Acta Cryst. (1973). B**29**, 659

The Crystal Structure of the 1:1 Complex of *p*-Phenylenediamine and 1,2,4,5-Tetracyanobenzene

BY H. TSUCHIYA, F. MARUMO AND Y. SAITO

The Institute for Solid State Physics, The University of Tokyo, Roppongi-7, Minato-ku, Tokyo 106, *Japan*

(*Received* 26 *July* 1972; *accepted* 3 *November* 1972)

The complex crystallizes in the space group $P2_1/a$ with $a=8{\cdot}992$, $b=12{\cdot}379$, $c=7{\cdot}318$ Å, $\beta=115{\cdot}2°$ and with $Z=2$. The structure has been refined with three-dimensional data from an automated four-circle diffractometer to an R value of 0·054. The component molecules are stacked alternately in infinite columns along the c axis. The average spacing between the overlapping molecules is 3·37 Å. The nitrogen atoms of the amino groups are out of the plane of the benzene ring by 0·09 Å, while the TCNB molecule is planar within experimental error. The structure seems to show the usual π–π interaction between the two aromatic rings. A difference-Fourier synthesis seems to indicate $p\pi$–$p\pi$ interaction around the C–N bonds.

Introduction

The complex of *p*-phenylenediamine (PD) and 1,2,4,5-tetracyanobenzene (TCNB) is the fifth member of the series of crystal structures of molecular complexes containing TCNB as an electron acceptor which we are investigating (Ohashi, Iwasaki & Saito, 1967; Kumakura, Iwasaki & Saito, 1967; Niimura, Ohashi & Saito, 1968; Tsuchiya, Marumo & Saito, 1972). Like the complex with *N,N,N′,N′*-tetramethyl-*p*-phenylenediamine (TMPD), the former is highly coloured, and this suggests a certain amount of charge transfer in the complex. The crystal structure analysis of the 1:1 complex of PD and TCNB was undertaken to study the intermolecular relationships between the component molecules and to compare them with those of the TMPD–TCNB complex (Ohashi, Iwasaki & Saito, 1967).

Experimental

Crystals were grown by slow evaporation of a solution of PD and TCNB in a mixture of dichloromethane and ethyl acetate. Dark needles elongated along the c axis were obtained. The approximate cell dimensions, crystal system and systematic absences were determined from oscillation and Weissenberg photographs. The cell dimensions obtained from a least-squares calculation, and other crystallographic data are as follows: $C_6H_4(NH_2)_2.C_6H_2(CN)_4$, F.W. 286, monoclinic, space group $P2_1/a$, $a=8{\cdot}992\pm0{\cdot}018$, $b=12{\cdot}379\pm0{\cdot}006$, $c=7{\cdot}138\pm0{\cdot}010$ Å, $\beta=115{\cdot}2\pm0{\cdot}1°$, $U=718{\cdot}9$ Å^3, $D_m=1{\cdot}324$ g cm^{-3} by flotation, $Z=2$, $D_x=1{\cdot}327$ g cm^{-3}, μ(Mo $K\alpha$, $\lambda=0{\cdot}7093$ Å$)=0{\cdot}82$ cm^{-1}.

Three-dimensional intensity data were collected on a Rigaku automated four-circle diffractometer using Mo $K\alpha$ radiation. A LiF monochromator was used. A crystal of dimensions $0{\cdot}37\times0{\cdot}34\times0{\cdot}32$ mm was mounted with the c axis approximately parallel to the φ axis of the goniostat. The ω–2θ scan technique with a scan speed of 0·5° per min was employed and the background measurements were taken for 10 sec at both ends of the scan range. Two standard reflexions were checked every 50 measurements. The fluctuations in the intensities of the standard reflexions were within 1·0%. Intensities of 1660 accessible reflexions below $2\theta=55°$ were collected. The data were corrected for the usual Lorentz and polarization effects. No correction was made for absorption. Reflexions for which the intensities were less than twice their standard deviations were regarded as 'unobserved' and were not included in subsequent calculations. The resulting number of 'observed' reflexions was 1026.

Structure determination

The structure was solved by obtaining phases with the aid of the symbolic addition procedure for centrosymmetric crystals (Karle & Karle, 1963). The program *SIGMA* written by T. Ashida (UNICS, 1967) was utilized to list the $\sum_2$ relationships for reflexions with $|E|\geq1{\cdot}3$ and to calculate the associated probabilities.

The six reflexions used to implement the $\sum_2$ relationship are listed in Table 1. In the course of phase determination, it turned out that $a=b=c=+$. With this assignment of the symbols, phases were determined for 180 reflexions with probabilities larger than 0·98. On the resulting E map the 11 strongest peaks defined all the carbon and nitrogen atoms of the component molecules.

Table 1. *Initial phase assignments*

h	k	l	$\|E\|$	Sign
$\bar{2}$	3	4	3·66	+
$\bar{1}$	1	2	3·38	+
$\bar{4}$	10	1	4·43	+
$\bar{9}$	2	5	3·53	a
$\bar{7}$	1	1	2·58	b
$\bar{3}$	5	8	2·97	c

Table 2. *Atomic parameters (heavy atoms × 10^4, hydrogen atoms × 10^3) with their estimated standard deviations*

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

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
C(1)	1684 (2)	−91 (2)	5787 (3)	132 (3)	70 (2)	217 (6)	6 (2)	81 (4)	−10 (3)
C(2)	943 (2)	868 (2)	4800 (3)	152 (4)	59 (2)	207 (6)	−7 (2)	92 (4)	−14 (3)
C(3)	4233 (2)	4062 (2)	4019 (3)	163 (4)	60 (2)	208 (6)	−13 (2)	90 (4)	−2 (2)
C(4)	1436 (2)	550 (2)	326 (3)	148 (3)	49 (1)	208 (5)	−20 (2)	88 (4)	−13 (2)
C(5)	−54 (2)	1068 (1)	9320 (3)	169 (4)	44 (1)	225 (5)	−8 (2)	100 (4)	−3 (3)
C(6)	3508 (2)	4481 (2)	8996 (3)	146 (3)	50 (1)	209 (5)	5 (2)	85 (4)	8 (2)
C(7)	2947 (2)	1107 (2)	690 (3)	178 (4)	53 (2)	290 (7)	−16 (2)	110 (4)	−8 (3)
C(8)	1944 (2)	3943 (2)	7970 (3)	172 (4)	57 (2)	326 (7)	5 (2)	104 (4)	−11 (3)
N(1)	1851 (2)	1699 (2)	4472 (3)	176 (4)	70 (1)	337 (6)	−17 (2)	113 (4)	−2 (3)
N(2)	4152 (2)	1532 (2)	999 (3)	199 (4)	79 (2)	481 (7)	−43 (2)	164 (5)	−20 (3)
N(3)	717 (2)	3514 (2)	7179 (3)	177 (4)	89 (2)	532 (8)	−18 (2)	110 (5)	−56 (3)

	x	y	z	B (Å^2)
H(1)	212 (2)	486 (2)	368 (2)	1·7 (4)
H(2)	368 (2)	335 (1)	329 (2)	2·1 (4)
H(3)	284 (2)	174 (2)	533 (3)	3·2 (5)
H(4)	138 (2)	233 (2)	413 (3)	4·7 (6)
H(5)	487 (2)	317 (1)	884 (2)	1·8 (4)

The coordinates and isotropic temperature factors for all the atoms except hydrogen atoms were then refined to $R=0{\cdot}20$ using a diagonal least-squares procedure. With the introduction of anisotropic temperature factors, the R value was reduced to 0·11. At this stage, a difference map was computed, which revealed all the hydrogen atoms. Further least-squares refinements were carried out with anisotropic temperature factors for carbon and nitrogen atoms and with isotropic temperature factors for hydrogen atoms. The final R value was 0·054 for the 1026 observed reflexions. The atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1962). The following weighting scheme was employed: $w=1$ if $|F_o|\geq 10{\cdot}0$, otherwise $w=0{\cdot}5$. Final atomic parameters and their standard deviations are listed in Table 2. The observed and calculated structure factors are compared in Table 3.

Description of the structure and discussion

The arrangement of the molecules viewed along the c axis in the structure is shown in Fig. 1. The component molecules are stacked alternately in infinite columns along the c axis. The TCNB molecule is planar with a maximum deviation of 0·01 Å. The plane of the TCNB molecule makes an angle of 70·8° with the c axis and the equation of the plane is given by

$$-0{\cdot}3426X+0{\cdot}3231Y+0{\cdot}8822Z=0{\cdot}0,$$

where X, Y and Z are the coordinates in Å units referred to the orthogonal crystal axes a, b and c^*. The PD molecule as a whole is not planar. However, apart from the amino groups, the aromatic ring and four hydrogen atoms bonded to the carbon atoms are coplanar. The nitrogen atom of the amino group is 0·09 Å above the plane of the aromatic ring, whereas the two hydrogen atoms of the amino group are situated 0·21 and 0·11 Å below the plane. Thus the lone-pair electron of the nitrogen atom comes close to

Table 3. *Observed and calculated structure factors*

H	FO	FC	H	FO	FC	H	FO	FC	H	FO	FC	H	FO	FC	H	FO	FC	H	FO	FC	H	FO	FC	H	FO	FC
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

Table 3 (*cont.*)

H	FO	FC
3	55	-54
4	35	36
5	18	12
6	16	-8
7	11	3
-1	144	141
-2	146	147
-3	189	187
-4	34	-32
-5	30	-30
-6	21	-18
-7	54	-51
-8*	0	0
-9*	0	9
-10	19	-21
-11	11	-11
K,L=	5	4
0	12	-4
1*	9	-6
2	36	-39
3	15	13
4	12	14
5	23	26
6	10	14
-1*	0	-4
-2	32	31
-3	15	10
-4	79	-79
-5	21	-23
-6	80	-79
-7	14	-16
-8	45	41
-9*	0	-7
-10	23	15
-11*	0	-6
K,L=	6	4
0	21	-22
1	91	-92
2	37	37
3	11	-10
4	19	23
5*	0	3
6	14	2
-1	18	20
-2	50	-49
-3	21	18
-4	19	18
-5	106	-105
-6	13	-8
-7	34	33
-8*	0	-3
-9	18	-12
-10	11	-10
K,L=	7	4
0	12	13
1*	0	-14
2	99	-96
3*	0	1
4*	0	18
5*	0	-3
6	23	23
-1*	9	0
-2	110	-114
-3	23	26
-4	37	-39
-5	38	40
-6	13	5
-7	12	-8
-8	12	-16
-9	25	-23
-10*	0	7
K,L=	8	4
0	22	-27
1	51	-49
2*	0	4
3	30	40
4	13	13
5	22	21
-1	53	-53
-2*	0	-6
-3	115	-112
-4*	0	-12
-5	74	-73
-6	30	25
-7	57	57

H	FO	FC
-8	13	11
-9	17	13
-10	16	-18
K,L=	9	4
0	18	-17
1	12	-19
2*	0	[illegible]
3	21	21
4*	0	11
5	15	-12
-1*	0	-9
-2	44	-44
-3	26	-27
-4	13	-12
-5	21	23
-6	25	24
-7	38	35
-8	14	19
-9	15	-16
K,L=	10	4
0*	[illegible]	-5
1*	[illegible]	19
2*	0	-7
3*	0	14
4	13	-14
-1	21	-19
-2*	0	-2
-3	18	-20
-4*	0	7
-5	27	27
-6	35	31
-7	17	22
-8*	5	-7
-9	18	[illegible]
K,L=	11	4
0*	0	-2
1	27	18
2	57	59
3*	0	1
4*	0	3
-1	26	-28
-2	21	25
-3*	0	-19
-4	18	-15
-5	14	7
-6	31	26
-7	11	6
-8	38	37
K,L=	12	4
0	15	11
1	51	51
2	17	15
3*	0	-17
-1	36	39
-2	20	-21
-3*	0	3
-4*	0	3
-5	21	[illegible]
-6	12	[illegible]
-7*	0	-1
K,L=	13	4
0	29	26
1*	0	16
2*	0	12
-1*	0	5
-2	19	14
-3*	0	5
-4*	0	9
-5	15	[illegible]
-6	28	[illegible]
K,L=	14	4
0*	0	7
-1	14	12
-2	16	[illegible]
-3	15	-8
-4	26	-23
K,L=	0	5
0	33	-33
2	56	-58
4	12	-6
6	14	16
-2	25	-23
-4	10	8
-6*	0	1
-8	19	-23

H	FO	FC
-10	18	-8
K,L=	1	5
0	42	-40
1	39	-37
2	29	25
3	11	-14
4	41	42
5*	0	-3
6*	0	-1
-1	77	77
-2	89	88
-3	10	12
-4	39	-38
-5	39	-38
-6*	0	-1
-7	48	-49
-8	40	39
-9	36	-36
-10*	0	6
-11	20	14
K,L=	2	5
0	21	25
1	22	25
2*	0	-4
3	46	44
4	15	-19
5	35	36
6	10	11
-1	75	-74
-2*	0	-11
-3	41	42
-4	50	53
-5*	0	-3
-6	30	-39
-7	39	35
-8	31	-29
-9	101	104
-10	19	16
-11	13	-9
K,L=	3	5
0	42	-38
1	30	26
2	25	22
3	15	-11
4	72	73
5	25	14
6*	0	6
-1	77	-78
-2	61	60
-3*	0	-2
-4	59	-59
-5	69	70
-6	38	37
-7*	0	5
-8	56	58
-9*	0	23
-10	25	28
-11	13	3
K,L=	4	5
0	44	47
1*	0	0
2	20	21
3	22	22
4	12	0
5	35	41
-1	15	-7
-2*	0	3
-3	16	10
-4*	0	0
-5*	0	3
-6	11	9
-7	15	-19
-8*	0	-10
-9	51	50
-10	19	17
-11*	0	6
K,L=	5	5
0	25	-24
1	47	41
2	27	-27
3	18	-12
4	22	27
5	10	10
-1	15	-14
-2	21	-18

H	FO	FC
-3	36	-38
-4*	0	0
-5	36	36
-6	25	-27
-7	28	28
-8	20	21
-9*	0	11
-10	27	31
K,L=	6	5
0*	0	-2
1	73	-76
2*	0	3
3*	0	7
4*	0	12
5*	0	-2
-1	25	22
-2	45	-41
-3	41	39
-4	38	-36
-5	73	-74
-6	87	86
-7	17	-19
-8	21	10
-9	17	-9
-10*	0	-1
K,L=	7	5
0	24	-26
1	34	42
2	31	-34
3*	0	-5
4	21	-24
-1	10	17
-2	25	24
-3	46	-46
-4	47	49
-5	24	23
-6	113	-111
-7*	0	-6
-8	15	-16
-9	21	-20
-10	12	0
K,L=	8	5
0	17	19
1	56	-56
2	10	16
3	19	-11
4	34	-33
-1	21	20
-2	68	-72
-3	42	41
-4	19	21
-5	46	-50
-6	23	19
-7*	0	-11
-8	14	-16
-9	12	-15
K,L=	9	5
0*	0	7
1	15	18
2*	0	-10
3*	0	-6
4	21	-22
-1	28	-25
-2	31	32
-3	38	-39
-4	26	24
-5	37	35
-6	28	-30
-7	14	-10
-8	26	-26
-9	29	-27
K,L=	10	5
0	35	35
1	24	28
2*	0	10
3	19	-19
-1*	0	12
-2	33	-34
-3	16	15
-4	20	17
-5	35	35
-6	14	-13
-7	29	-30
-8	45	-42
K,L=	11	5

H	FO	FC
0	14	11
1	[illegible]	3
2	[illegible]	18
-1	[illegible]	-1
-2*	[illegible]	5
-3	18	-17
-4*	[illegible]	-3
-5	[illegible]	14
-6	45	43
-7*	0	4
K,L=	12	5
0	15	13
1	47	48
-1	[illegible]	-23
-2*	[illegible]	-8
-3*	[illegible]	-1
-4	15	1
-5	33	35
-6	[illegible]	21
K,L=	3	6
-1*	[illegible]	4
-2	[illegible]	-21
-3	18	3
-4*	[illegible]	-5
-5*	[illegible]	13
K,L=	0	6
0	95	-95
2	23	22
4*	[illegible]	-9
-2	38	-37
-4	33	33
-6	94	-94
-8	64	62
K,L=	1	6
0	[illegible]	11
1	28	-30
2	29	-28
3	28	28
4*	[illegible]	[illegible]
-1	33	-28
-2	[illegible]	40
-3	[illegible]	-39
-4	29	30
-5	77	-78
-6	18	18
-7	17	-18
-8	26	-30
-9	55	54
-10	17	20
-11*	[illegible]	2
K,L=	2	6
0	30	-31
1*	[illegible]	-5
2*	[illegible]	9
3	19	-16
4	[illegible]	15
-1	16	12
-2	[illegible]	17
-3	98	97
-4	25	-26
-5	[illegible]	21
-6	47	-46
-7	[illegible]	-33
-8	34	32
-9	36	35
-10	19	20
-11*	[illegible]	1
K,L=	3	6
0	12	-12
1	24	-25
2	4	-43
3*	[illegible]	13
4*	[illegible]	13
-1*	[illegible]	3
-2	[illegible]	113
-3	73	81
-4	45	46
-5	1	4
-6*	[illegible]	-9
-7	15	[illegible]
-8	16	-15
-9*	[illegible]	5
-10	25	25
-11	16	-14
K,L=	4	6

H	FO	FC
0	17	14
1	54	-55
2*	0	-2
3	11	4
4	25	29
-1	22	28
-2	72	69
-3	[illegible]	129
-4*	9	3
-5	48	-45
-6	11	0
-7	28	-32
-8	13	-15
-9	26	27
-10	14	11
K,L=	5	6
0	44	-45
1	19	17
2	15	-16
3*	0	11
4	22	20
-1*	0	-6
-2	52	64
-3	116	119
-4*	0	17
-5	13	5
-6	71	-70
-7	22	-24
-8	21	16
-9	12	12
-10*	0	9
K,L=	6	6
0	19	-12
1	49	-51
2*	0	-6
3	11	12
-1	11	9
-2	47	48
-3*	0	7
-4	70	67
-5	34	-36
-6*	0	9
-7	29	-26
-8	14	-18
-9*	0	0
-10	15	-18
K,L=	7	6
0	31	-30
1*	0	-2
2	13	0
3*	0	8
-1*	0	-5
-2	21	-20
-3	25	22
-4	11	-7
-5*	0	-11
-6	65	-64
-7	27	-15
-8	10	7
-9*	0	0
K,L=	8	6
0	20	-26
1*	0	-12
2*	0	-2
-1	18	-9
-2*	0	-2
-3	45	-45
-4*	0	1
-5	13	-18
-6	13	-3
-7*	0	-2
-8*	0	5
-9*	0	9
K,L=	9	6
0	14	-14
1	31	-33
2*	0	10
-1*	0	-6
-2*	0	-9
-3	44	-44
-4	22	-22
-5	14	2
-6*	0	-1
-7	17	15
-8	14	21

H	FO	FC
K,L=	10	6
0	15	-10
1*	0	10
-1*	0	-7
-2	35	-37
-3*	0	-2
-4	26	-30
-5	12	-11
-6	20	-21
-7	24	23
K,L=	11	6
0	17	12
-1	15	-14
-2	14	8
-3	21	-25
-4	23	-20
-5	12	-8
-6	40	43
K,L=	12	6
-2	10	-11
-3	11	3
-4*	0	-5
-5	15	15
K,L=	0	7
0	19	-21
2	37	-33
-2	39	40
-4*	0	4
-6*	0	-4
-8	53	-50
-10	58	-58
K,L=	1	7
0	19	-10
1	29	-24
2*	0	5
3	34	-34
-1	26	23
-2	24	19
-3	32	-33
-4*	0	1
-5	33	35
-6	16	-11
-7	30	-29
-8*	0	-4
-9	45	-45
-10*	0	9
K,L=	2	7
0*	0	-3
1	14	-9
2	19	-12
3	18	26
-1	22	-20
-2*	0	6
-3	28	27
-4	14	4
-5	17	-21
-6*	0	0
-7*	0	7
-8*	0	-9
-9	14	20
-10	18	-14
K,L=	3	7
0	17	-16
1	14	9
2	13	15
-1	11	5
-2*	0	2
-3	22	21
-4	15	25
-5*	0	0
-6*	9	-14
-7*	0	10
-8	17	-13
-9	11	-2
-10	35	31
K,L=	4	7
0	39	39
1	10	-4
2*	0	4
-1	21	-22
-2	26	-26
-3	29	28
-4	18	-10
-5	13	10
-6	39	41

H	FO	FC
-7	44	-35
-8	20	19
-9	24	20
-10	[illegible]	29
K,L=	5	7
0	25	-29
1	24	26
2	[illegible]	9
-1*	[illegible]	6
-2	13	-12
-3	18	-15
-4	31	35
-5	16	-10
-6	27	-27
-7	59	59
-8	12	-4
-9	15	17
K,L=	6	7
0	41	39
1	19	-20
-1*	[illegible]	-11
-2	15	-20
-3	[illegible]	25
-4	34	-32
-5	11	4
-6	40	45
-7	35	-39
-8*	[illegible]	2
-9*	[illegible]	4
K,L=	7	7
0	30	-30
1*	[illegible]	9
-1*	[illegible]	3
-2	19	17
-3	40	-40
-4	10	21
-5	11	4
-6	30	-34
-7	24	29
-8*	9	-1
K,L=	8	7
0*	[illegible]	-4
-1*	[illegible]	-7
-2*	[illegible]	-6
-3	19	14
-4	19	-19
-5*	[illegible]	3
-6*	[illegible]	-6
-7*	[illegible]	-12
-8	15	3
K,L=	9	7
-1	17	5
-2	14	9
-3	12	-25
-4	17	12
-5*	[illegible]	15
-6*	[illegible]	-1
-7	27	-22
K,L=	10	7
-2*	[illegible]	5
-3*	[illegible]	1
-4*	[illegible]	-6
-5*	[illegible]	10
-6*	[illegible]	-6
K,L=	0	8
0	20	-22
-2	16	-15
-4	48	-48
-6	52	-50
-8*	[illegible]	12
K,L=	1	8
0*	[illegible]	-7
1	13	17
-1	20	-30
-2*	[illegible]	-2
-3	33	-33
-4*	[illegible]	5
-5	24	-23
-6	21	-17
-7	29	-33
-8*	[illegible]	-12
-9	30	35
K,L=	2	8
0*	[illegible]	-3
-1	[illegible]	-23

H	FO	FC
-2	19	-15
-3	20	19
-4*	0	-12
-5*	0	12
-6	19	-12
-7	22	-24
-8*	0	3
-9	19	15
K,L=	3	8
0	25	-27
-1*	0	1
-2*	0	8
-3	13	18
-4	16	20
-5	10	7
-6	21	-25
-7*	0	0
-8	11	-15
-9*	0	-2
K,L=	4	8
0*	0	8
-1	18	-13
-2*	0	2
-3	26	34
-4	54	61
-5*	0	-5
-6*	0	11
-7	27	-30
-8	16	-8
-9*	0	9
K,L=	5	8
-1*	0	2
-2	14	12
-3	57	63
-4	28	33
-5	21	24
-6*	0	-18
-7	11	12
-8	15	-10
K,L=	6	8
-1*	0	-9
-2	16	13
-3	28	28
-4	58	65
-5	11	4
-6*	0	-4
-7	30	-34
K,L=	[illegible]	8
-2*	0	2
-3	25	25
-4	29	28
-5	19	17
-6	21	-19
-7	13	-11
K,L=	8	8
-4	11	-1
-5*	6	8
K,L=	0	9
-4	17	-18
-6	25	21
K,L=	1	9
-3*	0	3
-4*	0	-1
-5*	0	1
-6*	0	4
-7*	0	0
K,L=	2	9
-3*	0	13
-4*	0	-10
-5	17	15
-6	20	0
-7	17	-14
K,L=	3	9
-4	14	17
-5	22	-13
-6*	0	5
K,L=	4	9
-5	14	23

the overlapping TCNB molecule. The equation of the plane of the aromatic ring is expressed as

$$-0{\cdot}3149X+0{\cdot}3708Y+0{\cdot}8737Z=3{\cdot}300\,.$$

This plane makes an angle of 67·6° with the c axis.

Intermolecular atomic distances less than 3·6 Å are listed in Table 4. The molecules illustrated in Fig. 3 were chosen as the original unit in Table 4. The mean interplanar spacing between the overlapping TCNB molecule and the aromatic ring of the PD molecule is 3·37 Å. This is the shortest interplanar spacing hitherto reported among the π–π type TCNB complexes. The atomic distances between overlapping molecules are of the order of generally accepted van der Waals distances, excepting the shortest, which is between N(1) and C(4) (3·16 Å). The same short atomic distance was observed in the crystal of TMPD–TCNB, where the mode of overlapping of the component molecules is very similar to that observed in PD–TCNB (Fig. 2). The usual π–π charge transfer interaction seems to be predominant in this complex. The n–π interaction, however, may exist to a small extent between the lone-pair electron of the amino group and the π-electron system of the aromatic ring of TCNB, since the distance from the nitrogen atom N(1) to the plane of TCNB is 3·13 Å.

Among the adjacent columns, short intermolecular contacts are observed between the nitrogen atom N(3) in the original unit and the amino group in unit 2 (Table 4). The distance N(3)···N(1) is 3·18 Å and

Table 4. *Intermolecular atomic distances less than* 3·6 Å

(*a*) Between the overlapping molecules in the original unit

C(1)···C(5′)	3·513 (4) Å		
C(1)···C(6′)	3·384 (4)	H(1)···C(6)	3·480 (15) Å
C(1)···C(8′)	3·599 (4)	H(1)···C(8′)	3·328 (17)
C(2)···C(4)	3·432 (4)	H(2)···C(5)	3·542 (20)
C(2)···C(6′)	3·417 (4)	H(2)···C(6)	3·307 (18)
C(3)···C(6)	3·397 (4)	H(2)···C(8)	3·520 (16)
C(1′)···C(7′)	3·515 (4)	H(4)···H(5)	3·496 (24)
C(1′)···C(4′)	3·435 (4)	H(4)···C(5)	3·489 (19)
C(3′)···C(5′)	3·564 (5)	H(3)···C(7)	3·447 (20)
N(1)···C(4)	3·164 (4)	H(5′)···C(3′)	3·419 (16)
N(1)···C(5)	3·425 (4)	H(1′)···C(7′)	3·461 (17)
N(1)···C(7)	3·330 (4)		

(*b*) From the original to unit 2

N(2)···N(3)	3·562 (4) Å	N(3′)···N(1′)	3·183 (3) Å
N(2)···H(1)	3·070 (13)	N(3′)···H(1′)	3·100 (15)
C(8′)···H(3′)	3·459 (15)	N(3′)···H(3′)	2·374 (15)

(*c*) From the original to unit 3

N(1)···H(2)	2·982 (18) Å	C(7)···H(4)	3·599 (16) Å
N(2)···N(1)	3·424 (3)	H(3)···C(3)	3·424 (19)
N(2)···H(2)	2·932 (18)	H(3)···H(2)	2·776 (26)
N(2)···H(4)	2·696 (16)	H(4)···C(3)	3·371 (20)
N(2)···C(5)	3·390 (3)	H(4)···H(2)	2·719 (28)
N(2)···H(5)	2·788 (17)	H(4)···H(1′)	3·250 (25)
C(5)···N(3)	3·591 (3)	H(5)···C(8)	3·419 (16)
C(7)···H(2)	3·270 (16)	H(5)···N(3)	2·668 (17)

Symmetry code:

1	x	y	z
2	$x+1$	y	z
3	$x+\frac{1}{2}$	$-y+\frac{1}{2}$	z

N(3)···H(3) is 2·37 Å. The three atoms N(1), H(3) and N(3) are approximately on a straight line. These observations indicate weak hydrogen bonding between N(1) and N(3).

Thermal motion

The thermal motion ellipsoids of the individual atoms are illustrated in Fig. 3, which was drawn using *ORTEP* (Johnson, 1965) and a plotter from the direct output of the HITAC 5020E computer at the Computer Centre of the University of Tokyo. The molecular motion has been analysed in terms of the rigid-body vibrations of translation (**T**) and libration (**ω**), using the approach described by Cruickshank (1956*a*). Rigid-body thermal parameters are given in Table 5. The libration around the axis, about which the moment of inertia is a minimum, has the largest r.m.s. amplitude in both molecules. The bond lengths have been

Table 5. *Rigid-body thermal parameters*

(*a*) Principal axes of the molecules in the form: $L\mathbf{a}+M\mathbf{b}+N\mathbf{c}$

TCNB Moment of inertia (A.W. × Å²)	L	M	N	PD Moment of inertia (A.W. × Å²)	L	M	N
384·5	0·1226	0·0010	0·0555	68·9	0·0662	0·0608	−0·0175
1018·3	0·0044	−0·0765	0·0473	292·5	0·1028	−0·0429	0·0738
1402·8	0·0082	0·0261	0·1367	361·3	0·0124	0·0314	0·1350

(*b*) Molecular vibrational tensors

	TCNB					PD			
	511	71	9			448	−13	1	
$\mathbf{T}\times10^4$		340	29	Å²	$\mathbf{T}\times10^4$		503	12	Å²
			267					268	
	269	−39	−21			293	18	0	
$\boldsymbol{\omega}\times10$		134	−9	(°)²	$\boldsymbol{\omega}\times10$		175	−7	(°)²
			78					67	

(*c*) Principal axes of the **T** and **ω** tensors relative to the molecular axes

TCNB R.m.s. amplitude	Direction cosines			PD R.m.s. amplitude	Direction cosines		
0·160 Å	0·068	−0·370	0·926	0·164 Å	−0·008	−0·052	0·999
0·180	0·345	−0·862	−0·370	0·211	−0·975	−0·221	−0·019
0·232	0·936	0·345	0·069	0·225	−0·222	0·974	0·048
2·70°	0·148	0·235	0·961	2·58°	−0·005	0·068	0·998
3·58	−0·217	−0·940	0·263	4·16	0·145	−0·987	0·068
5·30	0·965	−0·248	−0·088	5·43	0·989	0·145	−0·005

Table 6. *Bond lengths and angles with their estimated standard deviations*

PD	Obs.	Corrected for thermal motion	TCNB	Obs.	Corrected for thermal motion
C(1)–C(2)	1·392 (3) Å	1·398 Å	C(4)–C(5)	1·381 (3) Å	1·386 Å
C(2)–C(3)	1·396 (3)	1·402	C(4)–C(7)	1·447 (3)	1·450
C(1)–C(3′)	1·382 (3)	1·388	C(4)–C(6′)	1·400 (3)	1·405
C(2)–N(1)	1·399 (3)	1·402	C(5)–C(6)	1·391 (3)	1·396
C(1)–H(1)	0·97 (1)		C(6)–C(8)	1·446 (3)	1·449
C(3)–H(2)	1·01 (1)		C(7)–N(2)	1·136 (3)	1·137
N(1)–H(3)	0·83 (1)		C(8)–N(3)	1·133 (3)	1·134
N(1)–H(4)	0·86 (2)		C(5)–H(5)	0·99 (1)	
C(1)–C(2)–C(3)	117·9 (2)°		C(4)–C(5)–C(6)	119·0 (2)°	
C(2)–C(1)–C(3′)	121·2 (2)		C(5)–C(4)–C(6′)	120·2 (2)	
C(2)–C(3)–C(1′)	120·9 (2)		C(5)–C(6)–C(4′)	120·8 (2)	
C(1)–C(2)–N(1)	121·4 (2)		C(5)–C(4)–C(7)	120·1 (2)	
C(3)–C(2)–N(1)	120·5 (2)		C(5)–C(6)–C(8)	119·6 (2)	
C(2)–C(1)–H(1)	117·6 (8)		C(7)–C(4)–C(6′)	119·7 (2)	
C(2)–C(3)–H(2)	117·6 (9)		C(8)–C(6)–C(4′)	119·6 (2)	
H(1)–C(1)–C(3′)	121·2 (8)		C(4)–C(7)–N(2)	178·9 (2)	
H(2)–C(3)–C(1′)	121·5 (9)		C(6)–C(8)–N(3)	179·5 (2)	
C(2)–N(1)–H(3)	115·8 (10)		C(4)–C(5)–H(5)	122·0 (9)	
C(2)–N(1)–H(4)	117·4 (13)		C(6)–C(5)–H(5)	119·0 (9)	
H(3)–N(1)–H(4)	112·6 (16)				

corrected by rigid-body analysis for the effect of the thermal motion (Cruickshank, 1956*b*, 1961) and the lengths and angles are given in Table 6.

Molecular structure

No crystal structure of the complex formed by PD as a donor has yet been reported. The molecular structure of TMPD, however, has been studied in a number of complexes. The results are summarized in Table 7. From molecular orbital calculations (Monkhorst & Kommandeur, 1967), the difference between central and non-central bonds is estimated to be 0·014 Å for TMPD and 0·049 Å for $TMPD^+$. The molecular dimensions of TMPD in the complexes which are considered to have ionic ground states are also available (Hanson, 1965, 1968; de Boer, Vos & Huml, 1968; de Boer & Vos, 1968). In these complexes, some quinonoid character is observed in the ring of TMPD, and the differences in the bond lengths between central and non-central bonds range from 0·028 to 0·061 Å. This quinonoid character is also reflected in the shortening of the C–N bonds. In the molecule of PD in the present structure, the difference between the central and non-central bond lengths is 0·012 Å and the C–N bond length is 1·402 Å. Neither quinonoid structure in the ring nor shortening of the C–N bond is observed.

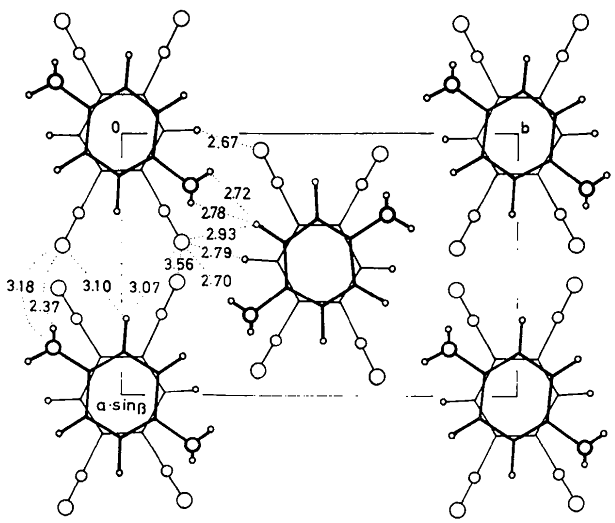


Fig. 1. The molecular arrangement viewed along the *c* axis.

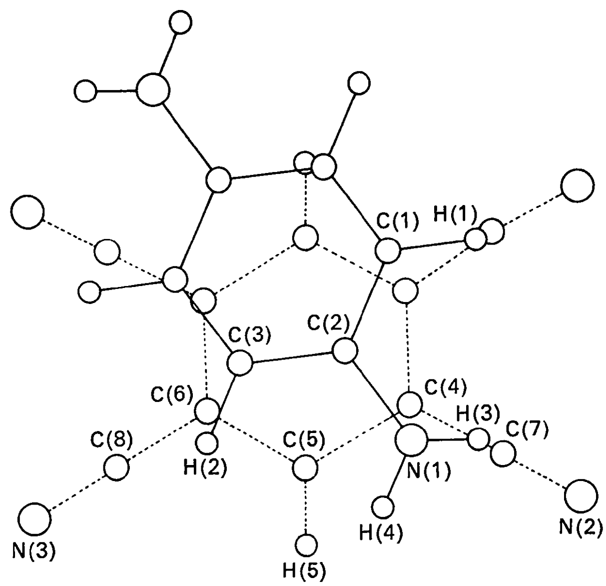
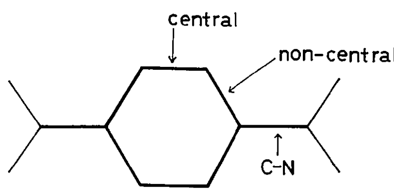


Fig. 2. The mode of overlapping of the component molecules in the crystal of PD–TCNB.

Table 7. *Bond lengths* (Å) *of TMPD and PD in various complexes*



	Central	Non-central	Δ	C–N		Reference
$TMPD^+I^-$	1·361	1·422	0·061	1·344	pyramidal	(1)
TMPD: TCNQ	1·374	1·416	0·042	1·365	pyramidal	(2)
TMPD: chloranil	1·374	1·402	0·028	1·357	planar	(3)
TMPD: $TCNQ_2$	1·367	1·417	0·050	1·373	pyramidal	(4)
TMPD: TCNB	1·377	1·380	0·003	1·430	pyramidal	(5)
PD: TCNB	1·388	1·400	0·012	1·402	pyramidal	(6)

(1) de Boer, Vos & Huml (1968).
(2) Hanson (1965).
(3) de Boer & Vos (1968).
(4) Hanson (1968).
(5) Ohashi, Iwasaki & Saito (1967).
(6) This investigation.

The molecular dimensions of s-triaminobenzene (TAB) in the complex with s-trinitrobenzene have been reported (Iwasaki & Saito, 1970). In the TAB molecule the mean C–N bond length is 1·398 Å, which is in accordance with that observed in the PD molecule. Thus, the ground state of PD seems to be non-ionic.

The amino group of the PD molecule exhibits tetrahedral character. The nitrogen atom is 0·09 Å above the plane of the aromatic ring; that is, the C–N bond makes an angle of 3·7° with this plane.

The molecular dimensions of TCNB in the π–π charge transfer complexes are compared in Table 8. All six complexes are considered to have non-ionic ground states. The skeleton of the TCNB molecule does not seem to differ significantly in the series, regardless of the ionization energy of the donor molecule. Averaging the dimensions of the TCNB molecules observed in the crystals of PD–TCNB and of anthracene–TCNB, bond lengths (1), (2) (4) and (6) are 1·392, 1·403, 1·446 and 1·135 Å respectively,

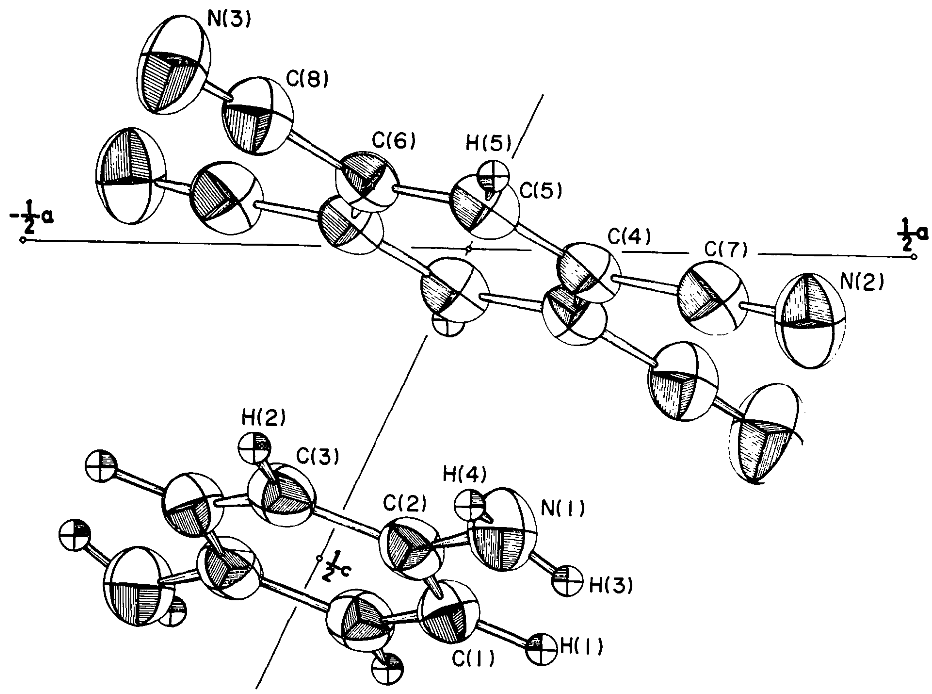
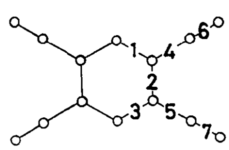


Fig. 3. The *ORTEP* plot of the thermal ellipsoid with a probablity of 50%, viewed along the b axis.

Table 8. *Molecular dimensions* (Å) *of TCNB in various complexes and ionization energies* (kcal mol^{-1}) *of the donor molecules*



Donor	Ionization energy	1	2	3	4	5	6	7	Reference
Durene	8·3	1·37	1·39	1·42	1·44	1·42	1·14	1·12	(1)
HMB	8·0	1·38	1·41	1·39	1·44	1·44	1·13	1·11	(2)
TMPD	6·5	1·36	1·39	1·39	1·47	1·44	1·12	1·12	(3)
Naphthalene	8·2	1·38	1·43		1·45		1·13	1·13	(4)
Anthracene	7·5	1·393	1·401		1·443		1·134		(5)
PD		1·386	1·405	1·396	1·450	1·449	1·137	1·134	

(1) Tsuchiya, Niimura & Saito , unpublished.
(2) Niimura, Ohashi & Saito (1968).
(3) Ohashi, Iwasaki & Saito (1967).
(4) Kumakura, Iwasaki & Saito (1969).
(5) Tsuchiya, Marumo & Saito (1972).

where the molecule is assumed to have the symmetry $2/m$. Bond (1) is shorter than bond (2) by 0·011 Å. This tendency is also observed in other TCNB molecules. Iwata, Tanaka & Nagakura (1966) showed that bond (1) should be shorter than bond (2) by about 0·03 Å.

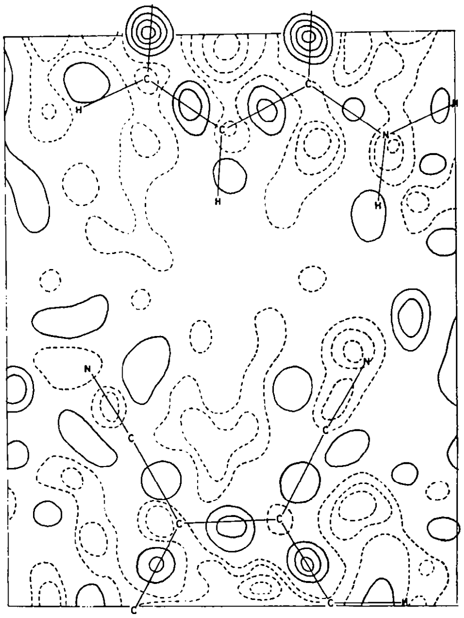


Fig. 4. The difference Fourier map through the plane ($\bar{1}12$). Solid contours show positive density at intervals of 0·05 e Å^{-3}, starting with 0·05 e Å^{-3}. Broken contours show negative density at the same intervals, starting with −0·05 e Å^{-3}.

Bonding electron effect

A difference Fourier synthesis was calculated in the plane ($\bar{1}12$). This section, passing nearly through the molecular plane, shows residual bonding electron peaks at the centre of each bond, excepting the C–N triple bond (Fig. 4). In the aromatic ring particularly, σ-bonding electrons definitely appear. The maximum values of the bonding electron density in the aromatic ring range from 0·11 to 0·21 eÅ^{-3}. A density of about 0·07 eÅ^{-3} appears between the carbon atom of the ring and the carbon atom of the cyano group or the nitrogen atom of the amino group. The C–N triple bond is characterized by a negative density region around the centre of the bond. This feature is the same as that observed in the crystals of *cis*-1,2,3-tricyanopropane (Hartman & Hirshfeld, 1966) and of anthracene–TCNB (Tsuchiya, Marumo & Saito, 1972). Sections of difference Fourier map through the middle of and perpendicular to the C–N triple bonds are shown in Fig. 5. Three positive blocks are observed surrounding each triple bond. A circle of a radius 0·7 Å can be drawn passing through these positive regions. As in the case of anthracene–TCNB, these residual peaks are thought to be due to the π-bonding electrons.

Fourier syntheses were carried out on the FACOM 270-30 computer at this Institute. The remaining calculations were performed on the HITAC 5020E

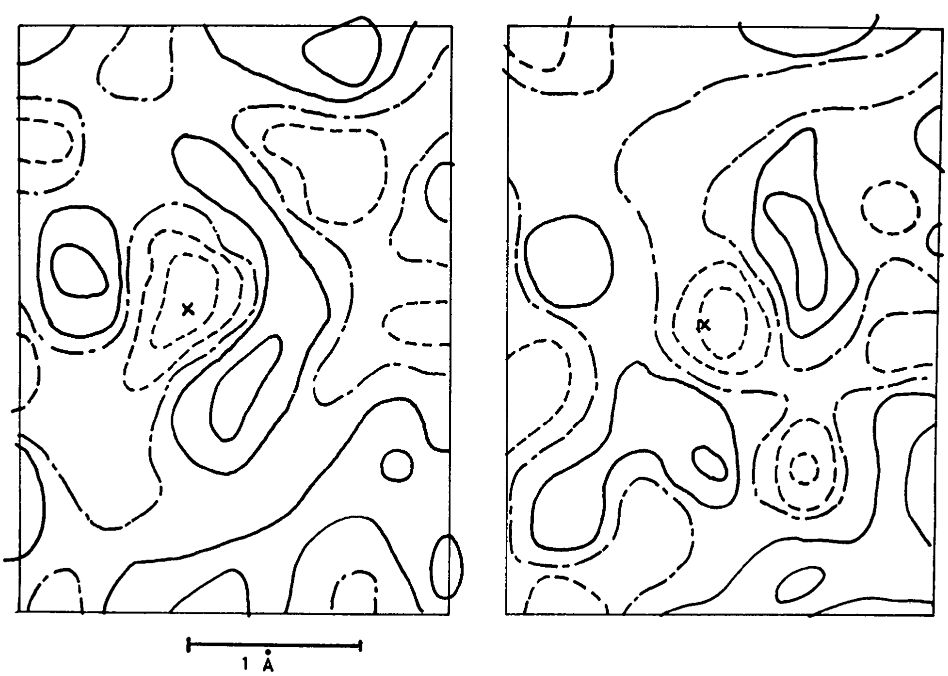


Fig. 5. Sections of difference Fourier synthesis perpendicular to and through the middle of C–N triple bonds. Crosses indicate the points of intersection of the triple bonds. Contours are at intervals of 0·04 e Å^{-3}. Broken and chain contours indicate negative and zero density respectively.

computer at the Computer Centre of the University of Tokyo with the program system UNICS (1967).

The authors are grateful to Professor Toshio Mitsui who kindly allowed them to use the X-ray diffractometer at Hokkaido University. This research was aided in part by a Scientific Research Grant from the Ministry of Education.

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Structure Cristalline du Dichloro-2,5 Phénol

PAR C. BAVOUX ET M. PERRIN

Laboratoire de Minéralogie-Cristallographie, Université Claude Bernard (Lyon I), 43 *boulevard du* 11 *Novembre* 1918, 621-*Villeurbanne, France*

(*Reçu le* 11 *octobre* 1972, *accepté le* 23 *novembre* 1972)

2,5-Dichlorophenol is monoclinic, space group $P2_1$, with $a=5{\cdot}702$ (4), $b=4{\cdot}887$ (3), $c=12{\cdot}439$ (9) Å, $\beta=107{\cdot}91$ (5); formula $C_6H_4OCl_2$, $Z=2$, $D_x=1{\cdot}64$ g cm^{-3}. 763 independent reflexions were measured. The structure was solved by Patterson methods and refined by least-squares to give a final R of 0·088. 2,5-Dichlorophenol is isotypic with 2,5-dimethylphenol. There are hydrogen bonds between molecules.

Introduction

Les cristaux ont été obtenus par évaporation lente d'une solution de dichloro-2,5 phénol dans le benzène à partir de produit préalablement purifié par sublimation; étant hygroscopiques, ils ont été placés dans des tubes de Lindemann.

Les paramètres de la maille ont été déterminés après dépouillement de clichés de Weissenberg. Ils ont été par la suite affinés d'après les données fournies par le diffractomètre. Les extinctions systématiques pour les réflexions $0k0$ ont été observées lorsque $k=2n+1$. Le groupe $P2_1/m$, possible avec ces lois d'extinction, a été rejeté dans la suite de l'étude.

Les intensités ont été obtenues avec un cristal de dimensions approximatives $0{,}2\times0{,}1\times0{,}4$ mm. Les mesures ont été effectuées au Laboratoire de Cristallographie de la Faculté des Sciences de Bordeaux sur un diffractomètre automatique Siemens. La radiation $K\alpha$ du cuivre a été utilisée; 763 réflexions indépendantes, dont 747 réellement observables, ont été mesurées. Les intensités obtenues ont été corrigées du facteur de Lorentz et du facteur de polarisation; on n'a pas tenu compte de l'absorption.

La structure a été résolue par les méthodes de Patterson qui ont permis de localiser facilement, d'abord les 2 chlores indépendants de l'unité assymétrique, puis ensuite les carbones et l'oxygène.

L'affinement par moindres carrés a été effectué en minimisant la quantité:

$$\sum w(|F_o|-|F_c|)^2\,,$$

le modèle final inclut le facteur de température anisotrope pour les atomes Cl, C et O, mais il n'a pas été possible d'obtenir les hydrogènes par séries différences, le point de fusion (55,3°C) étant trop proche de la température d'expérimentation et l'agitation thermique trop grande. L'indice

$$R=\frac{\sum|w(F_o)-(F_c)|}{\sum|w(F_o)|}$$