

The Crystal Structure of the 1:1 Complex formed by 2,6-Lutidine and Urea

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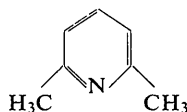
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(Received 18 December 1964)

Crystals of the complex $C_5H_3(CH_3)_2N \cdot CO(NH_2)_2$ are monoclinic, space group $C2/c$, with four lutidine and four urea molecules in a cell of dimensions $a = 11.34 \pm 0.03$, $b = 11.38 \pm 0.03$, $c = 7.48 \pm 0.02$ Å, $\beta = 99^\circ \pm 1^\circ$. The structure was obtained by Fourier-transform methods and refined by electron-density projections. It consists of urea molecules approximately parallel to (100) hydrogen-bonded into infinite bands parallel to the c axis, with lutidine molecules approximately parallel to (001) protruding on either side of each band along the [010] direction and held by $NH_2 \dots N$ hydrogen bonds. The interleaving of lutidine molecules between adjacent bands related by the b translation also contributes to the stability of the structure.

Introduction

The ability of urea $CO(NH_2)_2$, to form complexes with 2,6-lutidine,



provides a convenient method of separating the latter from other bases in coal tar (Riethof, 1944, 1945). The shape and size of the lutidine molecule would not permit it to form complexes of the well-known urea channel type (Zimmerschied, Dinerstein, Weitkamp & Marschner, 1949; Smith 1950, 1952), and this, together with the apparent specificity for 2,6-lutidine, makes it desirable to establish the structures of these complexes. The present report concerns the 1:1 complex. The structure of a second complex, in which there are two urea molecules for each lutidine molecule, is under investigation.

Experimental

The complex $C_5H_3(CH_3)_2N \cdot CO(NH_2)_2$ crystallizes when 2,6-lutidine is added to warm aqueous solutions containing less than about 20% of urea and the mixture is allowed to cool. It is also obtained by recrystallizing from water the 1:2 complex which separates when lutidine is added to more concentrated urea solutions. The crystals are in the form of colourless needles elongated along [001]. Since the crystals decompose by losing lutidine on exposure to the atmosphere, short sections cut from the needles were sealed inside thin-walled Pyrex glass capillaries for X-ray photography. Oscillation and zero-layer, multiple-film, Weissenberg photographs were obtained for crystals rotating about the b and c axes. In each case the specimen had an approximately cubic shape with each dimension ap-

proximately $\frac{1}{4}$ mm. Intensities of the $h0l$ and $hk0$ reflexions were measured by the photometric method of Wallwork & Standley (1954) and were converted into structure amplitudes $|F_o|$ (Table 2) in the usual way. No corrections were made for absorption of X-rays in view of the small size of the specimens.

Derivation of the structure

The crystal data are: monoclinic, $a = 11.34 \pm 0.03$, $b = 11.38 \pm 0.03$, $c = 7.48 \pm 0.02$ Å, $\beta = 99^\circ \pm 1^\circ$, $U = 953$ Å³, $D_m = 1.16 \pm 0.01$ (by flotation), $Z = 4$, $D_c = 1.165$, $F(000) = 360$. Space group Cc or $C2/c$ from absent reflexions; pyroelectric test and the $N(z)$ test indicate the centrosymmetric $C2/c$ (C_{2h}^6 , No. 15). Cu $K\alpha$ radiation ($\lambda = 1.542$ Å), $\mu = 6.6$ cm⁻¹.

Since the general position in $C2/c$ is eightfold, both molecules must lie in special positions. Of the possible positions, (a) to (d) all imply centrosymmetric molecules, and (e) implies that the molecules have twofold axes of symmetry parallel to the b axis of the crystal. Neither the urea nor the lutidine molecule possesses a centre of symmetry but both may have twofold axes of symmetry so they were assumed to be in positions (e) $0, y, \frac{1}{4}; 0, \bar{y}, \frac{3}{4}; \frac{1}{2}, \frac{1}{2} + y, \frac{1}{4}; \frac{1}{2}, \frac{1}{2} - y, \frac{3}{4}$. The weighted reciprocal lattice for the $hk0$ projection showed six intense regions at a distance of about 0.88 Å⁻¹, suggesting that the heterocyclic ring of the lutidine molecule is almost perpendicular to the c axis. On this basis, it was found possible to construct a satisfactory scale model in which each NH_2 group of urea was hydrogen-bonded both to the CO group of an adjacent urea molecule along the c axis and to the N atom of an adjacent lutidine molecule along the twofold axis parallel to b . This trial structure was shown to be approximately correct by comparing optically produced Fourier transforms (Hughes & Taylor, 1953) with the weighted $hk0$ and $h0l$ reciprocal lattice sections. The correspond-

ing two projections were then refined by Fourier and difference Fourier methods until agreement indices R of 0.14 and 0.13 respectively were obtained and positive areas in the difference maps could be ascribed mainly to hydrogen atoms.

The hydrogen atoms were then included in the structure factor calculations in positions which gave the best fit with the positive areas on the difference maps consistent with normal bond lengths and expected stereochemical configurations. Non-rotating methyl groups seemed to be indicated for the lutidine molecule. The R values for each projection were improved by about 0.04 on inclusion of the hydrogen atoms with isotropic temperature factors B of 5.0 \AA^2 and the final R values were 0.09 and 0.08 for the $hk0$ and $h0l$ projections respectively. The scattering factors of Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955) were assumed for carbon, nitrogen and oxygen atoms, and those of McWeeny (1951) were assumed for hydrogen atoms. Reflexions too weak to be observed were omitted from the calculation of R and from the $(F_o - F_c)$ Fourier maps.

The final atomic coordinates and the average isotropic temperature factors for all the atoms other than hydrogen are given in Table 1. Where the x/a values obtained from the two projections differed (maximum difference 0.002), they have been averaged.

Table 1. Final atomic fractional coordinates and isotropic temperature factors

Atom	x/a	y/b	z/c	B
C(1)	0.103	-0.027	0.232	5.5 \AA^2
C(2)	0.104	0.097	0.232	4.5
C(3)	0.000	0.158	0.250	4.5
C(4)	0.214	-0.097	0.207	5.0
C(5)	0.000	0.595	0.250	5.0
N(1)	0.000	-0.088	0.250	4.0
N(2)	0.028	0.645	0.400	4.5
O	0.000	0.483	0.250	5.0

The final calculated structure factors are compared with the observed amplitudes in Table 2. The values for the $h00$ reflexions, which are observed in both zones, have been averaged. The final electron-density projections are shown in Fig. 1 and one hydrogen-bonded layer of the structure as seen in the (100) projection is shown in Fig. 2. The bond lengths and angles and hydrogen-bond lengths shown in Fig. 3 are only approximate since they are based on two-dimensional X-ray data. The standard deviations of about 0.02 \AA for bond lengths (Cruickshank, 1949, 1954) and about 2° for bond angles (Darlow, 1960) almost certainly underestimate the errors.

Description of the structure

As shown in Fig. 2, the structure consists essentially of bands of hydrogen-bonded urea molecules (having $\text{NH} \cdots \text{O}$ distances of about 3.05 \AA) with lutidine molecules attached to these bands by each having its

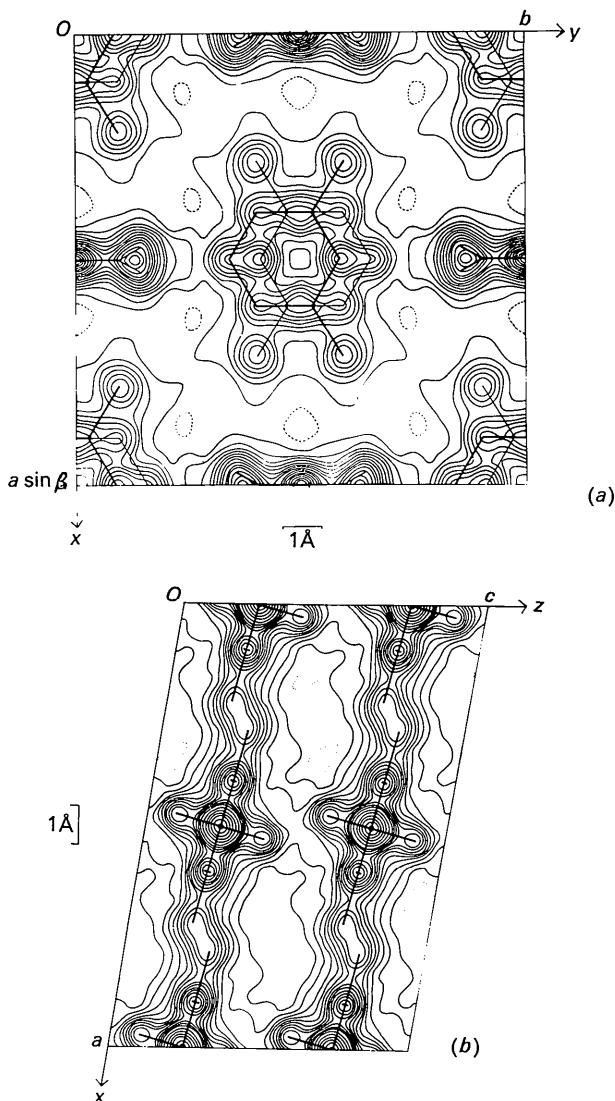


Fig. 1. Electron-density projections: (a) $hk0$, contours at intervals of 1 e. \AA^{-2} ; (b) $h0l$, contours at intervals of 1 \AA^{-2} up to 12 e. \AA^{-2} and thereafter at intervals of 3 e. \AA^{-2} . In both cases the zero contour is shown as a dotted line.

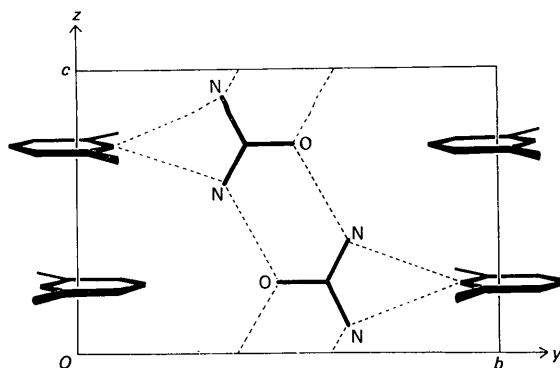


Fig. 2. View along the a axis of one hydrogen-bonded layer of the structure. Hydrogen bonds are represented by broken lines.

Table 2. Comparison of the final calculated structure factors F_c with the observed amplitudes F_o

hkl	$ F_o $	F_c	hkl	$ F_o $	F_c	hkl	$ F_o $	F_c	hkl	$ F_o $	F_c	hkl	$ F_o $	F_c
002	168	-166	206	12	-14	480	8	4	790	7	-6	1004	21	19
004	59	59	208	7	7	4120	5	5	800	27	31	1006	8	-7
006	37	-37	220	16	16	510	36	-37	802	7	-7	1008	7	6
008	14	12	240	14	-13	530	24	-23	804	9	9	1020	9	12
020	77	87	260	21	21	550	12	-11	806	7	-5	1040	4	-5
040	68	-66	280	11	9	570	11	-11	802	48	-48	1060	4	-5
060	9	-11	2100	5	-5	590	6	-5	804	26	26	10100	5	5
080	14	14	2120	4	3	600	29	26	806	21	-21	1110	3	3
0100	13	9	310	73	-75	604	10	11	808	11	14	1130	5	-5
0120	10	8	370	14	-13	606	9	-9	820	14	14	1200	4	3
110	25	21	390	9	-9	602	25	-25	840	3	-3	1202	5	-4
130	17	13	400	78	74	604	3	-3	8100	3	-2	1204	9	9
150	18	-18	404	5	4	606	7	-6	8120	3	3	1202	13	-10
170	22	-21	406	13	-11	608	5	9	910	13	15	1204	4	4
1110	9	8	408	3	2	620	6	-5	930	6	-6	1206	3	-1
200	113	118	402	48	-50	640	9	-8	950	9	-11	1220	4	3
202	55	-54	404	3	4	660	9	8	970	3	-4	1240	2	3
204	47	44	406	13	-10	6120	3	3	1000	23	27	1330	5	-5
206	41	-38	408	7	7	710	19	-19	1002	22	-20	1402	5	-4
208	12	15	420	4	-3	730	5	-5	1004	14	18	1404	2	2
202	30	-35	440	28	-29	770	3	-2	1002	37	35			

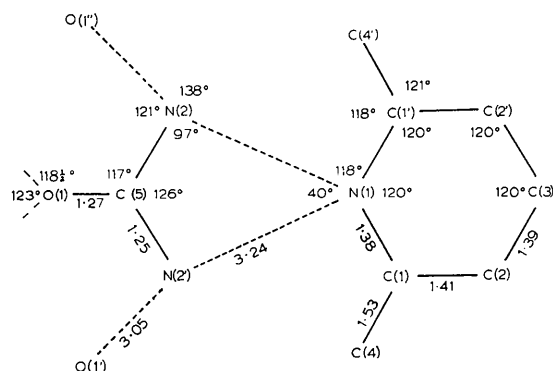


Fig. 3. Approximate bond lengths (Å) and bond angles. The two molecules are represented, for simplicity, in the same plane but, in the structure, they are in planes perpendicular to each other.

nitrogen atom linked to both NH_2 groups of the same urea molecule by weak hydrogen bonds of length approximately 3.24 \AA . Both molecules lie on twofold axes parallel to the b axis but their planes are perpendicular to each other. The plane of the urea molecule makes angles of 83° and 16° with the positive directions of the a and c axes respectively. The bands formed by hydrogen bonding of the urea molecules are therefore non-planar. Their mean plane is parallel to (100) and they link the molecules indefinitely in the c direction. Adjacent bands, related to each other by the b translation, have their lutidine molecules interleaved and the van der Waals attractions within each column of parallel lutidine molecules so formed, with an interplanar separation of about 3.59 \AA , must contribute to the coherence of the structure. One can only suppose that the requirements of hydrogen bonding and efficient packing cause this complex formation to occur

with 2,6-lutidine and not with other related pyridine derivatives.

It would not be appropriate to discuss the molecular dimensions since they were only obtained from two projections and few X-ray data. They are all reasonable with the exception of the rather short C-N distance in the urea molecule. Apart from the hydrogen bonds, there are no short intermolecular contacts.

The authors thank the University of Nottingham for the award of an F. S. Kipping Memorial Scholarship to J. D. L., during the tenure of which this work was carried out, and Dr B. D. Shaw for suggesting the problem. They are also grateful to the Council of the Royal Society for contributing to the cost of the apparatus, and to Mrs D. H. Thomas for assistance with some of the calculations.

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