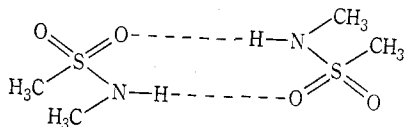


HYDROGEN BONDING IN ORGANIC COMPOUNDS*

III. THE EQUILIBRIUM CONSTANT FOR THE DIMERIZATION OF *N*-METHYLMETHANE SULPHONAMIDE†

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During an investigation of the infrared spectra of organic sulphonamides and related compounds we made some observations of the spectrum of *N*-methylmethane sulphonamide in dilute carbon tetrachloride solution. The compound showed absorption bands at 3404 and 3300 cm^{-1} which varied in relative intensity, when the concentration of the solution was changed, in a manner characteristic of a monomer-dimer equilibrium. The broader, lower frequency band that is characteristic of the dimer had a symmetrical contour, indicating that only a single species was involved. This we assume to have the formula (I).



The sample of *N*-methylmethane sulphonamide was prepared in 80% yield by the condensation of methylamine with methane sulphonyl chloride in ether solution at 0 °C (Baxter, Cymerman-Craig, and Willis 1955). It was purified by distillation, b.p. 162 °C, at 15 mm. The hygroscopic substance was stored over phosphorus pentoxide for several weeks and then solutions were made up in spectroscopic grade carbon tetrachloride just before the spectra were recorded.

The absorption bands were scanned with a Perkin Elmer 112, single-beam, double-pass, infrared spectrometer, fitted with a calcium fluoride prism, at the rate of 0.68 $\text{cm}^{-1} \text{sec}^{-1}$ for the monomer band and 0.62 $\text{cm}^{-1} \text{sec}^{-1}$ for the dimer band. Allowance for convergence of the beam through the specimen was shown to introduce a correction of about 0.3%. The computed (cm^{-1}) spectral slit-widths were 5.7 at 3400 cm^{-1} and 5.1 at 3300 cm^{-1} . The integrated band areas were calculated by the "triangular slit function" method of Ramsay (1952) which assumes that the contour of the absorption band is a Lorentz curve. The measurements are summarized in Table 1.

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† The experimental measurements were made in the Chemistry Laboratories of the University of Melbourne.

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TABLE 1

Soln. No.	Total Concentration* (mole l ⁻¹)	Cell Thickness (cm)	ln (T ₀ /T) _{max.}		Half Band-width, Δ√½ (cm ⁻¹)	
			Monomer	Dimer	Monomer	Dimer
1	2.693 × 10 ⁻²	0.268	0.431	0.610	25.2	83.4
2	1.077 × 10 ⁻²	0.550	0.503	0.341	24.3	75.0
3	5.386 × 10 ⁻³	1.00	0.539	0.211	25.7	73.8
4	1.346 × 10 ⁻³	4.00	0.628	0.078	24.3	64.0
5	6.73 × 10 ⁻⁴	4.00	0.330	—	24.8	—
6	1.966 × 10 ⁻²	0.400	0.538	0.622	26.6	80.8
7	9.83 × 10 ⁻³	1.00	0.759	0.447	26.5	77.4
8	4.914 × 10 ⁻³	1.00	0.507	0.165	25.8	71.2

* Solutions 2-5 were prepared by quantitative dilution of solution 1, and solutions 7, 8 by quantitative dilution of solution 6.

In computing the value of the equilibrium constant, it was first assumed that there was no appreciable concentration of dimer present in the 6.73×10^{-4} M solution 5 so that the apparent integrated absorption intensity for the monomer could be calculated as $4.7_1 \times 10^3$ mole⁻¹ l cm⁻² from the absorption coefficient of this solution. From this the concentrations of monomer, C_M , in the other solutions were found and then the concentration of the dimer, C_D , calculated as half the difference between the total concentration and the concentration of the monomer. A graph of $\log C_M$ v. $\log C_D$ showed all but two of the results grouped about a line of slope 2, the slope characteristic of a monomer-dimer equilibrium. These two results (solutions 3 and 8) were disregarded in equilibrium constant calculations.

The mean value of the equilibrium constant

$$K = C_D / C_M^2,$$

deduced from the remaining observations (3.3×10^1 moles l⁻¹) was then used to give an improved value of the monomer concentration in solution 5 and the calculations repeated. One further stage of approximation gave

$$K = 4.06 \pm 0.39 \times 10^1 \text{ l mole}^{-1},$$

at 25 °C.

A similar treatment of the results of Baxter, Cymerman-Craig, and Willis (1955) for *N*-phenylmethane sulphonamide gives the equilibrium constant for dimerization of that substance as $2.08_7 \pm 0.087 \times 10^2$ l mole⁻¹ compared with the value of 2.18×10^2 that they found by a different treatment of their observations. The approximately fivefold higher value of the equilibrium constant of the *N*-phenyl compared to the *N*-methyl derivative corresponds to almost 1 kcal difference in their standard free energies of dimerization. It is correlated with a difference of 125 cm⁻¹ between the monomer and dimer NH frequencies for the phenyl derivative compared to a corresponding difference of 104 cm⁻¹ for

the methyl derivative. The acidity of the N-H group in the phenyl compound is expected to be greater than that of the methyl compound so that its donor action in the formation of hydrogen bonds would be enhanced.

The monomer concentrations found when using the final value of the equilibrium constant gave the integrated absorption intensity

$$A_M = 4.94 \pm 0.17 \times 10^3 \text{ mole}^{-1} \text{ l cm}^2.$$

The large standard deviation, which is probably due to the fact that actual absorption curves do not correspond to the Lorentz function (Flynn, Werner, and Graham 1959; cf. Rank *et al.* 1960), and to a slight extension of a wing of the dimer band below the monomer band, does not warrant any attempt to extrapolate to infinite dilution. A similar treatment of the dimer concentrations and absorptions gives the integrated absorption intensity

$$A_D = 3.69 \pm 0.47 \times 10^4 \text{ mole}^{-1} \text{ l cm}^2.$$

The sevenfold increase in intensity of absorption for the dimer, compared to the monomer, corresponds to an increase in polarity in the NH bond produced by formation of a hydrogen bond of moderate strength.

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