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The Crystal Structure of 2,2′-Bipyridine*

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The crystal structure of 2,2′-bipyridine has been determined by single-crystal methods. The unit cell is monoclinic with $a = 5{\cdot}66$, $b = 6{\cdot}24$, $c = 13{\cdot}46$ Å, $\beta = 118^\circ\,44'$. The space group is $P2_1/c\text{–}C^5_{2h}$, and there are two molecules per unit cell.

Atomic positions were determined by electron-density projections and were refined by difference syntheses and by three-dimensional least-squares methods. Structure factors were obtained from visually estimated intensities on Weissenberg photographs taken with Cu $K\alpha$ radiation.

The molecule is planar and has a *trans* configuration. The C–N bonds average 1·36 Å and the C–C bonds in the pyridine ring average 1·39 Å. The C–C bond between the two rings is 1·50 Å. There are no short intermolecular distances, and binding must be due only to weak van der Waals forces.

Introduction

This report is the fourth in a series from these laboratories dealing with the crystal structure of organic reagents of analytical importance and the complexes they form with metallic ions. In addition to the well known complex which 2,2′-bipyridine forms with ferrous ions, this compound also reacts with cupric, cadmium, and zinc ions. The similar compound 2,2′-biquinoline does not react with ferrous ion, but does react with cuprous ion. A comparison of the structures of these two compounds and of some of their complexes should be of interest. Such studies are in progress in our laboratory.

Experimental technique, unit cell and space group

Single crystals of 2,2′-bipyridine were secured by recrystallization of the compound obtained from the G. Frederick Smith Chemical Company from a 50% ethyl alcohol–50% water solution at room temperature.

Preliminary X-ray studies of this compound had been made by Cagle (1948), who found $a = 5{\cdot}51$, $b = 6{\cdot}24$, $c = 13{\cdot}68$ Å, $\beta = 120^\circ$. He reported the space group $P2_1/c\text{–}C^5_{2h}$, with two molecules per unit cell.

The three principal indices of refraction, determined by the usual immersion methods, were found to be

$$n_\alpha = 1{\cdot}608,\ 1{\cdot}77 < n_\beta < 1{\cdot}78,\ n_\gamma > 1{\cdot}80\ ,$$

with β parallel to b and γ approximately parallel to c.

The unit-cell dimensions were obtained from oscillation photographs and from Weissenberg photographs. The results were

$$a = 5{\cdot}66,\quad b = 6{\cdot}24,\quad c = 13{\cdot}46\ \text{Å}\ .$$

The value of β was found to be $118^\circ\,44'$, as determined by the method of ω separations (Buerger, 1942).

The density, determined by flotation in a potassium iodide solution, was 1·28 g.cm.$^{-3}$, which gives 2·06, i.e. two molecules per unit cell.

Complete sets of equi-inclination Weissenberg photographs about the [100] and [010] axes were taken for intensity estimation. The crystals used were reduced to cylindrical form with diameter of about 0·5 mm. to minimize absorption effects. Since the crystals sublimed in the air in the period of a week, they were preserved by enclosing them in a thin formvar film after the method of Roth & Harker (1948). Copper $K\alpha$ radiation filtered through nickel was employed, and relative intensities were estimated visually by comparison with a standard intensity strip prepared by making a series of timed exposures of the $(20\bar{4})$ reflection. The multiple-film technique of Robertson (1943) was employed, using four sheets of Eastman No-Screen X-ray film and an experimentally determined factor of 3·85 for the decrease in intensity on passage of the beam through one layer of film. A total of 446 unique reflections were observed and there are another 149 reflections which should have been observed but were either absent or too weak to be seen. The usual corrections for the Lorentz and polarization factors, the oblique penetration of the film by the X-rays for the non-equatorial layer photographs, and the relative time factor of Cox & Shaw (1930) were applied. The zero-layer Weissenberg film about [010] was taken as the standard film, and by cross calibration all intensities were reduced to this common level. Relative F_o values were calculated.

Systematic absences were noted for $(h0l)$ when l is

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odd and (0k0) when k is odd, giving the space group $P2_1/c$–C_{2h}^5. Since there are only two molecules per unit cell, the molecules of 2,2′-bipyridine must have a center of symmetry. Assuming that the pyridine rings are planar and that the bond between the two rings lies in the plane of the rings, the fact that the molecule has a center of symmetry leads to the conclusion that the two rings must be coplanar. Furthermore, since the center of symmetry lies at the mid-point of the bond connecting the two rings, the two nitrogen atoms in one molecule must lie in the *trans* positions.

Determination of atomic positions

In order to obtain a trial structure, a Patterson projection upon (010) was calculated. Coefficients modified to remove the original peak and to sharpen the peaks were used, and were equal to

$$|F_m|^2 = k|F_o|^2 - \sum_{i=1}^{n} f_i^2 \exp\left(-2B\sin^2\theta/\lambda^2\right) \frac{\sum_i Z_i}{\sum_i f_i^2}\,.$$

The factors k and B were obtained by Wilson's method (1942). This Patterson is shown in Fig. 1. Crosses represent the ultimate positions of projected interatomic vectors within one molecule. This Patterson projection was easily solved. The projected length of the vector taken as representing the length of the pyridine ring, i.e. the C_1–C_4 vector, indicated that the molecule was tilted about 40° off the (010) plane. The x and z parameters estimated from this trial structure were used to calculate structure factors. Atomic scattering factors were obtained from the curves given by McWeeny (1951) for carbon and nitrogen. Five electron-density projections on (010) were used for the first refinements of the x and z parameters. Further refinements were made by calculation of five difference syntheses on (010). The final electron-density projection on (010) is shown in Fig. 2.

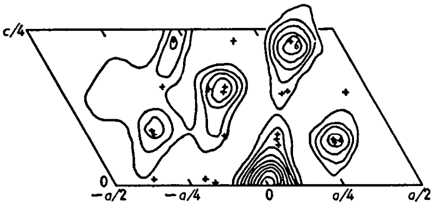

Fig. 1. Patterson projection upon (010) of one asymmetric unit of 2,2′-bipyridine. Contour values in arbitrary equal units. Crosses represent ultimate intramolecular vectors, all of approximately equal weight except cross marked 6, which has six times the weight of the others.

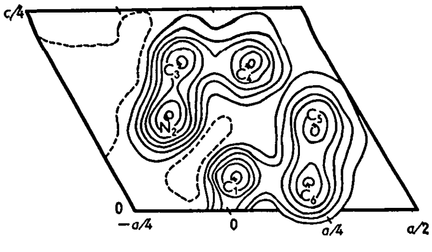

Fig. 2. Electron-density projection upon (010) of one asymmetric unit of 2,2′-bipyridine. The contours are drawn at intervals of 1 e.Å^{-2}, with the zero contour broken. Crosses represent ultimate centers of the atoms.

After each projection the constant B in the exponent of the temperature factor and a scale factor, k, were determined by the method of least squares using the following equation:

$$k|F_o| = |F_c| \exp\left[-B\sin^2\theta/\lambda^2\right].$$

The value of $R = \Sigma|F_o - F_c| \div \Sigma|F_o|$ was 0·21 after these refinements. The contribution of the hydrogen atoms was included in structure-factor calculations by assigning their position parameters, assuming a C–H distance of 1·08 Å. After the x and z parameters were established by the projection on (010) an estimate of the tilt of the molecule was made by measuring the bond lengths in the pyridine rings in projection and comparing these lengths with the expected values. It was estimated that the molecule was tilted 51° off the (010) plane and about 17° around its longest direction. From this information the y parameters were estimated and structure factors were calculated for all (0kl) reflections. An electron-density projection upon (100) gave a good picture of the molecule and further refinements were made by calculation of two difference syntheses on (100). The final electron-density projection on (100) is shown in Fig. 3. For the (0kl) data R was 0·22.

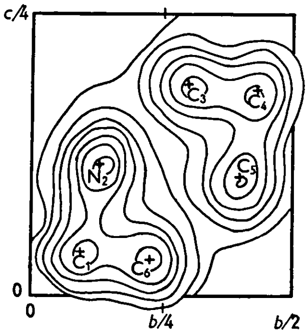

Fig. 3. Electron-density projection upon (100) of one asymmetric unit of 2,2′-bipyridine. The contours are drawn at intervals of 1 e.Å^{-2}, the lowest contour being the one-electron line. Crosses represent ultimate centers of the atoms.

Complete structure factors were calculated for all reflections and the correlation factor, R, was 0·23. Further refinements were carried out by three-dimensional least-squares calculations (Hughes, 1941), and two such refinements of parameters completed the structure determination. Only the diagonal and x_iz_i terms were used in solving the normal equations. The final corrections obtained from the least-squares method were small, with a maximum of 0·03 Å for the x parameter of C_5. Before the second least-squares refinement the six strongest low-angle reflections were investigated for possible secondary extinction effects to bring their F_o more in line with the respective F_c values. This was done by measuring the intensity of these reflections on powder diffraction photographs. The observed intensities for the (012), (110) and (111) reflections were found to be much greater than the intensities measured on the Weissenberg photographs, and these larger F_o values were used in the last least-squares refinement. The final parameters for the atoms are given in Table 1 and the values of F_o and F_c in Table 2.* The final value for B, the exponent in the temperature-factor expressions, was $4{\cdot}12\times10^{-16}$ cm.^{2}. The final correlation factor, R, for all the reflections was 0·15.

Table 1. *Atomic parameters for 2,2′-bipyridine*

Atom	x/a	y/b	z/c
C_1	0·062	0·094	0·039
N_2	−0·022	0·128	0·116
C_3	0·091	0·297	0·188
C_4	0·274	0·435	0·184
C_5	0·360	0·398	0·106
C_6	0·254	0·226	0·031
H_7	0·030	0·323	0·249
H_8	0·357	0·577	0·242
H_9	0·508	0·504	0·103
H_{10}	0·317	0·200	−0·029

Calculations of the electron-density projections, of the structure factors, and of the three-dimensional least-squares refinements were carried out with the aid of I.B.M. machines (Donohue & Schomaker, 1949; Shaffer, Schomaker & Pauling, 1946).

Discussion of the structure

The dimensions of a single asymmetric unit are presented in Fig. 4 and Table 3. The bond lengths in the pyridine ring, C–C (average) = 1·39 Å, C–N (average) = 1·36 Å, agree quite well with the values C–C = 1·40 Å, C–N = 1·36 Å, observed by Schomaker & Pauling (1939) for pyridine, pyrazine, and related six-membered heterocyclic molecules. None of the interatomic distances within the ring is of unusual length with only C_6–C_1 being longer than 1·40 Å. The length of the bond between the two pyridine rings, C_1–C_1' = 1·50 Å, is slightly greater than the length of 1·48 Å for the similar bond between the two benzene rings in biphenyl (Pauling, 1948). This indicates only about 10% double-bond character.

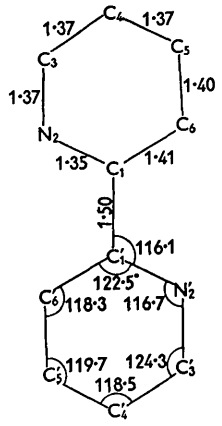

Fig. 4. Experimental bond lengths (in Å) and bond angles (in °) for 2,2′-bipyridine.

Table 3. *Interatomic distances and bond angles for 2,2′-bipyridine*

C_1–N_2	1·35 Å	C_1–N_2–C_3	116° 40′
N_2–C_3	1·37	N_2–C_3–C_4	124 17
C_3–C_4	1·37	C_3–C_4–C_5	118 32
C_4–C_5	1·37	C_4–C_5–C_6	119 40
C_5–C_6	1·40	C_5–C_6–C_1	118 17
C_6–C_1	1·41	C_6–C_1–N_2	122 28
C_1–C_1'	1·50	C_6–C_1–C_1'	121 25
		N_2–C_1–C_1'	116 08
(Assumed)			
C_3–H_7	1·08		
C_4–H_8	1·08		
C_5–H_9	1·08		
C_6–H_{10}	1·08		

Since the greatest variation of any C–C bond length in the pyridine ring is 0·03 Å from the accepted value, or 0·02 Å from the average value, and since the two C–N bonds differ in length by 0·02 Å and the largest deviation of any atom from the least-squares best plane is 0·014 Å, the error in any bond length is estimated to be not more than 0·025 Å. This would correspond to an error in any parameter of about 0·015 Å.

The bond angles within the pyridine rings approach the expected value of 120° for a hexagonal ring. However, owing to the fact that C–N bonds are shorter than C–C bonds there must be some distortion in the ring to compensate for the two shorter C–N bonds. The two angles adjacent to the C–N bonds are somewhat greater than 120°.

The equation for the least-squares best plane in terms of unit-cell vectors in the monoclinic system is

$$x-1{\cdot}219y+0{\cdot}699z = 0\ .$$

The largest deviation from this least-squares best plane is 0·014 Å for C_4. Therefore the molecule is undoubtedly planar.

The root-mean-square amplitude of thermal vibration of the atoms in the asymmetric unit was 0·23 Å, as calculated by the equation

$$B = 8\pi^2\overline{u^2}\ .$$

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* Table 2 has been withdrawn and is deposited as Document No. 4874 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D.C., U.S.A. A copy may be secured by citing the Document number and by remitting $1·25 for photoprints, or $1·25 for 35 mm. microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress. A copy may also be obtained from the authors.

The reaction yielding the ferrous complex which takes place in solution upon addition of 2,2′-bipyridine to a solution of a ferrous salt can only lead to the formation of a stable five-membered ring consisting of N_2–C_1–C_1'–N_2' and the Fe^{++} ion if the two nitrogen atoms are in the *cis* positions. Since in the solid crystalline form the nitrogen atoms lie in the *trans* positions, there must be rotation about the C_1–C_1' bond in solution in order for complex formation to be possible. The observed length of this bond would indicate that such rotation would be easily possible in solution.

The molecules in the unit cell of 2,2′-bipyridine show no unusually close approaches. The shortest intermolecular distances are 3·11 Å between the H_8 bonded to the C_4 in one ring and the C_3'' of the next molecule, and 3·12 Å between H_9 bonded to C_5 in one molecule and H_7'' bonded to C_3'' in the next molecule. Since the van der Waals radius of a carbon atom is about 1·7 Å and that of a hydrogen atom is about 1·3 Å, this indicates that the only forces between the molecules in the crystal are weak van der Waals forces. This is supported by the low melting point (69·5° C.) of this compound and also by the tendency of these crystals to sublime slowly in air at room temperatures.

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An Improvement of the 'Heavy-Atom' Method of Solving Crystal Structures

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For the normal heavy-atom method of solving crystal structures the Fourier series, whose coefficients are given in moduli by the observed intensities and in phase by the heavy-atom contribution, is summed. It is shown that a Fourier series with coefficients quite different from these shows the unknown part of the structure more clearly. A criterion for determining the degree of resolution of a structure is given and the advantage of the new series is demonstrated both theoretically and by means of practical examples.

Introduction

The 'heavy-atom' method of solving crystal structures is most frequently used for centrosymmetrical structures when one pair of atoms is sufficiently heavy to be detected by the Patterson function. With the observed structure amplitudes and phases given by the contribution of the known atom, a Fourier synthesis is calculated from which the position of the remaining atoms may be found. If the known atom is not heavy enough to dominate the phases of the complete structure, the remaining atoms will not show themselves. On the other hand, if the known atom is too heavy the relative contributions of the unknown atoms to the structure factors will be comparable in size with the experimental errors of the latter. The peaks of the Fourier synthesis due to random errors will then be of the same order as a peak height for one of the unknown atoms, whose positions will not be determined with any certainty.

Luzzati (1953) has given a theoretical treatment of the heavy-atom method as part of a more general

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