Intramolecular and Liquid Structures of Tetramethylurea Studied by Means of X-Ray Diffraction

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The intramolecular and liquid structures of tetramethylurea (TMU) were investigated by the liquid x-ray diffraction method. It is confirmed that in the liquid state the four methyl groups are out of the plane which is constructed by the O, C, and the two N atoms, the molecular structure being similar to what had been found in the gas phase. All structural parameters are in good agreement with those of TMU determined in the gas phase and with those of amide derivatives in the liquid phase. The liquid is characterized by a random distribution of molecules as predominant, but a weak molecular ordering characterized by approximately two intermolecular nonbonding Me ··· O distances at 340 pm is proposed.

Key words: Tetramethylurea, Liquid x-ray diffraction, Liquid structure, Molecular structure, Non-aqueous solvent.

1. Introduction

Almost 30 years ago A. Lüttringhaus and H. W. Dierksen [1] summarized the chemical properties of tetramethylurea (TMU). Their statement that TMU and other urea derivatives have attracted much less interest than formamide or acetamide derivatives and even other solvents such as dimethyl sulfoxide, is still valid. In particular, structural studies in the liquid and solid states have not been carried out at all, and only a few results can be found concerning the intramolecular structure of TMU in the gaseous state determined by means of gas electron diffraction (GED) [2, 3] and quantum chemical calculations [4, 5]. Interestingly, several recent publications have reported anomalous physico-chemical behavior of TMU-H_2O mixtures [6].

Tetramethylurea can be regarded as a dimethylamine derivative of dimethylformamide (DMF), in which the hydrogen atom in the formyl group is substituted with $-N(CH_3)_2$. On the basis of the molecular similarity between TMU and DMF, there are two interesting questions which arise in relation to the intramolecular structure of TMU. The first is how "bulky" the molecule is. In other words, one would expect that the four methyl groups located at the N atoms can result in a larger molecular size than, e.g., DMF, and if it is so, the bulkiness of the molecules may cause a significant steric hindrance in the structures of hydrates of TMU in its aqueous solutions, ionic solvates with TMU, and complexes in TMU solutions. Estimations have been reported for the average size of TMU molecules [6] derived from different experiments. The authors used different definitions of the size, which led to scattered results. The second question is whether or not the structure of TMU is planar, as it was believed earlier and is still believed in case of most amide derivatives, including DMF. In a detailed GED study [3] a non-planar structure is proposed for TMU in the gas phase, but it has not been confirmed in the condensed phase yet. On the other hand, a more recent study expressed serious doubts for the planar structure of dimethylacetamide [7], pointing out that the question is still worth investigating in more detail for the whole series of amides.

In our present work, an x-ray diffraction study on the intramolecular and liquid structures of TMU is reported. The liquid structure is compared with that of DMF studied by x-ray diffraction [8]. Both DMF and TMU have relatively large dipole moments (3.86 and 3.50 Debye, respectively), and thus, strong dipole-dipole interactions between adjacent molecules could be expected. Nevertheless, DMF proved to be an essentially disordered liquid at room temperature.

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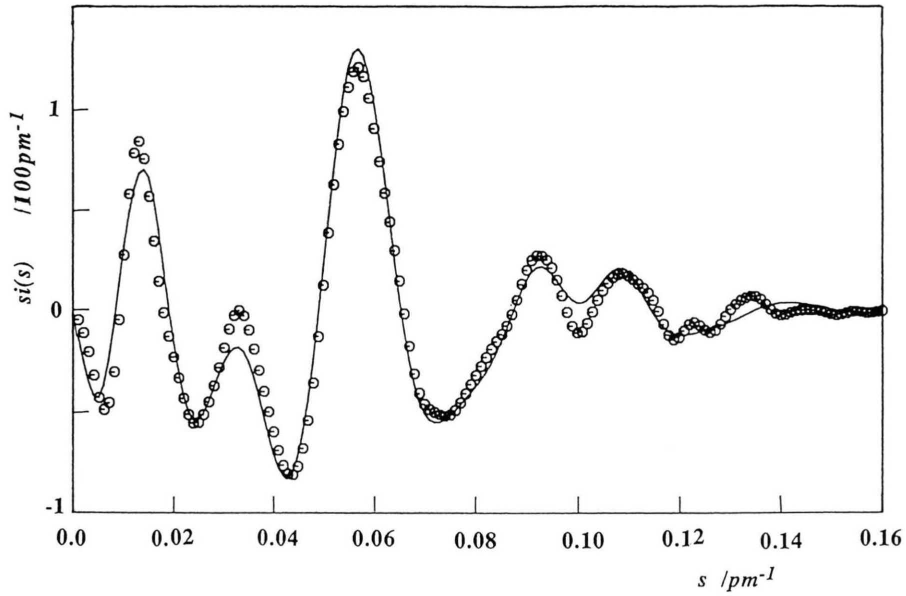

Fig. 1. Experimental structure function (circles) and the theoretical one from the best fitting model (solid line) for liquid TMU.

2. Experimental

2.1. Sample Solution

1,1,3,3-Tetramethylurea of reagent grade from Merck was used without purification. The water content of the sample was smaller than 0.5%. The density of the sample was determined to be 0.9627 g cm^{-3} at 23 °C.

2.2. X-ray Scattering Measurement

The scattering experiment was carried out with a Seifert $\Theta-\Theta$ diffractometer in a transmission arrangement by using the MoKα radiation with a wavelength of 71.07 pm at (25 ± 2) °C. The range of the scattering angle (2Θ) was between 1.5 and 110°. 120,000 counts at each of 150 selected angles were accumulated. The methods of measurement and data treatment were essentially the same as reported previously [9], including corrections for background, polarization, absorption, subtraction of the scattering pattern of the empty cell and conversion of the corrected intensities into absolute units.

2.3. Evaluation of Experimental Functions

The experimental structure function $si(s)$ was defined as

$$si(s) = s\,[I_{\text{abs}}(s) - \sum x_\alpha f_\alpha^2(s) - \sum x_\alpha I_{\alpha,\,\text{inc}}(s)]\,M(s)\,, \quad (1)$$

where s is the scattering variable, $s = (4\pi/\lambda)\sin\Theta$, λ the wavelength of the incident radiation, $I_{\text{abs}}(s)$ the corrected intensity converted to absolute units, x_α the atomic fraction of atom or atomic group α, $f_\alpha(s)$ the related coherent scattering factor, $I_{\alpha,\,\text{inc}}(s)$ the incoherent scattering, and $M(s)$ the modification function

$$M(s) = \exp(-ks^2)/[\sum x_\alpha f_\alpha(s)]^2\,, \quad (2)$$

where a value of $k = 100$ pm^2 was selected. The summation was extended over each type of four independent scattering units: O, N, double-bonded C atoms, and CH_3 group (abbreviated as Me). For the computations, analytical formulae were used in their usual form [9]. The necessary parameters were taken from the literature both for the coherent [10, 11] and incoherent [12] scattering intensities.

In this approach, H atoms of the molecule were not treated separately; instead, they were included in the methyl groups, which were treated as one scattering unit of atoms. The accuracy of this treatment was examined by Narten [10]. However, the contribution of hydrogen atoms to the intensity data is sometimes detectable by x-ray diffraction, as seen in DMF [8]. For TMU, the experimental structure function evaluated by using atomic scattering factors gave no significant difference between the two sets of the functions.

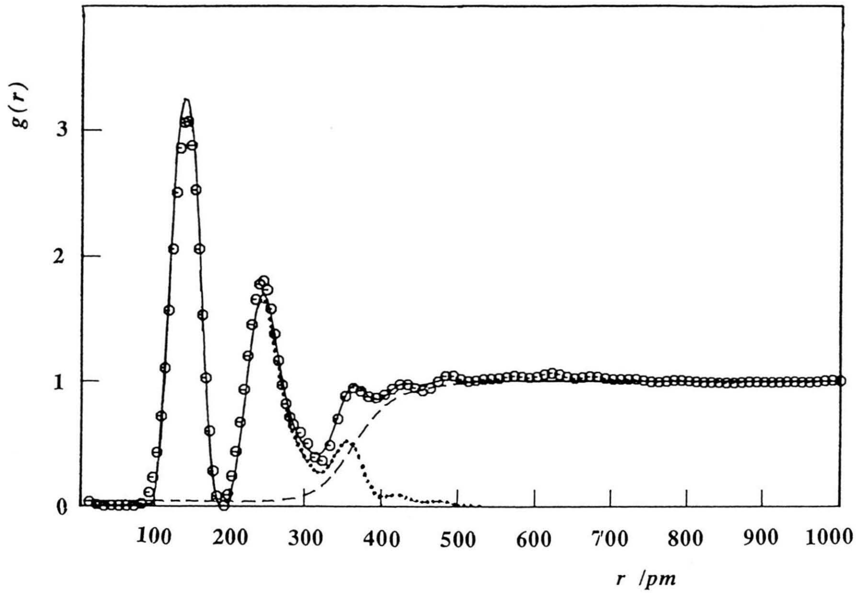

Fig. 2. Experimental pair correlation function (circles) and the theoretical one from the best fitting model (solid line) for liquid TMU. The sum of the intramolecular and discrete part of contribution (dots) and the continuum term (dashes) are also shown.

3. Structural Analysis and Results

3.1. Experimental Structure Functions and Pair Correlation Functions

The experimental structure function $si(s)$ and the related pair-correlation function $g(r)$ obtained by the Fourier transformation from the $si(s)$ function are shown in Figs. 1 and 2, respectively. The two main peaks of the $g(r)$ function can certainly be assigned to intramolecular contributions of the TMU molecule. The assignment can easily be done by considering the literature data [2, 3] and looking at the schematic view of the TMU depicted in Figure 3. Bonding distances C=O, C−N, and Me_i−N ($i=1$ to 4) contribute to the first peak of the $g(r)$ function, i.e., it arises from the "skeleton" of the molecule. The shape of the second peak is expected to be affected by the nonbonding intramolecular contributions only, since the distances in this range are too short to ascribe them to intermolecular interactions (the shoulder at about 300 pm might be an exception). As far as the intermolecular contributions are concerned, the $g(r)$ function shows that TMU is rather structureless beyond 300 pm.

The experimental difference radial distribution function $\Delta(r)$ of TMU is defined as

$$\Delta(r) = D(r) - 4\pi r^2 \varrho_0 = 4\pi r^2 \varrho_0 [g(r) - 1], \quad (3)$$

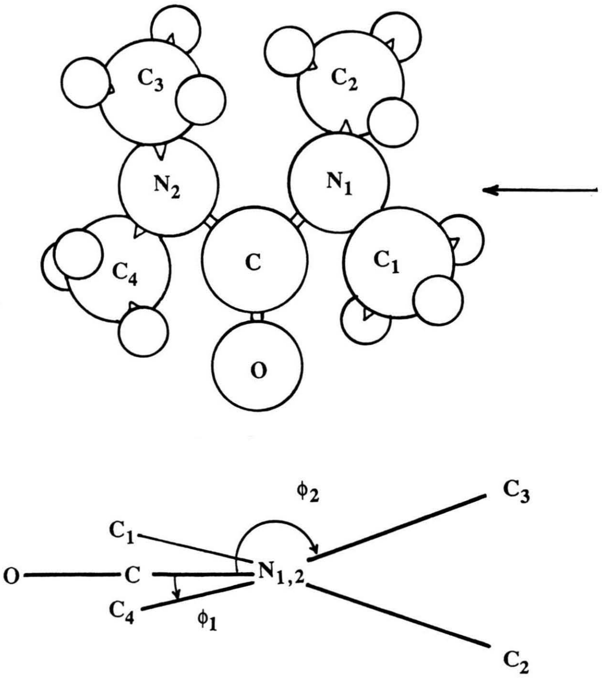

Fig. 3. Schematic view of the TMU molecule. The side projection in the direction of the arrow shows the definition of the dihedral angles describing the deviation from the planar structure. Hydrogen atoms are not numbered. Notations of C_1–C_4 change to Me_1–Me_4 when we consider the methyl groups as scattering units.

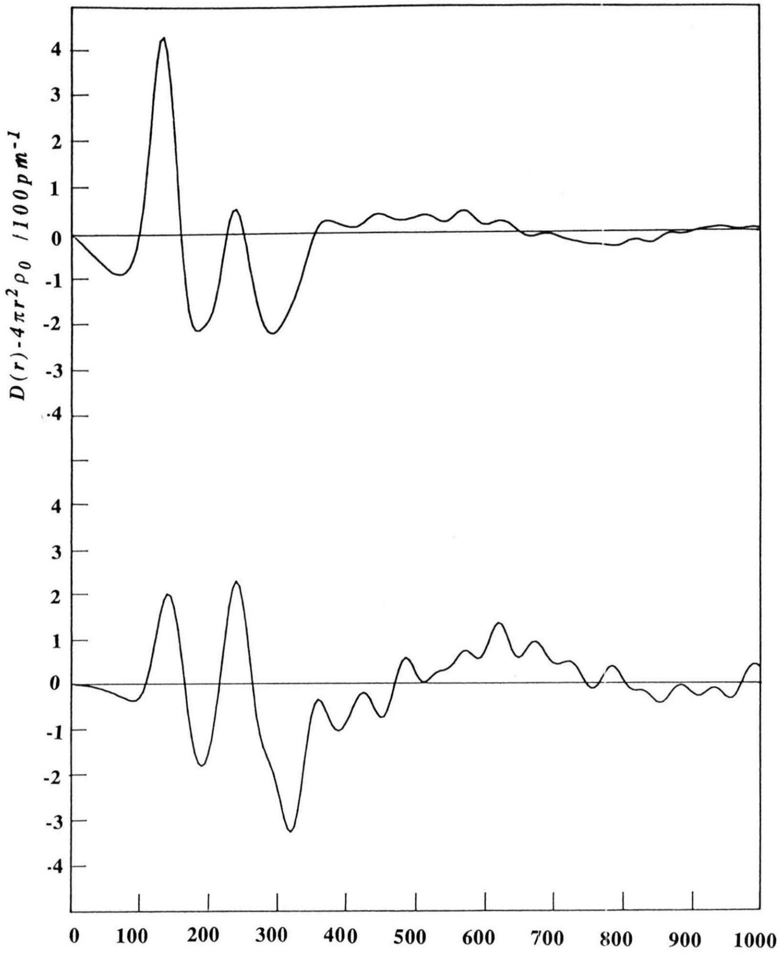

Fig. 4. Experimental difference radial distribution functions for liquid DMF (top, [7]) and TMU (bottom, this work).

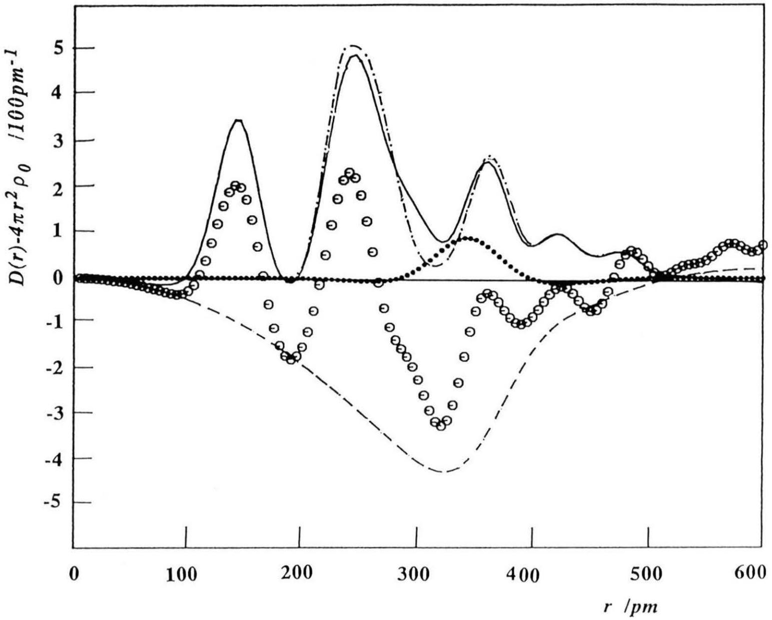

Fig. 5. The experimental difference radial distribution function for liquid TMU (circles) together with the separated intramolecular contribution (for planar structure: dash-dotted, and for non-planar structure: solid line). The intermolecular Me $\cdots$ O contribution is shown as dots. The theoretical continuum contribution, as obtained by the Fourier transformation of (7), is shown as the dashed line.

where $D(r)$ is the radial distribution function and ϱ_0 the particle density.

$\Delta(r)$ of liquid TMU is compared with $\Delta(r)$ of DMF in Figure 4. The overall character of the two curves is similar. Beyond the two peaks due to the intramolecular interactions, the patterns are almost structureless in both cases, but small differences can be observed. The $\Delta(r)$ function is flat and void of any significant structure of DMF beyond 370–380 pm; the flat maximum rises rather smoothly and extends up to about 700 pm. On the contrary, for TMU two rather clear peaks caused by intermolecular interactions can be observed from about 350–370 pm to 450–470 pm, followed by a broad maximum with many small peaks, most of which may be spurious, until about 800 pm. The boundary of the intermolecular region rises sharply, and the broad maximum extends up to longer distances. These features indicate that the molecular ordering must be slightly higher in liquid TMU than in DMF.

3.2. *Method of Structural Analysis*

A detailed analysis of the intramolecular and liquid structures of TMU was performed by model construction followed by fitting the model structure functions to the corresponding experimental ones by a nonlinear least-squares (LSQ) method. The fit was monitored through the R-factor as defined by

$$R = \frac{\sum [s\,i_{\mathrm{exp}}(s) - s\,i_{\mathrm{mod}}(s)]^2}{\sum [s\,i_{\mathrm{exp}}(s)]^2}, \tag{4}$$

where the summation is extended over the whole s-range used for the refinement.

The model structure functions comprised, in principle, three terms

$$s\,i_{\mathrm{mod}}(s) = s\,i_{\mathrm{I}}(s) + s\,i_{\mathrm{D}}(s) + s\,i_{\mathrm{C}}(s), \tag{5}$$

where $s\,i_{\mathrm{I}}(s)$ refers to the intramolecular contributions while the intermolecular contributions are divided into a discrete $s\,i_{\mathrm{D}}(s)$ and a continuum $s\,i_{\mathrm{C}}(s)$ part. For the first two terms the analytical form

$$s\,i(s) = \sum \varrho_0 x_\alpha n_{\alpha\beta} f_\alpha(s) f_\beta(s) \Delta_0(s r_{\alpha\beta}, l_{\alpha\beta}) M(s) \tag{6}$$

was used, while the continuum was described by

$$s\,i_{\mathrm{C}}(s) = -4\pi\varrho_0 \sum x_\alpha x_\beta f_\alpha(s) f_\beta(s) R^2_{\alpha\beta} \Delta_1(s R_{\alpha\beta}, L_{\alpha\beta}), \tag{7}$$

where

$$\Delta_m(s x, y) = j_m(s x) \exp(-1/2\, y^2 s^2), \tag{8}$$

and j_m is the m-th order spherical Bessel function. The summation runs over each $\alpha-\beta$ pair in the molecule in case of $s\,i_{\mathrm{I}}(s)$ and over the pairs included in the discrete structure in case of $s\,i_{\mathrm{D}}(s)$, and moreover, for selected $\alpha-\beta$ pairs for the continuum terms. The discrete structural parameters were distances $r_{\alpha\beta}$, their root-mean square deviations (r.m.s.d.) $l_{\alpha\beta}$, and frequency factors (or coordination numbers) $n_{\alpha\beta}$. The continuum contributions were characterized by the distances $R_{\alpha\beta}$ beyond which the β type scattering units can be considered to have a random distribution around a central α type one, and by the related $L_{\alpha\beta}$ values describing the sharpness of the $R_{\alpha\beta}$ boundaries.

3.3. *Models and Refinement Procedure*

Several geometrical models were constructed and tested gainst the experimental structure function.

For the fitting procedure, the s ranges from 0.02 to 0.155 pm^{-1} and 0 to 0.04 pm^{-1} were covered to adjust discrete and continuum parameters, respectively. Finally the overall fit was examined over the whole s range available.

a) At the first step our model included the intramolecular structure of TMU, beyond which the liquid structure was described by continuum terms. The molecule was supposed to be planar, i.e. dihedral angles $\phi_1 = 0$ and $\phi_2 = 180°$ (cf. Figure 3). The initial values for all structural parameters were taken from the previous GED study [3]. The adjustable parameters were the bonding distances $r_{\mathrm{C-O}}$, $r_{\mathrm{C-N}}$, and $r_{\mathrm{Me}_i\mathrm{-N}}$ (supposed to be identical for $i = 1$ to 4), the angles $\sphericalangle \mathrm{N_1CN_2}$, $\sphericalangle \mathrm{CN_1Me_1}$ ($= \sphericalangle \mathrm{CN_2Me_4}$), and $\sphericalangle \mathrm{CN_1Me_2}$ ($= \sphericalangle \mathrm{CN_2Me_3}$), and all $l_{\alpha\beta}$ values. It is worth noting that the r.m.s.d. values were treated as independent adjustable parameters, but in fact, they were only slightly changed in the course of the refinement in all cases. Attempts to refine them led to no detectable difference in the R-factor.

For the description of the continuum, the $R_{\alpha\beta}$ and $L_{\alpha\beta}$ parameters were adjusted for each $\alpha-\beta$ atom pair. At this level, a rather satisfactory R-factor of 0.097 could be obtained. This reflects that the real structure was not very far from that preliminarily assumed. Significant disagreements between the experimental and model structure functions were observed in the 0.02–0.04 and 0.08–0.12 pm^{-1} ranges, which resulted in a deviation of the theoretical radial distribution function from the experimental one in the 250–400 pm range.

b) At the next step, ϕ_1 and ϕ_2 were allowed to vary. A detectable improvement in the agreement was signalled by a drop in the R-factor to 0.086. The agreement between the experimental and theoretical $g(r)$ functions was improved, especially in the range where nonbonding intramolecular distances mainly contribute (200 to 320 pm). At this level of refinement slight changes in the bonding and nonbonding distances found in the preceding procedure were observed.

c) An unsatisfactory fit was still observed in the s-range from 0.02 to 0.04 pm^{-1} in the $s\,i(s)$ curves and in the range from 300 to 400 pm in the $g(r)$ functions. Moreover, some parameters resulted in unreasonable values, e.g., the small $R_{\mathrm{NMe}} = 300$ pm was accompanied by an unreasonably large $L_{\mathrm{NMe}} = 97$ pm (Table 2). The result was contradictory to our observation of a sharp rise in the $\Delta(r)$ function at about 300 pm.

In order to improve our model, we introduced a discrete intermolecular term, weighted as Me ··· O. The parameters $r_{\mathrm{Me} \cdots \mathrm{O}}$, $l_{\mathrm{Me} \cdots \mathrm{O}}$ and $n_{\mathrm{Me} \cdots \mathrm{O}}$ were adjusted. No other discrete contribution seemed to be necessary for further improvement.

d) Since several continuum parameters tended to common values, in the final attempt we aimed at reduction of the number of continuum parameters and, consequently, of the total number of fitted parameters. Three pairs of parameters were introduced in the 10 continuum terms, denoted by R_i and L_i, $i = 1, 2, 3$. In other words, the $\alpha - \beta$ pairs were organized in three groups and the terms in each groups used a common $R_i - L_i$ pair. The physical meaning of the distance parameters is as follows: R_1 is the distance beyond which an N, C, or O atom is randomly distributed around a central N, C, or O atom. R_2 is the boundary when an Me group is seen from an N atom or an Me group placed in the center, and R_3 was applied to Me groups seen from an O or C atom placed in the center. Accordingly, we can roughly interpret the three parameter pairs as expressing three different types of continuum distributions, namely, the distribution of small atoms ($i = 1$), more bulky parts ($i = 2$), and a cross-correlated term of the two first types ($i = 3$).

The refinement process was stopped when the R-factor converged to the lowest value of $R = 0.052$. The agreement between the experimental and theoretical structure functions is demonstrated in Fig. 1, and between the pair-correlation functions in Figure 2. Contributions of some pairs to the $g(r)$ function are also shown in Figure 2. Moreover, the $\Delta(r)$ functions obtained for the planar and nonplanar models are shown in Figure 5. The dashed line practically coincides with the residual curve after subtraction of the theoretical function calculated from the non-planar model from the experimental function; therefore the residual curve

Table 1. The best fit values of the intramolecular structural parameters for TMU and the gas phase GED data [3].

α, β	This work		GED [3]	
	$r_{\alpha\beta}$/pm	$l_{\alpha\beta}$/pm	$r_{\alpha\beta}$/pm	$l_{\alpha\beta}$/pm
C–H	–	7.5	111.7	7.5
C=O	123 (2) [a]	5.2 (4)	124.0	4.1
C–N	137 (2)	7.5 (7)	139.7	4.9
Me_1–N	146 (1)	8.1 (5)	146.1	5.0
$N_1 \cdots N_2$	235	7.3	245	7.3
$O \cdots N_1$	225	6.5 (2)	226	6.8
$N_1 \cdots Me_3$	286	10.7 (5)	287	11.7
$N_1 \cdots Me_4$	364	6.7	372	6.7
$C \cdots Me_1$	245	6.8	247	6.8
$C \cdots Me_2$	237	7.3	240	7.3
$O \cdots Me_2$	350	11.7 (9)	359	11.7
$O \cdots Me_1$	261	9.6 (9)	260	9.6
$Me_1 \cdots Me_2$	256	8.4 (6)	260	7.8
$Me_2 \cdots Me_3$	298	6.5 (5)	249	7.8
$Me_1 \cdots Me_4$	421	12.4 (7)	431	11.7
$Me_2 \cdots Me_4$	474	8.3	479	8.3
∢NCO	119.3° (5)		122.3°	
∢$CNMe_1$	114.0° (4)		114.3°	
∢Me_1NMe_2	119.7° (6)		119.8°	
ϕ_1	7° (6)		4.8°	
ϕ_2	144.2° (6)		138.4°	

[a] For the adjusted parameters the estimated errors are given in parantheses.

Table 2. Parameters describing the continuum parts of the structure of liquid TMU as derived from the best fitting model to the structure function and the continuum parameters reported for liquid DMF [8].

$\alpha - \beta$	TMU		DMF	
	$R_{\alpha\beta}$/pm	$L_{\alpha\beta}$/pm	$R_{\alpha\beta}$/pm	$L_{\alpha\beta}$/pm
Each terms fitted separately				
Me–Me	352 (4)	32 (3)	290	60
Me–N	300 (3)	97 (9)	269	86
Me–O	343 (4)	10 (1)	311	85
Me–C	356 (9)	47 (2)		
N–N	450 (8)	70 (5)		
N–O	425 (8)	91 (9)		
N–C	360 (5)	20 (3)		
O–O	468 (8)	50 (5)		
O–C	400 (9)	30 (5)		
C–C	380 (8)	30 (5)		
Common parameters for more terms				
1	452 (6)	69 (3)		
2	370 (5)	27 (2)		
3	354 (5)	32 (2)		

	FA	NMF	DMF	TMU	TMU	TMU	TMU
Method [a]	XD [a]	XD	XD	GED	GED	MNDO	MNDO
Reference	[13]	[14]	[7]	[2]	[3]	[4]	[5]
r_{C-H}/pm	–	–	109	110	111.7	–	–
$r_{C=O}$/pm	124	122	124	121	124	122.7	123.4
r_{C-N}/pm	133	134	135	133	139.7	142.5 [b]	139.3
r_{Me_1-N}/pm	–	145	145	145	146.1	146.7	
$\sphericalangle NCO$/°	122	120	130	120	122.3	122.1	
$\sphericalangle CNMe_2$/°	–		129	117.5	114.3	119.0 [b]	
$\sphericalangle Me_1NMe_2$/°	–		116	117.5	119.8	121.3 [b]	
ϕ_1/°	–				4.8	26.6, 36.8	
ϕ_2/°	–				138.4	134.4, 117.3	

Table 3. Comparison of several intramolecular parameters for formamide (FA), *N*-methylformamide (NMF), *N,N*-dimethylformamide (DMF) and tetramethylurea (TMU).

[a] The applied methods are: liquid x-ray diffraction (XD), gas electron diffraction (GED), and MNDO calculations.

[b] Average value of different ones.

is not shown in the figure. The final structural parameters are listed in Tables 1 and 2.

4. Discussion and Conclusions

4.1. *Intramolecular Structure of TMU*

As a result of the analysis, the non-planar geometry of the intramolecular structure could be verified even in the liquid state. One of the two dihedral angles ϕ_2 showed a stable convergence to a value of 144°. The other dihedral angle ϕ_1, however, is rather close to 0° and exhibits a large uncertainty (the final value is $(7 \pm 6)°$). We note that the values of this angle reported in the literature bear a similar uncertainty. Our result is in good agreement with the ϕ_1 value in a recent GED experiment [3], as shown in Table 1. However, if we compare the ϕ_1 value with those in other studies (Table 3), we see that the MNDO calculation led to even larger ϕ_1 values [4] and their errors seem to be large. On the other hand, the ϕ_2 values previously reported are somewhat smaller than that in the present work.

Other parameters such as bonding distances, angles and $l_{\alpha\beta}$ values show a good agreement with previous results. The three bonding angles $\sphericalangle N_1CN_2$, $\sphericalangle CN_1Me_1$, and $\sphericalangle CN_1Me_2$ were refined separately, but they did not deviate too much from the values in the gas phase. The same holds for the $l_{\alpha\beta}$ parameters (Table 1).

Thus, we can conclude that the intramolecular structural parameters of TMU are the same within the experimental errors in both the gas and liquid states.

If we compare the intramolecular structural parameters of TMU with those of formamide derivatives in the liquid state (Table 3), we see that the C–N distance in TMU is 2 to 4 pm larger than that in the amides, and somewhat smaller than that in TMU in the gas phase. The $\sphericalangle Me_1CMe_2$ bonding angles of DMF and TMU are similar. The $\sphericalangle NCO$ angle is by 10° larger and the $\sphericalangle CNMe_2$ angle is by 16° larger in DMF than the corresponding angles in TMU, which might be due to a lower symmetry in DMF and thus a larger deviation of the structure from the planar one. However, one has to keep in mind that in case of DMF the angles were calculated from nonbonding distances which were refined independently, and thus their uncertainty must be large.

4.2. *Intermolecular Structure and the Bulkiness of the Molecule*

The only discrete intermolecular contribution which was considered in the final step of the structural analysis was ascribed to Me ··· O interactions. The final values of the structural parameters were $r_{Me \cdots O} = 340$ pm, $l_{Me \cdots O} = 27$ pm, and the coordination number was determined to be 2.2. This result can be interpreted as a consequence of a certain kind of ordering between neighbouring TMU molecules, if we suppose that loose dimers can be formed in the liquid due to dipole-dipole interaction, where two molecules are situated in parallel planes in an antiparallel position. Another possible assumption is that one TMU molecule lies in a common plane with another one with its O atom approaching the Me_2 and Me_3 groups in the other molecule. An average number of 2 Me groups per oxygen atom is expected in both cases.

Many authors reporting results of liquid x-ray diffraction studies take less care of the meaning of the continuum parameters, which, however, may bear interesting information. The parameters are usually considered as artificial for improving the fit of models to the experimental data.

Table 2 shows the continuum parameters for TMU in comparison with the parameters reported for DMF [8]. In our explanation, the values of the applied

$R_1 - R_3$ parameters are correlated with the bulkiness of the TMU molecule or more precisely, with the space filled by a TMU molecule in the liquid. If we compare the continuum parameters of the DMF with those of TMU, we can observe that the DMF's boundaries of the continuum distribution are smaller than those of TMU, and thus DMF occupies a smaller space than TMU, i.e., the former is less bulky. Thus statement may be supported by the fact that the flat part in the $\Delta(r)$ function characteristic for intermolecular interactions in DMF appears at a lower r range than in the corresponding function of TMU.

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