

Aucune distance entre atomes lourds non liés n'a été trouvée inférieure à la somme des rayons de van der Waals.

Cette étude a été suggérée par M. le Professeur G. Ourisson, qui nous a fourni les cristaux. Qu'il soit remercié pour l'intérêt qu'il a bien voulu manifester pour ce travail.

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The Crystal and Molecular Structures of *N*-Methylchloroacetamide

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The crystal and molecular structures of *N*-methylchloroacetamide ($\text{ClCH}_2\text{CONHCH}_3$) which are stable at room temperature have been determined. The crystal has a monoclinic space group $P2_1/n$ and the lattice constants, $a = 7.55$, $b = 27.26$, $c = 5.11$ Å and $\beta = 106.1^\circ$. The asymmetric unit contains two crystallographically independent molecules I and II, in both of which the Cl-C bond takes *cis* conformation with respect to the C-N bond and the angle ψ defined by Edsall, Flory, Kendrew, Liquori, Némethy, Ramachandran & Scheraga [*J. Mol. Biol.* (1966). **15**, 339] is 179° in molecule I and 166° in molecule II. Molecules I form one kind of layer and molecules II form another, which stack together along the *b* axis. The packing of the molecules in each layer is almost identical. Some close interlayer contacts are found, which may be responsible for the existence of two kinds of molecular conformation.

Introduction

This is one of a series of studies on the conformation of simple peptide molecules (Koyama & Shimanouchi, 1968; Koyama, Shimanouchi, Sato & Tatsuno, 1971) which provide useful information on the internal rotation potentials about the $\text{C}^\alpha\text{-C}'$ and N-C^α axes adjacent to a peptide group -C'ONH- . In the present study, the crystal and molecular structures of the room temperature form of *N*-methylchloroacetamide ($\text{ClCH}_2\text{-CONHCH}_3$) have been analysed in order to determine the stable conformation about the C-C axis.

The molecular conformation of this compound was investigated by Mizushima, Shimanouchi, Ichishima, Miyazawa, Nakagawa & Araki (1956) on the basis of the vibrational spectroscopy and dipole moment

measurements. In the liquid state and in solutions, they found two rotational isomers, the less polar form and the more polar form. They also found two crystalline modifications. One form contains only the less polar form and is stable at room temperatures, and another contains only the more polar form and is stable at higher temperatures. They suggested that the rotational angle ψ about the C-C axis is near 150° for the less polar form and the Cl-C bond is situated at an intermediate position between *cis* and *gauche* with respect to the C-N bond. They also suggested that the angle ψ is near 0° for the more polar form and the Cl-C bond is *trans* to the C-N bond. The phase transformation between the two crystalline modifications was studied in detail by Miyazawa (1969) and the transition point was reported to be 38°C .

Table 1. Fractional atomic coordinates and temperature factors

Temperature factors are of the form:
 $T = \exp [-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

Standard deviations are listed in parentheses denoting the least significant digits.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Molecule I									
Cl	1-1615 (6)	0-0697 (2)	1-1245 (11)	0-0188 (11)	0-0023 (1)	0-0292 (43)	0-0001 (3)	0-0061 (18)	0-0014 (5)
O	0-7774 (19)	0-0524 (4)	0-4290 (34)	0-0263 (35)	0-0021 (3)	0-0180 (110)	0-0014 (7)	0-0003 (45)	0-0008 (12)
N	0-7586 (22)	0-0599 (5)	0-8739 (37)	0-0207 (39)	0-0015 (3)	0-0418 (149)	0-0008 (7)	0-0203 (57)	0-0014 (15)
C α	1-0653 (24)	0-0625 (7)	0-7685 (37)	0-0170 (42)	0-0027 (4)	0-0101 (161)	0-0004 (10)	0-0021 (60)	0-0024 (19)
C β	0-8475 (28)	0-0573 (6)	0-6740 (63)	0-0216 (53)	0-0006 (3)	0-0391 (201)	0-0004 (8)	0-0034 (84)	0-0016 (17)
C	0-5526 (24)	0-0564 (7)	0-7831 (42)	0-0138 (41)	0-0022 (4)	0-0686 (189)	0-0002 (9)	0-0029 (60)	0-0014 (19)
Molecule II									
Cl	1-2823 (6)	0-1855 (2)	1-6096 (11)	0-0165 (9)	0-0021 (1)	0-0394 (47)	0-0002 (2)	0-0019 (16)	0-0006 (5)
O	0-8912 (19)	0-1928 (5)	0-9047 (42)	0-0232 (43)	0-0023 (3)	0-0525 (131)	0-0010 (8)	0-0006 (58)	0-0008 (15)
N	0-8800 (17)	0-1846 (5)	1-3604 (35)	0-0147 (29)	0-0013 (2)	0-0353 (146)	0-0002 (7)	0-0150 (49)	0-0014 (14)
C α	1-1747 (22)	0-2005 (6)	1-2507 (37)	0-0168 (38)	0-0021 (3)	0-0155 (154)	0-0009 (9)	0-0125 (50)	0-0017 (15)
C β	0-9657 (26)	0-1917 (6)	1-1542 (71)	0-0178 (40)	0-0009 (3)	0-0423 (182)	0-0010 (8)	0-0086 (85)	0-0022 (17)
C	0-6682 (20)	0-1785 (6)	1-2578 (42)	0-0098 (30)	0-0020 (3)	0-0511 (155)	0-0003 (9)	0-0018 (50)	0-0004 (15)

Experimental

The crystals of *N*-methylchloroacetamide were grown from the melt in a glass bottle by slow cooling to room temperature. They are colourless pillars elongated along the *c* axis with cleavages on (001). Since the crystals are easily sublimated and deliquesced, the specimen was sealed in a glass capillary. The lattice constants were measured on the equatorial precession photographs of *h0l* and *0kl* taken with Cu *K* α radiation.

Crystal data

N-Methylchloroacetamide, C₃H₆ONCl;
 M.W. 107.55; m.p. 47°C; Monoclinic;
 $a = 7.55 \pm 0.02$, $b = 27.26 \pm 0.05$, $c = 5.11 \pm 0.01$ Å,
 $\beta = 106.1^\circ$;
 $U = 1010.4$ Å³;
 $D_x = 1.413$ g.cm⁻³;
 Systematic absences, *h0l* when *h* + *l* is odd,
0k0 when *k* is odd
 Space group: *P*2₁/*n*
 $Z = 8$.

The crystal density was not measured because the crystal dissolves in most liquids having appropriate density. From the density data of related compounds, the crystal density is supposed to be about 1.4 g.cm⁻³ in agreement with the calculated value. The intensity data of the *c* axis were collected from the multiple-film equi-inclination Weissenberg photographs of zero to second layer lines and those of the *b* axis (zero to second layer lines) and *a* axis (zero and first layer lines) were from the precession photographs of various exposure times. All the X-ray photographs were taken with Cu *K* α radiation. The intensities of the Weissenberg photographs were estimated by visual comparison with the standard intensity scale but those on the precession photographs were measured by using a Joyce flying spot integrating densitometer. These intensity data were corrected for Lorentz and polarization factors and scaled in a common base by correlating various layers. A total of 513 independent structure factors were finally derived.

Determination of the crystal structure

The *c*-axis projection of the Patterson map showed the layers of the molecules parallel to (010). However, the main peaks on the Patterson section at $v=0$, which must indicate the intramolecular vectors, could be interpreted equally well in terms of both 'cis' and 'trans' molecular models. It was therefore tried to fit on the Patterson section the common atomic disposition to both the models by assuming the molecules excluding the terminal methyl carbon atom. Fourier syntheses phased by these models were calculated for sets of trial structures, which made it possible to select the most probable one. The *R* value reduced to 0.21 after several cycles of least-squares refinement. Subse-

quent Fourier and difference Fourier syntheses revealed the terminal methyl carbon atoms at the positions expected for the 'cis' model (N is in the cis position with respect to Cl).

Refinement of the structure was carried out by the full-matrix least-squares method using the program ORFLS (Busing, Martin & Levy, 1962), in which the individual anisotropic thermal parameters were in-

Table 2. Observed and calculated structure factors

H	K	L	F _{obs.}	F _{calc.}	H	K	L	F _{obs.}	F _{calc.}	H	K	L	F _{obs.}	F _{calc.}	H	K	L	F _{obs.}	F _{calc.}	H	K	L	F _{obs.}	F _{calc.}	H	K	L	F _{obs.}	F _{calc.}
0	0	2	41.10	-35.59	1	1	-3	32.68	-31.16	2	1	1	37.68	38.74	3	1	6	11.28	10.66	5	1	-2	12.37	-13.05					
0	1	1	15.27	14.05	1	1	-2	28.02	28.35	2	1	-2	14.41	14.18	3	1	-2	13.70	-13.47	5	1	0	24.98	-25.77					
0	1	2	25.78	-23.80	1	1	-1	33.97	34.85	2	1	-2	44.00	43.21	3	1	-1	22.65	-21.53	5	1	-1	7.18	-12.25					
0	1	3	21.07	-21.31	1	1	0	15.56	15.20	2	1	0	6.76	-5.22	3	1	2	11.32	9.63	5	1	-2	6.28	-7.29					
0	2	1	5.66	-3.79	1	1	1	23.50	26.65	2	1	1	5.52	-9.73	3	1	0	10.99	11.94	5	1	0	23.50	-25.63					
0	3	1	29.50	28.18	1	1	2	24.21	-25.79	2	1	2	5.57	-9.11	3	1	2	9.28	7.20	5	1	2	16.17	15.93					
0	3	2	11.13	-9.74	1	1	-2	30.55	-32.01	2	1	-2	16.13	-18.73	3	1	-1	6.95	-8.63	5	1	-2	11.04	12.17					
0	3	3	21.07	-21.23	1	1	0	19.58	-18.54	2	1	-1	28.12	-26.88	3	1	0	19.50	-20.06	5	1	-1	14.18	-14.91					
0	4	1	29.71	35.05	1	1	1	11.18	13.33	2	1	1	20.50	18.30	3	1	1	7.09	11.60	5	1	-2	9.18	-8.94					
0	4	2	4.00	-1.52	1	1	2	15.98	15.83	2	1	2	33.78	-31.05	3	1	2	23.83	-23.48	5	1	-1	7.18	-10.18					
0	4	3	71.31	-78.40	1	1	-2	11.89	-12.75	2	1	-2	13.80	15.33	3	1	-2	15.89	15.38	5	1	0	11.66	12.26					
0	5	1	40.82	-43.82	1	1	-1	21.31	21.05	2	1	-2	13.80	15.33	3	1	-1	6.47	9.40	5	1	0	12.46	18.62					
0	5	2	21.55	22.08	1	1	0	10.32	-9.18	2	1	0	7.33	6.09	3	1	0	6.71	7.59	5	1	2	6.04	-9.80					
0	6	1	9.04	8.50	1	1	1	22.07	23.34	2	1	1	8.37	9.93	3	1	1	13.42	15.98	5	1	-1	21.74	22.38					
0	6	2	7.37	4.89	1	1	2	12.89	10.52	2	1	2	13.14	-12.57	3	1	-1	14.13	15.17	5	1	-2	6.47	10.39					
0	7	1	26.88	-29.20	1	1	-1	49.81	50.04	2	1	-1	17.34	15.06	3	1	-1	65.13	-61.56	5	1	0	13.27	13.90					
0	8	0	227.30	-262.56	1	1	0	15.08	16.87	2	1	0	31.45	-31.69	3	1	0	7.04	5.48	5	1	0	6.52	10.29					
0	8	1	17.03	16.72	1	1	1	38.75	-37.86	2	1	1	15.03	-16.46	3	1	1	24.88	24.21	5	1	-2	35.30	-34.94					
0	8	2	24.33	25.05	1	1	2	5.47	-9.50	2	1	2	12.08	-12.57	3	1	2	29.40	-26.83	5	1	0	12.70	10.58					
0	9	1	4.00	6.49	1	1	-2	16.70	18.98	2	1	-2	13.86	-12.77	3	1	-2	25.02	-26.14	5	1	-2	12.46	15.34					
0	9	2	31.58	32.93	1	1	-1	19.17	-18.53	2	1	-1	13.86	-12.77	3	1	-1	32.75	-32.14	5	1	0	9.28	8.31					
0	10	1	4.23	5.00	1	1	0	33.92	33.18	2	1	0	11.80	-12.53	3	1	0	55.42	-55.25	5	1	0	10.28	15.62					
0	11	1	7.75	-6.85	1	1	1	8.09	-8.65	2	1	1	8.85	9.98	3	1	1	27.59	25.54	5	1	-2	30.64	28.61					
0	11	2	12.70	12.82	1	1	2	29.45	-31.86	2	1	2	16.75	16.72	3	1	-2	36.06	-31.85	5	1	-1	16.94	16.18					
0	12	1	13.80	-13.71	1	1	-2	12.42	12.24	2	1	-2	8.61	-10.08	3	1	-2	28.40	27.17	5	1	2	24.07	-26.35					
0	13	1	30.92	31.86	1	1	-1	14.18	10.95	2	1	-1	11.23	-9.95	3	1	-1	11.27	-8.88	5	1	-2	31.97	32.28					
0	13	2	7.33	-8.10	1	1	0	29.54	-29.78	2	1	0	16.51	-16.18	3	1	0	49.62	47.21	5	1	-1	18.36	-16.99					
0	14	1	12.84	-14.51	1	1	1	5.95	10.67	2	1	-1	9.47	-8.77	3	1	-1	31.78	-30.68	5	1	1	10.28	11.71					
0	14	2	52.19	-47.82	1	1	-2	22.22	22.87	2	1	-2	18.60	-17.66	3	1	-2	21.36	-19.70	5	1	-2	14.13	-10.64					
0	15	1	22.05	22.05	1	1	0	22.60	20.56	2	1	0	11.05	-11.41	3	1	0	10.32	-9.11	5	1	0	12.08	11.83					
0	16	0	62.24	100.05	1	1	2	21.74	-20.89	2	1	2	15.57	-14.72	3	1	2	41.06	42.67	5	1	-2	31.64	30.77					
0	16	1	14.08	-15.12	1	1	0	19.22	-14.83	2	1	0	9.18	9.78	3	1	0	34.63	34.59	5	1	-1	9.90	9.26					
0	16	2	12.56	-11.10	1	1	1	18.17	-18.10	2	1	1	21.50	19.34	3	1	-1	9.49	11.83	5	1	1	12.56	-13.68					
0	17	1	6.04	-9.88	1	1	2	12.42	-13.42	2	1	2	9.23	-8.94	3	1	2	7.42	-7.10	5	1	2	12.51	-10.56					
0	17	2	26.07	-24.19	1	1	-2	20.41	-18.95	2	1	-2	17.74	18.90	3	1	-2	36.44	32.99	5	1	-2	24.64	-25.06					
0	21	1	16.94	-15.72	1	1	-1	13.03	-12.80	2	1	-3	42.39	41.36	3	1	-3	24.69	-22.72	5	1	-1	7.04	10.86					
0	22	1	7.09	11.51	1	1	1	17.93	16.17	2	1	0	23.07	-20.59	3	1	-2	14.32	12.40	5	1	0	9.42	-8.00					
0	23	1	7.18	-11.19	1	1	2	12.65	11.94	2	1	0	36.25	-40.03	3	1	0	49.29	51.07	5	1	0	21.74	-22.72					
0	24	0	32.83	-31.97	1	1	0	8.75	8.17	2	1	-2	24.55	-24.68	3	1	-2	14.13	-12.48	5	1	-2	9.04	11.73					
0	25	0	7.23	10.05	1	1	-1	24.50	-24.10	1	1	-1	35.08	-32.75	2	1	-1	20.74	-21.15	5	1	0	9.42	7.83					
0	25	2	9.05	11.52	1	1	2	11.32	11.15	2	1	2	24.12	-23.91	3	1	2	12.56	-11.52	5	1	0	7.14	-6.53					
1	0	-3	22.98	22.05	1	1	2	17.51	16.63	2	1	2	18.74	18.96	3	1	2	10.66	-11.68	5	1	0	7.23	1.77					
1	0	-1	43.96	48.04	1	1	0	13.27	-13.49	2	1	-1	9.37	-10.21	3	1	-1	10.66	-11.68	5	1	0	12.25	-10.09					
1	0	1	28.02	25.97	1	1	2	13.03	12.02	2	1	2	29.30	27.23	3	1	2	43.05	41.07	5	1	2	9.18	-12.77					
1	1	-2	79.21	74.47	1	1	0	14.99	14.80	2	1	0	4.95	7.96	3	1	0	16.70	-15.68	5	1	-2	9.18	-12.77					
1	1	-1	54.33	53.39	1	1	2	6.66	7.48	2	1	-1	4.23	-10.69	3	1	-1	20.41	-18.76	5	1	0	6.71	-6.97					
1	1	0	59.04	63.09	2	1	-2	18.60	17.87	2	1	3	42.67	-38.21	3	1	-2	20.08	19.29	5	1	-2	21.60	-21.28					
1	1	2	76.50	-72.31	2	1	0	82.68	-92.11	2	1	3	11.23	12.16	3	1	-2	15.46	14.30	5	1	-1	14.41	-14.08					
1	2	-3	21.22	22.19	2	1	0	46.95	-44.00	2	1	4	75.26	-74.89	3	1	0	5.71	-5.30	5	1	0	17.55	18.61					
1	2	-2	1.81	3.22	2	1	-3	31.40	26.90	2	1	-1	11.47	10.57	3	1	-1	37.15	-37.47	5	1	-2	21.69	-21.93					
1	2	-1	44.43	46.07	2	1	-2	3.78	-4.30	2	1	4	88.30	-94.45	3	1	-2	20.27	-17.74	5	1	-1	17.70	18.48					
1	2	0	6.66	-8.28	2	1	-1	47.33	44.19	2	1	4	5.09	5.50	3	1	-1	22.45	21.10	5	1	2	8.23	7.12					
1	2	1	61.99	-63.75	2	1	0	13.65	20.95	2	1	4	44.39	41.90	3	1	-1	23.64	-21.78	5	1	-2	7.23	-9.28					
1	2	2	9.99	-11.65	2	1	1	11.42	-11.90	2	1	5	37.77	33.92	3	1	0	5.92	-5.95	5	1	0	19.65	-19.14					
1	2	3	20.22	-20.53	2	1	2	47.10	45.08	2	1	5	22.55	20.29	3	1	2	32.30	-33.93	5	1	-2	19.65	8.99					
1	3	-3	34.87	35.75	2	1	-3	44.43	43.05	2	1	5	12.04	9.75	3	1	-2	17.74	17.02	5	1	2	9.56	7.64					
1	3	-2	32.21	-32.63	2	1	-2	13.99	-10.04	2	1	6	8.33	7.75	3	1	-2	28.50	-26.42	5	1	-2	13.03	12.94					
1	3	-1	55.80	-61.10	2	1	-1	52.28	-43.65	2	1	6	22.88	20.72	3	1	-2	22.64	-22.50	5	1	0	6.66	8.38					
1	3	0	27.12	-25.69	2	1	0	5.66	-2.87	2	1	6	24.74	22.80	3	1	0	6.57	-9.33	5	1	0	9.66	10.89					
1	3	1	52.90	-57.52	2	1	1	25.17	-28.17	2	1	6	9.47	-9.98	3	1	1	8.80	-9.94	5	1	-2	6.47	-5.75					
1	3	2	35.01	31.02	2	1	2	28.50	-26.44	2	1	7	10.56	9.50	3	1	2	14.03	-12.84	5	1	-2	7.28	-4.61					
1	4	-2	53.80	57.31	2	1	-2	8.99	5.65																				

cluded. After several cycles of calculation, the R value converged to 0.09. The final atomic parameters and their estimated standard deviations are listed in Table 1. A comparison of the observed and calculated structure factors is given in Table 2. Throughout the

present calculation, the following atomic scattering factors were used: for carbon, nitrogen and oxygen atoms, those of Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955) and for chlorine, those of Dawson (1960).

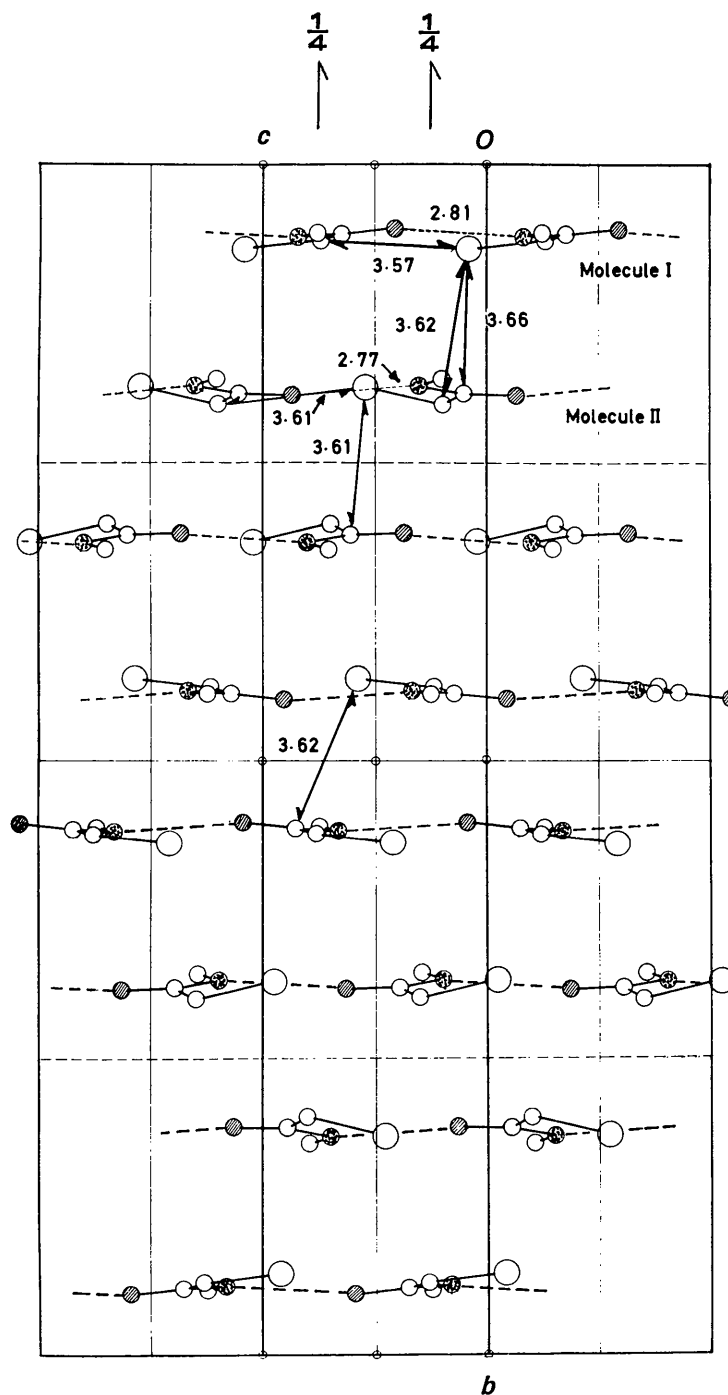


Fig. 1. a -axis projection of the crystal structure showing two kinds of layers stacked together in the b direction. Closest interatomic distances are shown by arrows and hydrogen bonds by broken lines. Large open circles indicate chlorine, small open circles carbon, shaded circles oxygen and dotted circles indicate nitrogen atoms.

Discussion of the structure

The present crystal contains two crystallographically independent molecules in the asymmetric unit, which we denote molecules I and II as shown in Fig. 1. In both molecules, the atoms belonging to the peptide group *i.e.* C α , C', O, N and C are in a plane within the limit of experimental error. The perpendicular distances of atoms from the plane are shown in Table 3. Molecule I takes a planar structure. Molecule II takes a slightly twisted structure, the chlorine atom being 0.36 Å out of the peptide plane.

Table 3. *Perpendicular distances of atoms from the peptide groups*

	Molecule I	Molecule II
C α	0.01 Å	0.02 Å
C'	-0.01	-0.01
O	0.00	0.00
N	-0.01	-0.02
C	0.01	0.02
Cl	0.00	-0.36

Chlorine atoms are not included in the calculation of the least-squares planes.

The bond lengths and the bond angles in molecules I and II are listed in Tables 4 and 5. The standard deviations of these values were calculated from those listed in Table 1. The internal rotation angles are also listed in Table 6. In Tables 4 and 5 the molecular parameters involved in the peptide group are compared

with those generally accepted (Corey & Pauling, 1953). The differences are within experimental error with the exception of the C'-N bond lengths. The longer C'-N bonds (1.37 and 1.39 Å) and the larger Cl-C α -C' angles (114.6 and 114.6°) may reflect the intramolecular interaction between the chlorine and nitrogen atoms which are arranged in the *cis* position.

Table 4. *Bond lengths and their standard deviations*

	Molecule I	Molecule II	Corey & Pauling (1953)
Cl-C α	1.77 (0.02) Å	1.83 (0.02) Å	—
C α -C'	1.59 (0.03)	1.54 (0.02)	—
C'-O	1.22 (0.03)	1.24 (0.04)	1.24 Å
C'-N	1.37 (0.04)	1.39 (0.04)	1.32
N-C	1.50 (0.02)	1.55 (0.02)	—

Table 5. *Bond angles and their standard deviations*

	Molecule I	Molecule II	Corey & Pauling (1953)
Cl-C α -C'	114.6 (1.4)°	114.6 (1.4)°	—
C α -C'-N	116.6 (1.9)	115.4 (1.9)	114°
C α -C'-O	116.0 (1.9)	117.2 (2.1)	121
O-C'-N	127.3 (2.1)	127.3 (2.2)	125
C'-N-C	116.5 (1.7)	114.3 (1.6)	—

The angle ψ about the C α -C' axis is found to be 179° for molecule I and 166° for molecule II, indicating that both molecules take the *cis* conformation. The difference in the ψ values is far beyond the experimental error and is explained by intermolecular interactions as described below.

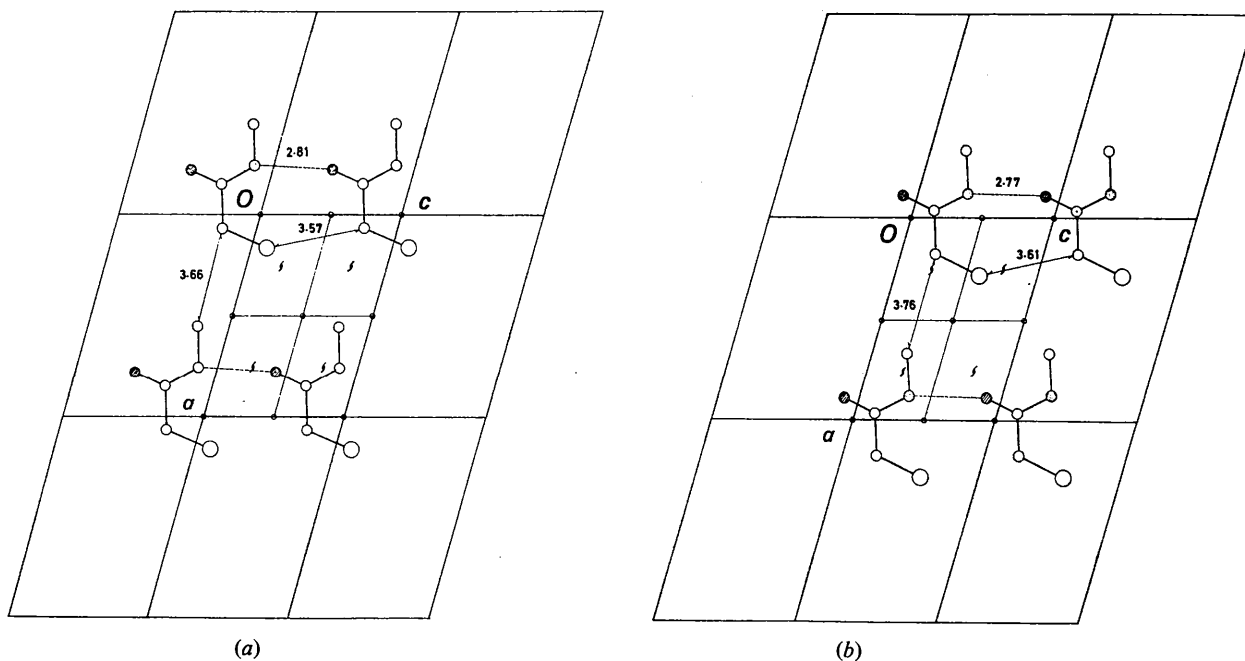


Fig. 2. Packing of the molecules within each layer. Hydrogen bonds are shown by broken lines. (a) Layer I formed by molecules I; (b) layer II formed by molecules II. Symbols as in Fig. 1

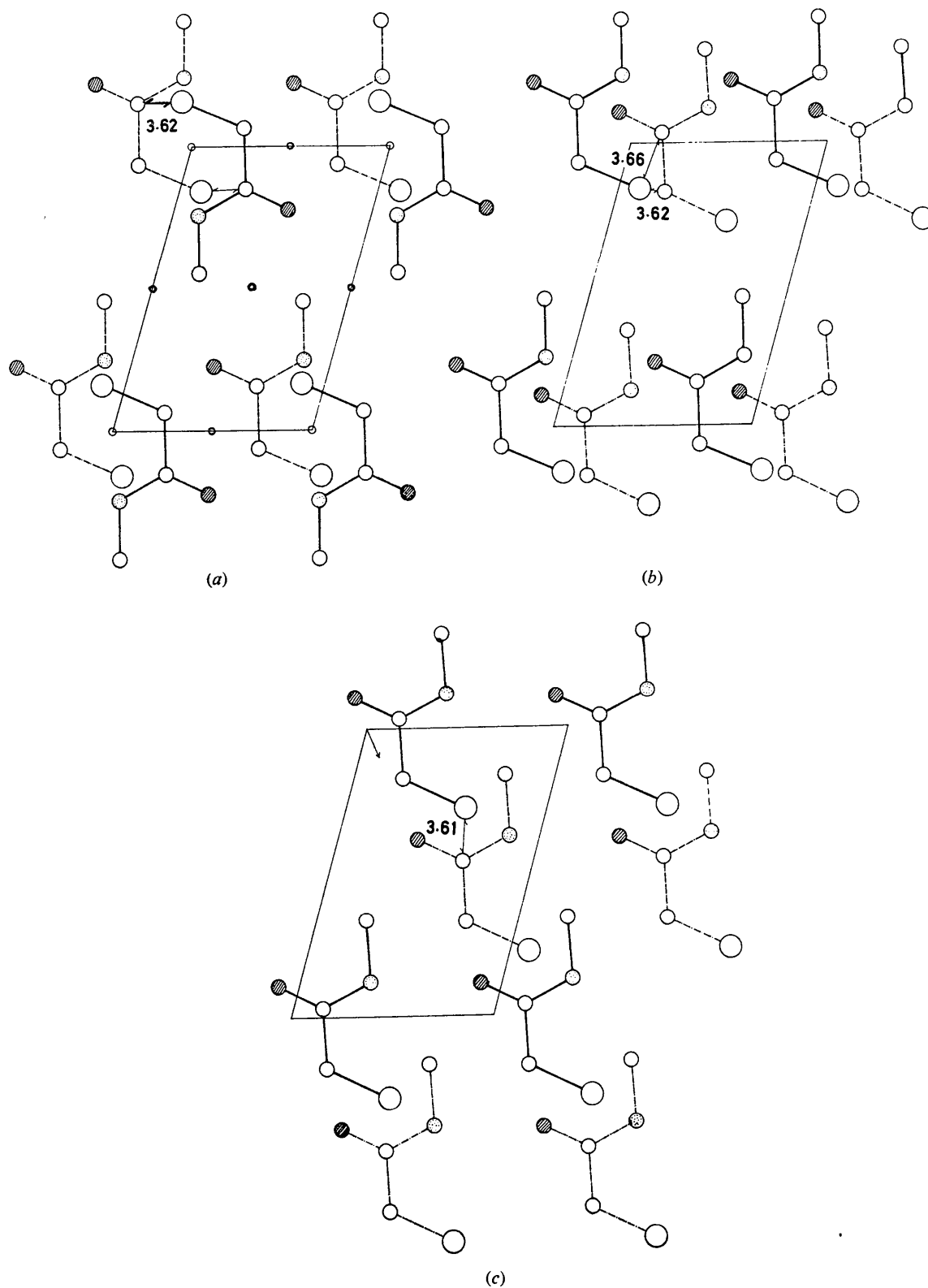


Fig. 3. Packing of the molecules between the layers. Molecules drawn by chain lines indicate those in the neighbouring layer. (a) Layer I — layer I, related by a centre of symmetry; (b) layer I — layer II, no strict crystallographic symmetry relation exists; (c) layer II — layer II, related by an n glide plane.

Table 6. *Internal rotation angles*

Internal rotation angle $A-B-C-D$, is defined as the angle between the projections of $A-B$ and $C-D$, when the projection is taken along the $B-C$ bond. The positive angle is taken in the same sense as that of the turning direction of a right handed screw advancing along the $B-C$ bond. To make the definition concordant with that defined by Edsall, Flory, Kendrew, Liquori, Némethy, Ramachandran & Scheraga (1966), the angle is taken as 0° in the case of exact *trans* conformation.

	Molecule I	Molecule II
Cl-C α -C'-N (ψ)	178.7°	165.8°
Cl-C α -C'-O	0.3	12.4
C α -C'-N-C	1.8	3.0
O-C'-N-C	180.1	181.1

The projection of the crystal structure along the a axis is shown in Fig. 1, in which the intermolecular contacts less than 3.8 Å are indicated. It is seen that two kinds of molecules I and II form different layers I and II, respectively, and they stack together along the b axis. The orientations and the packings of the molecules in the layers I and II are almost identical as shown in Fig. 2. Within each layer, the molecules are bound together in the c direction through N-H...O hydrogen bonds which must stabilize the close contacts between the chlorine atom and the α -carbon atom of the neighbouring in the same layer.

There are three kinds of interlayer interactions as shown in Fig. 3. The following Cl...C distances are distinctly short and may be responsible for the difference in the conformations of the two kinds of molecules.

- Cl (layer I) to C' (layer I, related by a centre of symmetry), 3.62 Å,
- Cl (layer I) to C α (layer II), 3.62 Å,
- Cl (layer II) to C' (layer II, related by a glide plane), 3.61 Å.

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The Crystal Structure of Anthanthrone

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The crystal structure of anthanthrone (C₂₂H₁₀O₂) has been solved by molecular transform methods using room temperature photographic data, and refined to a residual of 13.7% with the standard deviations of the atomic coordinates about 0.03 Å. The space group is $P2_1/c$ with $a = 20.9$, $b = 3.86$, $c = 33.2$ Å, $\beta = 92^\circ$, and $Z = 8$. The three independent molecules are planar and are arranged in stacks with different superpositions and interplanar spacings of 3.46, 3.54, 3.50 Å. Some recurring structural features are discussed.

The crystal structure of anthanthrone

Anthanthrone C₂₂H₁₀O₂ (Kalb, 1914) and similar compounds have been used as models in the study of the carbonization of coal. Knowledge of the crystal structure of these compounds is essential to a more com-

plete understanding of the mechanism of carbonization and the structure of a number of aromatic quinones have been determined in this laboratory.

We are indebted to I.C.I. Dyestuffs Division for a sample of the material. This was further purified and recrystallized by sublimation under partial vacuum, in

As will be understood from Fig. 1, the chlorine atom of molecule II would be located too close to the C' atom of molecule II in the neighbouring layer if molecule II took a planar conformation of $\psi = 180^\circ$.

It is to be noted that the molecules take the *cis* conformation in spite of the strong intramolecular steric hindrance between the chlorine and nitrogen atoms. This fact suggests that the internal rotation potential inherent to the C α -C' axis has one of the minima at $\psi = 180^\circ$ and takes an important role in stabilizing the *cis* conformation.

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