brentano geometry used in the θ–θ diffractometer requires essentially surface scattering in order to get agreement between the goniometer angle and the mean scattering angle 2θ from the liquid. This is an acceptable approximation for liquid *N*,*N*-dimethylthioformamide, which has a relatively high linear absorption coefficient, μ(Mo-Kα) = 4.0 cm^{-1}. However, for liquid *N*,*N*-dimethylformamide with $\mu = 0.72$ cm^{-1}, large corrections are needed of both intensity values and scattering angles, which tend to become unreliable. Measurements were therefore performed in transmission mode, by means of a recently developed Rigaku instrument equipped with an imaging plate area detector.[34] The liquids were contained in 1 mm thin-walled Lindemann capillaries, illuminated by a carefully centered 0.5 mm Mo-Kα X-ray beam. The intensity as a function of the scattering angle 2θ was obtained as a scaled sum over the exposed parts of the imaging plate detector corresponding to the same scattering angle. The intensity function was corrected for absorption in the sample and in the glass walls of the cylindrical capillary, corrected for polarization, and normalized to a stoichiometric volume corresponding to an oxygen or sulfur atom. No monochromatization could be made of the scattered beam, and the total Compton scattering was calculated and subtracted. It was found that only data below $\theta \approx 45°$ could be used because of instrumental factors and non-linearities in the detector efficiency. Liquid *N*,*N*-dimethylthioformamide was investigated both in transmission and reflection mode for comparison.

Table 2 Positional and isotropic displacement parameters (pm^2) for *N*,*N*-dimethylthioformamide (DMTF) with estimated standard deviations within brackets

DMTF	*x*	*y*	*z*	U_{eq} [a]
S	0.07826(3)	0.19556(2)	0.378818(8)	226.0(3)
N	0.41622(10)	0.55623(7)	0.37728(3)	218.4(7)
C1	0.31429(11)	0.37751(9)	0.41313(3)	200.6(8)
H11	0.3921(18)	0.3599(16)	0.4645(6)	303(21)
C2	0.33670(16)	0.62066(11)	0.29782(4)	302.6(12)
H21	0.258(2)	0.7696(18)	0.2992(7)	385(26)
H22	0.493(2)	0.615(2)	0.2644(6)	414(26)
H23	0.196(2)	0.516(2)	0.2778(6)	419(26)
C3	0.62445(12)	0.69898(11)	0.41587(5)	338.5(13)
H31	0.568(2)	0.8558(19)	0.4200(7)	449(27)
H32	0.806(2)	0.6923(19)	0.3851(7)	475(30)
H33	0.662(2)	0.6407(18)	0.4706(7)	405(26)

[a] U_{eq} is defined as 1/3 of the trace of the U_{ij} tensor. Hydrogen atoms were refined with isotropic displacement parameters.

The KURVLR program was used for the data treatment.[33] The reduced structure-dependent intensity, $i(s)$, with the scattering variable $s = (4\pi/\lambda)\sin\theta$, was obtained by subtracting the calculated coherent scattering from the free atoms of the sample from the scaled and corrected experimental intensity, using scattering factors from the same sources as before.[4] A Fourier transformation of the intensity function gives the radial distribution function, $D(r) - 4\pi r^2\rho_0$. Spurious peaks below 1.2 Å were removed by a Fourier back-transformation procedure,[35] to obtain a better alignment of the intensity function prior to a least-squares refinement of some of the model parameters used to calculate intensity contributions for distinct interatomic distances. Theoretical intensity values for pair-wise interactions between the atoms *p* and *q* within the molecular models were calculated according to eqn. (1):[33]

$$i_{\text{calc}}(s) = \Sigma\Sigma[f_p(s)f_q(s) + \Delta f_p''(s)\Delta f_p''(s)](\sin sd_{pq}/sd_{pq})\exp(-l_{pq}{}^2s^2/2) \quad (1)$$

The exponent of the Debye–Waller factor contains the root-mean-square variation, l_{pq}, of the interatomic distance d_{pq} assuming a Gaussian distribution. The $si_{\text{calc}}(s)$ model function was fitted to the experimental intensity data for $s \geq 5$ Å^{-1} with the program STEPLR.[36] The peak shapes corresponding to the model interactions were obtained by a Fourier transformation in the same way as for the experimental data, and were compared to the experimental radial distribution curves.

Vibrational spectroscopy

Raman spectra were recorded in the region 10–3400 cm^{-1} using a DILOR Z24 triple monochromator at a spectral bandwidth of 3 cm^{-1}. The light source was the 514.5 nm line of a Coherent Radiation Laboratories Innova Argon Ion Laser with an effective power of 500 mW at the sample. The low-temperature measurements of the solid *N*,*N*-dimethylthioformamide and *N*,*N*-dimethylformamide samples were made at about 110 K by means of an Oxford Instruments cryostat (DN1704). Infrared absorption spectra were recorded by Perkin-Elmer 1700 and Bruker IFS66v instruments. Raman and far-IR spectra of the solids and liquids are shown in the Supporting material, Figs. S1 to S4.

Results

Description of crystal structures

The atomic positions are given in Tables 2 and 3 for *N*,*N*-dimethylthioformamide and *N*,*N*-dimethylformamide, respectively, and bond distances and angles in Tables 4 and 5.

The structure of the planar *N*,*N*-dimethylthioformamide molecule is shown in Fig. 2. There is no significant deviation

Table 3 Positional and isotropic displacement parameters (pm^2) for the two *N*,*N*-dimethylformamide molecules (DMF1 and DMF2)

DMF1	x	y	z	U_{eq} [a]
O1	0.32890(7)	0.61982(6)	0.11632(4)	249.8(9)
C1	0.18759(8)	0.67672(7)	0.02323(5)	185.9(8)
H11	0.2340(12)	0.6666(11)	−0.0672(7)	221(17)
N1	−0.04167(7)	0.75373(6)	0.03204(4)	175.9(7)
C2	−0.14499(10)	0.77149(10)	0.15863(5)	254.1(11)
H21	−0.1978(17)	0.9106(15)	0.1682(9)	492(26)
H22	−0.2737(17)	0.7128(15)	0.1688(9)	481(26)
H23	−0.0366(18)	0.6970(15)	0.2269(10)	509(27)
C3	−0.19487(9)	0.82711(8)	−0.08411(5)	211.2(9)
H31	−0.2641(13)	0.9701(12)	−0.0970(7)	262(19)
H32	−0.3159(13)	0.7561(11)	−0.0747(7)	270(19)
H33	−0.1049(14)	0.8030(12)	−0.1627(8)	283(20)
DMF2				
O2	0.83027(7)	0.21167(7)	0.34272(4)	274.5(9)
C4	0.62022(8)	0.26785(8)	0.35979(5)	187.8(9)
H41	0.5087(13)	0.3290(12)	0.2864(7)	252(18)
N2	0.51875(6)	0.25245(6)	0.47723(4)	164.5(7)
C5	0.65339(8)	0.16506(8)	0.59959(5)	196.4(9)
H51	0.6418(14)	0.2683(12)	0.6505(8)	299(20)
H52	0.5897(13)	0.0564(12)	0.6505(7)	260(18)
H53	0.8130(14)	0.1067(12)	0.5840(8)	320(20)
C6	0.26806(8)	0.32025(9)	0.48729(5)	219.6(9)
H61	0.2306(13)	0.4271(11)	0.5343(7)	236(18)
H62	0.2074(13)	0.2087(12)	0.5308(8)	272(19)
H63	0.1973(15)	0.3744(13)	0.4016(8)	372(23)

[a] U_{eq} is defined as 1/3 of the trace of the orthogonalized U_{ij} tensor. Hydrogen atoms were refined with isotropic displacement parameters.

Table 4 Bond distances (pm) in the *N*,*N*-dimethylthioformamide (DMTF) and *N*,*N*-dimethylformamide molecules (DMF1 and DMF2). Estimated standard deviations given within brackets

DMTF		DMF1		DMF2	
S–C1	166.66(6)	O1–C1	123.09(6)	O2–C4	122.99(6)
N–C1	132.10(7)	N1–C1	134.07(6)	N2–C4	133.99(6)
N–C2	145.56(8)	N1–C2	145.20(7)	N2–C5	145.24(7)
N–C3	146.14(8)	N1–C3	145.37(7)	N2–C6	145.26(6)
C1–H11	95.5(10)	C1–H11	98.4(7)	C4–H41	97.5(8)
C2–H21	96.5(10)	C2–H21	97.1(10)	C5–H51	97.5(8)
C2–H22	93.6(11)	C2–H22	94.9(10)	C5–H52	97.9(8)
C2–H23	97.6(11)	C2–H23	94.2(10)	C5–H53	95.7(8)
C3–H31	97.7(11)	C3–H31	96.2(8)	C6–H61	95.9(8)
C3–H32	101.0(11)	C3–H32	96.5(8)	C6–H62	96.0(8)
C3–H33	101.0(11)	C3–H33	98.5(8)	C6–H63	95.4(8)

(<0.33 pm) of the non-hydrogen atoms from a least-squares plane. The N–C(thioformyl) bond distance 132.10(7) pm is much shorter than the mean bond distance to the methyl carbon atoms, N–C(methyl) 145.9 pm (*cf.* Table 4). The shortening is a result of the delocalized π-electrons over the N–C–S entity giving a partial double bond character to the N–C1 bond of the thioformyl group. Also the C–S bond distance, 166.66(6) pm, is shorter than the expected C–S single bond distance, 182 pm,[37] but longer than that found in the gas phase for thioformaldehyde, $H_2C{=}S$ 161 pm,[17] and much longer than the C=S double bond of 156 pm in carbon disulfide.[38]

Almost linear S···H–C hydrogen bonds between the thioformyl groups connect the *N*,*N*-dimethylthioformamide molecules in helix-shaped chains (*cf.* Fig. 3). The interplanar angle between the normals to the planes of two adjacent molecules is 84.5°, reflecting the directionality of the hydrogen bonds to the C=S group, see below. The parallel helical chains are probably held together by additional weak bifurcated hydrogen bond interactions between the sulfur atoms and methyl hydrogen atoms, the closest of which is S···H21, 300.5(1.1) pm, with the C2–H21···S angle being 154.3(9)°.

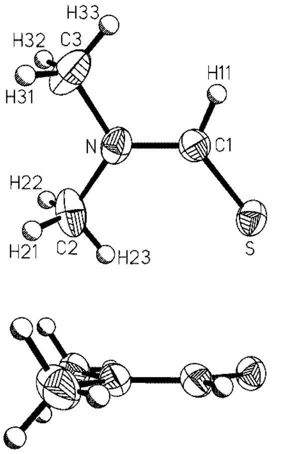

Fig. 2 The *N*,*N*-dimethylthioformamide molecule in two orientations with 50% probability thermal ellipsoids.

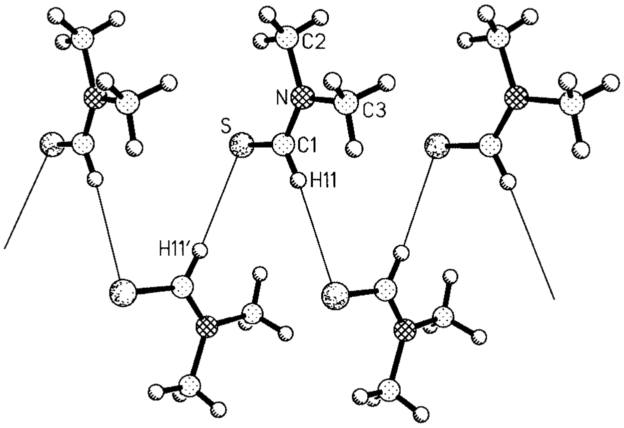

Fig. 3 The helix formation and hydrogen bonding in the *N*,*N*-dimethylthioformamide structure. The thin line denotes the hydrogen bond with C–(H)···S 378.10(7) pm, 175.4(7)°.

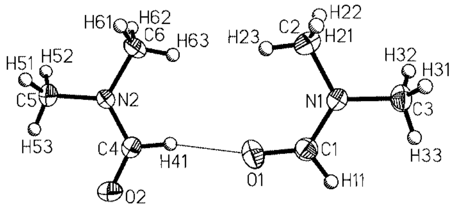

Fig. 4 The pair of crystallographically independent *N*,*N*-dimethylformamide molecules connected with a hydrogen bond *via* the formyl proton, C–(H)···O 329.41(9) pm, 149.3(8)°. The atomic positions are represented by 50% thermal ellipsoids.

The *N*,*N*-dimethylformamide structure comprises two crystallographically independent molecules. Both are planar with the non-hydrogen atoms deviating less than 0.9 and 0.4 pm, respectively, from the molecular planes which have an interplanar angle of 9.1° (*cf.* Fig. 4). The mean N–C(formyl) distance, 134.07 pm, is slightly longer, and the mean N–C(methyl) bond distance slightly shorter, 145.27 pm, than for *N*,*N*-dimethylthioformamide, *cf.* Table 4, indicating a somewhat weaker double bond character of the N–C–O entity. A centrosymmetric ring of four *N*,*N*-dimethylformamide molecules connected by weak C–H···O hydrogen bonds, all of which with oxygen atoms as acceptor, can be distinguished in the structure (*cf.* Fig. 5). The mean C–O bond distance is 123.04 pm.

In the dimethylamino groups the C–N–C angles between the two eclipsed methyl groups are significantly smaller than the value 120° expected for sp^2 hybridization of the nitrogen atom, Table 5. For both compounds one hydrogen atom of each

Table 5 Bond angles (deg) in the *N*,*N*-dimethylthioformamide (DMTF) and *N*,*N*-dimethylformamide molecules (DMF1 and DMF2)

DMTF		DMF1		DMF2	
S–C1–N	127.68(4)	O1–C1–N1	125.21(5)	O2–C4–N2	125.23(4)
S–C1–H11	120.6(6)	O1–C1–H11	122.1(4)	O2–C4–H41	122.1(5)
N–C1–H11	111.7(6)	N1–C1–H11	112.7(4)	N2–C4–H41	112.7(5)
C1–N–C2	123.19(5)	C1–N1–C2	120.80(4)	C4–N2–C5	121.67(4)
C1–N–C3	120.77(6)	C1–N1–C3	121.64(4)	C4–N2–C6	121.20(4)
C2–N–C3	116.02(5)	C2–N1–C3	117.53(4)	C5–N2–C6	117.13(4)
N–C2–H21	108.7(7)	N1–C2–H21	113.1(6)	N2–C5–H51	109.7(4)
N–C2–H22	110.4(7)	N1–C2–H22	108.9(6)	N2–C5–H52	108.6(4)
N–C2–H23	109.5(7)	N1–C2–H23	109.5(6)	N2–C5–H53	111.7(5)
N–C3–H31	114.0(7)	N1–C3–H31	111.1(4)	N2–C6–H61	109.8(4)
N–C3–H32	108.8(7)	N1–C3–H32	109.7(4)	N2–C6–H62	109.8(5)
N–C3–H33	109.4(6)	N1–C3–H33	109.5(5)	N2–C6–H63	110.1(5)
H21–C2–H22	110.8(9)	H21–C2–H22	108.7(8)	H51–C5–H52	109.1(6)
H21–C2–H23	109.5(8)	H21–C2–H23	109.3(8)	H51–C5–H53	110.2(7)
H22–C2–H23	107.9(9)	H22–C2–H23	107.0(8)	H52–C5–H53	107.4(6)
H31–C3–H32	108.0(10)	H31–C3–H32	109.4(6)	H61–C6–H62	110.7(6)
H31–C3–H33	108.2(9)	H31–C3–H33	108.0(6)	H61–C6–H63	107.0(7)
H32–C3–H33	108.3(8)	H32–C3–H33	109.1(6)	H62–C6–H63	109.4(7)

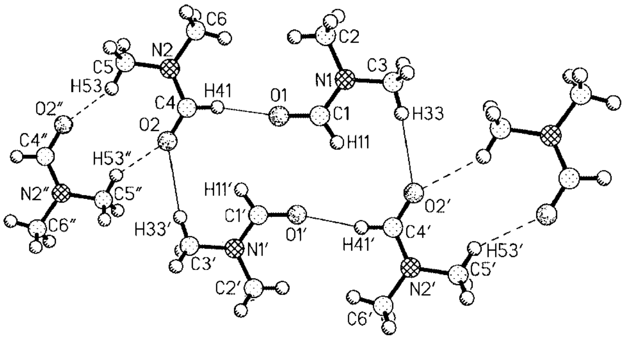

Fig. 5 The four-membered centrosymmetric ring of *N*,*N*-dimethylformamide molecules formed by weak C–H···O hydrogen bond interactions (thin solid lines) involving formyl protons (H41, see Fig. 4) and methyl protons, with C3′–(H33′)···O2 341.41(9) pm, 167.3(8)°. The rings are connected *via* a bifurcated hydrogen bond to O2 (dashes): C5″–(H53″)···O2 347.2(1) pm, 144.7(6)°.

methyl group is close to the molecular plane (*cf.* Figs. 2 and 4). Similar eclipsed conformations and C–N–C angles have previously been observed for other compounds with strongly bonded dimethylamino groups,[39,40] and should primarily be caused by electronic effects.

The formyl groups are tilted within the molecular plane. Since the deviation from regular trigonal coordination of the formyl carbon is largest for the thioformyl group, intramolecular contacts between the formyl and methyl groups may contribute to enlarge the S–C1–N angle to 127.68(4)° (*cf.* Table 5). Within the *N*,*N*-dimethylthioformamide molecule the S···H23 distance is 263.3(12) pm, the C–H···S angle 112.5(1)° and the H11···H33 distance 211.3(14) pm, while there seems to be less strain in the two *N*,*N*-dimethylformamide molecules where the corresponding mean distances are 244 pm for O1···H23 and O2···H53, the mean angle C–H···O is 103.2°, and the mean H11···H33 and H41···H63 distances are 216 pm. All these intramolecular contacts are shorter than the sum of the "classical" van der Waals radii (S 185, O 140 and H 120 pm).[41] However, an analysis of intramolecular C–H···O hydrogen bonds, where the orientation dependence of the van der Waals separation has also been taken into account, clearly shows that the C–H···O (and also C–H···S) contacts belong to the same type of 5-membered circular atomic arrangements found in carbohydrates.[42]

Structure of liquids

The structure-dependent reduced intensity functions, $si(s)$, of liquid *N*,*N*-dimethylthioformamide are shown in Fig. 6 for the two different scattering geometries. For this relatively highly absorbing liquid the θ–θ measurement in reflection geometry gives a more reliable weighting of the intensity values in the low s region than the transmission experiment, which required a large absorption correction. A better resolution is obtained in r-space for the data obtained in reflection geometry because a higher $s_{\max}$ value can be reached in the Fourier transformation procedure (see Experimental section), but the main features are very similar, *cf.* Fig. 7. The first three major peaks in the RDFs, at *ca.* 160, 260 and 410 pm, and also the small peak at 320 pm, correspond to distances within the *N*,*N*-dimethylthioformamide molecule. The calculated peak shapes for the model parameters (Table 6), with intramolecular distances from the crystal structure, are shown in Fig. 7. A broad peak at about 470 pm, and the residue of the prominent 410 pm peak, show intermolecular ordering to be present in the liquid. These peaks are satisfactorily described by assuming a hydrogen bonded S···(H)–C interaction, which is refined to 382(2) pm by least-squares fitting of the reduced intensity functions for $s > 5$ Å^{-1} (*cf.* Fig. 6). It is estimated from the peak fitting to the RDF

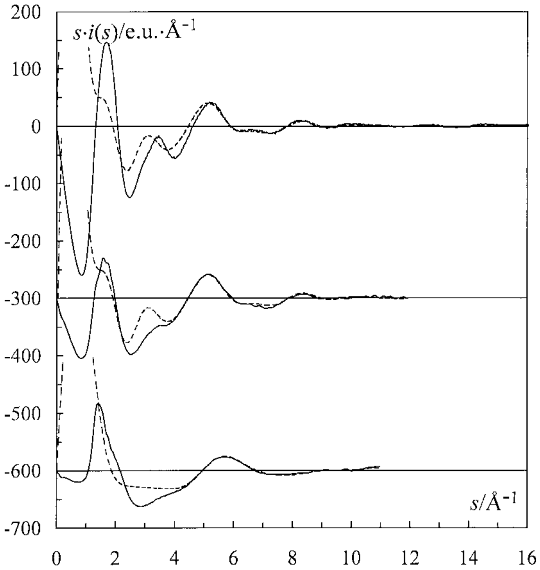

Fig. 6 Reduced LAXS intensity functions (solid line = experimental; dashed line = calculated) multiplied by the scattering variable, $si(s)$. *Upper*. Reflection (θ–θ) geometry data of *N*,*N*-dimethylthioformamide. *Middle*. Transmission X-ray data for *N*,*N*-dimethylthioformamide, offset: −300. *Lower*. Transmission data for *N*,*N*-dimethylformamide, offset: −600.

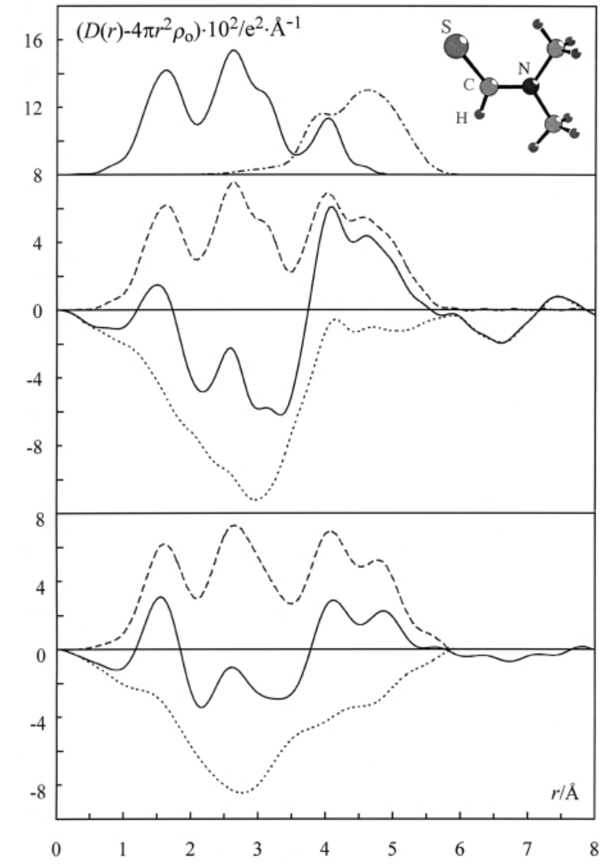

Fig. 7 *Upper*. Model peak shapes for liquid *N*,*N*-dimethylthioformamide: intramolecular distances (solid line), intermolecular hydrogen bonded distances (dash-dotted line). *Middle*. Experimental radial distribution function in reflection geometry (solid line), $D(r) - 4\pi r^2\rho_o$, calculated model function (dashed line) with parameters from Table 6, and the difference between the experimental and model function (dotted line). *Lower*. Experimental RDF from transmission measurement and the model functions; the line labels are the same as in the middle section.

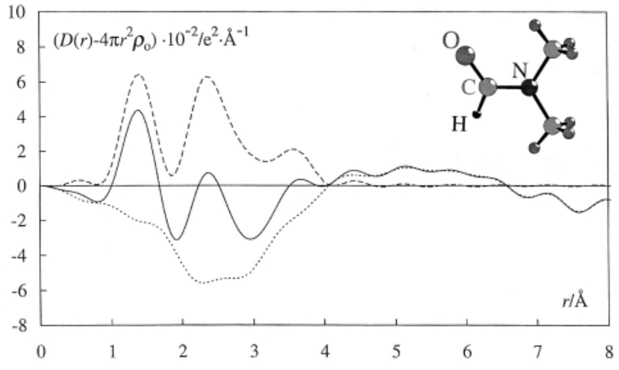

Fig. 8 Experimental differential radial distribution function, $D(r) - 4\pi r^2\rho_o$ and calculated peak shapes from transmission measurements of *N*,*N*-dimethylformamide; the line labels are the same as in Fig. 7.

that most, about 70%, of the *N*,*N*-dimethylthioformamide molecules form hydrogen bonds in the liquid.

The RDF of liquid *N*,*N*-dimethylformamide shows less intermolecular structure than for *N*,*N*-dimethylthioformamide, see Fig. 8. The intramolecular distances of the molecular model obtained from the crystal structure (Tables 4 and 5) gave a satisfactory fit to the three major peaks in the RDF, and consequently also to the high *s* part of the intensity function (Fig. 6). An almost featureless residual RDF remains after subtraction of the calculated model peak shapes. The agreement with the intensity function previously obtained in θ–θ reflection geometry is satisfactory.[9] The same conclusion emerges from the two diffraction studies of liquid *N*,*N*-dimethylformamide, no significant ordering giving rise to distinct intermolecular distances can be seen.

Vibrational spectroscopy

The Raman and infrared spectra of liquid *N*,*N*-dimethylthioformamide and *N*,*N*-dimethylformamide have been analysed by full normal coordinate calculations of the fundamentals, supported by *ab initio* calculations.[8] All 30 normal modes for the $(CH_3)_2NCHS$ and $(CH_3)_2NCHO$ molecules could be assigned to vibrational frequencies.[8] In the present work solid state low temperature Raman spectra, and also IR spectra of dilute solutions in benzene (5%), were measured in order to elucidate the effects of the hydrogen bonding, see Supporting Information.

The thioformyl C–H stretching in solid *N*,*N*-dimethylthioformamide at about 112 K is observed as a distinct peak at 2856 cm^{-1} in Raman (Fig. 9A). No splitting is observed since all the weakly hydrogen bonded molecules are crystallographically equivalent in the solid, and no Fermi resonance occurs.[43] Hydrogen bonding is not expected in a solution of 5% *N*,*N*-dimethylthioformamide in benzene and the frequency of the thioformyl C-H stretching measured by IR is shifted to 2872 cm^{-1}. The Raman spectrum of liquid *N*,*N*-dimethylthioformamide at room temperature shows a shoulder at 2860 cm^{-1} (in the IR at about 2853 cm^{-1}), consistent with intermolecular hydrogen bonding.

The C–S stretching will also to some degree be affected by the hydrogen bonding. The lowest Raman stretching frequency is found in the solid phase at 957 cm^{-1}, and at 967 cm^{-1} in the liquid (*cf.* Fig. 9B). The IR band of the liquid is centered at 970 cm^{-1}, but shifts for a 5% solution in benzene to a higher frequency, 976 cm^{-1}, as expected for a non-hydrogen bonded structure where the C–S stretching frequency should increase.

The formyl C–H stretching in *N*,*N*-dimethylformamide does not show as clear indications of intermolecular interactions as in *N*,*N*-dimethylthioformamide. In the solid state (100 K) a Raman band which can be assigned to this group frequency is found at 2868 cm^{-1}, possibly corresponding to the non-hydrogen bonded C1–H11 group. Two additional weak bands occur at 2855 and 2832 cm^{-1}, probably split by Fermi resonance with an overtone of the in-plane C–H bending.[37] The Raman band for the liquid is found at 2856 cm^{-1} (IR 2857 cm^{-1}).[8]

The most clearly visible changes for *N*,*N*-dimethylformamide occur for the normal mode dominated by C–O stretching, which splits into two sharp Raman bands at 1661 and 1645 cm^{-1} in the solid state where all C–O groups are weakly hydrogen bonded. In the Raman spectrum of the liquid this mode also shows two components, a strongly polarized band at 1659 cm^{-1}, and a shoulder at about 1674 cm^{-1} which becomes dominant in perpendicular polarization (*cf.* Fig. S5 Supporting Information). The IR spectrum shows only one strong band at 1677 cm^{-1}, which shifts to 1684 cm^{-1} for benzene solution, and to 1715 cm^{-1} in the gas phase.[44] Thus, it seems probable that the Raman and IR bands at about 1677 cm^{-1} originate from non–interacting C-O groups in the liquid. The polarized Raman band at 1659 cm^{-1}, however, would then correspond to C–O stretchings affected by hydrogen bonding in the liquid, although the amount is difficult to estimate and can be fairly small.

Discussion

The structural difference between the two molecular compounds and in particular the unexpectedly strong effects of hydrogen bonding found for both crystalline and liquid *N*,*N*-dimethylthioformamide will be the main subject of this discussion.

Mulliken charge distributions

Density functional theory (DFT) computations have previously

Table 6 Model parameters (based on the crystal structures) for the LAXS studies of liquid *N*,*N*-dimethylthioformamide (DMTF) and *N*,*N*-dimethylformamide (DMF): distances *d* (pm), atomic displacement parameters *l* (pm), and number of distances, *n*. Estimated standard deviations are given within brackets

DMTF						DMF		
Intramolecular			Intermolecular			Intramolecular		
S–C(1)	*d*	167.2	S···(H)–C	*d*	382(2)	O–C(1)	*d*	121.9
	l	10.1		*l*	16(2)		*l*	11.5
	n	1.0		*n*	0.7		*n*	1.0
N–C(1)	*d*	132.1	S···C	*d*	425	N–C(1)	*d*	132.1
	l	3.9		*l*	26		*l*	11.5
	n	1.0		*n*	0.7		*n*	1.0
N–C(2,3)	*d*	146.0	S···N	*d*	452	N–C(2,3)	*d*	144.1
	l	10.3		*l*	24		*l*	11.5
	n	2.0		*n*	0.7		*n*	2.0
C(1)···C(2)	*d*	244.7	S···S	*d*	485	C(1)···C(2,3)	*d*	240.8
	l	10.8		*l*	30		*l*	11.5
	n	1.0		*n*	0.7		*n*	2.0
C(1)···C(3)	*d*	241.7						
	l	10.8						
	n	1.0						
C(2)···C(3)	*d*	247.8				C(2)···C(3)	*d*	246.4
	l	13.9					*l*	11.5
	n	1.0					*l*	1.0
S···N	*d*	266.7				O–N	*d*	226.0
	l	9.6					*l*	11.5
	n	1.0					*n*	1.0
S···C(2)	*d*	308				O···C(2)	*d*	277.8
	l	13.3					*l*	11.5
	n	1.0					*n*	1.0
S···C(3)	*d*	401.6				O–N	*d*	356.5
	l	13.3					*l*	11.5
	n	1.0					*n*	1.0

Table 7 Mulliken population atomic charges of a single *N*,*N*-dimethylformamide (DMF) and *N*,*N*-dimethylthioformamide (DMTF) molecule, obtained from density functional theory calculations.[a] Atomic numbering as in Figs. 2 and 4

Atom	DMTF	DMF
S or O	−0.18	−0.35
C1	−0.07	+0.34
N	−0.32	−0.49
C2	0.21	0.21
C3	0.22	0.21
H11	0.039	−0.027
H21	0.017	0.012
H22	0.020	0.014
H23	0.013	0.034
H31	0.020	0.019
H32	0.021	0.020
H33	0.009	0.004

[a] Computational details of the DFT calculations are given in ref. 8.

been performed on single free *N*,*N*-dimethylthioformamide and *N*,*N*-dimethylformamide molecules, respectively, and comparisons of calculated and experimental vibrational frequencies were made.[8] The most stable conformation was in both cases found to correspond to eclipsed methyl groups, as indeed found in the crystal structures (Figs. 2 and 4). The methyl proton H23 (H53) which is close to the sulfur or oxygen atoms, is probably held in the molecular plane by intramolecular hydrogen bonding,[43] see Results section. The eclipsed conformation of the C3 (C5) methyl group with also the H33 (H63) protons in the molecular plane should then be an effect of the delocalized π-electron structure. The energy was calculated to be 7.5 and 9.6 kJ mol^{-1} lower for *N*,*N*-dimethylthioformamide and *N*,*N*-dimethylformamide, respectively, than with the C3 methyl group in the staggered conformation, which corresponds to a transition state for methyl rotation. Mulliken population analyses of the density matrices showed much smaller charge differences within the N–C–S thioformyl group than in N–C–O (Table 7). This implies an increase in the double bond character consistent with the significantly longer N–C bonds observed for *N*,*N*-dimethylformamide (mean 134.03 pm) than in *N*,*N*-dimethylthioformamide (132.10(7) pm, *cf.* Table 4).

As mentioned in the Introduction, a terminal oxygen atom generally forms stronger hydrogen bonds than the sulfur atom of the corresponding thio-compound. Also for the present molecules a comparison of the Mulliken charge distribution (Table 7) shows the oxygen atom to be more negatively charged than the sulfur atom ($\Delta e = -0.18$), which is consistent with the experimental evidence of stronger hydrogen bond *acceptor* properties for oxygen atoms.[11–14,17] Furthermore, the Mulliken analyses showed the thioformyl hydrogen atom of *N*,*N*-dimethylthioformamide to be more positively charged than the formyl one ($\Delta e = +0.07$, *cf.* Table 7). This is probably the reason why intermolecular ···S=C–H···S=C–H··· cooperative hydrogen bonds are formed. The strength of this interaction can probably be enhanced by further polarisation of the C=S electron cloud in the *N*,*N*-dimethylthioformamide molecules. Preliminary results of a DFT calculation of a cluster of hydrogen bonded *N*,*N*-dimethylthioformamide molecules also show a small increase in the charge separation due to the collective polarisation effect when a *N*,*N*-dimethylthioformamide molecule acts both as hydrogen bond donor *and* acceptor.[45]

The C=S polarisation of *N*,*N*-dimethylthioformamide is certainly larger than that for C=O in *N*,*N*-dimethylformamide, see discussion above. It is however difficult to judge whether the main increase in polarisation of the C=S–H entity is due to the delocalized S–C–N π-electron system, *i.e.* if it should be classified as a resonance-assisted (RAHB, π-cooperative) effect,[46] an induction-assisted (IAHB, σ-cooperative) effect,[47] or both. The more general terminology polarisation-assisted hydrogen bonding (PAHB),[48] therefore seems appropriate.

For *N*,*N*-dimethylformamide the poor hydrogen bond *donor* ability of the formyl hydrogen atom evidently makes it possible also for methyl protons, which for the isolated molecule are the more positively charged (*cf.* Fig. 5 and Table 7) to compete on

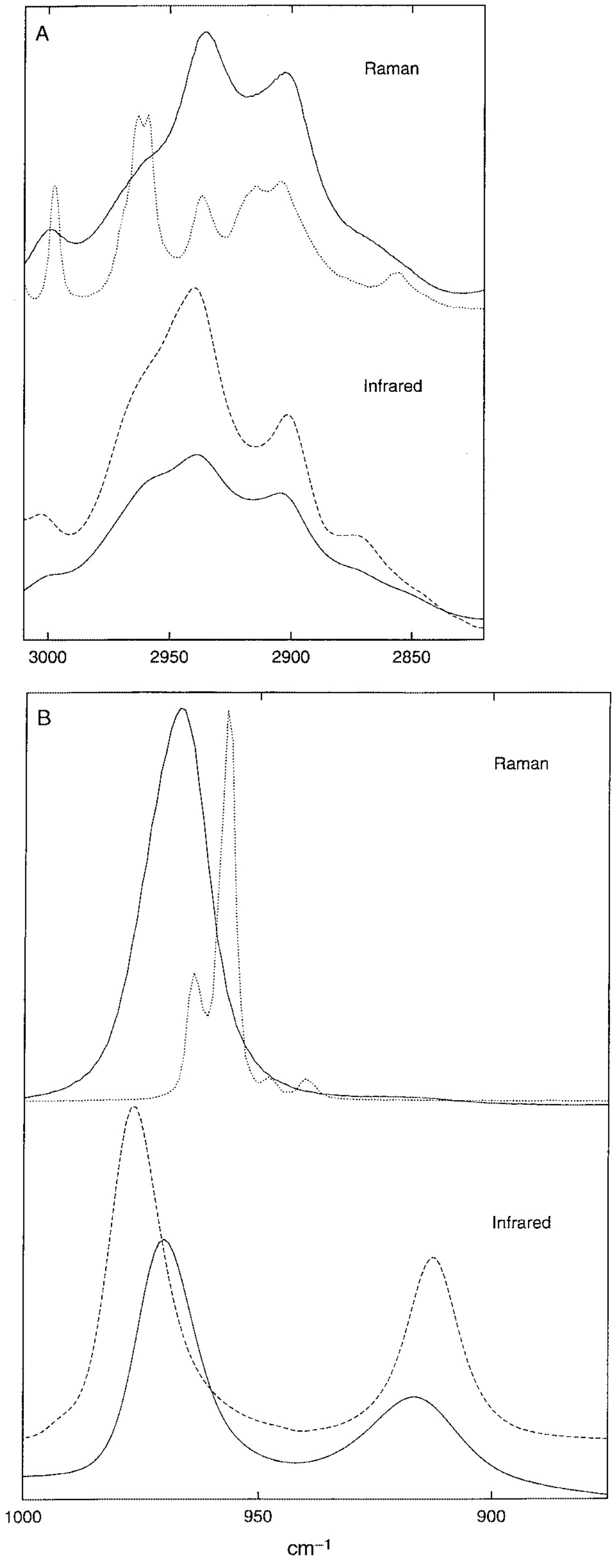

Fig. 9 Vibrational spectra of *N*,*N*-dimethylthioformamide. Liquid: solid lines; Raman of solid at 112 K: dotted line; IR of 5% solution in C_6D_6: dashes. A. C–H stretching region; B. C–S/O stretching region.

an equal basis for an interaction with the oxygen atom of neighboring molecules. It should be kept in mind, however, that the absolute values of the charges in Table 7 depend on the computational method, basis sets and partitioning scheme used, and it is only meaningful to discuss differences between directly comparable calculations.

Comparison based on the Mulliken population analysis of atomic charges given in Table 7 is concerned with the internal charge distribution and reflects changes in hybridization and polarization for single molecules. However, in cases with asymmetrical charge distribution as in the formyl groups, this approach is not always sufficient for a detailed discussion of intermolecular interactions, since induced polarization, atomic charge dipoles and higher terms should also be considered.[49] Computations of clusters with several interaction molecules should also be performed for more detailed descriptions of the unexpectedly strong effect of the C–H···S hydrogen bonding in the present system. Also, new additional criteria for more precise definitions of non-conventional hydrogen bonds depend on evaluation of charge densities between interacting atoms.[50]

Hydrogen bond geometry

The intermolecular packing arrangements of the two crystalline compounds are clearly influenced by their different ability to form hydrogen bonds *via* the formyl/thioformyl groups. The closest intermolecular S···H hydrogen bond distance in crystalline *N*,*N*-dimethylthioformamide is determined to be 282.8(9) pm by X-ray diffraction, with an almost linear C1–H11···S connection, 175.4(7)°, between the molecules, giving rise to helical chains parallel to the *a*-axis of the structure. Normalizing the C1–H11 distance to 1.08 Å,[22] since C–H distances appear too short,[51] gives a corrected S···H hydrogen bond distance of about 270 pm. The same motif also occurs in the crystal structure of *N*,*N*-dithioformylaniline, where the two thioformyl groups of the molecule form two parallel helix-shaped chains with similar S···H bond lengths, *ca.* 275 pm after normalization.[28] A polarisation-assisted enhancement of the cooperative intermolecular C–H···S hydrogen bonding occurs probably in ethylene trithiocarbonate as well.[29]

The hydrogen bond directionality has been investigated recently for C=S and C=O acceptors.[17,52] In both studies, it was found that the lone-pair directionality is weaker for the S···H than for the O···H interaction, and that a more perpendicular orientation is preferred for the C–S···H interactions than for C–O···H ones. It was also concluded that in $R_1R_2C{=}S$ systems the sulfur atom is an effective hydrogen bond acceptor only when R_1 and R_2 can form an extended delocalized system with C=S.[17] However, also for $R_2 = H$ these results are consistent with the present *N*,*N*-dimethylthioformamide and the previous *N*,*N*-dithioformylaniline structures,[28] with the C–S···H angles 88.3 and 95.3°, respectively, because of the polarizability of the thioformyl group.

The hydrogen bond formation in liquid *N*,*N*-dimethylthioformamide is also evident from the LAXS results, with features in the RDF functions corresponding to an intermolecular hydrogen bonded sulfur–carbon atom S···(H)–C distance of 382(2) pm (Table 6) which is comparable to that in the solid state, 378.10(7) pm. This is consistent with the estimation based on both the LAXS results and the vibrational spectra that the major part of the *N*,*N*-dimethylthioformamide molecules remains hydrogen bonded in the liquid.[6]

The packing arrangement in crystalline *N*,*N*-dimethylformamide is quite different. Two crystallographically independent *N*,*N*-dimethylformamide molecules form a pair *via* a O1···H41–C4 hydrogen bond (O···H 241.8(7) pm, O···H–C 149.3(8)°) (see Fig. 4). Two such centrosymmetrically related pairs are joined *via* O2···H33–C3 bridges, O···H 244.6(8) pm and O···H–C 167.3(8)°, between the formyl oxygen and a methyl hydrogen atom to form cyclic tetramers. Another weak bifurcated interaction between O2 and the methyl hydrogen H53 (O···H 264.6(7) pm, O···H–C 144.7(6)°) connects these rings and gives rise to bands perpendicular to the *b*-axis (*cf.* Fig. 5). The second formyl proton H11 is not involved in any hydrogen bond interaction.

Previously, from an MO-SCF calculation of a pair of *N*,*N*-dimethylformamide molecules using minimal basis sets a possible weak linear hydrogen bond interaction between the formyl groups was suggested with a shallow potential surface corresponding to a C–(H)$\cdots$O distance of about 320 pm,[9] *i.e.* at an O$\cdots$H distance of about 210 pm. The present crystal structure results, where the shortest O1$\cdots$H41 distance is 241.8(7) pm, show the hydrogen bonding to be very weak, and it is in fact of similar strength between the oxygen and methyl hydrogen atoms O2$\cdots$H33, 244.6(8) pm. This is also consistent with the present and previous LAXS results, which did not show significant hydrogen bonding in the liquid.[9] Furthermore, a recent study by low-frequency Raman spectroscopy indicated hydrogen bonded interactions (N–H$\cdots$O) in liquid formamide and *N*-methylformamide, but not for *N*,*N*-dimethylformamide.[53]

While the hydrogen bonding motif was quite similar in the *N*,*N*-dimethylthioformamide and *N*,*N*-dithioformylaniline compounds, the structures of their oxygen analogues show different types of arrangement. For the *N*,*N*-diformylaniline structure, as for *N*,*N*-dimethylformamide, there are two crystallographically independent molecules, but in *N*,*N*-diformylaniline they are held together in bands by means of bifurcated hydrogen bonds from an oxygen atom to the two formyl protons of a diformyl group.[28]

Conclusions

Cooperative hydrogen bonding is clearly shown by the packing arrangement of the molecules in the crystal structures of the thioformamides *N*,*N*-dimethylthioformamide and *N*,*N*-dithioformylaniline as well as in the liquid structure of *N*,*N*-dimethylthioformamide but not in the corresponding formamide structures. This apparent anomaly is a result of the better hydrogen-bond *donor* properties of the thioformyl proton, which more than outweigh the less favorable hydrogen-bond *acceptor* properties of the sulfur atom. Moreover, the *cooperative* effect when the more polarisable thioformyl group forms hydrogen bonds involving both the sulfur and hydrogen atoms, will to some extent give a polarisation-assisted enhancement of the hydrogen bond strength.

Evidently, the less positively charged formyl proton of *N*,*N*-dimethylformamide will only allow formation of very weak hydrogen bonds in the solid state, which are comparable in strength with interactions between the methyl protons and the oxygen atoms. For *N*,*N*-dimethylformamide the C–O stretching vibrations indicate no significant hydrogen bond interactions for most oxygen atoms, consistent with the lack of intermolecular ordering found from the LAXS studies on liquid *N*,*N*-dimethylformamide.

Acknowledgements

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