819. *The Hydrogen Bonding of Some Substituted Pyrazoles in Carbon Tetrachloride Solution.*

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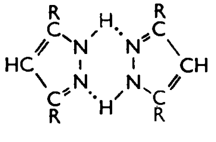
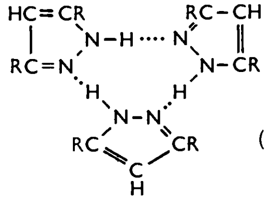
Analysis of the concentration-dependence of the infrared spectrum of 3,5-diphenylpyrazole in carbon tetrachloride solution at 21° ± 1° has shown that the fundamental N–H stretching band at 3475 ± 10 cm.$^{-1}$ is due to the free end groups of the monomer and polymers other than the dimer, which is cyclic. The hydrogen-bonding equilibria in the concentration range 10^{-4} to 2×10^{-3}M may be represented quantitatively by the hypothesis that the stepwise self-association constants for the acyclic polymers are all equal. The fundamental N–H stretching bands at 3485 ± 10 cm.$^{-1}$ for 3,5-dimethylpyrazole and at 3480 ± 10 cm.$^{-1}$ for 3,5-diethylpyrazole are, however, due to free monomer only. Hydrogen-bonding equilibria in these two systems have been quantitatively interpreted in terms of co-existing monomer, cyclic dimer, and cyclic trimer in the concentration range 10^{-4} to 1M. Values of the self-association constants are reported.

A RECENT infrared study[1] of the self-association of pyrazole in carbon tetrachloride solution has indicated that cyclic, hydrogen-bonded dimers (I; R = H) and trimers (II; R = H) are formed. A consideration of bond angles suggests that the hydrogen bonds in the cyclic trimer will be almost strainless, and indeed, the thermodynamic stability of the trimer was found to be considerably greater than that of the dimer. The effect which 3,5-disubstitution in the pyrazole ring has on the nature of the polymers formed and on the stability of the products has now been studied. White and Kilpatrick have reported[2] cryoscopic evidence for trimeric and possibly dimeric 3,5-dimethylpyrazole in benzene solution. These species were assumed to be cyclic and linear respectively.

Preliminary infrared spectroscopic examination of dilute solutions ($<10^{-2}$M) of 3,5-dimethyl- and 3,5-diethyl-pyrazole in carbon tetrachloride solution showed fundamental N–H stretching modes at 3485 and 3480 ± 10 cm.$^{-1}$, respectively, each with a half-band width of 20 cm.$^{-1}$, together with broad bonded N–H bands from 3400 to 2000 cm.$^{-1}$. These spectra were similar to that of pyrazole[1] for which the 3485 cm.$^{-1}$ mode was assigned to free monomer and the 3400—2000 cm.$^{-1}$ band to cyclic dimer and trimer. A shoulder at 3240 ± 10 cm.$^{-1}$ to the 3175 cm.$^{-1}$ band in the pyrazole system[1] was assigned to the cyclic dimer absorption. Absorptions at 3240 and 3250 ± 10 cm.$^{-1}$ are now assigned to the cyclic dimers of 3,5-dimethyl- and 3,5-diethyl-pyrazole respectively (see below).



(I)



(II)

Dilute solutions ($<2 \times 10^{-3}$M) of 3,5-diphenylpyrazole showed a fundamental N–H stretching mode at 3475 ± 10 cm.$^{-1}$, with a half-band width of 20 cm.$^{-1}$, a broader band at 3255 ± 10 cm.$^{-1}$ and a broad bonded band with fine structure in the region 3100—2700 cm.$^{-1}$. The 3255 cm.$^{-1}$ band is assigned to the N–H absorption of a hydrogen-bonded dimer. Now, it is well known[3] that non-linear hydrogen bonds are usually associated

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[1] Anderson, Duncan, and Rossotti, *J.*, 1961, 140.

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

[3] Nakamoto, Margoshes, and Rundle, *J. Amer. Chem. Soc.*, 1955, **77**, 6840.

with smaller frequency shifts than linear hydrogen bonds. We have found [4] that the frequency shift for the linear dimer of imidazole in carbon tetrachloride solution is 360 cm.$^{-1}$ (from 3485 to 3125 ± 10 cm.$^{-1}$) as compared with shifts of 230—245 cm.$^{-1}$ for the cyclic dimers of pyrazole and the two dialkylpyrazoles. It is therefore most probable that the frequency shift of 220 cm.$^{-1}$ in the 3,5-diphenylpyrazole system is due to a cyclic dimer. As the hydrogen bonds in cyclic trimeric pyrazoles are almost linear, the N-H spectrum of a cylic trimer will be expected to be much the same as those of linear polymers. Indeed, the spectra of the linear imidazole polymers are almost indistinguishable [4] from that of cyclic, trimeric pyrazole in the region 3400—2000 cm.$^{-1}$. It is therefore not possible to deduce the conformation of multimers of 3,5-diphenylpyrazole larger than the dimer from the broad bonded band. However, a consideration of molecular models suggests that, although the benzene rings will allow a cyclic dimer to be formed, larger polymers cannot cyclise (cf. I and II).

The hypotheses that the free end-groups arise from the free monomer only in the 3,5-dimethyl- and 3,5-diethyl-pyrazole systems, but from monomer plus polymers other than the dimer in the 3,5-diphenylpyrazole systems were tested by quantitative studies of the concentration-dependence of the free end-group bands.

EXPERIMENTAL

Materials.—A commercial sample of 3,5-dimethylpyrazole was recrystallised twice from cyclohexane; it had m. p. 107° (lit., 107—108°). 3,5-Diethylpyrazole was prepared by condensing equimolar amounts of dipropionylmethane (prepared by Zellars and Levine's method [5]) and hydrazine hydrate in ethanol; after distillation under reduced pressure, a colourless solid was obtained with m. p. 23—24° (lit., 22—24°). 3,5-Diphenylpyrazole was prepared similarly from dibenzoylmethane. The product was recrystallised twice from carbon tetrachloride and had m. p. 199—200° (lit., 200°). Reagent-grade carbon tetrachloride was used without further purification, since no infrared absorption was detectable in the region 4000—2400 cm.$^{-1}$ when the solvent was placed in 4·00 cm. cells.

Infrared Measurements.—The spectrometer, operating conditions, and the precision of the frequency and intensity measurements were the same as reported previously.[1] Carefully matched pairs of 4·00, 2·00, and 1·00 cm. Unicam quartz cells were used for precise measurements in the concentration range 10^{-4} to 10^{-2}M. A pair of cells of variable path-length, set at 5·000 ± 0·005 mm. and fitted with rock salt windows, was used for less precise measurements in the concentration range 10^{-2}—1M on the dialkylpyrazoles.

Stock solutions of the pyrazoles were prepared by semimicro-weighing, and dilutions were made by using an Agla micrometer syringe. Spectra of 3,5-dimethylpyrazole were obtained at 19° ± 1°, and all other spectra were obtained at 21° ± 1°.

The most dilute solutions that could be studied (total pyrazole concentration, $B \sim 10^{-4}$M) were still slightly (~5%) hydrogen-bonded. It was, therefore, impossible to confirm that the intensity of the fundamental N-H stretching bands of the free monomers adhered to Beer's law. However, by using 4·00, 2·00, and 1·00 cm. cells, and a range of values of B, it was shown that the intensities of the free end-group bands adhered to Lambert's law within ±1%. Values of the apparent molar extinction coefficients ε_1 of the monomers at the end-group frequencies were obtained by short graphical extrapolations [4] as $\lim_{B \to 0} (\log I_0/I)/Bl$, where I_0 and I are the intensities of the incident and transmitted radiation, and l is the cell length. On the reasonable assumption [4] that the values of the extinction coefficients of all non-cyclic polymers in a particular system are equal at the end-group frequency, the total end-group concentrations e may be calculated from the relation

$$\log I_0/I = \varepsilon_1 el. \quad (1)$$

The relevant data are given in Tables 1, 3, and 4 below.

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[4] Anderson, Duncan, and Rossotti, *J.*, 1961, 2165.
[5] Zellars and Levine, *J. Org. Chem.*, 1948, **13**, 161.

INTERPRETATION OF THE DATA

3,5-*Diphenylpyrazole*

Calculation of Concentration Variables.—The sum of the concentrations of the Q polymers, which coexist, is given by

$$S = \sum_1^Q B_q = \sum_1^Q \beta_{q0} b^q, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where B_q is the concentration of the qth polymer B_q, b is the free monomer concentration, and the self-association constants are defined by

$$\beta_{q0} = B_q b^{-q}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

The relation

$$e = b + \sum_3^Q B_q = b + \sum_3^Q \beta_{q0} b^q \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

is a quantitative expression of the hypothesis that the dimer is cyclic, but that all other polymers are linear. Combining eqns. (2), (3), and (4), we derive

$$e = S - B_2 = S - \beta_{20} b^2. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

The total solute concentration is given by

$$B = \sum_1^Q q B_q = \sum_1^Q q \beta_{q0} b^q \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

and related to S and b by the integral

$$\log (b/b_1) = (1/2{\cdot}303) \int_{S_1}^{S} (1/B)\, \mathrm{d}S \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

A method of finding a reference point (B_1, S_1, b_1) has been described previously.[4,6] The limiting forms of eqns. (2), (3), and (4), *viz.*

$$\lim_{b \to 0} [(B - b)/2b^2] = \lim_{b \to 0} [(S - b)/b^2] = \beta_{20}$$

and

$$\lim_{b \to 0} [(e - b)/b^2] = 0,$$

eqn. (5), and eqn. (7) were used to calculate values of S and b from the experimental values of B and e by an iterative procedure. Convergent values, obtained after five cycles of calculation, are included in Table 1.

TABLE 1. *Infrared absorbancies at* 3475 *cm.*$^{-1}$ *for associated* 3,5-*diphenylpyrazole at* 21° ± 1° *and concentration variables derived therefrom.*

$\varepsilon_1 = 258 \pm 1$

10^4B	$\log I_0/I$	10^4e	10^4S	10^4b	10^4B	$\log I_0/I$	10^4e	10^4S	10^4b
1·000	0·100	0·969	—	—	8·000	0·636	6·171	6·700	5·866
2·000	0·194	1·880	1·934	1·870	9·000	0·695	6·740	7·359	6·340
3·000	0·281	2·721	2·833	2·695	10·00	0·749	7·259	7·938	6·738
4·000	0·363	3·519	3·706	3·466	12·00	0·421 *	8·156	9·004	7·427
5·000	0·438	4·245	4·512	4·151	14·00	0·464 *	8·993	9·977	8·007
6·000	0·511	4·952	5·305	4·797	16·00	0·503 *	9·738	10·84	8·484
7·000	0·576	5·580	6·025	5·359	18·00	0·538 *	10·42	11·63	8·888

* 2·00 cm. cells; all other results refer to 4·00 cm. cells.

Determination of the Stability Constants.—The number-average degree of self-association $\bar{q} = B/S$ increases from 1 to 1·55 in the concentration range $10^{-4} \leqslant B \leqslant 2 \times 10^{-3}$M (saturated solution), and the average number of monomeric units in each polymer $\bar{\nu} = (B - b)/(S - b)$ increases from 2 to 3·3. Hence, the value of Q in the saturated solutions must be at least 4. An attempt to interpret the data $B(b)$ and $S(b)$ quantitatively in terms of co-existing monomer,

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[6] Rossotti and Rossotti, *J. Phys. Chem.*, 1961, **65**, 926.

dimer, trimer, and tetramer, by following the procedure described in ref. 6 for " systems containing few species," indicated that the system contained larger polymers than the tetramer. A similar attempt to interpret the data $e(b)$ indicated that the system contained larger polymers than the pentamer. This conclusion was not unexpected as the functions $\bar{q}(B)$ and $\bar{v}(B)$ are comparable with those for the imidazole system,[4] in which species as large as decamers are evident at a total concentration equal to the solubility of 3,5-diphenylpyrazole in carbon tetrachloride at 21° ($B = 2 \times 10^{-3}$M).

Consequently, it was assumed that Q has a very large value, and the data $B(b)$ and $S(b)$ were treated by the methods described in ref. 7 for " systems containing many species." The pair of experimental functions log T (log b) and log Θ (log b) were compared with pairs of normalised functions log $\boldsymbol{T}$ (log $\boldsymbol{b}$) and log $\boldsymbol{\Theta}$ (log $\boldsymbol{b}$) calculated by Rossotti and Rossotti [7] on a number of simple two-parameter hypotheses. The auxiliary concentration variables are defined by

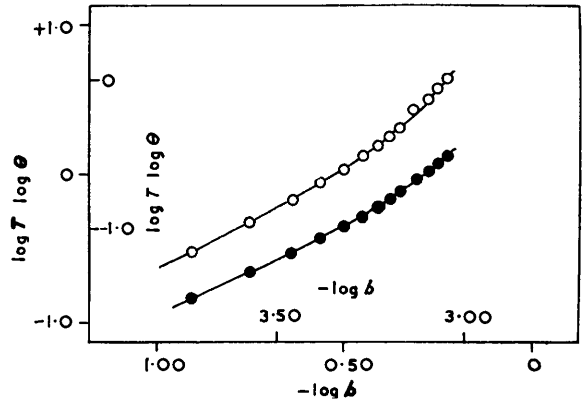

FIG. 1. *Experimental data* log T, log b (*open circles*) *and* log θ, log b (*closed circles*) *for the* 3,5-*diphenylpyrazole system superimposed in the position of best fit on normalised curves* log $\boldsymbol{T}$ (log $\boldsymbol{b}$) *and* log $\boldsymbol{\Theta}$ (log $\boldsymbol{b}$), *calculated by assuming Hypothesis I.*

$$T = (B - b)/b$$

and

$$\Theta = (S - b)/b$$

and the normalised variables by

$$\boldsymbol{T} = TK/\beta_{20},$$

$$\boldsymbol{\Theta} = \Theta K/\beta_{20},$$

and

$$\boldsymbol{b} = bK.$$

The required stability constants β_{q0} are related to β_{20} and the parameter K in different ways for each hypothesis (see below). The experimental functions were found to be of the same shape as portions of the normalised curves described in ref. 7 by hypotheses I, III, and IV (see Fig. 1). For these models, β_{q0}, β_{20} and K are inter-related by the equations

$$\beta_{q0} = \beta_{20}K^{q-2}, \quad \text{(8)}$$

$$\beta_{q0} = \beta_{20}K^{q-2}/(q-1)!, \quad \text{(9)}$$

and

$$\beta_{q0} = \beta_{20}(q-1)K^{q-2}, \quad \text{(10)}$$

respectively. Values of the parameters β_{20} and K for each hypothesis were obtained by the curve-fitting procedure,[7] and values of β_{q0} calculated by substitution into eqns. (8), (9), and (10).

The data $B(S)$ were also found to conform to Lassettre's two-parameter equation [8] and are well represented by the linear equation

$$(B - S)/S^2 = 610B/S - 440. \quad \text{(11)}$$

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[7] Rossotti and Rossotti, *J. Phys. Chem.*, 1961, **65**, 930.

[8] Lassettre, *J. Amer. Chem. Soc.*, 1937, **59**, 1383.

According to this model, the required stability constants are related to the slope C_B and intercept C_S of eqn. (11) by the relation

$$\beta_{q0} = \frac{\prod_{m=0}^{m=q-2} [qC_B + (q - m)C_S]}{q!} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (12)$$

Values of the first few self-association constants for the cyclic dimer and linear polymers of 3,5-diphenylpyrazole are collected in Table 2. Actual values of the equilibrium constants presumably lie within the ranges delineated by the various methods, which have given results in substantial agreement. It is often possible[9] to restrict the choice of two-parameter hypotheses by back-calculation of the function $B/S(B)$ by substituting the appropriate stability constants into eqns. (2) and (6). In the present system, back-calculation of the experimental function $B(e)$ provides an additional check. However, it was not possible to differentiate between the various sets of constants since the limited solubility of 3,5-diphenylpyrazole restricts the range over which B may be varied. In so far as Hypothesis I [cf. eqn. (8)] represents the simplest model, there is no valid reason for preferring the other less simple two-parameter models.

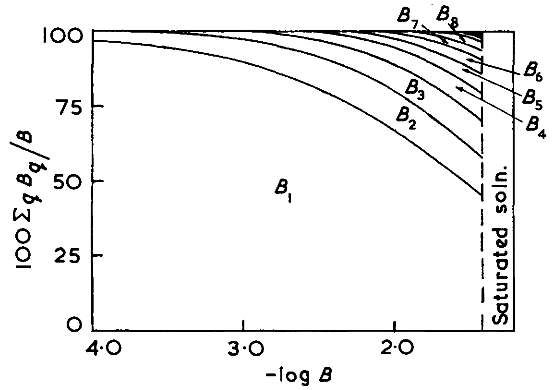

FIG. 2. *The percentage distributions* $(100\Sigma qB_q)/B$ *of the* 3,5-*diphenylpyrazole multimers in carbon tetrachloride at* 21° *plotted as a function of* log B.

TABLE 2. *Self-association constants on the molar scale for the* 3,5-*diphenylpyrazole system obtained by the various methods.*

	Hypothesis I	Hypothesis III	Hypothesis IV	Lassettre
$\log \beta_{20}$	2·19 ± 0·03	2·18 ± 0·04	2·15 ± 0·04	2·23 ± 0·03
$\log \beta_{30}$	5·01 ± 0·04	5·08 ± 0·06	5·06 ± 0·05	4·91 ± 0·03
$\log \beta_{40}$	7·83 ± 0·05	7·80 ± 0·08	7·85 ± 0·06	7·70 ± 0·04
$\log \beta_{50}$	10·65 ± 0·06	10·40 ± 0·10	10·58 ± 0·07	10·54 ± 0·04
$\log \beta_{60}$	13·47 ± 0·07	12·90 ± 0·12	13·29 ± 0·08	13·41 ± 0·05
$\log \beta_{q0}$	$2{\cdot}19 + (q - 2)2{\cdot}82$	$2{\cdot}18 + (q - 2)3{\cdot}20 - \log (q - 1)!$	$2{\cdot}15 + (q - 2)2{\cdot}61 + \log (q - 1)$	See eqn. (12)

The percentage distribution of 3,5-diphenylpyrazole between the various polymers has been calculated as a function of the total pyrazole concentration, B, by substituting the constants for Hypothesis I into eqn. (6). These data are shown in Fig. 2. Significant concentrations of all polymers up to the decamer appear to co-exist in saturated solutions. The lower solubility of 3,5-diphenylpyrazole than of pyrazole is therefore due, not only to the phenyl substituents, but also to the more extensive self-association. Apart from the fact that the dimer is cyclic, there is a close resemblance to the imidazole system over the same concentration range (compare Fig. 2 with Fig. 4 in ref. 4).

3,5-*Dimethylpyrazole and* 3,5-*Diethylpyrazole*

The experimental data $B(e)$ for 3,5-dimethylpyrazole could be represented by the linear equation

$$(B - e)/e^2 = 137{,}150e + 568. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (13)$$

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[9] Rossotti and Rossotti, *J. Phys. Chem.*, submitted for publication.

Standard deviations, found by an unweighted least-squares procedure, were ± 2150 and $\pm 3{\cdot}2$ in the slope and intercept respectively. By precisely the same argument as was used for pyrazole,[1] we infer that eqn. (13) is identical with eqn. (6) where $Q = 3$, *viz.*

$$F = (B - b)/b^2 = 2\beta_{20} + 3\beta_{30}b, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

and that the dimer and trimer are both cyclic. The data $B(e)$ for 3,5-diethylpyrazole could similarly be represented by

$$(B - e)/e^2 = 18{,}300e + 219 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

with standard deviations of ± 500 and $\pm 3{\cdot}0$ in the slope and intercept, and similar deductions follow.

TABLE 3. *Infrared absorbancies at* 3485 *cm.*$^{-1}$ *for associated* 3,5-*dimethylpyrazole at* 19° ± 1° *and concentration variables derived therefrom.*

$\varepsilon_1 = 295 \pm 2$

10^4B	1·000	2·000	3·000	4·000	5·000	6·000	7·000	8·000	9·000
$\log I_0/I$ ...	0·114 *	0·213 *	0·306 *	0·392 *	0·472 *	0·548 *	0·620 *	0·688 *	0·749 *
10^4e	—	1·810	2·591	3·322	3·998	4·641	5·248	5·831	6·352
10^4S	—	—	—	3·650	—	5·295	—	—	7·615
10^4B	10·00	12·00	14·00	16·00	18·00	20·00	22·00	24·00	26·00
$\log I_0/I$ ...	0·407 †	0·463 †	0·513 †	0·567 †	0·614 †	0·654 †	0·345	0·369	0·387
10^4e	6·857	7·848	8·711	9·612	10·41	11·09	11·69	12·51	13·12
10^4S	—	9·822	—	12·64	—	15·20	—	—	19·06
10^4B	28·00	30·00	32·00	36·00	40·00	45·00	50·00	55·00	60·00
$\log I_0/I$ ...	0·407	0·422	0·439	0·471	0·498	0·536	0·565	0·597	0·627
10^4e	13·80	14·31	14·88	15·97	16·89	18·18	19·15	20·23	21·25
10^4S	—	—	22·74	25·09	27·27	30·41	32·81	35·72	38·50
10^4B	70·00	80·00	90·00	100·00					
$\log I_0/I$ ...	0·680	0·730	0·775	0·820					
10^4e	23·04	24·75	26·26	27·79					
10^4S	43·74	49·26	54·16	59·63					

* 4·00 cm. cells } Other results refer to 1·00 cm. cells.
† 2·00 cm. cells }

TABLE 4. *Infrared absorbancies at* 3480 *cm.*$^{-1}$ *for associated* 3,5-*diethylpyrazole at* 21° ± 1° *and concentration variables derived therefrom.*

$\varepsilon_1 = 225 \pm 1$

10^4B	1·000	2·000	3·000	4·000	5·000	6·000	7·000	8·000	9·000
$\log I_0/I$ ...	0·088 *	0·172 *	0·254 *	0·332 *	0·408 *	0·481 *	0·552 *	0·621 *	0·687 *
10^4e	0·978	1·916	2·821	3·688	4·528	5·343	6·129	6·901	7·635
10^4S	—	—	—	3·829	—	5·666	—	—	8·310
10^4B	10·00	12·00	14·00	16·00	18·00	20·00	25·00	30·00	35·00
$\log I_0/I$ ...	0·751 *	0·439 †	0·498 †	0·553 †	0·608 †	0·662 †	0·390	0·447	0·501
10^4e	8·337	9·761	11·07	12·28	13·51	14·71	17·34	19·86	22·26
10^4S	—	10·87	—	14·06	—	17·29	20·96	24·69	28·39
10^4B	40·00	45·00	50·00	60·00	70·00	80·00			
$\log I_0/I$ ...	0·547	0·595	0·640	0·720	0·791	0·856			
10^4e	24·31	26·44	28·44	32·00	35·16	38·05			
10^4S	31·69	35·27	38·72	45·21	51·33	57·27			

*† See Table 3.

As a check on the interpretation of these data, values of S were calculated from the experimental data B (b) by using Kreuzer's analogue[10] of eqn. (7), *viz.*

$$S - S_1 = 2{\cdot}303 \int_{b_1}^{b} B \, \mathrm{d}(\log b).$$

The method of finding a convenient reference point (B_1, S_1, b_1) has been described in ref. 6. Values of S so calculated are given in Tables 3 and 4, and were used to construct the appropriate rearranged form of eqn. (2):

$$\phi = (S - b)/b^2 = \beta_{20} + \beta_{30}b. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

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[10] Kreuzer, *Z. phys. Chem.*, 1943, **53***B*, 213.

Substitution of the normalised variables

$$\boldsymbol{F} = F/\beta_{20},$$

$$\boldsymbol{\Phi} = \phi/\beta_{20},$$

and

$$\boldsymbol{b} = b\beta_{20}/\beta_{20}$$

into eqns. (14) and (16) gives

$$\log \boldsymbol{F} = \log (2 + 3\boldsymbol{b})$$

and

$$\log \boldsymbol{\Phi} = \log (1 + \boldsymbol{b}).$$

Values of β_{20} and β_{30} were obtained by simultaneously curve-fitting [6] the pair of experimental functions $\log F$ ($\log b$) and $\log \phi$ ($\log b$) with the normalised curves $\log \boldsymbol{F}$ ($\log \boldsymbol{b}$) and $\log \boldsymbol{\Phi}$ ($\log \boldsymbol{b}$) (see Fig. 3). Values of the stability constants for the cyclic dimers and trimers, calculated by using the linear equation and curve-fitting methods are given in Table 5. The agreement between the values found by the two methods confirms the identification of cyclic dimer and cyclic trimer.

FIG. 3. *Experimental data* $\log F$, $\log b$ *(lines) and* $\log \phi$, $\log b$ *(circles) for* (a) *the* 3,5-*dimethylpyrazole system and* (b) *the* 3,5-*diethylpyrazole system superimposed in the positions of best fit on normalised curves* $\log \boldsymbol{F}$ ($\log \boldsymbol{b}$) *and* $\log \boldsymbol{\phi}$ ($\log \boldsymbol{b}$). *The upper and right-hand scales refer to* (a) *and the lower and left-hand scales refer to* (b).

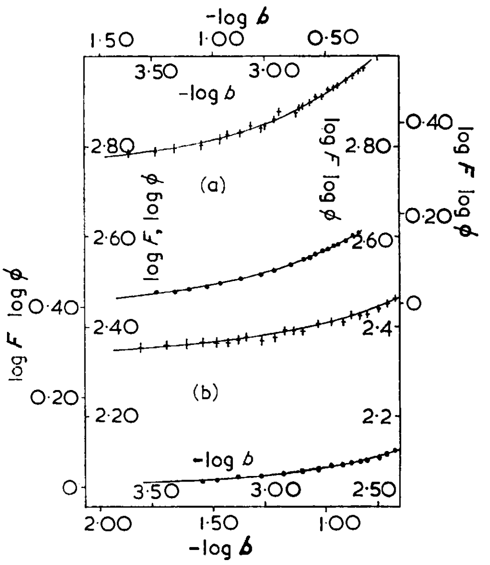
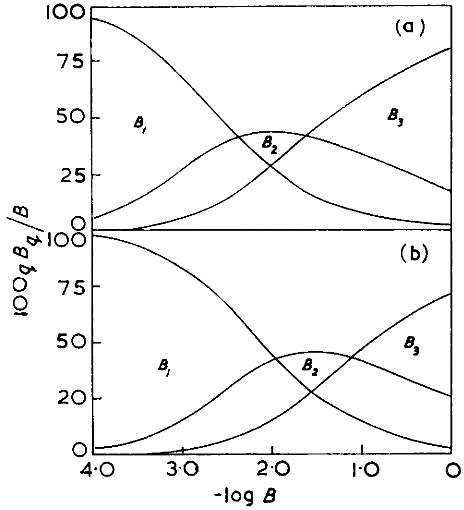


FIG. 4. *The percentage distributions* $100qB_q/B$ *of* (a) *the* 3,5-*dimethylpyrazole species and* (b) *the* 3,5-*diethylpyrazole species in carbon tetrachloride at* 18° *and* 19°, *respectively, plotted as functions of* $\log B$.



The percentage distributions of the 3,5-dialkylpyrazoles between monomer, cyclic dimer, and cyclic trimer have been calculated as functions of the total concentration of pyrazole, B, by using eqn. (14) (see Fig. 4). The precise infrared measurements from which the equilibria have been deduced extend over the concentration range $10^{-4} \leqslant B \leqslant 10^{-2}$M. However, the percentages of monomer, which may be calculated from less precise data in the range $10^{-2} \leqslant B \leqslant 1$M, are in good agreement (±5%) with those shown in Fig. 4. Our values of β_{20} and β_{30} are therefore considered valid for $B \leqslant 1$M, and there is no evidence for detectable concentrations of larger multimers than the trimer within this wider concentration range.

A comparison of the spectra with the data summarised in Fig. 4 suggests that the cyclic dimers are responsible for the bands at 3240 ± 10 and 3250 ± 10 cm.$^{-1}$ in the 3,5-dimethyl- and 3,5-diethyl-pyrazole system, respectively. No assignments have been made for the N–H peaks of the trimers, owing to the presence of the C–H peaks of the alkyl substituents. The spectra of the dialkylpyrazoles in other non-associated solvents, *e.g.*, chloroform and methylene dichloride, are qualitatively similar to those in carbon tetrachloride. It is therefore likely that cyclic dimers and trimers are formed in all solvents of this type.

TABLE 5. *Self-association constants on the molar scale for the* 3,5-*dialkylpyrazoles.*

	3,5-Dimethylpyrazole		3,5-Diethylpyrazole	
	Eqn. (13)	Curve-fitting	Eqn. (15)	Curve-fitting
$\log \beta_{20}$	$2{\cdot}453 \pm 0{\cdot}003$	$2{\cdot}454 \pm 0{\cdot}005$	$2{\cdot}041 \pm 0{\cdot}006$	$2{\cdot}042 \pm 0{\cdot}005$
$\log \beta_{30}$	$4{\cdot}660 \pm 0{\cdot}007$	$4{\cdot}662 \pm 0{\cdot}025$	$3{\cdot}785 \pm 0{\cdot}012$	$3{\cdot}774 \pm 0{\cdot}025$

DISCUSSION

The self-association of 3,5-dimethyl- and 3,5-diethyl-pyrazole in carbon tetrachloride, like that of pyrazole itself,[1] results in the formation of a cyclic dimer and a cyclic trimer. Although 3,5-diphenylpyrazole also forms a cyclic dimer, cyclisation of the trimer is prevented by steric hindrance between the benzene rings. Hence, an extensive series of larger polymers, which associate through a single hydrogen bond, is formed. The behaviour of this system may be regarded as intermediate between that of pyrazole and imidazole, which has been shown to form an extensive series of linear polymers.[4] (For simplicity, it is assumed that conformational equilibria between linear and cyclic forms are unimportant.)

The quantitative results of our infrared studies of the hydrogen bonding in these systems are summarised in Table 6. The cyclisation of the dimeric pyrazoles implies that the more negative enthalpy change accompanying the formation of two bent hydrogen bonds in place of one linear hydrogen bond, together with any positive entropy of desolvation of the monomers, more than offsets the entropy loss on cyclisation. 3,5-Disubstitution stabilises the cyclic dimers, the stabilisation being most pronounced with methyl groups between which steric interference is impossible. Free rotation of the ethyl substituents is probably restricted, and the phenyl substituents are probably forced slightly out of the plane of the dimeric ring.

TABLE 6. *Summary of self-association constants on the molar scale for imidazole and the pyrazoles in carbon tetrachloride solution.*

Compound	Temp.	$\log \beta_{20}$	$\log K_q$	$\log K_q$ ($q \geqslant 4$)	$\log (\beta_{20}/K_3)$
Pyrazole [1]	18°	$1{\cdot}677 \pm 0{\cdot}009$	$2{\cdot}20 \pm 0{\cdot}02$	$-\infty$	$-0{\cdot}523 \pm 0{\cdot}029$
3,5-Dimethylpyrazole	19	$2{\cdot}454 \pm 0{\cdot}005$	$2{\cdot}21 \pm 0{\cdot}02$	$-\infty$	$0{\cdot}244 \pm 0{\cdot}025$
3,5-Diethylpyrazole	21	$2{\cdot}042 \pm 0{\cdot}005$	$1{\cdot}73 \pm 0{\cdot}02$	$-\infty$	$0{\cdot}312 \pm 0{\cdot}025$
3,5-Diphenylpyrazole	21	$2{\cdot}19 \pm 0{\cdot}03$	$2{\cdot}82 \pm 0{\cdot}01$	$2{\cdot}82 \pm 0{\cdot}01$ *	$-0{\cdot}63 \pm 0{\cdot}02$
Imidazole [4]	18	$2{\cdot}37 \pm 0{\cdot}03$	$2{\cdot}88 \pm 0{\cdot}01$	$2{\cdot}88 \pm 0{\cdot}01$ *	$-0{\cdot}51 \pm 0{\cdot}02$

* On Hypothesis I.

It is noteworthy that the linear dimer of imidazole is comparable in stability with the cyclic dimers of the pyrazoles. This presumably implies that the hydrogen bond between two imidazole molecules is stronger than that between two pyrazoles. In the imidazole system, the equilibrium constant K_3 for the catenation

$$\mathrm{B}_2 + \mathrm{B} \rightleftharpoons \mathrm{B}_3 \qquad K_3 \quad . \ . \ . \ . \ . \ . \ . \ . \ . \quad (17)$$

is larger than the constant for the catenation

$$\mathrm{B} + \mathrm{B} \rightleftharpoons \mathrm{B}_2 \qquad \beta_{20} \quad . \ . \ . \ . \ . \ . \ . \ . \quad (18)$$

since the enthalpy change will favour [11] reaction (17) rather than (18) and the accompanying decrease in entropy will be less.[12] The entropy argument also applies in the pyrazole system, even though both the dimer and the trimer are cyclic. However, even though the

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[11] Coggeshall, *J. Chem. Phys.*, 1950, **18**, 978.

[12] Saroléa-Mathot, *Trans. Faraday Soc.*, 1953, **49**, 8.

methyl groups do not sterically hinder the dimerisation, they may hinder the trimerisation (cf. I and II; R = Me). Although β_{20} is larger for 3,5-dimethylpyrazole than for pyrazole, it is significant that the values of K_3 are approximately equal. Steric hindrance to trimerisation is even more pronounced with the larger ethyl substituents, and K_3 is even smaller, compared with β_{20}, than in the dimethyl system. However, with 3,5-diphenylpyrazole, K_3 is again larger than β_{20}, since the benzene rings completely prevent cyclisation of the trimer. The ratio K_3/β_{20} is even larger in this system than in the imidazole system, since the dimer is cyclic in the former and both dimer and trimer are linear in the latter system.

These arguments can be tested by determination of the heat and entropy changes. We have just learned that Kilpatrick and Vinogradov[13] have already studied the 3,5-dimethylpyrazole system in carbon tetrachloride and benzene over a wide temperature range, and agree with our conclusion that a cyclic dimer and cyclic trimer are the only polymers detectable.

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[13] Kilpatrick and Vinogradov, personal communication, April 1st, 1961.