

(Fig. 2). For all three molecules these angles are very similar and the same situation is found in BUT. These similarities are remarkable in view of the different nature of the molecules: SYNDIM and BUT are aromatic annulenes, while DIAL and SYNO are polyenes showing alternation of short and long bonds. Some significant parameters of these four molecules are collected in Table 5 to make the similarity of these systems more evident.

Despite the distortion from planarity of the ring, the distance $H(16') \cdots H(17'')$ in DIAL, SYNO and SYNDIM is very short.

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The Crystal and Molecular Structure of Phenylurea

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The crystal structure of phenylurea has been determined from visually estimated $Cu K\alpha$ X-ray data. The crystals are monoclinic, space group $P2_1$, with $a = 14.01$ (2), $b = 5.36$ (2), $c = 4.66$ (1) Å, $\beta = 94.7$ (3)° and $Z = 2$. The structure was solved by the Patterson method and refined by block-diagonal least-squares calculations to $R = 0.081$ for 573 non-zero reflexions. The molecules related by a c -translation are linked together by two kinds of N—H \cdots O hydrogen bonds [N \cdots O 2.924 (9) Å, N—H \cdots O 147 (11)°, H \cdots O 2.14 (13); N \cdots O 2.935 (9) Å, N—H \cdots O 154 (7)°, H \cdots O 2.10 (8) Å] to form a ribbon extending along c . The ribbons are held together by another N—H \cdots O hydrogen bond [N \cdots O 3.013 (9) Å, N—H \cdots O 161 (5)°, H \cdots O 2.14 (6) Å] between the molecules related by a twofold screw axis to form a sheet parallel to (100). The sheets are stacked along a by van der Waals interactions. The dihedral angle between the benzene ring and the urea moiety is 46.4°. The imino N—C(carbonyl) distance, 1.375 (10) Å, is longer than the amino N—C(carbonyl) 1.326 (10) Å. The C=O distance, 1.245 (9) Å, is longer than those in acetanilides.

Introduction

As part of a programme of investigation of the molecular structure and packing mode of the aromatic compounds containing the amide grouping, —NH—CO—X (X = CH₃, NH₂, etc.) (Haisa, Kashino, Kawai & Maeda, 1976), the structure of phenylurea has been determined by X-ray analysis. The molecule is

of interest since it is an activator as well as a competitive inhibitor of trypsin-catalysed hydrolysis (Sanborn & Heim, 1967). Its activity has been related by Pullman & Pullman (1963) and Amatuni & Krylov (1974) to the electronic structure of the amide group.

The present paper also extends the scope of study on the relation between the s -character of hybrid orbitals and the bond lengths, explored in a previous paper (Kawai, Kashino & Haisa, 1976).

Experimental

The crystals were grown from an ethanol solution by slow evaporation as tabular plates with well formed (100).

Crystal data

Phenylurea, $C_7H_8N_2O$, $M_r = 136.2$, m.p. 152–153 °C. Monoclinic, space group $P2_1$, $a = 14.01(2)$, $b = 5.36(2)$, $c = 4.66(1)$ Å, $\beta = 94.7(3)^\circ$, $V = 348.8(17)$ Å³, $D_m = 1.30$ (by flotation in aqueous KI solution), $D_x = 1.297$ g cm⁻³ for $Z = 2$; $\mu = 7.5$ cm⁻¹ for Cu $K\alpha$ ($\lambda = 1.5418$ Å), $F(000) = 144$. Systematic absence: $0k0$ with k odd. The higher symmetry was ruled out by the determination of the structure.

With a specimen of dimensions $0.2 \times 0.4 \times 0.2$ mm, intensity data were collected on equi-inclination Weissenberg photographs for the layers $h0l$ to $h4l$. Specimens cut along c gave reflexions elongated by about 4° in ω on the Weissenberg photographs and hence were not used for data collection. In total 573 reflexions (67% of those accessible in the Cu sphere) were observed as non-zero reflexions. The intensities were estimated visually and corrected for Lorentz–polarization factors and for spot shape.

Structure determination and refinement

The structure was solved from a sharpened Patterson map and refined by the block-diagonal least-squares method. At the stage of $R = 0.108$, all the H atoms were located by a difference Fourier synthesis. Further refinement including the H atoms gave a final R value of 0.081 for 573 non-zero reflexions.* The weighting

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32122 (3 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. The final positional ($\times 10^3$) and isotropic thermal parameters of the hydrogen atoms with standard deviations in parentheses

	x	y	z	B (Å ²)
H(1)	322 (6)	695 (26)	-65 (20)	6.2 (2.5)
H(2)	147 (6)	651 (20)	-60 (15)	3.7 (1.7)
H(3)	20 (5)	370 (20)	85 (14)	3.3 (1.6)
H(4)	50 (6)	46 (27)	441 (20)	5.9 (2.2)
H(5)	221 (5)	30 (19)	662 (14)	3.7 (1.8)
H(6)	342 (5)	290 (21)	523 (15)	4.0 (1.7)
H(7)	502 (3)	984 (11)	272 (10)	0.1 (0.9)
H(8)	444 (4)	912 (16)	-37 (12)	1.8 (1.2)

scheme used was: $w = 1.0$ for $0 < |F_o| \leq 3.6$ and $w = (3.6/|F_o|)^2$ for $|F_o| > 3.6$. One reflexion, $\bar{1}11$, was excluded from the refinement because it suffered from extinction.

The final atomic parameters are given in Tables 1 and 2. The atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1962). The computation was carried out on an NEAC 2200-500 computer at the Okayama University Computer Center. The programs used were *HBL5-5* and *DAPH* (Ashida, 1973).

Results and discussion

Crystal structure

The crystal structure projected along b is illustrated in Fig. 1. The molecules related by a c -translation are linked together by two kinds of N–H...O hydrogen bonds in a similar manner to those in urea (Caron & Donohue, 1969) to form a ribbon extending along c . The plane of the urea portion through the N(1), C(7), O and N(2) atoms makes an angle of only 4.5° with the c axis, which compares with 0° in urea. This results in the similarity of the cell constants c .

The ribbons are held together by another N–H...O hydrogen bond between the molecules related by the

Table 1. The final positional and thermal parameters ($\times 10^4$) with standard deviations in parentheses

The anisotropic coefficients have the form: $\exp(-\beta_{11}h^2 - \beta_{22}k^2 - \beta_{33}l^2 - \beta_{12}hk - \beta_{13}hl - \beta_{23}kl)$.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
O	3978 (2)	7581 (11)	5611 (6)	65 (2)	418 (19)	228 (13)	-4 (12)	37 (8)	32 (27)
N(1)	3255 (3)	6484 (12)	1184 (8)	63 (3)	434 (24)	259 (15)	-40 (14)	70 (10)	28 (34)
N(2)	4543 (3)	9089 (14)	1564 (9)	69 (3)	452 (24)	275 (16)	-78 (15)	59 (11)	-86 (36)
C(1)	2524 (4)	4964 (12)	2196 (10)	57 (3)	281 (28)	342 (21)	13 (14)	81 (13)	-99 (37)
C(2)	1602 (5)	5324 (17)	929 (14)	74 (4)	470 (37)	543 (32)	-33 (20)	40 (18)	199 (58)
C(3)	885 (5)	3776 (20)	1761 (17)	66 (4)	560 (43)	781 (40)	-67 (23)	89 (20)	-76 (75)
C(4)	1074 (5)	1966 (18)	3788 (16)	82 (5)	496 (51)	792 (46)	-103 (22)	192 (23)	-104 (68)
C(5)	1991 (6)	1680 (20)	5074 (18)	104 (6)	432 (39)	720 (40)	-50 (25)	155 (24)	205 (65)
C(6)	2731 (5)	3200 (15)	4267 (13)	71 (3)	328 (33)	535 (29)	-41 (17)	90 (16)	71 (46)
C(7)	3935 (3)	7727 (14)	2937 (9)	54 (3)	254 (23)	298 (19)	39 (14)	58 (11)	16 (35)

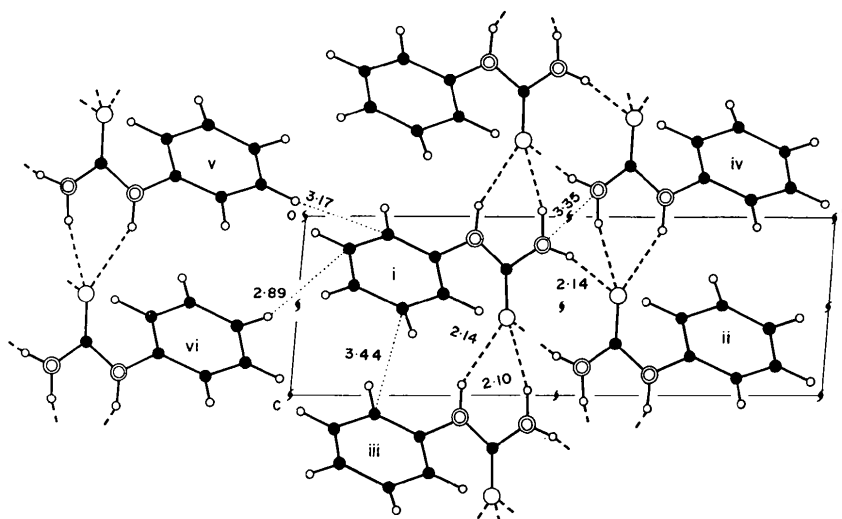


Fig. 1. Projection of the crystal structure along *b*. Broken lines show hydrogen bonds; dotted lines are intermolecular contacts. Symmetry code: (i) x, y, z ; (ii) $1 - x, \frac{1}{2} + y, 1 - z$; (iii) $x, y, 1 + z$; (iv) $1 - x, \frac{1}{2} + y, -z$; (v) $-x, \frac{1}{2} + y, -z$; (vi) $-x, \frac{1}{2} + y, 1 - z$; (vii) $1 - x, -\frac{1}{2} + y, 1 - z$.

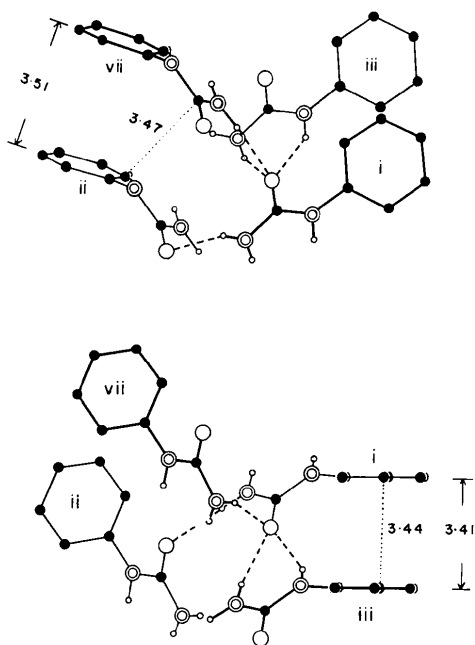


Fig. 2. Molecular arrangement viewed along an axis perpendicular to the benzene ring plane (i) and an axis parallel to the plane, together with inter-plane spacings (Å) and intermolecular distances (Å). The hydrogen atoms attached to the benzene rings are omitted. Symmetry code is given in Fig. 1.

twofold screw axis at $x = \frac{1}{2}$ to form a sheet consisting of double molecules parallel to (100). The geometry of the hydrogen bonds is summarized in Table 3. The carbonyl O atom accepts three H atoms as in biurea (Brown & Russell, 1976) and hydroxyurea (Arman, Richards & Uraz, 1976), and that in urea ac-

cepts four, all the available H atoms being used for the hydrogen-bond formation.

In the sheet the benzene rings of the molecules related by the *c* and *b*-translations do not overlap each other, as shown in Fig. 2; their interplanar spacings are 3.41 and 3.51 Å respectively. The sheets are stacked along *a* by van der Waals interactions between the benzene rings of the molecules related by the twofold screw axis at $x = 0$. This loose packing causes a lower density and melting point than in DL-allantoin (Mootz, 1965), where a three-dimensional hydrogen-bond network is formed.

Molecular structure

Bond lengths and angles are shown in Fig. 3. Both the benzene ring and the urea portion are planar within experimental error, as shown in Table 4. The exocyclic bond C(1)–N(1) makes an angle of 3.2° with the benzene-ring plane. The bond lengths C(3)–C(4) and C(1)–C(6) in the ring are somewhat smaller than the other four, the respective average values being 1.365 and 1.387 Å. However, the *p*-quinonoid structure as suggested by Hampson & Mathias (1968) is not apparent. The torsion angle C(6)–C(1)–N(1)–C(7) is 48.2° , which is caused by the hydrogen bond $O \cdots H(7^{vii})-N(2^{vii})$. The C(1)–N(1)–C(7) angle is larger than that in DL-allantoin and smaller than that in acetanilide (Brown, 1966). This angle decreases with increase in the torsion angle. The C(1)–N(1) distance is close to that in DL-allantoin in spite of the difference in the nature of the C(1) atom, and also to that in acetanilides (Brown, 1966; Haisa, Kashino & Maeda, 1974; Haisa, Kashino, Kawai & Maeda, 1976) irrespective of the torsion angle.

Table 3. *Geometry of hydrogen bonds*

See Fig. 1 for symmetry code.

N—H...O=C	N...O (Å)	H...O (Å)	N—H...O (°)	H...O=C (°)
N(1 ⁱⁱⁱ)—H(1 ⁱⁱⁱ)...O	2.924 (9)	2.14 (13)	147 (11)	147 (3)
N(2 ⁱⁱⁱ)—H(8 ⁱⁱⁱ)...O	2.935 (9)	2.10 (8)	154 (7)	149 (2)
N(2 ^{vii})—H(7 ^{vii})...O	3.013 (9)	2.14 (6)	161 (5)	113 (2)

The geometry of the urea moiety is close to that found in DL-allantoin. The bond N(1)—C(7) is longer than C(7)—N(2). This is in harmony with the results from ¹⁴N chemical shifts (Hampson & Mathias, 1968) and implies a greater delocalization of the lone-pair electrons in the N(2) atom than in the N(1). The bond N(1)—C(7) is longer than that in the acetanilides in which only the lone-pair electrons of N(1) are delocalizable. The C=O lengths of the present compound and DL-allantoin are longer than those in the acetanilides.

The lengths of carbonyl C=O bonds in some X—CO—Y derivatives (X and Y = C or N) taken from the literature are plotted as a function of the *s*-character (*S*) of the C atom toward the O atom in Fig. 4. The *s*-character can be estimated from the angles O=C—X, α , and O=C—Y, β , to be $\cot \alpha \cot \beta$, as shown in the Appendix, provided that the three non-equivalent sp^2 hybrids are constructed from 2*s*, 2*p_x*, and 2*p_y* orbitals. In most cases the difference between α and β is less than 10° and the X—C—Y angle γ near $2\pi/3$, so that by assuming that $\cos(\alpha - \beta) = 1$ and then expanding the *S* given by equation (5) in the Appendix about the point $\gamma = 2\pi/3$, we obtain

$$S = \frac{1}{3} - \frac{4}{3\sqrt{3}}(\gamma - \frac{2}{3}\pi) + \frac{1}{3}(\gamma - \frac{2}{3}\pi)^2.$$

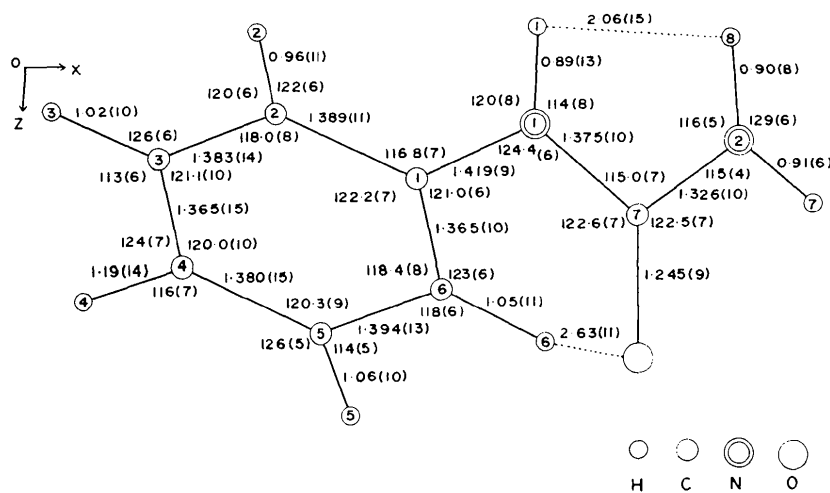


Fig. 3. Bond lengths (Å) and bond angles (°), with their e.s.d.'s in parentheses. Intramolecular contacts are shown by dotted lines.

Since the *s*-character expected for equivalent hybrids is 0.333, the carbonyl C atom in most ureas withdraws the *s*-character from the bonds with N atoms. It is seen that the C=O length increases as the *s*-character decreases. At a given *s*-character the C=O lengths are

Table 4. *The least-squares planes and the displacement (Å) of the atoms from the planes*

Atoms marked with an asterisk were used for the calculation of the plane.

$$X = ax + cz \cos \beta, Y = by, Z = cz \sin \beta.$$

Plane I

$$\text{Benzene ring: } 0.2513X - 0.6543Y - 0.7133Z + 1.6115 = 0$$

C(1)*	0.0107	C(6)*	-0.0035	H(2)	0.052
C(2)*	-0.0082	N(1)	0.0801	H(3)	0.096
C(3)*	-0.0013	C(7)	-0.7139	H(4)	0.122
C(4)*	0.0089	O	-1.5589	H(5)	0.028
C(5)*	-0.0064	N(2)	-0.5095	H(6)	0.017

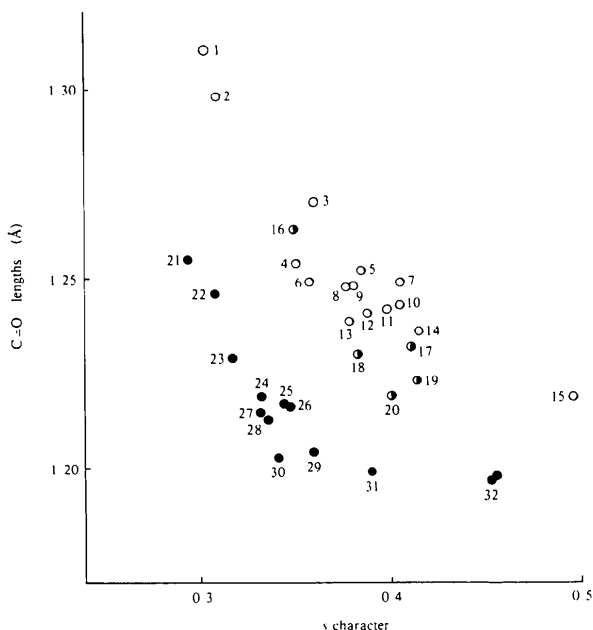
Plane II

$$\text{Urea portion: } -0.6166X + 0.7868Y + 0.0280Z + 0.0341 = 0$$

N(1)*	-0.0002	N(2)*	-0.0004	H(7)	-0.053
C(7)*	0.0010	C(1)	0.0275	H(8)	0.035
O*	-0.0004	H(1)	0.158		

Dihedral angle between the planes I and II: 46.4°.

longer for X, Y = N,N or N,C than for X, Y = C,C. This trend is consistent with delocalization of the lone-pair electrons of the N atoms.



- References: (1) 2-Methylpseudourea hydrochloride (White & Mason, 1970). (2) Urea nitrate (Korsham & Busing, 1969). (3) Urea (Caron & Donohue, 1969). (4) Hydroxyurea (Armagan, Richards & Uraz, 1976). (5) N,N'-Dicyclohexylurea (Coiro, Giacomello & Giglio, 1971). (6) Biurea (Brown & Russell, 1976). (7) Phenylurea (this work). (8) DL-Allantoin (Mootz, 1965). (9) Monomethylurea (Huissoon & Tiemessen, 1976). (10) L-Homocitrulline hydrochloride (Ashida, Funakoshi, Tsukihara, Ueki & Kakudo, 1972). (11) Acetone semicarbazone (Naik & Palenik, 1974). (12) L-Citrulline hydrochloride (Ashida, Funakoshi, Tsukihara, Ueki & Kakudo, 1972). (13) Benzaldehyde semicarbazone (Naik & Palenik, 1974). (14) Potassium allantoinate (Ringertz, 1968). (15) 1,1'-Azobiscarbamide (Cromer & Larson, 1974). (16) N-Methylacetanilide (Pedersen, 1967). (17) p-Hydroxyacetanilide, monoclinic form (Haisa, Kashino, Kawai & Maeda, 1976). (18) N-methyl-2,4,6-trinitroacetanilide (Christoph & Fleischer, 1973). (19) p-Hydroxyacetanilide, orthorhombic form (Haisa, Kashino & Maeda, 1974). (20) Acetanilide (Brown, 1966). (21) 2-Hydroxy-4-methoxybenzophenone (Liebich & Parthé, 1974). (22) 2-Hydroxy-4-methoxy-4'-chlorobenzophenone (Liebich, 1976). (23) 2,2',2''-Dicyclohexenyl ketone (Holbrook & Helm, 1975). (24) Δ^6 -6-Azidobetumethasone-21-acetate (Nassimbeni, Scheldrick & Kennard, 1974). (25) Pipamperone (Deslercq, Germain & Koch, 1975). (26) Acetophenone (Tanimoto, Kobayashi, Nagakura & Saito, 1973). (27) p-Aminoacetophenone (Haisa, Kashino, Yuasa & Akigawa, 1976). (28) Chloralminone acetate (Chandross & Bordner, 1975). (29) 9 α -Methoxycortisol (Becks & Duax, 1976). (30) Cyproterone acetate (Chandross & Bordner, 1975). (31) 17-Desoxymethasone (Dupont, Dideberg & Campsteyn, 1974). (32) Dichloroacetone (Sørensen, 1974).

Fig. 4. Plot of the C=O lengths vs the s-character of the carbonyl C atom toward the O atom. Examples for X, Y = N, N (○) are selected from urea derivatives, those for X, Y = C, N (◐) from acetanilides, and those for X, Y = C, C (●) from aromatic and aliphatic ketones, all of whose structures have recently been determined with fair accuracy.

APPENDIX

Relation between the s-character and bond angles

Three non-equivalent sp^2 hybrids constructed from $2s$, $2p_x$ and $2p_y$ orbitals are expressed as follows:

$$\varphi_1 = as + (1 - a^2)^{1/2} p_x \quad (1)$$

$$\varphi_2 = (1 - b^2 - c^2)^{1/2} s - bp_x + cp_y \quad (2)$$

$$\varphi_3 = (c^2 + b^2 - a^2)^{1/2} s - (a^2 - b^2)^{1/2} p_x - (1 - c^2)^{1/2} p_y. \quad (3)$$

By combining the orthogonality condition of the hybrids and the expressions for cosines of the inter-hybrid angles $\varphi_1\varphi_2 = \alpha$, $\varphi_1\varphi_3 = \beta$, $\varphi_2\varphi_3 = \gamma$, the square of the coefficient a , that is, the s-character (S) of the C atom toward the O atom can be expressed by

$$S = a^2 = \cot \alpha \cot \beta. \quad (4)$$

Since $\alpha + \beta + \gamma = 2\pi$, S can also be expressed by

$$S = [\cos(\alpha - \beta) + \cos \gamma] / [\cos(\alpha - \beta) - \cos \gamma]. \quad (5)$$

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The Crystal Structure of (–)₅₈₉-Bis[(*S,S*)-*trans*-1,2-diaminocyclohexane]-(*R,R*)-*trans*-1,2-diaminocyclohexanecobalt(III) Chloride Pentahydrate

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Crystals of the title compound are hexagonal, space group $P6_1$ with $a = 12.472(1)$, $c = 32.594(2)$ Å and $Z = 6$. The crystal structure has been refined by block-diagonal least-squares calculations to an R value of 0.040 on the basis of 2595 independent reflexions collected by diffractometry. The crystal structure resembles that of the chloride pentahydrate of the lel_3 -isomer. The complex ion takes the lel_3ob conformation, and has an approximate twofold axis of rotation through the central Co atom and bisecting the C–C bond in the ob chelate ring. All the bond distances and angles are normal: the mean Co–N distance is 1.972(5) Å and the mean N–Co–N angle in the chelate ring is 84.5(2)°. The absolute configuration of the complex ion can be designated as $A(\delta\delta\lambda)$ according to the IUPAC convention. The plane formed by Co and two N atoms of the ob ring is inclined at an angle of 35.7° with respect to the pseudo threefold axis of the complex ion, which is larger by about 4° than that of the lel_3 -isomer as well as the ob_3 -isomer. Such a large inclination may be ascribed to the non-bonded H–H interaction between the lel and ob -chelate rings.

Introduction

The isomers of the tris[(±)-*trans*-1,2-diaminocyclohexane]cobalt(III) ion consist of two catoptric series with absolute configurations A and Δ around the Co atom. For each of the configurational series there exist four diastereoisomers: lel_3 , lel_2ob , ob_2lel and ob_3 . These eight isomers were recently isolated and characterized (Harnung, Sørensen, Creaser, Maegaard, Pfenninger & Schäffer, 1976). The crystal structures of the A - lel_3 and A ob_3 -isomers are already reported (Marumo, Utsumi & Saito, 1970; Kobayashi, Marumo & Saito, 1972). This paper deals with the crystal structure of the chloride pentahydrate of the A - lel_2ob -isomer.

Experimental

Crystals were kindly provided by Dr S. E. Harnung. They are orange-red hexagonal bipyramids.

Crystal data: (–)₅₈₉-(lel_2ob)-[Co(chxn)₃]Cl₃·5H₂O. C₁₈H₅₂N₆O₅CoCl₃, F.W. 597.9. Hexagonal, $a = 12.472(1)$, $c = 32.594(2)$ Å, $U = 4391.0$ Å³, $D_m = 1.35$ (floatation, benzene/carbon tetrachloride), $D_c = 1.36$ g cm⁻³, $Z = 6$, μ for Mo $K\alpha$ ($\lambda = 0.7107$ Å) = 9.16 cm⁻¹, space group $P6_1$ (No. 169).

Intensity data were collected on a Rigaku automated four-circle diffractometer using Mo $K\alpha$ radiation monochromated by a graphite plate. A crystal specimen was approximately shaped into a sphere of