

## The Crystal and Molecular Structure of Pyrazole

By H. W. W. EHRLICH

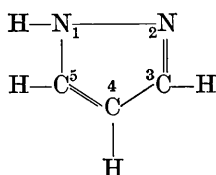
Department of Chemistry, The University, Edinburgh 9, Scotland

(Received 14 March 1960)

The space group of pyrazole is  $P2_1cn$  with eight molecules in the unit cell. There are two crystallographically independent molecules and good agreement is obtained for the lengths of corresponding bonds. The bond lengths of the molecule indicate that there is a large contribution from the betaine form to the resonance hybrid. The molecules are hydrogen-bonded together in a figure-8 spiral, these helices forming a close-packed array in the crystal.

### Introduction

Pyrazole, whose molecular formula is



melts at 70 °C., in spite of its low molecular weight. A point of chemical interest is that substitution derivatives at the 3 and at the 5 position are indistinguishable from one another, whereas this property disappears immediately the hydrogen atom on the nitrogen atom is replaced by an alkyl group.

Both these peculiarities can be explained by assuming that there exists a strong hydrogen bond between the nitrogen atoms of different molecules, and that perhaps the hydrogen is placed symmetrically between them. It was primarily to examine this hydrogen bond that the study of the crystal structure of pyrazole was undertaken.

### Experimental

Pyrazole sublimes rapidly at room temperature, and during photography the sample was enclosed in a gelatine capsule together with an atmosphere saturated with the vapour. Whereas a crystal exposed to the air had completely sublimed after 15 minutes at room temperature, an enclosed specimen of the same dimensions maintained its size over a period of weeks.

All the  $|F_o|^2$  were obtained from Weissenberg photographs (filtered Cu  $K\alpha$  radiation was used) the intensities being estimated visually by comparison against a calibrated scale.

As pyrazole is extremely soluble in most solvents, its density was only approximately determined by measuring and weighing one crystal.

### Crystal data

Pyrazole crystallises in the orthorhombic system, with absent spectra,  $hk0$  when  $h+k$  is odd, and  $h0l$  when  $l$  is odd. The  $0kl$  reflexions are systematically weak when  $k$  is odd, and the method of Howells, Phillips & Rogers (1950) for the determination of a centre of symmetry indicated that the (001) projection was centrosymmetric. However, pyrazole is piezoelectric, and therefore the space group is the non-centrosymmetric  $P2_1cn(C_{2v}^9)$ , but the arrangement of the molecules is such that it approximates to  $Pbcn(D_{2h}^{14})$ .

The cell dimensions are

$$a = 8.232 \pm 0.004, \quad b = 12.840 \pm 0.006, \\ c = 7.054 \pm 0.004 \text{ \AA}.$$

With  $Z=8$  the calculated density is 1.22 g.cm.<sup>-3</sup>. The approximate density is 1.15 g.cm.<sup>-3</sup>.

### Determination of structure

To obtain an approximate structure the space group was taken to be  $Pbcn$ , and the lower symmetry was

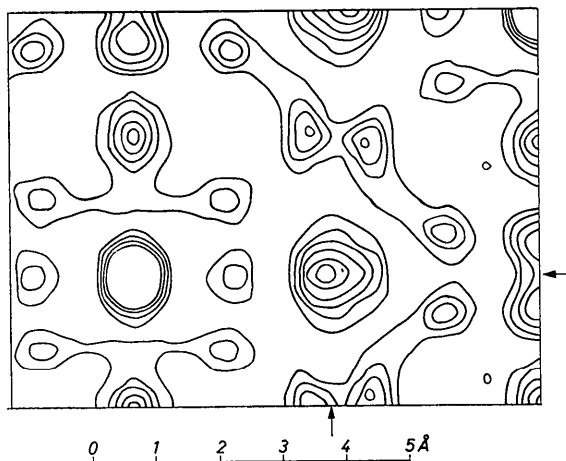


Fig. 1. The  $hk0$  Patterson synthesis of pyrazole. The diffuse peak is indicated by the two arrows.

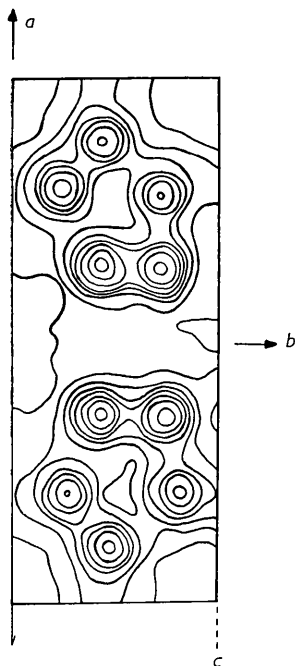


Fig. 2(a). The  $hk0$  Fourier synthesis of pyrazole. Contours every  $1 \text{ e.}\text{\AA}^{-2}$ .

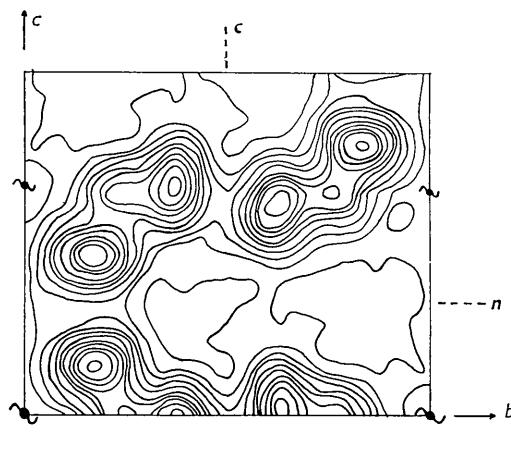


Fig. 2(b). The  $0kl$  Fourier synthesis of pyrazole. Contours every  $1 \text{ e.}\text{\AA}^{-2}$ .

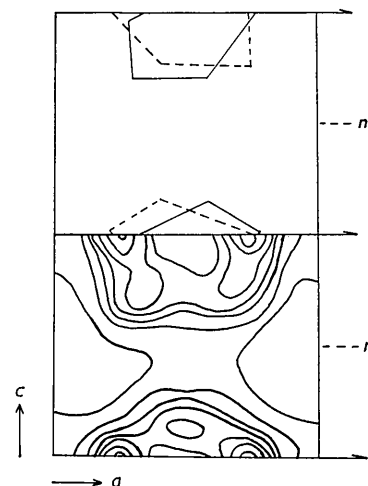


Fig. 2(c). The  $h0l$  Fourier synthesis of pyrazole. Contours every  $2 \text{ e.}\text{\AA}^{-2}$ .

later assumed during the refinement. The  $hk0$  Patterson synthesis is shown in Fig. 1, and this was solved by looking for diffuse peaks. The broadest peak in the map corresponds to unresolved but non-coincident vectors from one five-membered ring to another (Beever & Ehrlich, 1959). The  $h0l$  Patterson synthesis was interpreted by a similar procedure.

For the purposes of solving the Patterson projections the molecule of pyrazole was assumed to be a planar regular pentagon. Initially no distinction was made between carbon and nitrogen atoms, but the difference between them became apparent during refinement.

The symmetry imposed on the trial structure was destroyed by considering the weak  $0kl$  reflexions. Trial-and-error methods involving figure fields were used.

The refinement was carried out by means of  $(F_o - F_c)$  maps; contributions from hydrogen atoms have been included in the  $F_c$ , but only isotropic thermal vibration has been assumed for all the atoms. At a late stage in the refinement corrections were made for secondary extinction, the extinction coefficient being found by trial. The final values for  $R = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$  (unobserved reflexions assumed to have intensity of  $0.707 \times$  minimum observed) are 0.085, 0.132 and 0.113 for the  $hk0$ ,  $0kl$  and  $h0l$  reflexions respectively.

#### Positions of the hydrogen atoms

There is little doubt about the position of those hydrogen atoms which are bonded to carbon atoms,

as they can be predicted on theoretical grounds. The original coordinates have been modified as indicated by the  $(F_o - F_c)$  syntheses.

However, the remaining hydrogen atom in each molecule can be attached to either nitrogen atom, or be placed centrally along the hydrogen bond, in which case the molecule would have symmetry  $mm$ . The bond lengths in the pentagon show that the molecule is asymmetric and therefore the latter possibility is rejected. Hence there are only two possible structures,



Fig. 3. The  $0kl (F_o - F_c)$  synthesis showing the positions of the hydrogen atoms in the hydrogen bond. Contours every  $0.25 \text{ e.}\text{\AA}^{-2}$ .

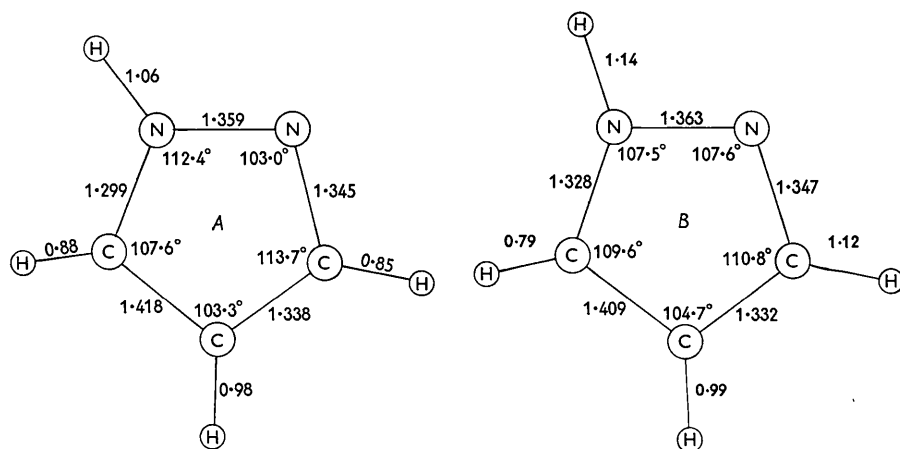


Fig. 4(a). The bond lengths and bond angles in the two crystallographically independent molecules.

and structure factors have been calculated for both of them. By comparing  $\sum[|F_o| - |F_c|]^2$  for both structures, a choice was made for that one with the lower value for this sum. The values were

$hk0$	213	246
$0kl$	558	615
$h0l$	383	392

The three  $F_o$  syntheses are shown in Fig. 2, and the  $0kl$  difference synthesis showing the position of these hydrogen atoms is shown in Fig. 3. The other two projections are non-centrosymmetric and previous work by the author has shown that such projections are not suitable for demonstrating hydrogen atoms (cf. also McGeachin & Beevers, 1957).

#### Atomic coordinates and molecular dimensions

The final atomic coordinates are listed in Table 1; the scattering curve used for carbon and nitrogen was

Table 1. *Atomic coordinates*

Atom	1000x	1000y	1000z
N <sub>1</sub>	856	184	000
N <sub>2</sub>	862	100	117
N <sub>3</sub>	141	180	484
N <sub>4</sub>	145	103	351
C <sub>1</sub>	710	062	108
C <sub>2</sub>	612	116	993
C <sub>3</sub>	712	199	930
C <sub>4</sub>	290	058	361
C <sub>5</sub>	383	107	503
C <sub>6</sub>	287	182	570

Atom	120x	120y	120z
H <sub>1</sub>	112	30	0
H <sub>2</sub>	83	1	21
H <sub>3</sub>	60	12	115
H <sub>4</sub>	83	30	102
H <sub>5</sub>	2	10	36
H <sub>6</sub>	38	2	34
H <sub>7</sub>	60	12	64
H <sub>8</sub>	37	29	82

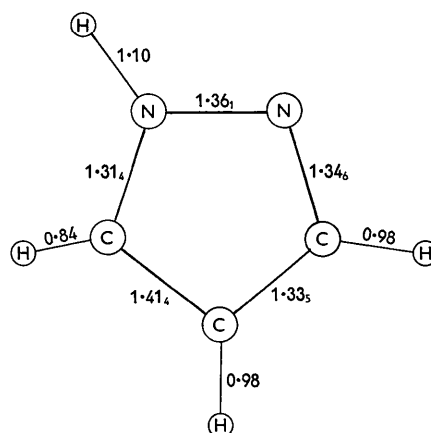


Fig. 4(b). The mean bond lengths in the pyrazole molecule.

that of Hoerni & Ibers (1954), with a Debye factor,  $B$ , of  $4.5 \text{ \AA}^2$ , and for the hydrogen atoms  $B$  was taken to be  $5.5 \text{ \AA}^2$ .

The values of  $A_c$ ,  $B_c$ ,  $|F_c|$  and  $|F_o|$  are listed in Table 2.

The two independent molecules are both planar, molecule  $A$  lying on the plane

$$2.189x - 7.268y - 5.504z + 1.671 = 0,$$

and molecule  $B$  on the plane

$$2.877x + 8.254y - 4.808z + 0.425 = 0,$$

where  $x$ ,  $y$  and  $z$  are the fractional coordinates of  $a$ ,  $b$  and  $c$ . The coefficients of  $x$ ,  $y$  and  $z$  in these equations have been chosen so that  $tx_1 + uy_1 + vz_1 + w$  gives the distance in  $\text{\AA}$  of any point  $x_1, y_1, z_1$  from the plane.

The bond lengths and bond angles are shown in Fig. 4(a) and the average bond lengths in Fig. 4(b).

**Estimation of accuracy**

The standard deviations of the atomic coordinates and electron density were estimated by the method of Cruickshank (1949). The values obtained were

$$\begin{aligned} \sigma(x) = \sigma(y) = \sigma(z) &= 0.011 \text{ \AA} \text{ for nitrogen atoms} \\ &= 0.015 \text{ \AA} \text{ for carbon atoms} \\ &= 0.25 \text{ \AA} \text{ for hydrogen atoms} \end{aligned}$$

$$\sigma(\rho) = 0.26 \text{ e. \AA}^{-2} \text{ for the (100) projection}$$

$$\sigma(\rho) = 0.68 \text{ e. \AA}^{-2} \text{ for the (010) projection}$$

$$\sigma(\rho) = 0.28 \text{ e. \AA}^{-2} \text{ for the (001) projection.}$$

Hence the standard deviation for the bond lengths in Fig. 4(a) are 0.016 Å for an N-N bond, 0.018 Å for an N-C bond, 0.021 Å for a C-C bond, and 0.25 Å for a C-H or N-H bond, and in Fig. 4(b) these values are 0.011, 0.013, 0.015 and 0.18 Å respectively.

The standard deviation of the bond angles between the heavy atoms is 1.4°. Hence some of the corresponding angles in the two molecules are significantly different from one another, and therefore average values for the angles are not quoted.

Table 2. *Calculated and observed values of F*

<i>hk0</i> reflexions					<i>h k</i>						
<i>h</i>	<i>k</i>	<i>A<sub>c</sub></i>	<i>B<sub>c</sub></i>	<i> F<sub>c</sub> </i>	<i> F<sub>o</sub> </i>	<i>h</i>	<i>k</i>	<i>A<sub>c</sub></i>	<i>B<sub>c</sub></i>	<i> F<sub>c</sub> </i>	<i> F<sub>o</sub> </i>
0	0	288	0	288	—	6	12	1.6	-0.6	1.7	<2.1
0	2	-11.0	0	11.0	11.7	7	1	-0.3	18.9	18.9	17.3
0	4	-55.3	0	55.3	56.5	7	3	-1.4	5.6	5.8	6.4
0	6	-13.1	0	13.1	12.1	7	5	0.6	0.4	0.7	<3.1
0	8	-21.1	0	21.1	22.2	7	7	0.9	6.1	6.2	7.7
0	10	19.5	0	19.5	19.3	7	9	-0.8	-8.0	8.0	8.0
0	12	0.1	0	0.1	<2.8	7	11	-0.4	0.3	0.5	<2.0
0	14	-9.1	0	9.1	7.4	8	0	7.4	-0.1	7.4	8.9
0	16	4.0	0	4.0	3.3	8	2	-0.6	0.7	0.9	<3.0
1	1	2.4	12.3	12.5	13.3	8	4	-6.9	-0.8	6.9	8.6
1	3	-8.8	-12.3	15.1	15.7	8	6	-1.1	0.5	1.2	<2.7
1	5	6.0	-8.1	10.1	9.3	8	8	2.3	-0.1	2.3	2.1
1	7	-3.4	7.0	7.8	8.1	8	10	3.9	-0.7	4.0	3.6
1	9	-1.7	-7.5	7.7	7.6	9	1	-0.3	-6.8	6.8	6.9
1	11	2.6	-0.9	2.8	3.0	9	3	-0.2	-4.0	4.0	4.3
1	13	-3.5	4.5	5.7	4.9	9	5	-0.1	0.0	0.1	<2.3
1	15	1.5	0.4	1.6	<2.2	9	7	0.5	-0.4	0.6	<1.9
2	0	-75.4	-1.8	75.4	72.8	10	0	0.2	-0.6	0.6	<1.2
2	2	6.1	-1.6	6.3	5.8	10	2	1.3	-0.5	1.4	<1.9
2	4	-6.5	-2.4	6.9	8.1	10	4	1.0	0.7	1.2	<1.5
2	6	-3.7	2.5	4.5	4.2	<i>h0l</i> reflexions					
2	8	21.1	2.7	21.3	21.3						
2	10	-1.2	-1.0	1.6	<2.9	<i>h</i>	<i>l</i>	<i>A<sub>c</sub></i>	<i>B<sub>c</sub></i>	<i> F<sub>c</sub> </i>	<i> F<sub>o</sub> </i>
2	12	0.4	-2.1	2.1	<3.0	1	2	35.9	-1.8	35.9	30.7
2	14	0.8	1.1	1.4	<2.7	2	2	-11.8	-4.8	12.7	12.2
2	16	-2.7	0.7	2.8	2.1	3	2	9.7	2.6	10.0	11.4
3	1	2.0	-10.2	10.4	10.6	4	2	-23.5	-0.6	23.5	23.6
3	3	1.6	-1.8	2.4	3.1	5	2	-13.8	-1.6	13.9	16.1
3	5	-2.9	18.2	18.4	19.4	6	2	1.2	2.9	3.1	<2.2
3	7	0.7	3.4	3.5	4.2	7	2	0.7	-0.8	1.1	<2.3
3	9	2.4	6.3	6.7	7.1	8	2	5.7	-2.1	6.1	9.4
3	11	-0.9	-2.8	2.9	3.6	9	2	2.8	0.8	2.9	3.2
3	13	0.6	-7.1	7.1	6.8	10	2	0.3	0.0	0.3	<1.1
3	15	-1.2	-0.1	1.2	<2.4	1	4	-14.0	2.3	14.2	13.2
4	0	-37.5	-0.7	37.5	34.0	2	4	15.1	-0.7	15.1	17.1
4	2	4.7	1.4	4.9	4.9	3	4	6.9	0.3	6.9	9.1
4	4	28.7	-1.9	28.8	30.1	4	4	-13.9	1.6	14.0	14.2
4	6	3.3	3.7	5.0	4.9	5	4	-2.0	-2.4	3.1	3.3
4	8	-8.5	-1.0	8.6	9.1	6	4	-0.9	-0.8	1.2	2.7
4	10	-11.9	-1.6	12.0	11.3	7	4	-0.2	2.3	2.3	3.6
4	12	-1.1	0.7	1.3	<2.8	8	4	3.3	-0.7	3.4	5.0
4	14	6.7	-1.3	6.8	5.4	9	4	1.1	-0.5	1.2	<1.2
5	1	1.0	-16.3	16.3	15.7	1	6	-11.6	-2.3	11.8	9.6
5	3	0.6	1.3	1.4	3.6	2	6	3.5	1.6	3.9	3.6
5	5	0.4	-8.5	8.5	8.3	3	6	2.7	2.2	3.5	3.2
5	7	-1.9	-14.0	14.1	13.5	4	6	-11.7	1.2	11.8	10.2
5	9	0.1	7.1	7.1	6.5	5	6	0.6	0.4	0.7	<2.0
5	11	0.5	3.7	3.7	4.3	6	6	2.0	-2.9	3.5	3.5
5	13	0.0	1.3	1.3	<2.2	7	6	0.1	-1.1	1.1	<1.4
6	0	9.8	1.0	9.9	11.4	8	6	3.9	1.5	4.2	2.0
6	2	-1.9	0.5	2.0	<2.8	1	8	1.9	-1.4	2.4	1.8
6	4	-2.9	1.1	3.1	<2.9	2	8	-0.1	-1.5	1.5	<1.6
6	6	0.9	-4.0	4.1	4.3	3	8	-0.4	1.3	1.4	<1.5
6	8	-2.3	-0.5	2.4	2.6	4	8	-5.9	0.6	5.9	5.1
6	10	2.4	2.4	3.4	4.4	5	8	-2.2	1.6	2.7	<0.8

Table 2 (cont.)

0kl reflexions											
<i>k l</i>	<i>F<sub>c</sub></i>	<i> F<sub>o</sub> </i>	<i>k l</i>	<i>F<sub>c</sub></i>	<i> F<sub>o</sub> </i>	<i>k l</i>	<i>F<sub>c</sub></i>	<i> F<sub>o</sub> </i>	<i>k l</i>	<i>F<sub>c</sub></i>	<i> F<sub>c</sub> </i>
1 1	2.3	6.0	12 2	-0.6	<2.7	7 4	2.6	<3.0	6 6	-1.3	2.8
2 1	-42.4	40.3	13 2	-1.8	<2.5	8 4	1.6	3.1	7 6	-0.3	<2.6
3 1	0.7	<1.9	14 2	-7.5	4.7	9 4	0.7	3.0	8 6	3.0	4.0
4 1	-46.1	46.1	15 2	-0.2	<1.8	10 4	3.6	3.4	9 6	-1.6	2.2
5 1	0.7	<2.4	16 2	3.2	2.3	11 4	2.0	<2.6	10 6	2.1	<2.0
6 1	4.9	6.3	1 3	7.6	8.2	12 4	-0.2	<2.3	11 6	0.6	<1.7
7 1	-5.0	5.2	2 3	-10.0	11.3	13 4	-1.3	<2.0	12 6	0.0	<1.4
8 1	7.6	9.2	3 3	-1.7	<2.7	14 4	-3.0	1.8	1 7	-2.6	<2.7
9 1	5.0	6.3	4 3	-30.1	28.3	1 5	-7.2	6.7	2 7	3.2	3.7
10 1	1.4	<3.0	5 3	-2.2	<2.9	2 5	16.9	18.0	3 7	-1.3	<2.6
11 1	-2.5	<3.0	6 3	5.5	5.7	3 5	-1.0	<3.0	4 7	4.4	5.1
12 1	0.4	<2.8	7 3	-2.1	2.9	4 5	5.5	5.1	5 7	2.1	2.5
13 1	-0.7	<2.6	8 3	2.8	4.3	5 5	5.8	5.6	6 7	-0.3	<2.3
14 1	-0.3	<2.3	9 3	1.5	3.1	6 5	1.0	<3.0	7 7	2.4	1.9
15 1	2.9	3.0	10 3	1.5	<2.9	7 5	4.4	4.6	8 7	-1.5	<1.9
16 1	1.8	<1.5	11 3	-2.2	<2.8	8 5	-5.3	5.3	9 7	-0.7	<1.7
0 2	88.6	87.6	12 3	3.2	3.7	9 5	-1.4	<2.7	10 7	0.2	<1.4
1 2	5.4	8.6	13 3	-1.7	<2.3	10 5	-0.9	<2.4	0 8	6.9	4.6
2 2	-36.1	36.1	14 3	-1.0	<1.9	11 5	-1.1	<2.2	1 8	3.2	1.9
3 2	-3.6	3.7	15 3	1.4	<1.5	12 5	2.1	<1.9	2 8	2.5	2.3
4 2	-24.9	25.7	0 4	0.6	<1.8	13 5	-0.6	<1.6	3 8	3.7	3.1
5 2	1.9	2.7	1 4	-2.2	<2.9	0 6	10.4	9.8	4 8	-4.1	2.6
6 2	14.5	15.0	2 4	-20.6	22.9	1 6	3.1	<3.0	5 8	0.5	<1.8
7 2	0.2	<2.9	3 4	-13.2	12.8	2 6	0.4	<3.0	6 8	-2.7	2.2
8 2	-11.7	11.4	4 4	-2.6	3.0	3 6	0.9	<2.9	7 8	-0.1	<1.4
9 2	0.4	<3.0	5 4	-2.8	3.0	4 6	-7.4	7.1	1 9	2.5	1.2
10 2	11.0	10.5	6 4	16.8	17.5	5 6	-0.7	<2.8	2 9	-3.1	1.4
11 2	2.7	<2.9									

### Discussion of structure

#### Crystal structure

In crystals of pyrazole the molecules are hydrogen-bonded together to form long chains. These chains form an arrangement which is related to the figure 8 as a helix is related to the figure 0, that is a translation perpendicular to the plane of the 8 takes place as the figure is described.

Another way of looking at this 8-helix is to consider it as a combination of a left-handed and a right-handed helix, the hand changing after every one complete turn of an ordinary spiral. This 8-helix is not distinguishable from its mirror image although it possesses neither a centre of symmetry, a mirror plane nor an alternating axis. It does, however, have a glide plane.

If we regard these 8-spirals as having a cylindrical form, then the crystal is a close-packed arrangement of cylinders. The principal axes of these cylinders are parallel to the crystallographic *c* axis, and they pack in layers perpendicular to the *b* axis. As the 8-helix is non-centrosymmetric these cylinders are polar, and in alternate layers the polarity is reversed.

The contacts between molecules in an 8-helix are shown in Fig. 5(a); the contacts between cylinders are shown in Fig. 5(b).

#### Molecular structure

The analysis reveals that the molecule is planar, and that the bond lengths are those expected in an aromatic system. The bond angles are significantly

different in the two molecules, but strong hydrogen bonds exist, and the different environments of the crystallographically distinct molecules lead to this distortion. It is perhaps significant that the distortion

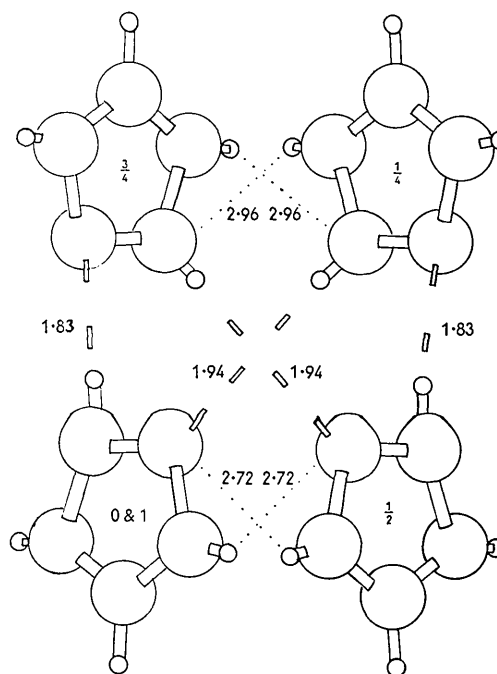
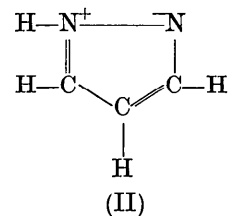
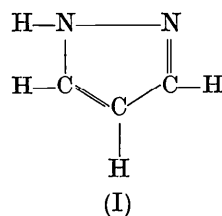


Fig. 5. (a) Diagrammatic representation of the 8-helix, showing the contacts between molecules within this arrangement.

of molecule *A* is such as to reduce the stress imposed on it by the packing of the cylinders. As the positions of the nitrogen atoms are determined by the fairly rigid requirements of the 8-helix, this is the only way in which this stress can be alleviated.

The interesting feature of this analysis is the unexpected distribution of long and short bonds in the molecule. This indicates that, in the solid state at least, the aromatic molecule resembles the betaine (II), more than the uncharged form (I).



Alternatively we may say that the betaine contributes more to the resonance hybrid than does (I).

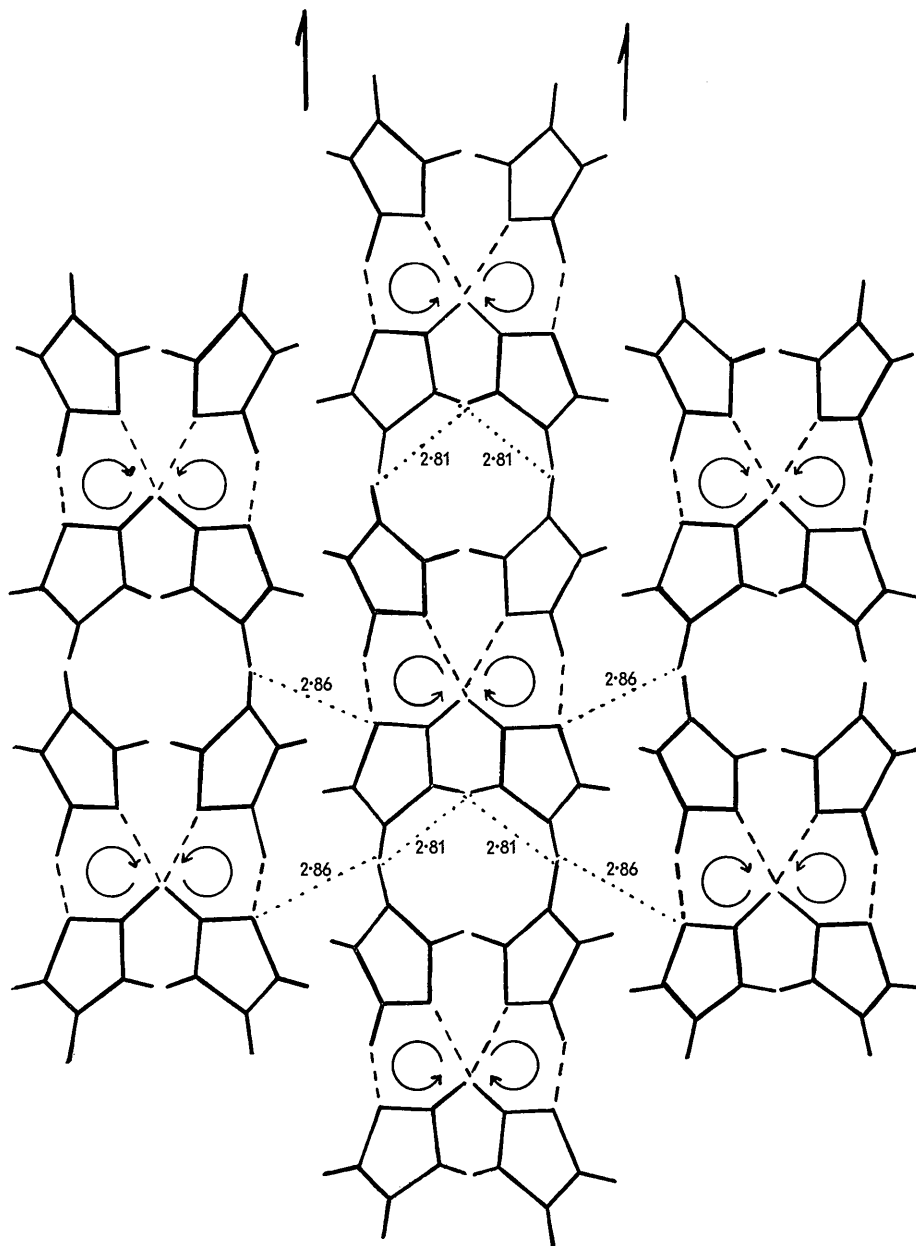
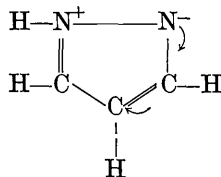


Fig. 5(b). The contacts between cylinders of pyrazole molecules. On going round the spiral in direction  $\odot$  an upwards translation is effected.

The hydrogen-bond hydrogen atoms are only  $14^\circ$  and  $16^\circ$  out of the plane of their molecules, and this again favours the betaine. It is just possible that the strong hydrogen bonds which exist (lengths  $N \cdots N$  are 2.93 Å and 2.86 Å) may force the hydrogens into the plane of the ring, thus biasing the molecule towards the betaine form. However, infra-red spectroscopy studies of solid pyrazole and of solutions of pyrazole in non-polar solvents show that the spectra of the hydrogen-bonded species are identical in the two states. Hence it is assumed that this is indeed an analysis of the pyrazole molecule in the ground state.

Many other crystal-structure studies of nitrogen heterocyclics have led to results which can be interpreted by assuming a large contribution from the betaine form. All N-methyl heterocyclic compounds have their methyl groups coplanar with the ring, examples involving five-membered rings being 2-methyl 5-aminotetrazole (Bryden, 1956), 1:3-dimethyl 5-iminotetrazole hydrochloride (Bryden, 1955) and caffeine (Sutor, 1958). Bond lengths in adenine hydrochloride (Cochran, 1951) and in 2-methyl 5-aminotetrazole are consistent with this concept. Furthermore there is also some evidence for the existence of a charged nitrogen atom from a consideration of the hydrogen bond lengths, as  $N \cdots N$  distances are shorter if one of the nitrogen atoms is charged. Table 3 lists some  $N^+ \cdots N$  distances.

The chemistry of pyrazole is readily explained on the basis of this structure. Substitution by electrophilic groups takes place in the 4-position, which is accounted for by an electron migration from the negatively charged nitrogen atom.



On reacting with alkyl halides, the positively charged alkyl group adds on to position 2. This molecule is unstable and loses a proton, leaving N-alkyl pyrazole, thus giving the effect of substitution. Subsequent attack with more alkyl halide gives rise to pyrazolium salts of which the cation is 1:2-dialkyl pyrazole.

Table 3.  $N^+ \cdots N$  distances

Compound	$N^+ \cdots N$ bond length	Reference
Hydrazinium chloride	2.95 Å	Sakurai & Tomiie, 1952a
Hydrazinium bromide	2.93 Å	Sakurai & Tomiie, 1952b
Ammonium azide	2.94 & 2.99 Å	Frevel, 1936
Hydrazine salt of 5-aminotetrazole	2.90, 2.90 Å & 2.88 Å	Bryden, 1958

One cannot distinguish between 3 and 5 substituted pyrazoles because the hydrogen bond is also present in solution, and thermal energy is sufficient to move the hydrogen atom in the hydrogen bond from one nitrogen atom to the other.

Although the results of this analysis seem, at first sight, to be surprising, pyrazole is not the only example in which the distribution of double bonds is unexpected. The molecular structure deduced from the study of its crystals explains the chemical behaviour of pyrazole, and examination of other nitrogen heterocyclic compounds with an  $-NH-$  in an aromatic ring also indicates that the main contribution to the resonance hybrid comes from the betaine form.

The infra-red spectroscopy studies mentioned above have been carried out by Mr J. L. Duncan, and I wish to record my gratitude to him. I also wish to thank Dr C. A. Beevers for much helpful discussion and encouragement.

### References

- BEEVERS, C. A. & EHRLICH, H. W. (1959). *Z. Kristallogr.* **112**, 414.  
 BRYDEN, J. H. (1955). *Acta Cryst.* **8**, 211.  
 BRYDEN, J. H. (1956). *Acta Cryst.* **9**, 874.  
 BRYDEN, J. H. (1958). *Acta Cryst.* **11**, 31.  
 COCHRAN, W. (1951). *Acta Cryst.* **4**, 81.  
 CRUICKSHANK, D. W. J. (1949). *Acta Cryst.* **2**, 65.  
 FREVEL, L. K. (1936). *Z. Kristallogr.* **94**, 197.  
 HOERNI, J. A. & IBERS, J. A. (1954). *Acta Cryst.* **7**, 744.  
 HOWELLS, E. R., PHILLIPS, D. C. & ROGERS, D. (1950). *Acta Cryst.* **3**, 210.  
 MCGEACHIN, H. MCD. & BEEVERS, C. A. (1957). *Acta Cryst.* **10**, 227.  
 SAKURAI, K. & TOMIIE, Y. (1952a). *Acta Cryst.* **5**, 293.  
 SAKURAI, K. & TOMIIE, Y. (1952b). *Acta Cryst.* **5**, 289.  
 SUTOR, D. J. (1958). *Acta Cryst.* **11**, 453.