A Study of the Liquid Structure of Dimethyl Sulfoxide by the X-Ray Diffraction

Sumiko Itoh and Hitoshi Ohtaki
Department of Electronic Chemistry, Tokyo Institute of Technology at Nagatsuta, Nagatsuta-cho, Midori-ku, Yokohama 227, Japan

Z. Naturforsch. **42 a,** 858–862 (1987); received April 28, 1987

The liquid structure of dimethyl sulfoxide (DMSO) was investigated by X-ray diffraction. The intramolecular structure parameters were obtained as follows: S=O 150(1) pm, C—S 180(1) pm, nonbonding C···O 267(4) pm and C···C 271(7) pm. It is suggested that the molecular arrangement in the liquid state is similar to that in the solid state. It is pointed out that not only the value but also the position of the dipole moment vector in the molecule is essential for dipole-dipole intermolecular interactions and that the latter factor results in a higher melting point of DMSO than of N,N-dimethylformamide in spite of their similar dipole moments.

1. Introduction

There are a number of investigations dealing with the structure of liquid dimethyl sulfoxide (DMSO) not only in the pure state but also in binary mixtures. Liquid DMSO is found to be associated according to cryoscopic [1], spectroscopic [2], relaxation [3], viscosity [4] and neutron inelastic scattering [5] measurements. From recent Raman and infrared spectroscopic data, the existence in pure DMSO of cyclic and linear dimers including linear polymers is reported, although the assignment of the bands is still in controversy [6–9]. The result of an NMR measurement suggested the formation of cyclic dimers of 2-thiaindan 2-oxide in $CDCl_3$ [10]. Lumbroso *et al.* measured the dipole moment of DMSO in cyclohexane and explained their result in terms of a mixture of linear dimers and cyclic chain aggregates [11].

Although some X-ray diffraction investigations on the structure of solvated metal ions in DMSO have been carried out [12–16], an analysis of the liquid structure of pure DMSO has not been reported. In the present work this is done by means of X-ray diffraction.

2. Experimental

Commercially available DMSO of analytical grade was distilled on calcium hydride under a reduced pressure.

X-Ray scattering measurements were carried out with a JEOL $\theta-\theta$ diffractometer using Mo$K\alpha$ radiation ($\lambda = 71.07$ pm) at (25 ± 1) °C. The range of the scattering angle (2θ) was from 4° to 140°. 80,000 counts were recorded over the whole angle range. The method of corrections and data treatment were essentially the same as those described previously [17]. The scattering and correction factors were quoted from the literature [18]. The reduced intensities $i(s)$ were obtained from the equation

$$i(s)_{\text{obsd}} = K I_{\text{corr}}(s) - \sum n_i [\{f_i(s) + \Delta f_i'\}^2 + (\Delta f_i'')^2], \quad (1)$$

where n_i is the number of atoms i in the stoichiometric volume V, and $f_i(s)$ denotes the atomic scattering factor at the angle s. $\Delta f_i'$ and $\Delta f_i''$ are the real and imaginary parts of the anomalous dispersion of atom i, respectively. I_{corr} denotes the measured scattering intensity corrected for the back ground, absorption, polarization, multiple and incoherent scattering. K is a factor for converting measured intensities to absolute ones and was obtained by the high angle method and the Krogh-Moe-Norman method [19, 20]. The radial distribution function $D(r)$ was then obtained from

$$D(r) = 4\pi r^2 \varrho_0 + (2r/\pi) \int_0^{s_{\max}} s\, i(s)\, M(s) \sin(s r)\, ds, \quad (2)$$

where ϱ_0 is the average electronic density of the sample solutions. $s_{\max}$ corresponds to the maximum values of s for the Fourier transform. In the present case $s_{\max}$ was 16.7×10^{-2} pm^{-1}. $M(s)$ is a modifica-

---

Reprint requests to Prof. H. Ohtaki, Department of Electronic Chemistry, Tokyo-Institute of Technology at Nagatsuta, Nagatsuta-cho, Midori-ku, Yokohama 227, Japan.

0932-0784 / 87 / 0800-0858 $ 01.30/0. – Please order a reprint rather than making your own copy.

tion function given by

$$M(s) = [\sum_i \{(f_i(0) + \Delta f_i')^2 + (\Delta f_i'')^2\} / \sum_i \{(f_i(s) + \Delta f_i')^2 + (\Delta f_i'')^2\}] \cdot \exp(-k\, s^2), \quad (3)$$

where the damping factor k is set to be 100 pm^2. Theoretical reduced intensities were calculated according to

$$i(s)_{\text{calcd}} = \sum\sum n_{ij} [\{f_i(s) + \Delta f_i'\}\{f_j(s) + \Delta f_j'\} + \Delta f_i''\, \Delta f_j''] \cdot \{\sin(s\, r_{ij})/(s\, r_{ij})\} \exp(-b_{ij} s^2), \quad (4)$$

where r_{ij}, b_{ij} and n_{ij} stand for the distance, temperature factor and frequency factor of the $i-j$ atom pair, respectively. The program KURVLR [21] was employed for the intensity calculations.

3. Results and Discussion

The $s\,i(s)$ curve and differential radial distribution function $D(r) - 4\pi r^2 \varrho_0$ are shown in Figs. 1 and 2, respectively. In the differential radial distribution function the first peak at 170 pm is ascribed to the 1 $S{=}O$, 2 C—S, and 6 C—H bonds per DMSO molecule, the small second peak and the area under the peak around 270 pm is attributable to the nonbonding 2 C···O, 1 C···C and 6 S···H interactions per molecule. The large peak centered at about 530 pm is due to various intermolecular atom-pair interactions, which will be discussed later.

The intramolecular interactions were first analyzed from the radial distribution curve, as well as from the reduced intensities under the following assumptions:

(1) The initial structure parameters within a DMSO molecule which are refined in the course of the least-squares method are assumed to be the same as those found in the solid state: S=O 150 pm, C—S 178 pm, C···O 265 pm, C···C 272 pm. The temperature factors for these four interactions are tentatively assumed to be 30 pm^2, 40 pm^2, 60 pm^2 and 70 pm ^{2}, respectively.

(2) The distance and the temperature factor of the C—H bond are fixed at 108 pm and 10 pm^2, respectively. The S···H distance is taken from the solid data: 240 pm [22]. The temperature factor is set to be the sum of those of the C—S and C—H bonds.

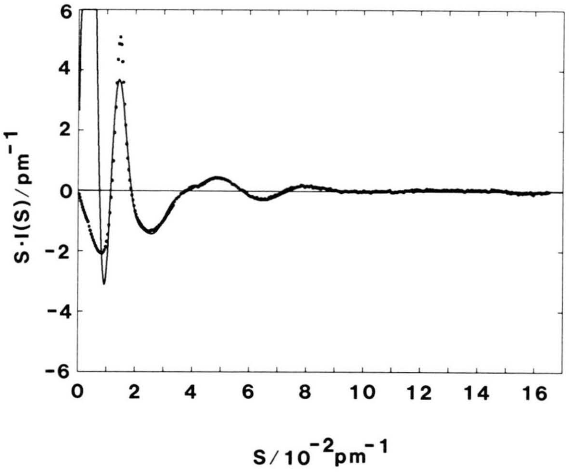


Fig. 1. Experimental (dots) and the theoretical (solid line si(s) curves.

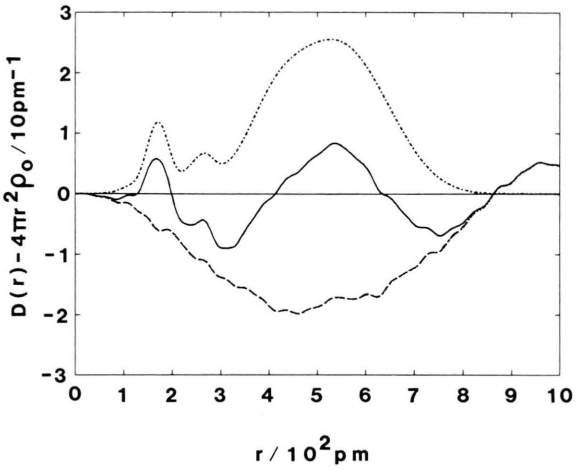


Fig. 2. Experimentally obtained $D(r) - 4\pi r^2 \varrho_0$ curve (solid line) and the theoretical one (dotted line). The difference between them is given by the broken line.

(3) The methyl groups are tetrahedral. Nonbonding interactions for the 6 S···H atom-pairs within a molecule are taken into account.

After the removal of the spurious peaks appearing at $r < 100$ pm in the radial distribution curve, the parameters for the intramolecular interactions were refined by applying the least-squares method with the program NLPLSQ [23] to the structure function in order to minimize the error-square sum

$$U = \sum_{s_{\min}}^{s_{\max}} w(s)\,[i(s)_{\text{obsd}} - i(s)_{\text{calcd}}]^2\,, \qquad (5)$$

where the weighting function $w(s)$ is set to be s^2. No appreciable change of the result was found when the $s_{\min}$ value was varied from $6.0 \times 10^{-2}\,\text{pm}^{-1}$ to $4.0 \times 10^{-2}\,\text{pm}^{-1}$. The obtained intramolecular structure parameters are tabulated in Table 1. These values coincide with the literature data [12–16] within the experimental error.

In the next step of the analysis, the intermolecular interactions were estimated. According to Lindemann [24], melting occurs when the thermal vibration of the lattice of a solid causes an expansion of its amplitude by more than about 10% of the molecular distance. Therefore, a liquid at a temperature just above the melting point may have a structure similar to that of the solid state. The rule could be applied to most of molten alkali metals [25], although exceptions have been seen for some cases, e.g., $CaCl_2 \cdot 6H_2O$ hydrate melt, which is easily supercooled, has a structure largely different from that in the crystalline state even just above the melting point [26].

Since DMSO has a sharp melting point and is not easily supercooled, the molecular arrangement of liquid DMSO may not be much different from that in the solid state at room temperature according to the Lindemann rule, because the temperature in the present study (25 °C) is not very far from the melting point of DMSO (18.54 °C). Thus we assumed that the liquid structure of DMSO is similar to that in the solid state. The mean-square amplitude Δr_{ij} for the intermolecular atom-pair interactions was assumed to be 13% of the corresponding atomic distances of each pair. The temperature factors b_{ij} in (4) were thus calculated by the equation

$$b_{ij} = (\Delta r_{ij})^2/2\,. \qquad (6)$$

The calculated si(s) and differential radial distribution functions fitted well the experimental ones, as shown in Figs. 1 and 2, and therefore the assumptions adopted for the structure of liquid DMSO seem reasonable. The interatomic distances and the temperature factors of liquid DMSO used in the calculations are given in Table 1. The molecular arrangement thus estimated for liquid DMSO is depicted in Figure 3. As is seen in the picture, the nearest neighbours of an oxygen atom of a DMSO molecule are four H atoms of methyl groups of three neighboring molecules. The discrete molecular aggregates of DMSO so far proposed [6–11] are not seen in the solid-like structure.

Table 1. The structure parameters of liquid DMSO. *r*, *b* and *n* denote the distance, the temperature factor and the frequency factor, respectively. The values in parentheses are their standard deviations. The intermolecular structure parameters are obtained from the crystal data [22] and fixed in the course of the calculations.

Interactions	*r*/pm	*b*/10² pm²	*n*	interactions	*r*/pm	*b*/10² pm²	*n*
Intramolecular interactions							
S=O	150(1)	0.4(1)	1	C—S	180(1)	0.5(1)	2
C···O	267(4)	0.9[a]	2	C···C	271(7)	1.1[b]	1
Intermolecular interactions							
C···O	336	9.6	1	C···O	345	10.3	1
C···O	353	10.5	1	C···O	357	10.8	1
C···O	372	11.7	1	S···O	376	11.9	1
C···C	381	12.2	1	C···C	383	12.4	1
S···O	384	12.5	1	S···C	387	12.6	1
S···O	396	13.2	1	C···C	399	13.5	1
S···C	401	13.6	1	O···O	407	14.0	2
C···C	419	14.8	1	S···S	421	14.9	1
S···C	428	15.4	1	S···C	430	15.6	1
C···C	434	15.9	1	C···C	441	16.4	1
S···C	442	16.5	1	C···O	451	17.2	1
O···O	452	17.3	1	S···O	460	17.9	1
C···O	467	18.4	1	S···C	470	18.6	1
C···C	478	19.3	2	C···C	480	19.5	1
S···C	481	19.6	1	S···C	483	19.7	1
S···C	492	20.4	1	S···S	497	20.9	2
C···O	514	22.3	1	S···S	514	22.3	1
S···C	521	22.9	1	S···C	522	23.0	1
C···O	526	23.4	1	S···S	530	23.8	2
O···O	530	23.8	2	C···C	530	23.8	2
C···O	541	24.7	1	C···O	546	25.2	1
C···O	567	27.2	1	C···O	568	27.3	1
S···C	575	27.9	1	S···C	579	28.3	1
O···O	580	28.4	1	S···C	587	29.1	1
C···C	588	29.2	2	O···O	588	29.5	1
S···C	593	29.7	1	S···C	595	29.9	1
C···O	595	29.9	1	C···C	595	29.1	1
S···C	596	30.1	1	C···O	596	30.1	2
S···S	598	30.2	2	S···O	602	30.6	1
C···C	603	30.7	2	O···O	603	30.7	1
S···O	606	31.2	1	C···O	615	32.0	1
S···O	619	32.3	1	S···S	619	32.4	1

[a] $b_{CO} = b_{S=O} + b_{C-S}$. [b] $b_{CC} = 2\,b_{C-S}$.

Some physicochemical properties of DMSO are shown in Table 2 together with those of N,N-dimethylformamide (DMF) for comparison [27, 28]. It has been shown that liquid DMF has no significant intermolecular interactions and that the molecules are practically randomly distributed at room temperature according to an X-ray diffraction study

Table 2. Comparison of physicochemical properties: m.w. the molecular weight, m.p. the melting point (°C), b.p. the boiling point (°C), ε the relative dielectric constant, μ the dipole moment (Debye), η the viscosity (centipoise), D_N the donor number, A_N the acceptor number, v the molar volume (10^{-6} m^3/mol), g the dipole correlation parameter, α the polarizability (10^{-30} m^3/molecule).

Property	DMSO	DMF
m.w.	78.134	73.095
m.p.	18.54	− 60.43
b.p.	189.0	153.0
ε	46.68	36.71
μ [a]	3.9	3.86
η	1.996	0.802
D_N	29.8	26.2
A_N	19.3	16.0
v	71.3	77.4
g	1.06	1.00
α	7.97	7.91

[a] 1 Debye = 3.33×10^{-30} C m.

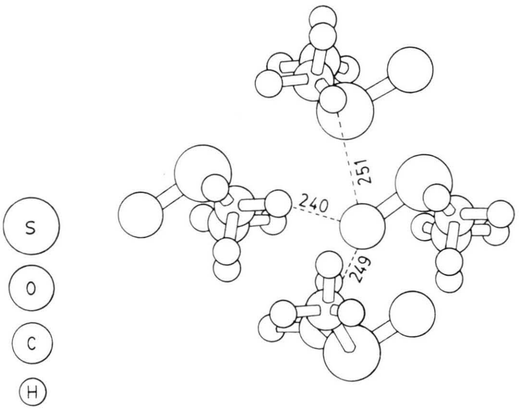
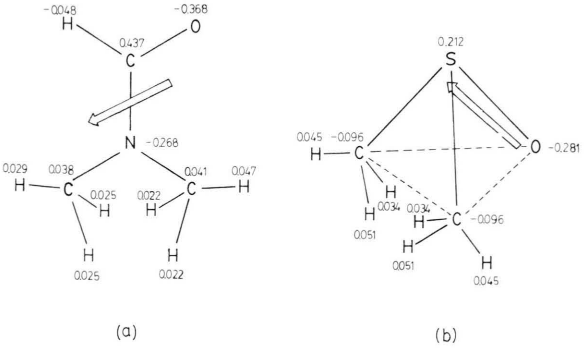


Fig. 3. The liquid structure of dimethyl sulfoxide deduced from Ref. [22].



(a)

(b)

Fig. 4. The charge distributions of DMF (a) and DMSO (b) molecules [30, 31]. The arrows indicate the dipole moments.

[29]. DMSO has a dipole moment similar to that of DMF, but it has long-range intermolecular interactions at 25 °C. The former has a higher melting point in spite of their similar dipole moments, molecular weights and molar volumes (see Table 2).

In Fig. 4 the charge distributions of DMSO and DMF molecules calculated by the CNDO/2 method are shown [30, 31]. All atoms within a DMF molecule except the hydrogen atoms lie in a plane and the vector of the dipole is located at almost the center of the molecule directing from the oxygen atom within the carbonyl group toward the methyl group in the *trans*-position as indicated by an arrow in the figure [32]. On the other hand, a DMSO molecule has a trigonal pyramid structure in which the dipole lies almost along the S=O bond, i.e. along an edge of the pyramid (cf. Fig. 4(b)). The location of the dipole of DMSO indicates that the dipole-dipole interaction between two DMSO molecules can be stronger than that between two DMF molecules because in the former case the dipole-dipole distance can be shorter.

It may be generally expected that molecules in which the dipole is deeply embedded show weak interactions, while molecules in which an exposed dipole exists may easily associate [33]. The low melting point and relatively low viscosity of DMF may thus be due to weak dipole-dipole interactions. Similar values of the g-parameter, the polarizability, the dipole moment and the molecular volume of DMSO and DMF and a more ordered structure of the former result in the slightly larger relative dielectric constant of DMSO compared with DMF. Slightly larger D_N and A_N values of DMSO than those of DMF may partly contribute to larger donor-acceptor interactions between DMSO molecules, which lead also to a more structured molecular arrangement of DMSO than of DMF molecules.

Acknowledgement

The work has partially been financially supported by the Grant-in-Aid for Scientific Research (No. 61134043) from the Ministry of Education, Science and Culture of Japan. Computer calculations have been carried out at the Tokyo Institute of Technology at Nagatsuta and partly at the Institute for Molecular Science at Okazaki. Professor A. D. Kowalak kindly corrected the English.

[1] J. J. Lindberg, J, Kenttämaa, and A. Nissema, Suom. Kemistil. **B 34,** 98 (1961); **B 34,** 156 (1961).

[2] W. D. Horrocks, Jr. and F. A. Cotton, Spectrochim. Acta **17,** 134 (1961).

[3] E. Cebe, D. Kaltenmeier and H. G. Hertz, Z. Phys. Chem. N.F. **140,** 181 (1984).

[4] R. T. M. Bicknell, D. B. Davies, and K. G. Lawrence, J. Chem. Soc., Faraday Trans. 1, **78,** 1595 (1982).

[5] G. J. Safford, P. C. Schaffer, P. S. Leung, G. F. Doebbler, G. W. Brady, and E. F. X. Lyden, J. Chem. Phys. **50,** 2140 (1969).

[6] R. H. Figueroa, E. Roig, and H. H. Szmant, Spectrochim. Acta **22,** 587 (1966).

[7] M.-T. Forel and M. Tranquille, Spectrochim. Acta **26 A,** 1023 (1970).

[8] M. I. S. Sastry and S. Singh, J. Raman Spect. **15,** 80 (1984).

[9] J. B. Gill, D. C. Goodall, B. Jeffreys, and P. Gans, J. Chem. Soc., Dalton Trans., **1986,** 2597.

[10] R. F. Watson and J. F. Eastham, J. Amer. Chem. Soc. **87,** 664 (1965).

[11] H. Lumbroso, J. Curé, T. Konakahara, and K. Sato, J. Mol. Struct. **98,** 277 (1983).

[12] F. Gaizer and G. Johansson, Acta Chem. Scand. **22,** 3013 (1968).

[13] M. Sandström, Acta Chem. Scand., Ser. A **A 32,** 627 (1978).

[14] S. Pocev, R. Triolo, and G. Johansson, Acta Chem. Scand. Ser. A, **A 33,** 179 (1979).

[15] S. Ahrland, E. Hansson, Å. Iverfeldt, and I. Persson, Acta Chem. Scand. **A 35,** 295 (1981).

[16] I. Persson, Å. Iverfeldt, and S. Ahrland, Acta Chem. Scand. **A 35,** 295 (1981).

[17] H. Ohtaki, M. Maeda, and S. Ito, Bull. Chem. Soc. Japan **47,** 2217 (1974).

[18] "International Tables for X-Ray Crystallography," Kynoch Press, Birmingham 1974, vol. **4,** D. T. Cromer and J. B. Mann, J. Chem. Phys. **47,** 1892 (1967). D. T. Cromer, J. Chem. Phys. **50,** 4857 (1969).

[19] J. Krogh-Moe, Acta Crystallogr. **9,** 951 (1956).

[20] N. Norman, Acta Crystallogr. **10,** 370 (1957).

[21] G. Johansson and M. Sandström, Chem. Scr. **4,** 195 (1973).

[22] R. Thomas, C. B. Shoemaker and K. Eriks, Acta Crystallogr. **21,** 12 (1966). M. A. Viswamitra and K. K. Kannan, Nature, London **209,** 1016 (1966).

[23] T. Yamaguchi, Doctor Thesis, Tokyo Institute of Technology, March 1978.

[24] F. A. Lindemann, Physik. Z. **11,** 609 (1910).

[25] J. N. Shapiro, Phys. Rev. **B 1,** 3982 (1970).

[26] T. Yamaguchi, S. Hayashi, and H. Ohtaki, to be published.

[27] J. A. Riddick and W. B. Bunger, Organic Solvents, Wiley-Intersci. Press, New York 1970, 3rd edn.

[28] Y. Marcus, Introduction to Liquid State Chemistry, Wiley-Intersci. Press, New York 1977.

[29] H. Ohtaki, S. Itoh, T. Yamaguchi, S. Ishiguro, and B. M.Rode, Bull. Chem. Soc. Japan **56,** 3406 (1983).

[30] G. Robinet, C. Leibovici, and J.-F. Labarre, Theor. Chim. Acta (Berl.) **26,** 257 (1972).

[31] J. F. Yan, F. A. Momany, R. Hoffmann, and H. A. Scheraga, J. Phys. Chem. **74,** 420 (1970).

[32] J. Applequist, J. Chem. Phys. **71,** 4324 (1979).

[33] Ref. [28], p. 105.