26. *The Hydrogen Bonding of Pyrazole in Carbon Tetrachloride Solution.*

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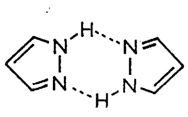
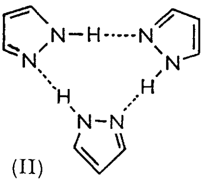
Analysis of the concentration-dependence of the infrared spectrum of pyrazole in carbon tetrachloride at 18° ± 1° has shown that the fundamental N–H stretching band at 3485 ± 10 cm.$^{-1}$ is due to monomeric pyrazole only. Hydrogen-bonding equilibria in the concentration range 10^{-4}—1M have been interpreted quantitatively in terms of co-existing monomer, cyclic dimer, and cyclic trimer, with overall formation constants of $\beta_{20} = 47{\cdot}5 \pm 1{\cdot}0$ l. mole^{-1} and $\beta_{30} = 7540 \pm 240$ l.^{2} mole^{-2}.

HÜCKEL and his co-workers [1] have suggested, on the basis of cryoscopic, viscometric, and dielectric measurements, that pyrazole consists predominantly of a cyclic, hydrogen-bonded dimer (I) at moderate concentrations in non-associated solvents. It was also suggested that more than two monomers might form chains at higher concentrations.



(I)



(II)

Hunter [2] has recently criticised the non-linear hydrogen bond in (I) and suggested that the strainless cyclic trimer (II) would be more stable. A cryoscopic study of 3,5-dimethylpyrazole in benzene by White and Kilpatrick [3] has given convincing evidence for the existence of a stable trimer, and dubious evidence for an unstable dimer. These authors consider that the trimer is almost certainly cyclic, and the dimer most probably linear. An X-ray analysis by Ehrlich [4] has now shown that pyrazole exists in the solid state as long, parallel, hydrogen-bonded chains, which describe figure-of-eight spirals. The present study was undertaken to investigate the nature of the pyrazole oligomers which exist in carbon tetrachloride solution.

A preliminary study of dilute solutions of pyrazole in carbon tetrachloride showed a fundamental N–H stretching mode at 3485 ± 10 cm.$^{-1}$ with a half-band width of 20 cm.$^{-1}$. The intensity of this band decreased with increasing total concentration, B; concurrently, a broad, bonded N–H band of increasing intensity appeared in the region 3400—2000 cm.$^{-1}$

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[1] Hückel, Datow, and Simmersbach, *Z. phys. Chem.*, 1940, **186**, *A*, 129; Hückel and Jahnentz, *Ber.*, 1942, **75**, 1438.

[2] Hunter, in " Progress in Stereochemistry," ed. Klyne, Butterworths, London, 1954, p. 223.

[3] White and Kilpatrick, *J. Phys. Chem.*, 1955, **59**, 1044.

[4] Ehrlich, *Acta Cryst.*, 1960, **13**, 946.

Bonded N–H *absorption bands of pyrazole (all peaks strong)*

Solid (cast film)	3135	3050	2960	2900	2860	2810(sh)
CCl_4 solution	3175	3070	2995	2930	2905	2825(sh)

(see Fig. 1); this showed six major peaks [excluding that due to C–H at 3120 cm.$^{-1}$ (w)], which were remarkably similar to the infrared N–H absorption bands of a solid, cast film of pyrazole. A quantitative study was therefore made of the concentration-dependence of the intensity of the 3485 cm.$^{-1}$ band.

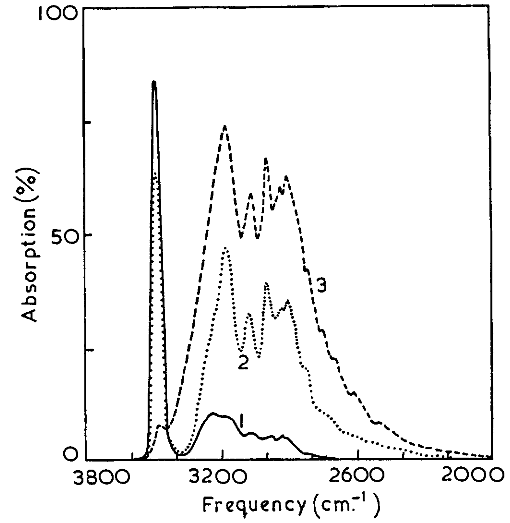

Fig. 1. *Infrared absorption spectra in the region 3800—2000 cm.$^{-1}$ for carbon tetrachloride solutions of pyrazole at various total concentrations, B, at* 18°.

1, B = 0·001M. 2, B = 0·010M.
3, B = 1·00M.

Experimental

Materials.—Pyrazole was recrystallised twice from cyclohexane; it had m. p. 70° (lit., 70°). Reagent-grade carbon tetrachloride was used without further purification; no O–H absorption spectrum was detectable on using 4 cm. cells.

Infrared Measurements.—The spectrophotometer was a Hilger H800 double-beam instrument. A rock-salt prism was used for preliminary studies, and a quartz prism for precise measurements on dilute solutions (B <10^{-2}M). The quartz prism gave a theoretical slit-width of 8 cm.$^{-1}$ at 3485 cm.$^{-1}$ with a spectrometer slit-width of 0·30 mm. The frequency scale was calibrated with reference to the N–H stretching frequency of pyrrole vapour (3530 cm.$^{-1}$). The spectrophotometer was not thermostatically controlled, and wave-number estimates are considered to be accurate to $\pm$10 cm.$^{-1}$ within the region 3500—3000 cm.$^{-1}$. Run-to-run reproducibility was $\pm$5 cm.$^{-1}$. Instrumental conditions were: gain, 4; damping, 2; speed of scan, 68 cm.$^{-1}$/min. Variable path-length cells, set at 5·000 $\pm$ 0·005 mm. and fitted with

Table 1. *Infrared absorbancies at* 3485 *cm.$^{-1}$ of associated pyrazole in carbon tetrachloride at* 18° $\pm$ 1°.

10^4B ...	0·9947	1·989	2·984	3·979	4·974	5·968	6·963	7·958	8·952	9·947	
log I_0/I...	0·0894 *	0·174 *	0·260 *	0·347 *	0·417 *	0·494 *	0·574 *	0·646 *	0·721 *	0·0985	
10^4B......	11·94	13·93	15·92	17·91	19·89	21·88	23·87	25·86	27·85	29·84	31·83
log I_0/I...	0·118	0·134	0·150	0·167	0·179	0·193	0·210	0·222	0·235	0·244	0·257
10^4B......	33·82	35·81	37·80	39·79	41·78	43·77	45·76	47·75	49·74	51·72	53·71
log I_0/I...	0·271	0·287	0·295	0·305	0·314	0·329	0·336	0·346	0·351	0·363	0·373
10^4B......	55·70	57·69	59·68	61·67	63·66	65·65	67·64	69·63	79·58	89·52	99·47
log I_0/I...	0·385	0·394	0·399	0·408	0·419	0·426	0·434	0·438	0·478	0·507	0·539

* 4·00 cm. cells: all other results refer to 0·500 cm. cells.

rock-salt windows, were used for most of the measurements. However, a carefully matched pair of 4·00 cm. Unicam quartz cells was necessary for the most dilute solutions. Evaporation losses were negligible. The instrument was operated with pure solvent in the reference beam.

Two stock 0·09947M-solutions of pyrazole in carbon tetrachloride were prepared by semi-micro-weighing. Subsequent dilution was effected by using an Agla micrometer syringe. More concentrated solutions ($B > 0{\cdot}1$M) were prepared by direct weighing. No interaction between the pyrazole and decomposition products of the solvent was detectable. Solution temperatures were 18° ± 1°.

Procedure.—By using 4·00 cm. cells in the concentration range $1 \times 10^{-4} \leqslant B \leqslant 4 \times 10^{-4}$M, where no hydrogen bonding was detectable, the intensities of the free N–H band at 3485 cm.$^{-1}$ were found to obey Beer's law. A mean value of $\varepsilon = 220 \pm 3$ was obtained for the apparent molar extinction coefficient of the monomer, on using the relation

$$\log (I_0/I) = \varepsilon e l \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where I_0 and I are the intensities of the incident and transmitted radiation, e is the free N–H end-group concentration, and l is the cell length. In measuring the ratio I_0/I, frequent checks were made upon the constancy of the absorption base-line. The value of ε was also obtained graphically as $\lim_{B \to 0} (\log I_0/I)/Bl$: a value of $\varepsilon = 220 \pm 2$ was found, in good agreement with the previous value.

As a further check upon the optics of the system, it was confirmed that the intensity of the 3485 cm.$^{-1}$ band adhered to Lambert's law in the region where hydrogen bonding was detectable. Solutions of $B = 8 \times 10^{-4}$ and 1×10^{-3}M were used in conjunction with the 4·00 and 0·500 cm. cells. The results obeyed Lambert's law to ±1%.

The concentration dependence of the intensity of the 3485 cm.$^{-1}$ band was then studied. Forty-three solutions ($10^{-4} \leqslant B \leqslant 10^{-2}$M) were prepared in duplicate, one from each stock solution. Intensities were reproducible to ±1%, and the mean values are given in Table 1. Intensities for the concentration range $10^{-2} \leqslant B \leqslant 1$M were less precise, as the bonded N–H band interfered with the base line of the free N–H band. These data are therefore not reported.

INTERPRETATION OF THE DATA

It cannot be assumed *a priori* that the free N–H band at 3485 cm.$^{-1}$ in associated pyrazole solutions is due to the monomer only.[5,6] It is, however, valid to assume that the band is due to free N–H end-groups, and, further, that the apparent molar extinction coefficients of all linear oligomers B_q are equal. End-group concentrations, e, were therefore calculated by using the experimental value of $\varepsilon = 220 \pm 3$ for the monomer. Overall association constants are defined as

$$\beta_{q0} = B_q/b^q \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where B_q is the concentration of B_q, and b the concentration of monomer. For simplicity, we anticipate our conclusions by limiting subsequent consideration to monomeric, dimeric, and trimeric species. Two mass-balance expressions follow from eqn. (2):

$$B = B_1 + 2B_2 + 3B_3 = b + 2\beta_{20}b^2 + 3\beta_{30}b^3 \quad . \quad . \quad . \quad . \quad . \quad (3)$$

$$S = B_1 + B_2 + B_3 = b + \beta_{20}b^2 + \beta_{30}b^3 \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where S is the sum of the concentrations of all species. It was found that the experimental data could be represented by the linear equation

$$(B - e)/e^2 = 22{,}620e + 94{\cdot}8 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

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[5] Coggeshall and Saier, *J. Amer. Chem. Soc.*, 1951, **73**, 5414; Huggins and Pimentel, *J. Phys. Chem.*, 1956, **60**, 1615; Coburn and Grunwald, *J. Amer. Chem. Soc.*, 1958, **80**, 1318.

[6] Pimentel and McClellan, "The Hydrogen Bond," Freeman and Co., San Francisco, 1960, pp. 97, 207.

The standard deviations of the slope and intercept were found to be ±716 and ±2 by an unweighted least-squares treatment.

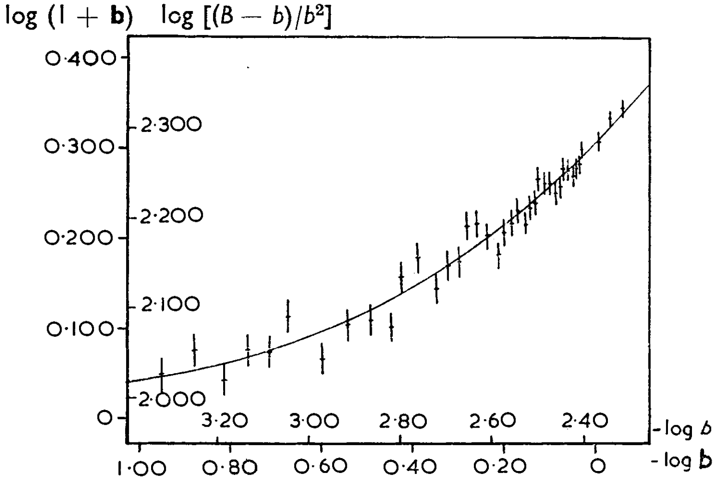
The significance of the experimental eqn. (5) follows from a consideration of the four possible combinations of linear and cyclic oligomers, B_2 and B_3. The experimental variables $(B - e)/e^2$ and e are expressed in terms of b by using eqns. (3) and (4) for the four possibilities in Table 2.

TABLE 2. *The possible variables of eqn.* (5) *for the pyrazole system in carbon tetrachloride.*

B_2	B_3	$(B - e)/e^2$	e
Cyclic	Cyclic	$2\beta_{20} + 3\beta_{30}b$	b
Linear	Linear	$(\beta_{20} + 2\beta_{30}b)/(1 + \beta_{20}b + \beta_{30}b^2)^2$	$b + \beta_{20}b^2 + \beta_{30}b^3$
Cyclic	Linear	$(2\beta_{20} + 2\beta_{30}b)/(1 + \beta_{30}b^2)^2$	$b + \beta_{30}b^3$
Linear	Cyclic	$(\beta_{20} + 3\beta_{30}b)/(1 + \beta_{20}b)^2$	$b + \beta_{20}b^2$

It is apparent that $(B - e)/e^2$ will be linear in e if the free N–H band is in fact due to monomeric pyrazole only, and the dimer and trimer are both cyclic. However, it is extremely unlikely that a linear representation of the data according to eqn. (5) would have been found, if either or both the associated species were linear. We therefore derive from eqn. (5) values of

FIG. 2. *The experimental data log* $[(B - b)/b^2]$ *plotted as a function of* log b *superimposed in the position of best fit on the normalised curve* log $(1 + \mathbf{b})$ *as a function of* log $\mathbf{b}$.



$$\beta_{20} = 47{\cdot}4 \pm 1{\cdot}0 \text{ l. mole}^{-1} \text{ and } \beta_{30} = 7540 \pm 240 \text{ l.}^2 \text{ mole}^{-2}$$

The values of the association constants were checked by the curve-fitting method suggested by Rossotti and Rossotti.[7] The expression

$$\log\left(\frac{B - b}{b^2}\right) - \log 2\beta_{20} = \log\left(1 + \frac{3\beta_{30}}{2\beta_{20}}\mathbf{b}\right)$$

is a rearrangement of eqn. (3). The experimental data, log $\{(B - b)/b^2\}$ plotted as a function of log b, will therefore be of the same shape as the normalised curve log $(1 + \mathbf{b})$

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[7] Rossotti and Rossotti, " The Determination of Stability Constants," McGraw-Hill, New York, in the press, Chap. 16.

plotted as a function of log **b**. The experimental and normalised curves are superimposed, and, in the position of best fit (see Fig. 2), the equations

$$\log (1 + \mathbf{b}) = \log [(B - b)/b^2] - \log 2\beta_{20}$$

and

$$\log \mathbf{b} = \log b + \log (3\beta_{30}/2\beta_{20})$$

may be solved for β_{20} and β_{30}/β_{20}. The permissible relative displacements of the experimental and the normalised curves, parallel to the co-ordinate axes, give estimates of the errors in the two parameters. Hence, we obtain values of

$$\beta_{20} = 47{\cdot}5 \pm 1{\cdot}0 \text{ l. mole}^{-1} \text{ and } \beta_{30} = 7540 \pm 300 \text{ l.}^2 \text{ mole}^{-2}$$

in excellent agreement with the values obtained from the linear equation. This treatment therefore confirms that monomer, cyclic dimer, and cyclic trimer are the only species co-existing in the concentration range $10^{-4} \leqslant B \leqslant 10^{-2}$ M. There is no evidence for detectable concentrations of larger oligomers.

DISCUSSION

The percentage distribution of pyrazole between the monomer, cyclic dimer, and cyclic trimer has been calculated as a function of the total concentration of pyrazole by using eqn. (3), and is shown in Fig. 3. The precise infrared measurements from which the equilibria have been deduced only extend up to $B = 10^{-2}$M, where the pyrazole is approximately 25% dimeric and 37% trimeric. However, the percentages of monomer, which may be derived from the less precise data in the range $10^{-2} \leqslant B \leqslant 1$M, are in good agreement (±4%) with the values calculated by using eqn. (3). Our values of β_{20} and β_{30} therefore represent the pyrazole system at 18° in carbon tetrachloride for total concentrations $B \leqslant 1$M.

It is evident from the value of β_{20} and β_{30} that the trimer is much more stable than the dimer. The equilibrium constant for the reaction

$$B_2 + B_1 \rightleftharpoons B_3$$

is given by $\beta_{30}/\beta_{20} = 159 \pm 6$ l. mole^{-1}, as compared to the dimerisation constant of 47·5 l. mole^{-1}.

As the pyrazole molecule is planar, the cyclic dimer and trimer will also be planar. Consideration of Ehrlich's structure [4] for the long chains of pyrazole molecules in the solid state suggests that the N–H–N bond in the cyclic trimer may not be quite linear.

An examination of the bonded N–H region, from the viewpoint of the calculated distribution of pyrazole oligomers, suggests that the bands at 3175, 3070, 2995, 2930, 2905, and 2825 cm.$^{-1}$ may be assigned to the trimer. The relative intensities of these bands remain unchanged as B varies. The dimer appears to contribute a leading edge to the band at 3175 cm.$^{-1}$. This absorption becomes a significant shoulder when $B < 10^{-2}$M, and the concentration of dimer exceeds that of trimer. However, the absorption of the trimer is much stronger than that of the dimer, and the shoulder is not detectable for $B > 10^{-2}$M (cf. Figs. 1 and 3). The absorption band of the dimer would be expected to be at a higher frequency than that of the trimer on the basis of Badger's correlation [8] of frequency shift with the energy of the hydrogen bond. Moreover, it has been shown [9] that non-linear intramolecular hydrogen bonds are associated with smaller frequency shifts than linear hydrogen bonds. The frequency shifts for both dimer and trimer clearly correspond to

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[8] Badger, *J. Chem. Phys.*, 1940, **8**, 288.

[9] Nakamoto, Magoshes, and Rundle, *J. Amer. Chem. Soc.*, 1955, **77**, 6480.

very short N–H–N bond lengths (cf. ref. 9). Indeed, the figure-of-eight spirals of pyrazole in the solid state [4] contain N–H bonds of length ~2·9 Å. The shortness of these bonds, and also the tendency to self-association in solution, are presumably both due to a markedly unequal distribution of charge on the two nitrogen atoms of a molecule of pyrazole. The assignment of six bands in the bonded N–H region to a single species is of some interest in connection with current theories of the structure of X–H stretching modes.[10,11]

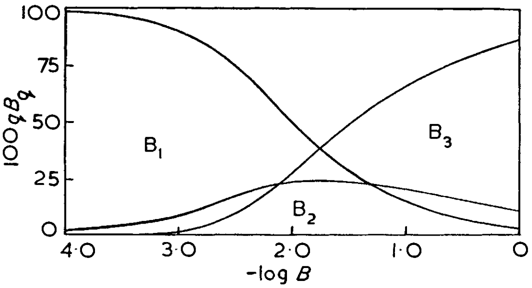

FIG. 3. *The percentage distributions* $100qB_q/B$ *of the pyrazole species in carbon tetrachloride at* 18° *plotted as a function of* log B.

The intensities of the observed N–H bands were markedly sensitive to temperature. With increase of temperature, the intensity of the 3485 cm.$^{-1}$ band due to free pyrazole increased, and that of the broad, bonded N–H band decreased. This implies that the enthalpy changes on association are negative, always provided that the temperature variation of the apparent extinction coefficients is not a dominant factor.[12] As the temperature coefficient of the dielectric constant of carbon tetrachloride is approximately zero,[13] the negative enthalpies appear to be partly due to non-environmental exchange forces. It is therefore possible that the covalent contribution to the hydrogen bond is more important than is commonly supposed.

The infrared spectra of pyrazole in other non-associated solvents, *e.g.*, carbon disulphide and chloroform, are qualitatively similar to that in carbon tetrachloride. It is therefore likely that the same equilibria obtain.

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[10] Bratož and Hadži, *J. Chem. Phys.*, 1957, **27**, 991; Pimentel and McClellan, ref. 6, p. 102.

[11] Sheppard, in " Hydrogen Bonding," eds. Hadži and Thompson, Pergamon Press, London, 1959, p. 85.

[12] Becker, in ref. 11, p. 155; Pimentel and McClellan, ref. 6, p. 76.

[13] Landolt–Börnstein, " Tabellen," II, (6), " Elektrische Eigenschaften 1," Springer-Verlag, Berlin, 1959, p. 625.