

The Crystal Structure of Pyridoxine Hydrochloride. A Comparison of the Symbolic Addition Procedure and the Heavy Atom Method

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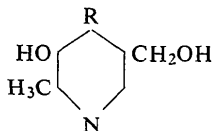
The crystal structure of pyridoxine hydrochloride was determined directly by means of the heavy atom method and by the symbolic addition procedure from three-dimensional data, and the efficiency of both methods was compared. The space group is $P\bar{1}$ and the cell dimensions are:

$$a = 9.52, b = 5.803, c = 9.56 \text{ \AA}; \alpha = 93.9, \beta = 115.4, \gamma = 98.6^\circ.$$

The pyridoxine molecule is truly planar with the exception of the oxygen atom from the CH_2OH group participating in an intramolecular hydrogen bond. The increase of the C-N-C bond angle in the pyridine ring is discussed. The pyridoxine ions are connected by intermolecular hydrogen bonds of the type $\text{O-H} \cdots \text{O}$, $\text{N-H} \cdots \text{Cl}$, $\text{O-H} \cdots \text{Cl}$. The estimated standard deviations for bond lengths and angles are 0.005 \AA and 0.3° respectively.

Introduction

The classical studies of Rabinowitz & Snell (1948) demonstrated that vitamin B_6 exists in three forms in the tissues of animals and plants, *viz.* pyridoxine ($\text{R} = \text{CH}_2\text{OH}$), pyridoxamine ($\text{R} = \text{CH}_2\text{NH}_2$), and pyridoxal ($\text{R} = \text{CHO}$):



All of them are converted to pyridoxal phosphate in tissue. Deficiency of pyridoxine has been reported to result in a decrease in serum protein synthesis (Pike & Brown, 1959). It has been suggested that pyridoxine is an important regulator in glutathione metabolism (Hsu, Buddemeyer & Chow, 1964). The isolation of several micro-organisms that grow with pyridoxine, pyridoxal, or pyridoxamine as sole sources of carbon and nitrogen has been described (Rodwell, Volcani, Ikawa & Snell, 1958). Stebbins (1951) demonstrated an impaired water metabolism in animals deprived of vitamin B_6 . Anaemia from vitamin B_6 deficiency has been reported in several species (Fouts, Helmer, Lepkovsky & Jukes, 1938; Kornberg, Tabor & Sebrell, 1945; Chick, Macrae, Martin & Martin, 1938; Hegsted & Rao, 1945; Luckey, Briggs, Elvehjem & Hart, 1945). Riggs, Coyne & Christensen (1953) and Christensen, Riggs & Coyne (1954) have proposed that vitamin B_6 may function as a carrier substance in amino acid transport in Ehrlich mouse ascites tumour cells.

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The purpose of this paper is a detailed study of the crystal and molecular structure of pyridoxine hydrochloride.

Crystal data

Crystals of pyridoxine hydrochloride were kindly supplied by Dr Liska. The material is colorless. The unit-cell dimensions were determined from rotation, Weissenberg and precession photographs. It was found that the unit cell is triclinic with the following dimensions: $a = 9.52 \pm 0.04$, $b = 5.803 \pm 0.007$, $c = 9.56 \pm 0.04 \text{ \AA}$; $\alpha = 93.9$, $\beta = 115.4$, $\gamma = 98.6^\circ$; $V = 471.8 \text{ \AA}^3$; M.W. 205.6; $D_m = 1.439 \text{ g.cm}^{-3}$; D_x (with $Z = 2$) = 1.447 g.cm^{-3} .

The intensities of the reflexions were measured on a Hilger and Watts automatic linear diffractometer using a scintillation counter and $\text{Mo K}\alpha$ radiation with balanced filter operation. The crystal was mounted on the b axis and the intensities of 2211 reflexions were collected for the layers $h0l$ through $h7l$. All the intensities were corrected for background. No absorption corrections were applied as X-ray absorption was negligible. Lorentz and polarization corrections were made in the usual way. The different layers of b -axis data were brought to an approximately common scale by comparison with $0kl$ and $hk0$ spectra. The method of Wilson (1942) was used to bring the coefficients to an approximately absolute scale, and to determine the value of the overall temperature exponent as $B = 2.82$. With this B value the scattering factors f_{jh} of all atoms were corrected and the E values were computed with the formula (Karle & Karle, 1964):

$$E_h^2 = F_h^2 / \varepsilon \sum_{j=1}^N f_{jh}^2, \quad (1)$$

N being the number of atoms in the unit cell, E_h normalized structure factors, F_k structure factors cor-

responding to the reflexions hkl . ε is an integer which is introduced to allow for the presence of symmetry elements and centring effects in the reciprocal lattice. For the space group $P\bar{1}$, $\varepsilon=1$. A computer program was used (Daly, 1965) which calculated statistical averages for normalized structure factors $\langle|E|\rangle$, $\langle|E^2-1|\rangle$, $\langle|E^2|\rangle$ (Table 1) and evaluated the fraction of the normalized structure magnitudes larger than 1.0, 1.2, 1.4, 1.6, 1.8, 2.0, 2.5, and 3.0 (Table 2) with evidence for centrosymmetrical distribution. The space group is therefore $P\bar{1}$. The same program listed all triplet interactions E_h, E_k and E_{h-k} with E values greater than a chosen limit to facilitate the application of the Σ_2 formula for the symbolic addition method. The limit $\langle|E|\rangle 1.5$ allowed 249 reflexions to be used for the symbolic addition procedure.

Table 1. Statistical average for the normalized structure factors

	Experimental	Theoretical	
		Centrosym-metric	Non-centrosym-metric
$\langle E \rangle$	0.832	0.798	0.886
$\langle E^2-1 \rangle$	0.895	0.968	0.736
$\langle E^2 \rangle$	0.999	1.000	1.000

Table 2. The distribution of the normalized structure magnitudes $|E|$

$ E $	Experimental	Theoretical	
		Centrosym-metric	Non-centrosym-metric
$ E > 3.0$	0.36 %	0.27 %	0.01 %
$ E > 2.5$	1.35	1.24	0.19
$ E > 2.0$	3.83	4.55	1.83
$ E > 1.8$	6.26	7.19	3.92
$ E > 1.6$	8.96	10.96	7.73
$ E > 1.4$	13.55	16.15	14.09
$ E > 1.2$	21.45	23.01	23.69
$ E > 1.0$	32.09	31.73	36.79

Phase determination

The phases were determined by the heavy atom method and by the symbolic addition procedure (Karle & Karle, 1963, 1964) to compare the efficiency of both methods. We expected to find 78.3% correct signs with the heavy atom method according to the probability relation of Sim (1957).

The starting set for the symbolic addition procedure included the signs of three origin specifying linearly independent reflexions (Hauptman & Karle, 1953) and the assignment of signs to four other reflexions with letters a, b, c, d . Each letter represented + or -. All selected signs were associated with large values for $|E|$ and they had many relationships applicable to the Σ_2 formula (Hauptman & Karle, 1953):

$$sE_h \sim s \sum_k E_k E_{h-k} \quad (2)$$

This basic set of the seven assignments for applying the Σ_2 formula is shown in Table 3.

Table 3. Assignment of three origin specifying reflexions and four other reflexions as a starting set for the application of Σ_2

hkl	$ E $	Sign
$\bar{1}24$	3.71	+
527	3.32	-
216	2.78	+
$\bar{2}5\bar{2}$	3.51	a
811	3.22	b
535	3.20	c
$\bar{3}4\bar{2}$	2.65	d

The probability that the sign of E_h is plus is determined by the formula (Woolfson, 1954; Hauptman & Karle, 1953):

$$P_+(E_h) = \frac{1}{2} + \frac{1}{2} \tanh \frac{\sigma_3 |E_h| \sum_k E_k E_{h-k}}{\sigma_2^{3/2}} \quad (3)$$

where

$$\sigma_n = \sum_{j=1}^N Z_j^n \quad (3a)$$

Z_j being the atomic number of the j th atom in a cell containing N atoms. σ_3/σ_2 is a constant which had in the present case a value 0.2575. The formula (3) indicates that the reflexions whose $|E_h| \sum_k E_k E_{h-k}$ is more than 10 have a correct sign determined with a probability of 0.99.

In the course of application of the starting set of 7 reflexions (Table 3) to the determination of further phases the predominant influence of these basic reflexions was accepted only if their contribution to $\sum_k E_k E_{h-k}$ was larger than 9. In this manner, the phases for 16 further reflexions were determined (Table 4).

Table 4. Determination of phases for 16 further reflexions

Σ_2 represents the contribution of the basic set of 7 reflexions listed in Table 3.

hkl	$ E $	Sign	Σ_2
012	2.28	-c	10.62
31 $\bar{1}$	1.79	-	9.22
619	2.81	c	11.87
713	2.59	b	11.94
6.0. $\bar{1}\bar{1}$	2.56	-	12.31
935	2.33	b	11.94
336	1.96	-b	10.69
$\bar{1}\bar{3}\bar{6}$	2.53	a	13.02
132	2.76	+	10.31
444	1.54	a	9.75
44 $\bar{3}$	2.96	-	12.31
643	2.67	ab	11.30
45 $\bar{1}$	2.87	c	11.87
$\bar{1}\bar{0}.6.\bar{1}$	1.68	ab	11.30
$\bar{3}\bar{7}\bar{2}$	2.36	a	13.02
379	3.69	-a	11.65

Further useful information on phases gave the Σ_1 formula for space group $P\bar{1}$ (Hauptman & Karle, 1953):

$$sE_{2h} \sim s(E_h^2 - 1) \quad (4)$$

The probability that E_{2h} is positive can be computed from the relationship:

$$P_+(E_{2h}) = \frac{1}{2} + \frac{1}{2} \tanh \frac{\sigma_3 |E_{2h}| (E_h^2 - 1)}{2\sigma_2^{3/2}}. \quad (5)$$

The application of (4) and (5) to the reflexion $\bar{2}48$, whose $|E| = 1.99$, indicated that it had a positive sign with a probability of 0.99.

The 24 phases found in the first stage of symbolic addition procedure were used to determine the signs of 48 further reflexions and the phases found in the earlier stage were confirmed by additional contributors to Σ_2 . Two important conclusions followed from these results: (1) many interactions $E_k E_{h-k}$ showed that $s a = -s b$, (2) it was necessary to introduce a new symbol e for further progress of the symbolic addition procedure. This symbol was assigned to the reflexion $\bar{2}35$. With these four symbols a , c , d and e the rest of the 177 phases for reflexions with $|E| > 1.5$ were determined. Many interactions $E_k E_{h-k}$ showed again that probably $s a = -s c = s d = -s e$. This relationship between the letters a , b , c , d , and e gave rise to two possibilities:

	a	b	c	d	e
I	-	+	+	-	+
II	+	-	-	+	-

The correct combination of signs could be proved in the following way. If the origin were chosen to be: $s(\bar{1}24) = +$, $s(52\bar{7}) = +$, and $s(21\bar{6}) = +$ instead of $+ - +$, then all signs in groups $u g u$, $g g u$, $u u u$ and $g u u$ would change. Hence the signs of letters b , c and e should change giving rise to the two possibilities for phases:

	a	b	c	d	e
I	-	-	-	-	-
II	+	+	+	+	+

From these two sets it is easily recognized that set II is impossible since all phases would be $+$ and there is no atom at the origin in this structure.

With set I, 121 positive and 127 negative signs were obtained. It was shown later that all 249 phases were correctly determined.

The position of the Cl atom (heavy atom method) was found from the three-dimensional Patterson function. The x_{Cl} , y_{Cl} , z_{Cl} coordinates were fixed in such a manner that the selected origin was identical with the origin specified by the three linearly independent reflexions $\bar{1}24$, $52\bar{7}$ and $21\bar{6}$.

The signs of structure factors calculated with the contribution of Cl atoms only were used as phase angles of three-dimensional Fourier coefficients. It was shown later on that 77.9% of all signs were correctly determined (the theoretical value is 78.3%). The Fourier synthesis computed with these signs showed the positions of all 13 atoms of pyridoxine hydrochloride but another 10 false peaks appeared of the same heights as those of light atoms. Only the known shape of the pyridine ring enabled us to distinguish between the true and false maxima.

The three-dimensional E map, based on 20 phases per atom, showed clearly the positions of all 13 atoms. Only one spurious peak appeared there with a rather lower value for its maximum. The result of the $E(x, y, z)$ -synthesis was in the present case much clearer and more unequivocal than the result of the electron density calculation by the heavy atom method.

Further refinement of the parameters of the structure has been carried out by a least-squares program of Daly, Stephens & Wheatley (1963) on an Elliott 803 computer. We started with the set of atomic positions from the $E(x, y, z)$ and $\rho(x, y, z)$ syntheses. The scattering factors for the atoms were taken from *International Tables for X-ray Crystallography* (1962). First, the coordinates and the individual isotropic temperature factors of 13 atoms, together with the scale factor were refined. The least-squares program used the block diagonal approximation and weighting scheme proposed by Cruickshank, Pilling, Bujosa, Lovell & Truter (1961). During the 4 cycles of refinement the reliability index $R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$ decreased from 0.35 to 0.20. In this stage of refinement individual anisotropic temperature factors were introduced with a 6×6 matrix for the thermal parameters. During another 4 cycles the reliability factor R decreased to 0.093, and the residual $R' = \Sigma w \Delta F^2 / \Sigma w F_o^2$ fell to 0.016.

Table 5. Final atomic coordinates (\AA), with standard deviations

Atom	x	σ_x	y	σ_y	z	σ_z
Cl	4.314	0.001	1.908	0.001	1.957	0.001
O(1)	-2.443	0.003	-1.640	0.003	3.537	0.003
O(2)	0.163	0.003	-1.942	0.003	3.928	0.003
O(3)	-1.881	0.004	2.384	0.004	-0.032	0.004
N(1)	1.490	0.003	0.552	0.003	2.206	0.003
C(1)	1.450	0.004	-0.474	0.003	3.000	0.004
C(2)	0.139	0.004	-0.920	0.003	3.100	0.004
C(3)	-1.106	0.004	-0.348	0.003	2.365	0.004
C(4)	-0.991	0.004	0.712	0.003	1.538	0.004
C(5)	0.338	0.004	1.152	0.003	1.491	0.004
C(6)	-2.587	0.005	-0.824	0.004	2.374	0.004
C(7)	2.811	0.004	-1.074	0.004	3.734	0.005
C(8)	-2.303	0.004	1.369	0.004	0.708	0.004

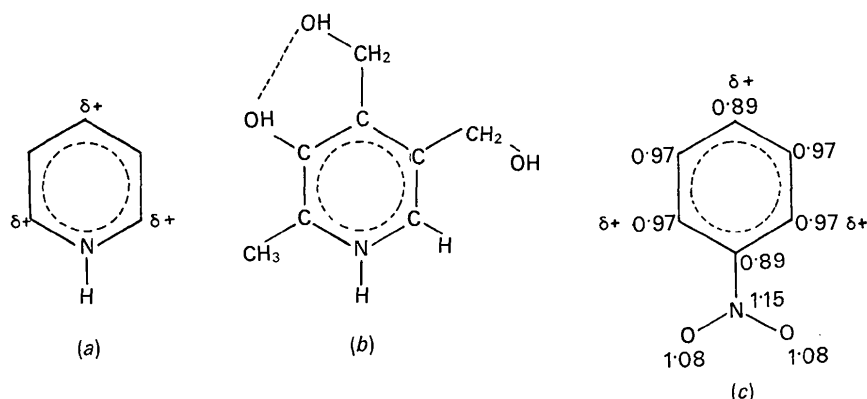


Fig. 1. (a) Pyridine hydrochloride. (b) Pyridoxine hydrochloride. (c) Charge distribution in nitrobenzene (Nagakura & Tanaka, 1954).

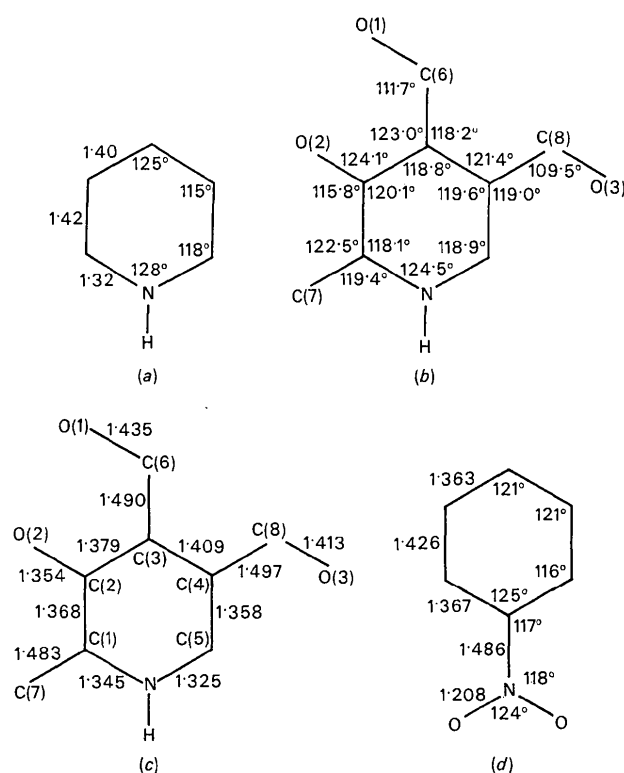


Fig. 2. (a) Bond lengths and valence angles in pyridine hydrochloride (Rérat, 1962). (b) Valence angles in pyridoxine hydrochloride. (c) Bond lengths in pyridoxine hydrochloride. (d) Bond lengths and valence angles in nitrobenzene (Trotter, 1959).

Description of the structure and discussion

The bond lengths and angles obtained from the coordinates in Table 5 are shown in Table 8 together with their standard deviations. The crystal structure is governed by the presence of the nitrogen atom in the aromatic ring system and by the behaviour of the ring substituents which give rise to hydrogen bond systems in the structure.

Table 6. The components of the mean square vibration tensor (\AA^2)

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cl	0.038 0.001	0.062 0.001	0.058 0.001	0.019 0.001	0.040 0.001	0.040 0.001
O(1)	0.054 0.002	0.072 0.002	0.050 0.001	0.001 0.003	0.037 0.002	0.050 0.002
O(2)	0.055 0.002	0.068 0.002	0.061 0.002	0.031 0.002	0.070 0.003	0.049 0.003
O(3)	0.059 0.002	0.087 0.002	0.089 0.002	0.060 0.003	0.107 0.004	0.073 0.003
N(1)	0.041 0.001	0.054 0.001	0.045 0.001	0.015 0.002	0.025 0.002	0.038 0.002
C(1)	0.042 0.002	0.054 0.002	0.036 0.001	0.017 0.003	0.020 0.002	0.028 0.002
C(2)	0.044 0.002	0.048 0.001	0.037 0.001	0.015 0.002	0.027 0.002	0.032 0.003
C(3)	0.041 0.002	0.046 0.001	0.037 0.001	0.011 0.002	0.014 0.002	0.036 0.002
C(4)	0.039 0.001	0.045 0.001	0.038 0.001	0.014 0.002	0.014 0.002	0.034 0.002
C(5)	0.042 0.002	0.053 0.002	0.042 0.002	0.017 0.003	0.028 0.002	0.037 0.003
C(6)	0.043 0.002	0.063 0.002	0.054 0.002	0.014 0.003	0.041 0.003	0.049 0.003
C(7)	0.044 0.002	0.073 0.002	0.055 0.002	0.040 0.003	0.040 0.003	0.033 0.003
C(8)	0.044 0.002	0.056 0.002	0.055 0.002	0.031 0.003	0.043 0.003	0.045 0.003

Some parallel behaviour might be expected between pyridoxine hydrochloride (Fig. 1b), pyridine hydrochloride (Fig. 1a) and nitrobenzene (Fig. 1c). This parallel behaviour results from similarity in electron distribution; in all three molecules π -electrons are removed primarily from three positions on the ring by electronegative atoms. A common feature of all three structures is a large value of the valence angle in the position of the atom at which electron withdrawal occurs (Fig. 2a-d) (nitrogen or carbon atom with NO_2 -substituent). This value is 125 – 128° . It is interesting that a weaker donor-acceptor bond between a transition metal and

Table 7. Observed and calculated structure factors

L	F _o	F _c	L	F _o	F _c	L	F _o	F _c	L	F _o	F _c	L	F _o	F _c	L	F _o	F _c	
0 0 L			453	466		661	-491		9	516	564		9	647	-477	1	2265	2265
1 786	683		92	-106		157	-114		11	591	-631		1	11 L		3	610	477
2 4808	-4878		1137	1128		11 L			6	1 L			4	1710	-1707	5	1150	-1208
3 132	284		1017	927					6	406	-396		5	55	24	6	1229	1178
4 231	284		314	-304		194	54		6	194	201		7	157	194	8	101	164
5 2672	2591		2330	-2180		147	52		7	573	-540		8	127	94	9	813	884
6 714	-77		665	571		453	-376		8	416	-367		9	194	-191	10	397	418
7 647	-603		1024	2791		767	569		9	1229	-1117		11	127	127	12	175	-149
8 129	132		1082	961		499	407		10	554	-498		13	110	-110	14	2173	2165
9 55	62		101	185		499	377		11	1544	-1390		15	184	196	16	543	925
10 231	-230		106	-106		397	266		12	1128	-1209		17	240	335	18	92	42
11 157	154		110	-117		804	-640		13	1712	508		19	277	-225	20	2894	-2972
			952	932		-471	435		14	1442	1288		21	416	296	22	81	5
			1146	1084		120	-14		15	2681	-2739		23	943	-139	24	969	781
			161	-69		1766	-1676		16	1174	3538		25	1017	-1007	26	639	764
			212	-118		120	0		17	1646	1894		27	527	308	28	327	-519
			194	-92		613	572		18	2472	-2664		29	147	17	30	164	-182
			504	-684		718	1058		19	2284	-2122		31	747	798	32	684	-690
			129	-34		11	-91		20	4172	1097		33	610	-623	34	73	-71
			342	239		739	-753		21	5803	-57		35	1507	-1500	36	363	423
			739	-517		101	-82		22	860	851		37	2210	2101	38	527	-526
			314	-314		11	314		23	453	-431		39	1399	-1322	40	499	-545
			767	569		1292	-1111		24	825	-813		41	240	357	42	240	357
			1396	1299		246	288		25	932	-918		43	110	173	44	1376	-1351
			591	531		157	-177		26	1166	183		45	2490	-1914	46	212	186
			323	294		212	-233		27	184	-179		47	134	179	48	1035	1043
			869	-877					28	434	34		49	786	1081	50	786	1081
			490	-322					29	514	266		51	416	404	52	312	312
			1591	992					30	258	279		53	1128	-1119	54	286	-267
			1363	1168					31	1692	-1583		55	1692	-1583	56	1368	-1378
			1424	-1128					32	1488	1392		57	1488	1392	58	1488	1392
			808	808					33	1784	-1804		59	1784	-1804	60	1784	-1804
			98	-176					34	841	818		61	841	818	62	453	666
			249	-238					35	1122	-1172		63	1122	-1172	64	867	-1090
			147	-47					36	1645	1060		65	1645	1060	66	2524	-3109
			203	-221					37	120	111		67	120	111	68	2080	2195
			610	531					38	231	-258		69	231	-258	70	231	-258
			249	231					39	1248	-1344		71	1248	-1344	72	1248	-1344
									40	1886	1886		73	1886	1886	74	1886	1886
									41	560	315		75	560	315	76	560	315
									42	147	181		77	147	181	78	147	181
									43	527	533		79	527	533	80	527	533
									44	231	-282		81	231	-282	82	231	-282
									45	312	312		83	312	312	84	312	312
									46	436	-384		85	436	-384	86	436	-384
									47	114	147		87	114	147	88	114	147
									48	406	447		89	406	447	90	406	447
									49	169	-122		91	169	-122	92	169	-122
									50	861	861		93	861	861	94	861	861
									51	258	-268		95	258	-268	96	258	-268
									52	998	-1027		97	998	-1027	98	998	-1027
									53	2358	-2366		99	2358	-2366	100	2358	-2366
									54	1311	1366		101	1311	1366	102	1311	1366
									55	1603	-1542		103	1603	-1542	104	1603	-1542
									56	2515	-3275		105	2515	-3275	106	2515	-3275
									57	64	99		107	64	99	108	64	99
									58	573	602		109	573	602	110	573	602
									59	369	406		111	369	406	112	369	406
									60	221	208		113	221	208	114	221	208
									61	2562	-1907		115	2562	-1907	116	2562	-1907
									62	591	-621		117	591	-621	118	591	-621
									63	2654	-2251		119	2654	-2251	120	2654	-2251
									64	379	414		121	379	414	122	379	414
									65	564	570		123	564	570	124	564	570
									66	1312	-1322		125	1312	-1322	126	1312	-1322
									67	508	-521		127	508	-521	128	508	-521
									68	32	-103		129	32	-103	130	32	-103
									69	604	753		131	604	753	132	604	753
									70	416	396		133	416	396	134	416	396
									71	887	-947		135	887	-947	136	887	-947
									72	286	236		137	286	236	138	286	236
									73	147	151		139	147	151	140	147	151
									74	1979	-2886		141	1979	-2886	142	1979	-2886
									75	2191	-1912		143	2191	-1912	144	2191	-1912
									76	864	-761		145	864	-761	146	864	-761
									77	628	613		147	628	613	148	628	613
									78	1079	2198		149	1079	2198	150	1079	2198
									79	212	233		151	212	233	152	212	233
									80	776	686		153	776	686	154	776	686
									81	379	318		155	379	318	156	379	318
									82	632	-394		157	632	-394	158	632	-394
									83	92	-11		159	92	-11	160	92	-11
									84	231	-245		161	231	-245	162	231	-245
									85	924	893		163	924	893	164	924	893
									86	527	569		165	527	569	166	527	569
									87	434	-496		167	434	-496	168	434	-496
									88	1424	-1446		169	1424	-1446	170	1424	-1446
									89	212	88		171	212	88	172	212	88
									90	1627	1357		173	1627	1357	174	1627	1357
									91	1794	1647		175	1794	1647	176	1794	1647
									92	3486	-3022		177	3486	-3022	178	3486	-3022
									93	1318	-1344		179	1318	-1344	180	1318	-1344
									94	397	-285		181	397	-285	182	397	-285
									95	166	-266		183	166	-266	184	166	-266
									96	2164	-2174		185	2164	-2174	186	2164	-2174
									97	2820	-2620		187	2820	-2620	188	2820	-2620
									98	2293	2761		189	2293	2761	190	2293	2761
									99	360	573		191	360	573	192	360	573
	</																	

Table 7 (cont.)

L	F _o	F _c	L	F _o	F _c	L	F _o	F _c	L	F _o	F _c	L	F _o	F _c	L	F _o	F _c	L	F _o	F _c	L	F _o	F _c	L	F _o	F _c									
9	6	L	3	240	242	7	305	260	1	27	-24	4	157	-144	3	277	252	2	277	252	1	175	-154	4	332	315	7	295	222	1	7	L			
0	258	-258	4	92	-92	5	166	-187	3	351	337	2	6	L	0	212	-208	0	258	-224	6	64	-64	5	125	111	6	296	235	9	212	173			
1	194	189	7	64	-53	6	166	143	0	453	-511	2	6	L	1	114	-141	2	175	179	2	92	-75	4	129	-161	4	7	L	8	179	-311	8	92	97
1	203	198	8	129	-44	7	730	621	2	388	381	10	342	335	2	92	-75	4	129	-161	4	7	L	5	73	-108	4	175	153	7	168	-207			
3	84	-114	4	101	-111	5	641	482	5	120	-121	6	332	-309	5	6	L	6	166	185	5	5	5	5	73	-108	0	101	-117	4	277	259			
4	101	-111	5	92	89	6	184	-158	4	231	-276	7	277	-244	6	166	185	5	5	5	5	5	5	5	73	-108	1	194	-162	3	286	261			
5	92	89	6	166	153	7	83	-57	6	166	185	7	277	-244	6	166	185	5	5	5	5	5	5	5	73	-108	2	120	-93	1	582	-549			
6	166	153	7	83	-57	8	83	-32	7	129	92	8	332	-309	7	277	-244	6	166	185	5	5	5	5	73	-108	3	120	-93	0	129	-127			
7	83	-32	8	83	-32	9	118	-134	8	129	92	9	332	-309	8	129	92	7	129	92	6	166	185	7	277	-244	4	194	-162	3	286	261			
8	129	92	9	83	-32	10	184	-158	9	231	-276	11	184	145	10	342	335	9	231	-276	10	342	335	11	184	145	5	73	-108	4	277	259			
9	83	-32	10	184	-158	11	231	-276	10	342	335	12	184	145	11	231	-276	11	231	-276	10	342	335	12	184	145	6	166	185	5	582	-549			
10	184	-158	11	231	-276	12	184	145	11	231	-276	13	203	193	12	184	145	11	231	-276	10	342	335	13	203	193	6	166	185	5	582	-549			
11	231	-276	12	184	145	13	203	193	12	184	145	14	314	319	13	203	193	12	184	145	11	231	-276	14	314	319	7	129	92	6	129	-127			
12	184	145	13	203	193	14	314	319	13	203	193	15	314	319	14	314	319	13	203	193	12	184	145	15	314	319	8	129	92	7	129	-127			
13	203	193	14	314	319	15	314	319	14	314	319	16	314	319	15	314	319	14	314	319	13	203	193	16	314	319	9	129	92	8	129	-127			
14	314	319	15	314	319	16	314	319	15	314	319	17	314	319	16	314	319	15	314	319	14	314	319	17	314	319	10	129	92	9	129	-127			
15	314	319	16	314	319	17	314	319	16	314	319	18	314	319	17	314	319	16	314	319	15	314	319	18	314	319	11	129	92	10	129	-127			
16	314	319	17	314	319	18	314	319	17	314	319	19	314	319	18	314	319	17	314	319	16	314	319	19	314	319	12	129	92	11	129	-127			
17	314	319	18	314	319	19	314	319	18	314	319	20	314	319	19	314	319	18	314	319	17	314	319	20	314	319	13	129	92	12	129	-127			
18	314	319	19	314	319	20	314	319	19	314	319	21	314	319	20	314	319	19	314	319	18	314	319	21	314	319	14	129	92	13	129	-127			
19	314	319	20	314	319	21	314	319	20	314	319	22	314	319	21	314	319	20	314	319	19	314	319	22	314	319	15	129	92	14	129	-127			
20	314	319	21	314	319	22	314	319	21	314	319	23	314	319	22	314	319	21	314	319	20	314	319	23	314	319	16	129	92	15	129	-127			
21	314	319	22	314	319	23	314	319	22	314	319	24	314	319	23	314	319	22	314	319	21	314	319	24	314	319	17	129	92	16	129	-127			
22	314	319	23	314	319	24	314	319	23	314	319	25	314	319	24	314	319	23	314	319	22	314	319	25	314	319	18	129	92	17	129	-127			
23	314	319	24	314	319	25	314	319	24	314	319	26	314	319	25	314	319	24	314	319	23	314	319	26	314	319	19	129	92	18	129	-127			
24	314	319	25	314	319	26	314	319	25	314	319	27	314	319	26	314	319	25	314	319	24	314	319	27	314	319	20	129	92	19	129	-127			
25	314	319	26	314	319	27	314	319	26	314	319	28	314	319	27	314	319	26	314	319	25	314	319	28	314	319	21	129	92	20	129	-127			
26	314	319	27	314	319	28	314	319	27	314	319	29	314	319	28	314	319	27	314	319	26	314	319	29	314	319	22	129	92	21	129	-127			
27	314	319	28	314	319	29	314	319	28	314	319	30	314	319	29	314	319	28	314	319	27	314	319	30	314	319	23	129	92	22	129	-127			
28	314	319	29	314	319	30	314	319	29	314	319	31	314	319	30	314	319	29	314	319	28	314	319	31	314	319	24	129	92	23	129	-127			
29	314	319	30	314	319	31	314	319	30	314	319	32	314	319	31	314	319	30	314	319	29	314	319	32	314	319	25	129	92	24	129	-127			
30	314	319	31	314	319	32	314	319	31	314	319	33	314	319	32	314	319	31	314	319	30	314	319	33	314	319	26	129	92	25	129	-127			
31	314	319	32	314	319	33	314	319	32	314	319	34	314	319	33	314	319	32	314	319	31	314	319	34	314	319	27	129	92	26	129	-127			
32	314	319	33	314	319	34	314	319	33	314	319	35	314	319	34	314	319	33	314	319	32	314	319	35	314	319	28	129	92	27	129	-127			
33	314	319	34	314	319	35	314	319	34	314	319	36	314	319	35	314	319	34	314	319	33	314	319	36	314	319	29	129	92	28	129	-127			
34	314	319	35	314	319	36	314	319	35	314	319	37	314	319	36	314	319	35	314	319	34	314	319	37	314	319	30	129	92	29	129	-127			
35	314	319	36	314	319	37	314	319	36	314	319	38	314	319	37	314	319	36	314	319	35	314	319	38	314	319	31	129	92	30	129	-127			
36	314	319	37	314	319	38	314	319	37	314	319	39	314	319	38	314	319	37	314	319	36	314	319	39	314	319	32	129	92	31	129	-127			
37	314	319	38	314	319	39	314	319	38	314	319	40	314	319	39	314	319	38	314	319	37	314	319	40	314	319	33	129	92	32	129	-127			
38	314	319	39	314	319	40	314	319	39	314	319	41	314	319	40	314	319	39	314	319	38	314	319	41	314	319	34	129	92	33	129	-127			
39	314	319	40	314	319	41	314	319	40	314	319	42	314	319	41	314	319	40	314	319	39	314	319	42	314	319	35	129	92	34	129	-127			
40	314	319	41	314	319	42	314	319	41	314	319	43	314	319	42	314	319	41	314	319	40	314	319	43	314	319	36	129	92	35	129	-127			
41	314	319	42	314	319	43	314	319	42	314	319	44	314	319	43	314	319	42	314	319	41	314	319	44	314	319	37	129	92	36	129	-127			
42	314	319	43	314	319	44	314	319	43	314	319	45	314	319	44	314	319	43	314	319	42	314	319	45	314	319	38	129	92	37	129	-127			
43	314	319	44	314	319	45	314	319	44	314	319	46	314	319	45	314	319	44	314	319	43	314	319	46	314	319	39	129	92	38	129	-127			
44	314	319	45	314	319	46	314	319	45	314	319	47	314	319	46	314	319	45	314	319	44	314	319	47	314	319	40	129	92	39	129	-127			
45	314	319	46	314	319	47	314	319	46	314	319	48	314	319	47	314	319	46	314	319	45	314	319	48	314	319	41	129	92	40	129	-127			
46	314	319	47	314	319	48	314	319	47	314</																									

Table 9. Interatomic distances and bond angles in pyridine derivatives

Compound	Me-N (Å)	Bonds (Å)				Angles (°)			Literature
		N-C(1) N-C(2)	C(1)-C(2) C(4)-C(5) (pyridine ring)	C(2)-C(3) C(3)-C(4)	C-N-C	N-C-C (pyridine ring)	C-C-C		
Monopyridinecopper(II) acetate Cu ₂ (CH ₃ · CO ₂) ₄ · 2C ₅ H ₅ N, orthorhombic	2.186	1.311 1.349	1.396 1.426	1.339 1.379	119.2	121.4 122.5	119.7 121.6 115.3	Hanic, Štampelová & Hanicová (1964)	
Monopyridinecopper(II) acetate Cu ₂ (CH ₃ · CO ₂) ₄ · 2C ₅ H ₅ N, monoclinic	2.122 2.129	1.377 1.379	1.411 1.381	1.412 1.433	117.9 116.4	121.5 125.2	113.7 120.5 124.2 116.5 113.7 120.5	Barclay & Kennard (1961)	
Dipyridineselenium oxychloride SeOCl ₂ · 2C ₅ H ₅ N	2.19 2.20	1.32 1.32	1.36 1.36	1.40 1.40	120.5	122.5 122.5	117.3 119.5 117.3	Lindqvist & Nähringbauer (1959)	
Pyridinium dicyanomethylide C ₅ H ₅ N · C · (CN) ₂	1.42	1.37 1.37	1.39 1.39	1.39 1.39	120.3	119.5 119.5	120.5 118.9 120.5	Bugg & Sass (1965)	
Pyridine C ₅ H ₅ N by microwave spectroscopy		1.342 1.342	1.391 1.391	1.398 1.398	116.7	124.0 124.0	118.6 118.6	Bak <i>et al.</i> (1954)	

pected on account of the smaller atomic radius of the nitrogen atom.

With orthogonal atomic coordinates, a least-squares plane was fitted to the atoms constituting the pyridoxine ion. The arrangement of atoms is truly planar with the exception of O(1) (an atom from the CH₂OH group). The equation of the plane is:

$$-0.0696x + 0.5741y + 0.8158z = 1.6783.$$

The atoms deviate from the mean plane as follows: N(1) 0.001, C(1) -0.009, C(2) 0.009, C(3) -0.001, C(4) -0.007, C(5) 0.007, C(6) -0.033, C(7) -0.037, C(8) -0.015, O(1) 0.314, O(2) 0.015, O(3) -0.029, Cl 0.164 Å.

The Cl⁻ ion is only slightly displaced from the plane of the pyridoxine ion (0.16 Å) and it occurs close to the extension of the straight line connecting N(1) and C(3) atoms, the Cl-C(1) and Cl-C(5) distances being 3.98 and 3.75 Å, respectively.

From the considerable shortening of the bond length (1.354 Å in comparison with the pure single-bond value) it may be inferred that the C-OH bond possesses a partial double-bond character distinct from what it has in CH₂OH groups, where there are no conventional π-electrons, the C(6)-O(1) and C(8)-O(3) bond lengths being 1.435 and 1.413 Å respectively.

A close intramolecular contact between O(1) and O(2) atoms suggests the presence of a strong hydrogen bond (2.53 Å). Another system of hydrogen bonds connects the pyridoxine ions and Cl⁻ among themselves, as follows from the interatomic distances Cl-N(1) 3.064, Cl-O(1) 3.024, and Cl-O(3) 3.064 Å. Two O(2) atoms from different molecules are connected by a hydrogen bond of length 2.724 Å.

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Crystal Structure of Dibenzoylmethane*

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The crystal structure diffraction phase problem for dibenzoylmethane ($C_{15}H_{12}O_2$) has been solved by packing analysis. The three-dimensional scintillation counter data have been refined by anisotropic least-squares analysis. The positions of all hydrogen atoms, including the enolic hydrogen, have been found and refined by least-squares analysis. The final discrepancy index for the 865 observed reflections was 5.9%.

The molecule was found to be nonplanar, with the planes of the two phenyl groups making angles of -3.8 and $+16.9^\circ$ respectively with the enol ring. The hydrogen bond was found to be very short, 2.47 Å, and appears to be nonlinear, asymmetric, and nonstatistical. The thermal analysis showed rather large librations of the phenyl groups about their connecting bonds and a large libration of the enol ring about an axis through the carbonyl carbon atoms. Intramolecular distances were corrected for the observed librations.

The crystals are orthorhombic, space group *Pbca*, with lattice constants $a = 10.857$, $b = 24.446$, $c = 8.756$ Å, and eight molecules in the unit cell.

Introduction

Dibenzoylmethane is used as an analytical reagent for the determination of uranium (Harton & White, 1958; Maeck, Booman, Elliott & Rein, 1959). It has also been investigated for use in the determination of plutonium and neptunium (Kolthoff, Elving & Sandell, 1962) and several other metal ions because of its chelating ability. Williams, Dumke & Rundle (1962) and Engebretson & Rundle (1964) have shown that the symmetrically substituted *m*-bromo and *m*-chloro-dibenzoylmethanes are completely enolized in the crystal and possess a strong, possibly symmetric, intramolec-

ular hydrogen bond. Dibenzoylmethane crystallizes in a different space group from either the *m*-chloro or the *m*-bromo compound, with twice as many molecules in the unit cell. The unit cell of the *m*-chloro compound does not have a center of symmetry, but centers of symmetry are present in the *m*-bromo compound and in dibenzoylmethane itself.

Collection and treatment of X-ray data

Crystals suitable for X-ray analysis were obtained by recrystallization from carbon tetrachloride solution. Weissenberg and precession X-ray photographs indicated the unique centric orthorhombic space group *Pbca*. Data for the lattice constants were obtained with a single-crystal orienter-scintillation counter, which

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