

The Crystal and Molecular Structure of Succinimide C₄H₅O₂N

BY R. MASON

Department of Chemical Crystallography, University College, London W. C. 1, England

(Received 16 December 1955 and in revised form 16 January 1956)

Succinimide crystallizes with $a = 7.50$, $b = 9.62$, $c = 12.75$ Å, $\rho_o = 1.420$ g.cm.⁻³, $Z = 8$ and space group $Pbca$. The crystal structure was determined by a combination of analytical, optical transform and difference Fourier methods. A chemically tenable, but incorrect structure was refined to a stage where $R = 0.21$. The final co-ordinates of a structure which refines to $R = 0.104$ have been derived by least-squares methods and some account has been taken of thermal anisotropy in the molecule and crystal. This structure is built up through N-H...O bonds of length 2.85 Å and the usual van der Waals forces. Short intramolecular C-C distances are observed and the C-N distances are less than those usually found in analogous compounds. Values are given for the principal molecular magnetic susceptibilities.

Experimental

Suitable crystals for an X-ray examination were grown from a solution of succinimide in methyl ethyl ketone; the larger crystals necessary for magnetic measurements were grown by seeding the solution. The crystals were orthorhombic bipyramids with faces {111}, and subordinate {001}, {110}, {102} and {201}.

Unit-cell dimensions were determined from high-order axial reflexions on Weissenberg photographs:

$$a = 7.50 \pm 0.04, \quad b = 9.62 \pm 0.05, \quad c = 12.75 \pm 0.05 \text{ Å};$$

$$a:b:c = 0.780:1:1.325,$$

in agreement with Yardley's (1924) earlier observations but differing from Groth's (1910) values. The volume V of the unit cell is 919 Å³. $\rho_o = 1.420$ g.cm.⁻³, $\rho_c = 1.428$ g.cm.⁻³ for $Z = 8$. $F(000) = 416$.

The space group is $Pbca$, uniquely determined by the systematic absences $\{hk0\}$ for $h = 2n+1$, $\{h0l\}$ for $l = 2n+1$ and $\{0kl\}$ for $k = 2n+1$. The eight asymmetric molecules in the unit cell must lie in general positions.

The equi-inclination Weissenberg method gave intensity values for some 850 reflexions, approximately 90% of those occurring within the Cu $K\alpha$ reflecting sphere; they were assigned $|F_o|$ values by employment of the multiple-film and visual-estimation techniques. A range of amplitudes of some 50:1 was observed.

Absorption, and primary and secondary extinction effects were neglected until calculated structure factors revealed large discrepancies for several strong reflexions. Use of a smaller crystal and powder photography led to revised values for several amplitudes. In some cases the change was large: $|F(040)|$ was increased from 12.2 to 33.4, for example.

Diamagnetic anisotropy

Measurement of the diamagnetic anisotropy should suggest an orientation for the plane containing the

atoms O=C-N-C=O which might be expected to have a $\Delta\chi$ of about 10×10^{-6} c.g.s.e.m.u., the susceptibility being numerically greatest normal to the plane of the group.

The method of Krishnan, Guha & Banerjee (1933) gave

$$\chi_a - \chi_c = -5.54 \times 10^{-6} \text{ c.g.s.e.m.u.}$$

$$\chi_b - \chi_c = -0.98 \times 10^{-6}$$

$$\chi_a - \chi_b = -4.53 \times 10^{-6}.$$

The *International Critical Tables* give

$$\bar{\chi} = \frac{1}{3}(\chi_a + \chi_b + \chi_c) = -47.3 \times 10^{-6} \text{ c.g.s.e.m.u.}$$

Hence,

$$\chi_a = -50.7 \times 10^{-6} \text{ c.g.s.e.m.u.}$$

$$\chi_b = -46.1 \times 10^{-6}$$

$$\chi_c = -45.1 \times 10^{-6}.$$

These values show the crystal to be approximately magnetically uniaxial; they suggest that the molecular plane is not parallel to any of the axial planes but may be nearest to (100). The unitary values of the $\{h00\}$ reflexions offer some confirmation of the magnetic results.

The refractive indices listed by Hinch & MacCrone (1953) are

$$\alpha = 1.505 \pm 0.002 \text{ along } a \text{ (referred to this unit cell),}$$

$$\beta = 1.537 \pm 0.002 \text{ along } b,$$

$$\gamma = 1.623 \pm 0.002 \text{ along } c.$$

The maximum (numerical) crystal diamagnetic susceptibility coincides with the minimum refractive index, which is typical of nearly parallel molecules containing conjugated bonds; on the other hand the crystal is optically positive.

Determination of the crystal structure

Three projections of the Patterson function were evaluated, but could not be interpreted.

In an effort to determine the structure analytically, the usual equation,

$$|U_H| = \sigma_H / (F_H^2 / \overline{F^2}),$$

was used to determine the unitary structure-factor values. All atoms were assumed of equal scattering power (neglecting the hydrogen atoms).

8% of the two-dimensional reflexions had unitary values $|U| \geq 0.32$ (1.7σ), while 11% of the hkl reflexions had values $|U| \geq 0.23$. The values are in accord with Hughes' (1949) estimates; according to Zachariasen (1952), Harker-Kasper inequalities will not effect an unequivocal analysis, and this is the case.

The 150 reflexions with unitary values $|U| \geq 1.5\sigma$ were, following Zachariasen, nominated strong and useful from an inequality viewpoint, and the origin of the unit cell was fixed uniquely by assigning, arbitrarily, a positive sign to the three reflexions 223, 529 and 212. A dozen or so more reflexions were then given signs a, b, \dots, p and the signs of remaining 'strong' reflexions were derived by assuming the equation $S_H S_K = S_{H+K}$ to be true. Discrepancies must arise in this operation but several relations between different symbols appeared valid from different combinations. Eventually, after eliminating the majority of symbols and using the more reliable statistical relationship, enough reflexions in the three principal zones could be assigned phases.

These signs were used to compute the electron densities for the $(h00)$, $(h0l)$, $(0kl)$ projections, but although the syntheses were physically acceptable in that they possessed little negativity, the molecular configurations could not be identified from them. It was later realized that extinction effects had so falsified the $|F_o|$ values as to cause the almost complete disappearance of one oxygen atom.

Optical methods were used at this stage in an effort to determine the structure independently. First an attempt was made to obtain the $\rho(0, Y, Z)$ synthesis by use of the optical Fourier synthesizer, but after a hopeful start the method proved abortive. Then several configurations suggested by inspection of the projections obtained by the inequality methods were

tested by the optical-transform method, and one configuration led to good agreement with the weighted reciprocal lattice. Phases were determined optically and the $\rho(0, Y, Z)$ synthesis was computed. The molecule thus obtained was, however, stereochemically improbable. A difference Fourier at this stage shifted one 'oxygen peak' to a chemically possible position and this new structure refined very slowly to about $R = 0.21$ for all projections.

This structure (Fig. 1) might easily have been accepted at this stage, although it would refine no further, but it is in fact incorrect. In view of the importance of recognizing that a structure refining to a reliability factor of about 0.21 may still be incorrect, it seems worthwhile to consider some features of this incorrect structure and the process that led to its rejection.

The two C=O bond distances differed significantly, but this could be accounted for by assuming enolization of the molecule. This suggestion was apparently confirmed by the occurrence of an intermolecular O...O distance of 2.7 Å, the crystal consisting of a compact array of molecules joined in chains by zigzag O-H...O bonds, the chains being separated by van der Waals distances. The molecules were not planar, the CH₂ groups being about 0.5 Å out of the mean molecular plane.

A difference Fourier on (100) showed a persistent peak of height 3 e.Å⁻² in the position from which one oxygen atom had previously been moved (as described earlier), and the inclusion of probable hydrogen contributions did not remove this peak. It was at this stage that new intensity measurements were made with a smaller crystal and a powder, to eliminate probable extinction effects. The resulting Fourier projections were found to lead to a structure in which six of the atoms were identical in position, though not in kind, with those in the false structure, the shift of the seventh atom permitting a new assignment of molecular orientation which did not imply enolization, and which refined to $R = 0.104$.

The atomic co-ordinates given in Table 1 were

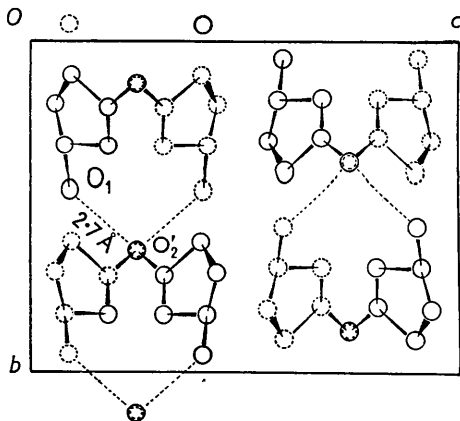


Fig. 1. The incorrect structure projected on (100). Broken lines represent directions of short intermolecular bonds.

Table 1. Final atomic co-ordinates

	x/a	y/b	z/c
N	0.041	0.108	0.109
O ₁	0.212	0.127	0.250
O ₂	-0.146	0.154	-0.025
C ₁	0.112	0.180	0.181
C ₂	-0.061	0.184	0.055
C ₃	0.055	0.328	0.174
C ₄	-0.071	0.333	0.079
H ₁	0.06 ₀	0.01 ₅	0.08 ₁
H ₂	0.15 ₀	0.41 ₀	0.17 ₂
H ₃	-0.03 ₀	0.35 ₀	0.24 ₀
H ₄	-0.19 ₅	0.38 ₀	0.10 ₀
H ₅	0.01 ₀	0.41 ₀	0.03 ₄

obtained by successive least-squares treatment of the new and complete two-dimensional data. McWeeny's

Table 2. Comparison of observed and calculated structure factors

<i>hkl</i>	$ F_o $	F_c	<i>hkl</i>	$ F_o $	F_c	<i>hkl</i>	$ F_o $	F_c
200	16.6	16.8	102	7.9	-8.3	029	0.3	-0.3
400	4.0	-3.0	202	11.8	12.1	0,2,10	0.5	0.7
600	3.8	-3.8	302	6.4	-6.9	0,2,11	2.6	2.4
800	3.2	-3.4	402	5.6	-5.9	0,2,12	3.1	-2.4
020	24.0	-24.6	502	1.7	-1.5	0,2,13	0.4	0.7
040	33.4	-33.8	602	2.5	2.0	0,2,14	1.5	1.3
060	16.0	16.4	702	1.0	-1.0	0,2,15	3.8	4.0
080	2.2	-1.4	802	0.5	-0.5	041	3.9	-2.9
0,10,0	1.6	-0.6	902	1.9	-2.0	042	3.9	3.6
0,12,0	1.4	1.6	104	4.6	5.1	043	5.4	-5.8
210	3.0	2.2	204	15.4	-15.9	044	3.6	-5.2
220	6.4	-6.4	304	9.0	8.5	045	1.7	-1.7
230	7.0	-5.8	404	2.5	1.9	046	5.9	5.9
240	0.6	0.2	504	5.8	5.4	047	3.3	2.9
250	2.6	-3.0	604	2.9	2.1	048	4.2	-4.2
260	4.8	3.4	704	1.4	-1.4	049	0.4	0.5
270	5.0	4.0	804	0.0	0.1	0,4,10	2.2	0.9
280	5.2	-4.8	106	5.1	-4.7	0,4,11	2.9	-3.2
290	0.4	0.6	206	0.6	0.7	0,4,12	0.5	-1.1
2,10,0	2.0	1.8	306	3.5	2.5	0,4,13	2.4	-2.5
2,11,0	2.4	-2.2	406	4.8	-5.4	0,4,14	2.6	2.8
2,12,0	1.8	1.8	506	4.2	4.7	0,4,15	1.8	-2.6
410	3.4	1.8	606	1.9	2.5	061	6.2	6.1
420	3.8	4.2	706	3.2	3.0	062	2.4	2.8
430	2.0	-1.8	806	2.4	2.4	063	3.9	-4.1
440	0.8	-1.0	108	5.2	-5.6	064	3.2	3.9
450	0.8	-0.8	208	7.9	-7.8	065	0.4	-0.9
460	4.8	-5.4	308	2.3	-2.5	066	2.4	2.8
470	1.6	1.0	408	3.2	3.4	067	7.9	-8.2
480	2.6	3.0	508	5.5	5.5	068	5.6	-5.7
490	0.6	0.4	608	2.5	2.6	069	0.4	0.8
4,10,0	1.8	1.4	708	1.4	1.3	0,6,10	2.1	-1.3
610	3.8	-4.0	1,0,10	0.4	0.4	0,6,11	0.4	-0.5
620	2.8	2.6	2,0,10	4.9	3.1	0,6,12	2.6	2.7
630	5.4	-5.6	3,0,10	1.4	-0.8	0,6,13	1.4	1.3
640	0.8	0.6	4,0,10	0.4	-0.6	0,6,14	1.0	-1.1
650	3.0	3.0	5,0,10	0.4	-0.4	081	3.4	3.4
660	2.6	-2.2	1,0,12	3.4	-3.4	082	1.8	-2.0
670	3.0	3.4	2,0,12	3.6	-3.3	083	4.9	5.3
680	2.2	2.2	3,0,12	3.7	-4.4	084	1.3	1.9
690	2.0	-2.2	4,0,12	1.5	-1.0	085	2.4	1.2
810	1.8	2.4	5,0,12	0.6	-0.6	086	4.6	-4.7
820	0.4	1.0	1,0,14	1.5	-1.5	087	0.0	-0.1
830	0.4	0.4	2,0,14	1.2	-0.7	088	6.2	6.1
840	1.4	1.6	3,0,14	1.0	-0.6	089	0.8	-0.3
002	2.3	3.4	4,0,14	0.5	0.4	0,8,10	0.5	-0.4
004	6.8	7.2	021	12.9	-13.3	0,8,11	1.5	1.0
006	7.5	-7.4	022	2.5	-3.0	0,8,12	1.6	-1.3
008	2.3	-0.6	023	11.5	11.7	0,10,1	3.3	-3.2
0,0,10	2.7	-2.5	024	4.4	-4.0	0,10,2	0.7	-0.6
0,0,12	4.1	4.3	025	1.9	-1.9	0,10,3	0.0	0.0
0,0,14	5.1	-6.0	026	2.3	-3.7	0,10,4	0.7	-1.9
0,0,16	1.3	1.4	027	14.7	14.6	0,10,5	1.7	-1.3
			028	5.9	6.1	0,10,6	0.9	-0.9
						0,10,7	2.6	2.6
						0,10,8	0.5	0.5

(1951) atomic scattering factors were used to compute F_c , which values include hydrogen contributions.

Table 2 gives a comparison of observed and calculated structure factors for this structure, which was finally accepted as correct.

Table 3 gives the values of B_j of the individual atoms for the different zones. Here we use

$$f_j = f_{j(\text{rest})} \exp(-2M_j),$$

where $2M_j = B_j \sin^2 \theta / \lambda^2$.

θ is the usual Bragg angle and φ is the angle between the normal to the mean molecular plane (assumed to be the direction of maximum vibration) and the normal to the crystal plane ($h0l$). γ is the angle

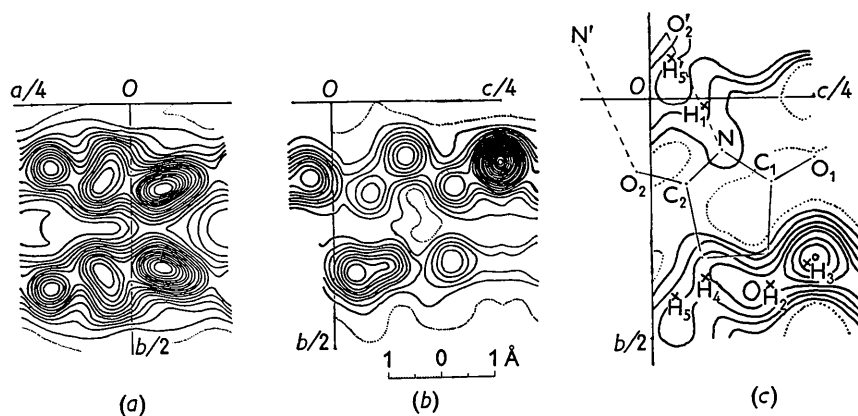


Fig. 2(a, b). The electron density projected (a) on (001), (b) on (100). The contours are drawn at equal intervals of $1 \text{ e.}\text{\AA}^{-2}$; the zero level is broken. (c) The difference synthesis $D(0, Y, Z)$. The contours are drawn at equal intervals of $0.25 \text{ e.}\text{\AA}^{-2}$; the zero level is broken.

Table 3. Values of B_j

	(Values in \AA^2)		
	$hk0$	$h0l$	$0kl$
N	2.6	$0.8 (1.78 + 4.4 \cos^2 \varphi)$	$1.4 + 2.4 \sin^2 \gamma$
O_1	2.6	$1.0 (1.78 + 4.4 \cos^2 \varphi)$	$3.0 + 1.2 \sin^2 \gamma$
O_2	2.6	$1.0 (1.78 + 4.4 \cos^2 \varphi)$	$1.9 + 2.5 \sin^2 (\gamma + 75)$
C_1	2.6	$1.25(1.78 + 4.4 \cos^2 \varphi)$	$1.7 + 1.7 \sin^2 (\gamma - 70)$
C_2	2.6	$1.25(1.78 + 4.4 \cos^2 \varphi)$	$3.0 + 2.0 \sin^2 (\gamma + 65)$
C_3	2.6	$2.0 (1.78 + 4.4 \cos^2 \varphi)$	$1.9 + 1.4 \sin^2 (\gamma + 70)$
C_4	2.6	$2.0 (1.78 + 4.4 \cos^2 \varphi)$	$1.9 + 1.2 \sin^2 (\gamma - 70)$

between the crystal plane ($0kl$) and the (010) plane. These thermal factors represent a trial-and-error result of fitting the calculated amplitudes to the observed data in the last stages of refinement. They may include actual deviations from spherical symmetry of the atoms due to bond effects.

For the $h0l$ reflexions the calculations were made in the form of

$$\sum f_{j(\text{rest})} \cos 2\pi(hx_j + lz_j) \exp(-2M_j) + \sum f_{j(\text{rest})} \cos 2\pi(h(x_j + \frac{1}{2}) - lz_j) \exp(-2M'_j).$$

$2M_j$ and $2M'_j$ are the respective atomic vibration factors for the j th atom corresponding to the angles φ and φ' for the molecules at (x, z) and $(\frac{1}{2} + x, \bar{z})$. A similar expression was used in calculating the ($0kl$) structure factors.

The final electron-density syntheses $\rho(X, Y, 0)$ and $\rho(0, Y, Z)$ are shown in Fig. 2(a, b). $\rho(X, 0, Z)$ is not included because of the severe overlap of atoms in this projection. $D(0, Y, Z)$ is shown in Fig. 2(c). Regions of electron density of height ranging from 0.8 to $1.1 \text{ e.}\text{\AA}^{-2}$ occur at the expected hydrogen positions, which are marked by crosses.

The three-dimensional series $\rho(X, Y, Z)$ has not been computed as the work involved was thought to be unjustified in this analysis; a complete set of $F(hkl)$'s is available on application to the author.

Results

A schematic drawing of the molecule projected on to the molecular plane is shown in Fig. 3. Representa-

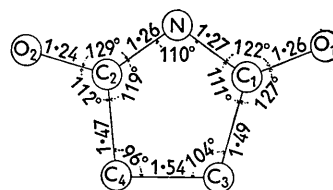


Fig. 3. Intramolecular bond lengths and bond angles.

tive intermolecular bond distances are collected in Table 4.

Table 4. Intermolecular bond lengths

(Values in Ångström units)	
N-H... O_2'	2.85
O...O (shortest)	3.75 ($O_1 \cdots O_1$ and $O_2 \cdots O_2'$)
(longest)	4.23 ($O_2 \cdots O_2'$)
C...C (shortest)	3.91 ($C_2 \cdots C_2'$)
(longest)	4.22 ($C_3 \cdots C_3'''$)
C...O (shortest)	3.26 ($C_4 \cdots O_2'''$)
(longest)	4.61 ($C_1 \cdots O_1'''$)

The atomic co-ordinates can be expressed in the form $lx + my + nz = -p$, where l , m and n are now the direction cosines of the normal to the plane. 'Least squares' give

$$0.7823x + 0.1889y - 0.5940z + 0.4051 = 0,$$

and the deviations of the atoms from this mean plane are:

N +0.017 Å	$O_1 - 0.014$ Å	$C_1 + 0.018$ Å
	$O_2 + 0.018$ Å	$C_2 - 0.035$ Å
		$C_3 + 0.006$ Å
		$C_4 - 0.005$ Å

Molecular magnetic susceptibilities

The three principal molecular diamagnetic susceptibilities are taken as follows:

K_1 perpendicular to the molecular plane
(direction cosines 0.7823, 0.1889, -0.5940);

K_2 along the line $C_1 \cdots C_2$
(direction cosines 0.6282, -0.0187, 0.7778);

K_3 perpendicular to K_1 and K_2
(direction cosines -0.1360, 0.9836, 0.1184).

For an orthorhombic crystal, the molecular susceptibilities are related to the principal crystal susceptibilities by the equations (Lonsdale & Krishnan, 1936),

$$K_1 l_1^2 + K_2 l_2^2 + K_3 l_3^2 = \chi_a = -50.7 \times 10^{-6} \text{ c.g.s.e.m.u.},$$

$$K_1 m_1^2 + K_2 m_2^2 + K_3 m_3^2 = \chi_b = -46.1 \times 10^{-6} \text{ c.g.s.e.m.u.},$$

$$K_1 n_1^2 + K_2 n_2^2 + K_3 n_3^2 = \chi_c = -45.1 \times 10^{-6} \text{ c.g.s.e.m.u.}$$

From the listed values of l_r , m_r and n_r we have

$$K_1 = -54.5 \times 10^{-6} \text{ c.g.s.e.m.u.},$$

$$K_2 = -42.1 \times 10^{-6} \text{ c.g.s.e.m.u.},$$

$$K_3 = -45.6 \times 10^{-6} \text{ c.g.s.e.m.u.}$$

Discussion of the results

The limit of error of bond distances is thought to be ± 0.02 – 0.03 Å, with a probable error of $\pm 2^\circ$ in the bond angles. These estimates have been formulated by changing the positional and thermal parameters in such a way that several configurations could be obtained having approximately equal reliability indices. It is possible to derive several structures whose bond distances differ by up to 0.02 Å from those quoted but whose agreement with the observed data are not significantly different (differences of up to 0.004 in R taken to be insignificant). In this particular analysis, severe overlap has prevented the use of successive 'difference' syntheses, which might otherwise have proved of considerable help. The atomic thermal anisotropies (especially those associated with the $h0l$ projection) are such that co-ordinate changes play a secondary role in obtaining a good value for the agreement factor. The temperature factors corresponding to the related molecule at, for example, (x, z) and $(\frac{1}{2} + x, \bar{z})$ are quite different; this effect of non-equivalence of orientation of molecules related by space-group symmetry seems sometimes to have been overlooked in crystal-structure determinations, although it has been recognized by Davies (1955) in the analysis of parabanic acid.

The arrangement of the molecules in the crystal projected along $[100]$ is shown in Fig. 4. Two molecules related by a centre of symmetry form a dimer through N–H \cdots O bonds of length 2.85 Å. The difference synthesis (Fig. 2(c)) does not indicate clearly that the hydrogen is attached to the nitrogen; there

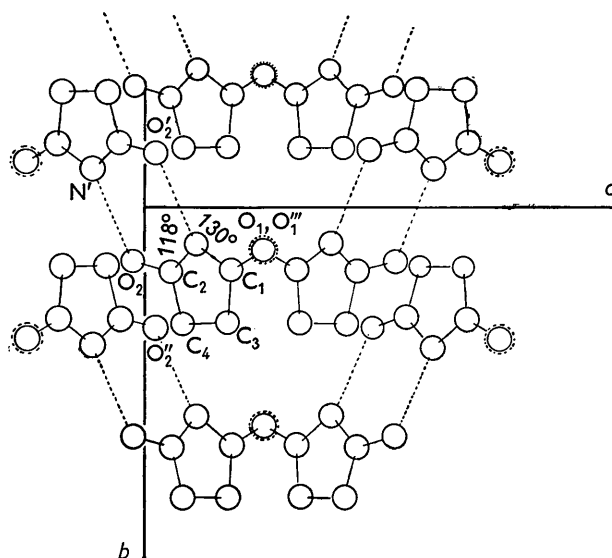
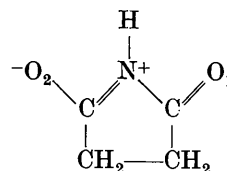


Fig. 4. The crystal structure projected on (100). Broken lines represent N–H \cdots O bond directions.

is a region of uniform electron density ($\sim 0.8 \text{ e.}\text{\AA}^{-2}$) stretching from the expected H_1 hydrogen position to the position of H_5' . The hydrogen bond distance is comparable with the distances 2.873 and 2.837 Å found for parabanic acid (Davies, 1955), 2.83 and 2.88 Å for cyanuric acid (Wiebenga, 1952), 2.81 Å for adenine hydrochloride (Cochran, 1951), 2.87, 2.81 and 2.79 Å in DL-serine (Shoemaker, Barieau, Donohue & Lu, 1953), 2.81 and 2.86 Å in uracil (Parry, 1954), 2.84 Å in DL-alanine (Donohue, 1950), 2.86 and 2.88 Å in glycyl-L-asparagine (Pasternak, Katz & Corey, 1954) and 2.84 Å in diketopiperazine (Corey, 1938). The hydrogen-bond arrangement forms an eight-membered ring system for succinimide which is also the case for diketopiperazine and cyanuric acid. Only one oxygen atom (O_2) engages in hydrogen-bond formation.

The effects of the hydrogen-bond formation should presumably have been such that the molecule received a major contribution from the resonance structure



but the C–O distances are not significantly different. The unusually short values for the C–N distances suggest a high double-bond character for these bonds, but the C–O distances do not confirm the suggestion. The nitrogen is not trigonal planar. Large values for bond angles, such as 129° (N–C₂–O₂), have been found in parabanic acid and analogous structures; from an angle viewpoint the molecule is significantly asymmetric.

An explanation of the apparently anomalous values for the bond distances may be that the hydrogen-bond proton tends to attract electrons from the nitrogen and oxygen atoms, thus making these atoms more electronegative in character; there would then be a shrinking of the C-O and C-N distances. Cochran & Penfold (1952) have found that in L-glutamine the shorter C-O bond involves the oxygen to which the greater number of hydrogen bonds are directed. This appears to be the case also in this structure.

Although the C₁-C₃ and C₂-C₄ distances are only reliable to ± 0.02 Å, there seems to be a significant shortening of these bond distances from the normal single-bond distance. This shortening of C-C bonds adjacent to carbonyl groups has been observed in acetanilide (Brown & Corbridge, 1954) and acetyl glycine (Carpenter & Donohue, 1950).

The maximum (numerical) molecular diamagnetic susceptibility is normal to the molecular plane, a result in common with all conjugated systems. K_3 , the second largest value, is almost along the hydrogen-bond direction. Angus & Hill (1940, 1943) have observed the increase in diamagnetism which occurs with hydrogen-bond formation; Anantakrishnan & Varadachari (1944) have pointed out the possible influences of hydrogen bonding on diamagnetism; of these, the spreading of the electron cloud may be the most important. It is not possible to infer from the magnetic values whether the protonic attraction of electrons from nitrogen and oxygen, and the subsequent change of the π electron orbitals around these atoms, is real or not.

Prof. Kathleen Lonsdale has followed this work with constant advice and encouragement and the author is deeply grateful to her. Facilities at the Manchester College of Technology and invaluable help were provided by Prof. H. Lipson and his staff. Dr W.

Cochran stimulated an interest in analytical methods.

The Merthyr Tydfil Education Committee provided a Major Award during the initial stages of this investigation and the work was completed during the tenure of a grant from the British Empire Cancer Campaign.

References

- ANANTAKRISHNAN, S. V. & VARADACHARI, P. S. (1944). *Proc. Ind. Acad. Sci. A*, **20**, 128.
- ANGUS, W. R. & HILL, W. K. (1940). *Trans. Faraday Soc.* **36**, 923.
- ANGUS, W. R. & HILL, W. K. (1943). *Trans. Faraday Soc.* **39**, 185.
- BROWN, C. J. & CORBRIDGE, D. E. C. (1954). *Acta Cryst.* **7**, 711.
- CARPENTER, G. B. & DONOHUE, J. (1950). *J. Amer. Chem. Soc.* **72**, 2315.
- COCHRAN, W. (1951). *Acta Cryst.* **4**, 81.
- COCHRAN, W. & PENFOLD, B. R. (1952). *Acta Cryst.* **5**, 644.
- COREY, R. B. (1938). *J. Amer. Chem. Soc.* **60**, 1598.
- DAVIES, D. R. (1955). *Acta Cryst.* **8**, 129.
- DONOHUE, J. (1950). *J. Amer. Chem. Soc.* **72**, 949.
- GROTH, P. (1910). *Chemische Krystallographie*, vol. 3, p. 270. Leipzig: Engelmann.
- HINCH, R. J. & MACCRONE, W. C. (1953). *Analyt. Chem.* **4**, 675.
- HUGHES, E. W. (1949). *Acta Cryst.* **2**, 34.
- KRISHNAN, K. S., GUHA, B. C. & BANERJEE, S. (1933). *Philos. Trans. A*, **231**, 235.
- LONSDALE, K. & KRISHNAN, K. S. (1936). *Proc. Roy. Soc. A*, **156**, 597.
- MCWEENY, R. (1951). *Acta Cryst.* **4**, 513.
- PARRY, C. S. (1954). *Acta Cryst.* **7**, 313.
- PASTERNAK, R. A., KATZ, L. & COREY, R. B. (1954). *Acta Cryst.* **7**, 225.
- SHOEMAKER, D. P., BARIEAU, R. E., DONOHUE, J. & LU, C.-S. (1953). *Acta Cryst.* **6**, 241.
- WIEBENGA, E. H. (1952). *J. Amer. Chem. Soc.* **74**, 6156.
- YARDLEY, K. (1924). *Proc. Roy. Soc. A*, **105**, 451.
- ZACHARIASEN, W. H. (1952). *Acta Cryst.* **5**, 68.