Acta Cryst. (1971). B**27**, 1360

The Crystal and Molecular Structure of 11,11,12,12-Tetracyano-1,4-naphthaquinodimethane

BY FUJIKO IWASAKI

Department of Materials Science, The University of Electro-Communications, Chofu-shi, Tokyo, Japan

(*Received* 27 *July* 1970)

Crystals of 11,11,12,12-tetracyano-1,4-naphthaquinodimethane, $C_{16}H_6N_4$, are orthorhombic, space group *Pbca* with cell dimensions: $a=13·210$, $b=7·209$, $c=26·629$ Å and $Z=8$. The structure was determined by a three-dimensional X-ray analysis using visually estimated Cu $K\alpha$ data. Phases were found by the symbolic-addition procedure and the subsequent refinement was carried out by the block-diagonal least-squares method with anisotropic temperature factors, the final R value being 0·085 for 1999 observed reflexions. Bond distances are in reasonable agreement with the corresponding values for the related substances, but the bond angles related to dicyanomethylene groups are significantly different because of relieving intramolecular overcrowding. The naphthalene skeleton is folded out by 15·3° and the quinonoid ring is distorted into the shape of a boat. Non-bonded intramolecular distances C···C (2·966 Å) are close to the typical value of 3·0 Å for non-bonded interactions of this type.

Introduction

11,11,12,12-Tetracyano-1,4-naphthaquinodimethane (TCNNQ) forms charge-transfer complexes with aromatic hydrocarbons, similar to the analogous compounds tetracyanoethylene (TCNE) and 7,7,8,8-tetracyanoquinodimethane (TCNQ). TCNNQ acts as a strong acceptor of electrons and its electronegativity is estimated as 1·5 eV (Chatterjee, 1967).

In contrast with TCNE and TCNQ which are planar, TCNNQ is considered subject to molecular deformation as a consequence of the intramolecular overcrowding from the addition of an aromatic ring to TCNQ moiety. The crystal-structure analysis was undertaken to investigate the detailed molecular geometry of TCNNQ itself and provide a standard for a series study on its charge-transfer complexes.

Experimental

The crystals of TCNNQ supplied were obtained from methylene bromide solution as yellow plates. Cell dimensions were calibrated with copper powder lines superposed on Weissenberg photographs (Cu K, $\bar{\alpha}=1·5418$, $\alpha_1=1·5405$, $\alpha_2=1·5443$ and $\beta=1·3922$ Å). The crystal data are: $C_{16}H_6N_4$, M.W. 254·25; orthorhombic, $a=13·210\pm0·003$, $b=7·209\pm0·003$, $c=26·629\pm0·005$ Å, $V=2535·8$ Å^3, $Z=8$; $D_m=1·34$ g.cm^{-3}, $D_x=1·332$ g.cm^{-3}; $F(000)=1040$; $\mu=8$ cm^{-1} (Cu $K\alpha$); systematic absences: $k=2n+1$ for $0kl$, $l=2n+1$ for $h0l$, $h=2n+1$ for $hk0$; space group: *Pbca* (No. 61–D_{2h}^{15}).

Intensity data were collected from integrated equi-inclination Weissenberg photographs around the a and b axes, $0kl\sim9kl$ and $h0l\sim h4l$, using Cu $K\alpha$ radiation. The intensities were estimated visually by comparison with a standard scale. A total of 1999 non-zero reflexions were observed. The crystals used for intensity-data collection were approximately cylindrical in form having an average radius of 0·2 mm. No absorption corrections were made. The usual Lorentz, polarization and spot-shape corrections were applied and interlayer scale factors were refined by a least-squares method.

Structure determination

An approximate scale factor and average temperature factor were obtained by Wilson's method. After an unsuccessful effort to obtain a trial structure through interpretation of the sharpened Patterson function, the structure was solved by the symbolic-addition procedure (Karle & Karle, 1963). Program *SIGMA* written by Dr T. Ashida was utilized to list the Σ_2 relationships for each reflexion and to calculate the associated probabilities. Signs of 134 reflexions out of 318 with $|E|\geq1·5$ were determined manually. The naphthalene skeleton and a part of the dicyanomethylene groups were found from an E map based on computations using these phases. The remaining three atoms, C(13), N(1) and N(3), were located by assuming that the molecule was almost planar. Five cycles of block-diagonal least-squares refinement of these atoms with isotropic temperature factors gave an R value of 0·35 for all reflexions but temperature factors of C(13), N(1) and N(3) atoms became enormously large. A three-dimensional Fourier synthesis was calculated and from the resultant map it was found that these three atoms had been misplaced by about 1 Å. The parameters of these atoms were corrected in accordance with the Fourier synthesis. After additional cycles of isotropic least-squares refinement the R value decreased to 0·145. At this stage anisotropic temperature factors were introduced and refinement was continued to reduce the R value to 0·12. Hydrogen atoms were located from a difference Fourier synthesis (Fig. 1) and were included in the least-squares refinement with isotropic temperature factors. The R value was reduced to 0·086 after four cycles of least-squares refinement excluding 24 strong reflexions which needed extinction corrections. They were corrected according to the formula $I_o = I_{\text{corr}} \exp(-g\, I_{\text{corr}})$. The constant g was estimated graphically. Four more cycles of block-diagonal least-squares refinement 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 0·085 for all the observed reflexions. Atomic scattering factors for carbon and nitrogen were taken from *International Tables for X-ray crystallography* (1962). For hydrogen, the values given by Stewart, Davidson & Simpson (1965) were used. The quantity $\Sigma w(kF_o - F_c)^2$ was minimized where w is the weight function and k is the scale factor. The weighting scheme employed was $w = (30/|F_o|)^2$ if $|F_o| > 30$, $w = 1$ if $30 \geq |F_o| \geq 8$ and $w = 0{\cdot}2$ if $|F_o| < 8$.

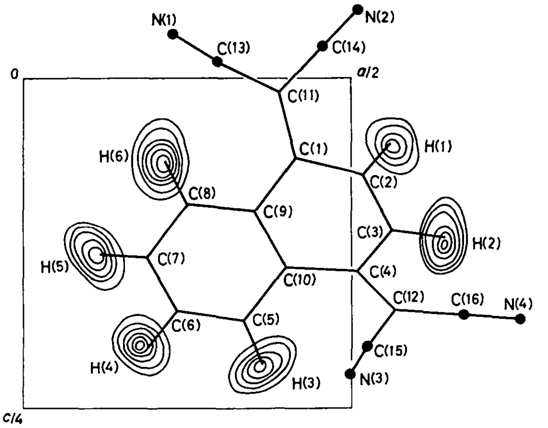


Fig. 1. Sections of the three-dimensional difference Fourier synthesis through the atomic centres parallel to (010). Contours are at intervals of 0·1 e.Å^{-3}, starting with 0·1 e.Å^{-3}.

Final atomic parameters are listed in Tables 1 and 2. Standard deviations in positional coordinates were: C = 0·0035, N = 0·004 and H = 0·04 Å. A comparison of the observed and calculated structure factors is given in Table 3.

Table 2. *Fractional coordinates* (× 10^3) *and thermal parameters* (Å^2) *of hydrogen atoms*

	x	y	z	B
H(1)	562 (3)	−292 (6)	049 (2)	4·3 (1·0)
H(2)	643 (3)	−174 (5)	121 (1)	3·8 (0·9)
H(3)	364 (3)	104 (6)	215 (1)	4·0 (0·9)
H(4)	191 (3)	110 (5)	204 (1)	3·3 (0·9)
H(5)	119 (3)	−012 (5)	133 (1)	2·6 (0·7)
H(6)	217 (3)	−133 (6)	063 (1)	3·9 (0·9)

Results and discussion

Thermal motion

Thermal-motion ellipsoids of the individual atoms are shown in Fig. 2. 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*). Some rigid parameters for the 12 innermost atoms [C(1)–C(12)] of the molecule are given in Table 4. The translational motion is not markedly anisotropic, while libration is quite anisotropic and the axis of the greatest libration corresponds approximately to the long axis of the whole molecule. The bond lengths were corrected for the thermal-motion effect indicated by the rigid-body analysis (Cruickshank, 1956*a*; 1961). A similar analysis was carried out for the entire TCNNQ molecule. This analysis has been used for correcting the remaining C–C bond lengths. (The differences in bond distances cor-

Table 1. *Final atomic parameters of non-hydrogen atoms and their estimated standard deviations* (*all quantities* × 10^4)

The anisotropic temperature factors are of the form:

$$\exp\,[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$$

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(1)	4175 (2)	−1499 (5)	0592 (1)	30 (2)	95 (6)	10 (0)	−9 (3)	−0 (1)	0 (2)
C(2)	5191 (3)	−2082 (5)	0738 (1)	32 (2)	125 (7)	12 (1)	7 (3)	−1 (1)	−2 (2)
C(3)	5632 (3)	−1404 (5)	1156 (1)	36 (2)	152 (8)	12 (1)	9 (3)	−1 (1)	−2 (2)
C(4)	5099 (3)	−0074 (5)	1468 (1)	39 (2)	127 (7)	9 (0)	−4 (3)	−2 (1)	5 (2)
C(5)	3384 (3)	0522 (5)	1832 (1)	44 (2)	150 (8)	9 (0)	−2 (4)	1 (1)	−1 (2)
C(6)	2338 (3)	0480 (5)	1788 (1)	38 (2)	162 (9)	11 (1)	3 (4)	4 (1)	−1 (2)
C(7)	1893 (3)	−0114 (5)	1346 (1)	30 (2)	150 (7)	10 (0)	3 (3)	1 (1)	1 (2)
C(8)	2482 (2)	−0725 (5)	0948 (1)	31 (2)	128 (7)	9 (0)	−0 (3)	1 (1)	2 (2)
C(9)	3534 (2)	−0697 (5)	0981 (1)	35 (2)	90 (6)	8 (0)	2 (3)	−1 (1)	2 (1)
C(10)	3990 (2)	−0034 (5)	1431 (1)	39 (2)	107 (6)	8 (0)	−4 (3)	−0 (1)	4 (1)
C(11)	3902 (2)	−1735 (5)	0094 (1)	29 (2)	112 (6)	9 (0)	−6 (3)	2 (1)	−3 (2)
C(12)	5665 (3)	1112 (5)	1764 (1)	39 (2)	167 (8)	8 (0)	−8 (3)	−2 (1)	4 (2)
C(13)	2997 (3)	−1058 (5)	−0134 (1)	39 (2)	163 (8)	9 (0)	−5 (3)	1 (1)	−6 (2)
C(14)	4586 (3)	−2592 (5)	−0253 (1)	40 (2)	134 (7)	10 (0)	−1 (3)	3 (1)	−7 (2)
C(15)	5260 (3)	2657 (6)	2028 (1)	45 (2)	189 (9)	11 (1)	−14 (4)	−6 (1)	−9 (2)
C(16)	6740 (3)	0949 (6)	1798 (2)	47 (2)	201 (9)	12 (1)	−14 (4)	−5 (1)	2 (2)
N(1)	2295 (2)	−0514 (6)	−0334 (1)	50 (2)	279 (11)	13 (1)	23 (4)	−4 (1)	−0 (2)
N(2)	5127 (3)	−3237 (5)	−0535 (1)	53 (2)	222 (9)	14 (1)	−7 (4)	6 (1)	−12 (2)
N(3)	4973 (3)	3945 (6)	2244 (2)	64 (3)	263 (10)	21 (1)	−8 (4)	−7 (1)	−35 (2)
N(4)	7604 (3)	0832 (7)	1830 (2)	40 (2)	347 (13)	25 (1)	−11 (4)	−8 (1)	−1 (3)

Table 3. *Observed and calculated structure factors* (×4)

* indicates reflexions for which $w=0{\cdot}2$.
† denotes the 24 reflexions corrected for extinction.

L	|FO|	FC
H,K= 0 0		
2	211	216
4	179	-228
6†	594	635
8†	380	-416
10	161	153
14	142	-133
16	149	133
18	55	-49
20	62	-66
22	187	177
24	191	-190
26	147	-146
28	101	97
30	45	-44
32*	19	-20
34	49	70
H,K= 1 0		
2†	343	-368
4	89	-82
6†	458	449
8	294	337
10	120	115
12	210	215
14*	28	18
16	57	-52
18	96	85
20	64	68
22	118	-120
24	152	-153
26*	21	13
28	60	59
30*	16	19
32*	22	-20
34*	22	-29
H,K= 2 0		
0	139	198
2	46	45
4	134	132
6†	421	-421
8*	29	19
10	318	-347
12	227	-223
14	374	401
16*	23	-16
18	127	124
20	65	60
22	176	-177
24*	28	-23
26	61	64
28*	16	-18
30*	25	-30
32	46	-55
H,K= 3 0		
2	136	146
4	180	-198
6	262	-282
8	287	-312
10	150	-136
12	157	147
16	111	-95
18*	17	8
22	139	-137
24	38	-40
26*	19	-16
28	43	-43
32	40	-45
H,K= 4 0		
0†	574	725
2	47	-47
4	183	188
6	84	-73
8	310	-348
10	91	-86
12	102	-96
14	47	-44
16	123	-117
18	65	-61
20	67	-66
22	35	-25
28*	12	-2
H,K= 5 0		
2	315	387
4	131	-130
6	129	128
8	119	111
10	151	154
12	229	241
16	83	77
18	43	35
20	33	-28
22	49	-41
24	79	-76
26	51	-55
28*	16	-4
30	34	34
H,K= 6 0		
2	173	-190
4	60	50
6	121	-110
8*	20	3
10*	27	-24
12	59	-52
14	186	179
16*	30	-21
18	32	-29
24*	29	-21
26*	20	18
30*	12	-13
H,K= 7 0		
2	222	228
4	44	43
6	33	26
8*	15	5
12	92	82
14	149	145
16	150	152
18	44	45
20	83	84
22	69	74
24	33	31
26*	16	-9
30	37	43
H,K= 8 0		
0	176	185
2*	23	-20
4	46	45
6	132	-124
8	79	-75
10*	23	17
12	46	51
14	92	87
16	127	-131
18*	26	-22
20	117	120
22	55	55
24*	29	-23
26	33	32
H,K= 9 0		
2	61	49
4*	28	-24
6	70	62
8	109	103
10	69	58
12	185	-188
14	132	-132
16	174	178
18*	13	4
20*	22	-16
22*	17	-20
24	95	-101
26	31	-32
28*	22	-28
H,K= 10 0		
2	68	68
4	91	84
6	47	42
8	152	146
10	186	-197
12	42	-31
14	288	311
16	32	35
18*	23	25
20	46	40
22*	28	-19
24*	14	-6
H,K= 11 0		
4	71	78
6	49	46
8	107	-108
10	63	-62
12	32	27
14	63	68
16	85	83
18	50	-54
22	36	35
24*	17	-15
H,K= 12 0		
0	154	162
2	97	-102
4	103	-106
6	44	-43
8	158	-152
10*	30	-31
12	38	29
14	38	-38
16	40	37
18	37	41
20*	20	17
22	73	83
24	42	-50
H,K= 13 0		
2	55	-48
4	61	-55
6*	25	23
8	55	-52
10	73	-66
12*	27	-28
16	36	41
18	32	-31
20*	8	-9
H,K= 14 0		
0	43	-35
4*	16	-19
6	83	-75
10	39	-43
14*	20	-17
16*	19	-16
18	76	80
H,K= 15 0		
6	63	-57
10	38	33
12	36	-27
14	38	38
16	80	96
H,K= 16 0		
0	37	38
2*	26	-22
4	49	-47
8	38	40
10*	14	11
H,K= 1 1		
1†	416	-450
2*	10	3
3†	319	364
4†	362	-438
5	93	85
6†	405	468
7	276	-307
8	131	122
9	144	135
10	115	109
11	203	-217
12	83	72
13	49	-37
14*	30	-1
15	44	-34
16	49	-39
17*	14	-12
18	67	-54
19*	22	4
20	67	-63
21	75	-63
22*	24	-19
23	52	49
24	38	32
25	81	76
27	61	-60
28	53	-51
29*	26	-22
30*	22	-25
31	61	65
32	39	-43
33*	31	-37
H,K= 2 1		
0†	328	-368
2	168	-185
3	105	105
4	234	-264
5	152	163
6	216	-244
8	47	44
9	61	-51
10	112	-117
11*	23	-20
12	132	-131
14*	21	-19
15	84	76
16*	12	-18
17	66	-49
18*	16	-13
19	114	-110
20*	16	-22
21	69	66
22*	18	-15
23	79	72
24	33	35
25	42	-40
26	75	77
27*	25	-20
30*	13	-13
33*	20	25
H,K= 3 1		
1	104	107
2	76	74
3	80	80
4*	11	-8
5	250	277
6	249	273
7	247	-273
9	131	133
10	206	213
11	211	220
13	39	-26
15	107	-96
16	39	-35
17	119	112
18	120	-115
19	45	43
20*	28	20
21	46	44
22	47	41
23*	17	10
24*	22	21
25	69	-67
26	32	30
27*	14	-12
28	56	-58
29	42	-44
30	37	-35
H,K= 4 1		
0	93	-90
1*	11	-11
2*	17	12
3*	15	20
4	174	-165
5	41	-41
6	153	-147
7	36	27
8	132	125
9	149	151
10	49	35
11	55	-45
12	38	35
13	142	-137
15	118	115
17	132	131
18	64	56
21	55	41
23	69	66
24*	20	19
25	65	66
26	50	47
27*	17	-2
29*	10	-14
30*	29	-31
31*	28	28
32*	19	-20
H,K= 5 1		
1	229	255
2	160	156
3	110	-107
4	78	74
5*	16	17
6	216	226
7	77	-68
8	40	30
9*	13	6
10	157	168
11	185	-189
13	44	-37
14	48	-37
17	37	33
18	43	37
20	112	108
22	116	119
23	60	58
24	79	80
25	42	-41
26	51	55
27*	19	-21
29	42	44
30*	13	-14
31*	20	24
H,K= 6 1		
0*	20	18
1	246	-266
2	142	138
3	137	-131
4	113	-108
5	159	158
6	167	-173
7*	25	22
8	46	37
9	36	-29
10	63	-61
11*	15	8
12	44	39
13*	30	-28
14	38	38
15	46	-36
16	50	46
17	63	-67
18	74	71
19	48	-38
20	34	34
21*	19	-16
22	39	37
23	112	-121
24*	17	17
25	49	-48
26	47	47
27*	27	24
28*	8	14
29	46	-48
30*	11	0
31*	23	-27
H,K= 7 1		
1	80	-73
2	85	84
3	135	129
4*	15	-16
5	35	18
6	123	124
7	74	-63
8*	31	-22
9	80	74
10	58	53
11	93	-87
12	91	-84
13	49	49
14	138	-138
15	59	52
16	93	-90
17	105	109
18*	18	-19
19	67	65
20	33	29
21	79	-77
22*	21	21
23*	17	-9
25*	19	22
27	40	-41
29	32	-38
30*	28	-32
H,K= 8 1		
0	57	46
1*	24	-21
2	115	109
3	74	-68
4*	22	2
5	47	-43
6	53	-51
7	67	-67
8*	24	-24
9	149	-153
10	88	-82
11	76	67
12	86	79
13	131	129
14	90	86
15	46	-40
16	109	108
17*	16	-10
18	90	85
19	46	38
21*	22	-9
22	39	31
23*	12	14
25	37	40
29*	11	-14
H,K= 9 1		
1	98	90
2*	30	-28
3	115	-118
4	71	67
5	111	121
6	74	-71
7	155	-163
8	121	-123
9	72	-70
10	73	73
11	130	130
12	113	-116
13	158	-170
14	67	-63
15	131	-136
16	49	-46
17	132	135
18	79	-77
19	65	-65
20	52	44
21	41	-37
22*	30	23
23	59	61
24*	17	-18
25	40	-35
26*	29	28
27*	19	20
28*	10	-3
H,K= 10 1		
0	61	56
1*	29	33
2	50	40
4	44	-28
5	44	-40
6	68	-63
8	131	-134
9	33	36
10	125	-117
11	95	91
12	52	46
13	64	57
14*	19	-3
16	41	36
18	36	29
20	35	-33
21	39	-38
22	38	36
23	38	-31
24*	18	-17
25*	17	15
26*	10	-11
H,K= 11 1		
1	85	-82
2	32	32
3*	22	31
4	58	-56
5	104	-102
6*	31	-21
7	60	-52
8*	29	-24
9	138	136
11	40	-42
16	60	-63
19	38	35
20*	10	-14
21*	10	-9
22*	11	-12
23*	12	14
24*	27	30
25*	23	25
H,K= 12 1		
0	32	-28
1	37	-34
3	58	-54
4	50	-48
5	45	-43
6	83	-79
8	80	-77
9*	31	-28
10	78	-78
12	43	38
15*	26	-20
19	46	46
20*	22	-19
21*	12	15
22	31	30
23*	17	-16
H,K= 13 1		
2	47	-45
3	67	68
4	31	-33
5	99	100
6*	23	-20
8*	25	-22
10*	19	-15
11*	16	26
12	37	-36
15*	30	-31
18*	11	10
19*	10	-8
21*	25	-26
H,K= 14 1		
0	42	42
1	42	41
2	52	52
3	32	34
4	40	35
6*	17	17
7*	30	23
8*	16	-10
9	34	29
11	44	45
12	43	41
15*	20	-16
17*	25	27
18*	19	-20
H,K= 15 1		
1	41	-37
6*	23	21
8*	26	24
10*	20	-17
11	45	-50
12*	19	-16
13	32	32
14*	25	30
15	43	51
H,K= 16 1		
0*	20	21
1*	14	-18
2*	27	31
4*	19	17
5*	11	10
7*	31	-32
9	59	-66
H,K= 0 2		
0†	449	519
2†	406	-450
3†	504	587
4†	508	-585
5†	429	468
6†	345	403
7†	632	-707
8	120	123
9	86	84
10	79	-76
12	76	67
13	292	-328
14	140	-128
15	144	133
16	91	-85
17	144	-143
18	129	-126
19*	16	-17
21	184	187
22	232	247
24	95	-95
26	53	-54
27	48	53
28	105	112
29	89	-96
30*	25	-19
32*	16	18
33*	18	24
H,K= 1 2		
1†	511	540
2†	326	-375
3	140	155
4	143	149
5	123	124
6	262	293
7	36	25
8	145	132
10	50	41
11	184	183
12*	18	16
13*	26	19
14*	22	27
15	79	-70
16	37	-35
20	96	94
21	73	69
22*	29	-27
23*	26	21
24	83	-76
25	68	-75
26	53	44
27	55	-55
28	48	45
31*	25	21
32*	11	6
H,K= 2 2		
0†	835	-844
1†	405	464
2	221	-254
3*	17	4
4	135	-135
5	218	237
6*	23	-19
7†	328	363
8	276	313
9	61	54
10	158	-155
11	80	77
12	51	49
13	57	-52
14	180	184
15	91	-84
16	77	-75
17	77	71
18	68	72
19	145	141
20	92	91
23	44	35
25	40	-36
26	64	61
27*	28	31
28*	20	9
29	52	53
30	39	-41
31*	11	-11
32*	10	-10
H,K= 3 2		
1	77	-72
2	105	-105
3	55	51
4*	25	-26
5	119	114
6	105	-114
7	39	-36
8	120	-115
9	185	-194
10	155	-159
11*	13	-15
12*	26	-27
13	107	101
14*	20	5
15	65	61
16	88	-80
17	119	119
18	55	53
19	44	44
20	42	42
21*	29	28
22*	25	26
23	38	37
24	97	101
25	57	-57
26	44	47
27*	24	-23
28*	15	8
29*	23	24
31*	15	-13
H,K= 4 2		
0*	17	-3
1	95	89
3	68	-60
4	56	49
5	125	123
6	179	172
7	140	-136
8	91	86
9	84	-76
11	97	-98
12	66	60
13	140	-137
14	83	-77
15	33	25
16	56	-49
17	71	-67
18	32	33
19*	16	-18
21	44	-42
22	63	53
25*	13	-18
26*	12	15
29*	24	-14
30*	25	-20
31*	20	-24
32*	19	26
H,K= 5 2		
1	70	65
2	44	38
4	35	-23
5	145	138
6	77	-71
7	109	-108
8	79	75
9	189	-182
11*	24	-19
12	63	-55
13*	23	-25
14	61	-58
15	31	-31
16	68	-65
18*	23	-25
19*	25	-25
20	52	-50
21	44	41
22*	28	27
23	37	35
24	38	38
25	34	-33
26*	21	-22
27*	20	-19
28*	11	14
30*	10	2
H,K= 6 2		
0	80	-75
1	110	106
2	60	-54
3	115	-109
4	41	-41
5	48	40
6	77	69
7	83	75
8	134	138
11	45	-41
13	31	-23
14	37	33
15*	14	6
16*	25	23
17	58	-58
18	32	27
19*	24	-25
20*	14	12
21	80	-81
22*	21	23
23*	26	-24
24	37	-37
25*	19	-14
27*	20	-23
29*	11	-2
30*	18	-20
31*	22	29
H,K= 7 2		
1	125	-119
2	36	-37
3	38	-25
4	56	-45
5	48	37
6	180	-176
7	41	39
9	60	-55
10	85	-84
11	47	-46
12	98	-96
14	32	31
15	32	-34
16	75	-71
17	43	36
18	64	-67
20*	20	-24
22	52	49
23*	28	26
24	55	56
25*	22	-18
26*	20	-23
28*	20	22
29*	5	0
30*	11	12
H,K= 8 2		
0	86	77
1	98	95
2*	21	-19
3*	11	-2
4	46	-42
5	74	72
6*	13	14
7	42	33
9	44	-40
11*	11	-11
13	97	99
14	77	-74
15	97	92
16	110	-111
18*	22	-29
19	34	26
20	47	40
23	85	92
24	45	-50
25	63	69
26*	13	15
27*	14	-6
28*	16	16
H,K= 9 2		
1	38	-30
2	44	-40
3	42	-35
4	55	-46
5	111	-113
6	113	-121
7	37	-35
8	125	127
9	85	83
10	86	82
12	132	-135
13	57	-54
14	67	-64
15	95	-92
17	66	-65
18*	18	-19
19	46	40
20	54	-50
21	66	63
24*	9	11
25*	26	28
28*	20	26
H,K= 10 2		
1	88	78
2*	20	-24
3	99	-95
4	43	-44
5*	23	20
6	89	87
7	156	151
8	127	134
9*	21	-24
10	122	-123
11	82	-77
12	88	-85
13	71	-72
14	107	102
15	63	-63
16	41	-38
17	43	37
18	69	-72
19	44	43
21	44	-46
22	33	-31
23*	26	25
24*	19	-19
25*	17	-16
H,K= 11 2		
3	104	100
4*	24	21
5	52	50
6*	19	-27
7	105	108
9	87	84
11	47	-53
12	73	71
14	47	47
15	40	38
16	59	-60
17	37	39
19*	14	16
21*	19	-17
22	42	47
23*	11	-16
24	41	49
H,K= 12 2		
0	119	119
2*	28	-30
3	69	73
5	100	102
6	67	72
7	62	-68
9	34	32
10	44	43
13	51	-51
14	37	-41
15	55	55
16*	26	-26
17	39	-39
18	48	-48
21	50	54
22*	24	21
H,K= 13 2		
1	35	34
2	31	-35
4*	16	14
5	31	-30
8	38	38
9*	13	12
10*	15	19
11*	22	-19
13	32	-28
16	46	-45
17*	29	30
18*	10	-7
19*	24	25
20*	17	16
H,K= 14 2		
1	37	36
2*	27	27
4	61	63
6*	20	24
7*	21	-18
9*	30	-27
10	32	36
13	39	-42
15	47	-51
16*	31	-33
17*	20	-25
H,K= 15 2		
2*	25	23
3	33	27
4*	13	17
5	36	-33
6	33	-33
7*	19	-22
8	47	52
10	43	45
11	53	-60
12*	29	-29
13*	13	-17
H,K= 16 2		
0*	31	40
3*	11	12
7	36	-44
H,K= 1 3		
1	82	76
3	146	140
4	171	-179
5	69	-60
6	66	58
7*	22	-15
8*	26	-23
9	101	100
10	150	-142
11	182	184
12	92	-84
13	44	-37
14	68	61
15	51	50
16	64	-57
17	150	148
18	141	135
19*	30	-28
20*	26	-27
21	132	-128
22	61	-56
23	43	35
24	72	67
25	40	34
26*	28	-22
27*	15	-14
28	67	73
29*	19	13
30	38	42
31*	19	18
32*	10	11
H,K= 2 3		
0	89	-85
1	111	117
2*	25	-27
4	87	81
5	143	-140
6	35	34
7	31	-25
8	68	60
9	54	-51
10	38	-36
12	135	-132
13	76	65
14*	25	25
15	52	-50
17	50	-40
18	66	-60
19	48	-44
20	33	-20
21	61	-49
22	54	-47
25	60	-61
26	61	62
27*	26	-22
29	44	46
31*	10	-13
H,K= 3 3		
1	187	-192
2*	25	-26
3*	20	-21
4	140	144
5	119	-118
6	91	-83
7	140	-139
8	182	-190
10*	21	-20
11	169	172
12	129	-131
13	50	-42
14	87	81
15	56	-48
16	80	-78
17*	14	8
18	92	-83
19*	29	-26
20*	25	-13
21	72	-66
22	40	-39
25*	22	23
26*	16	-16
27	40	39
29*	17	13
H,K= 4 3		
0	103	105
1	95	86
2	61	55
3	59	54
4	80	75
5	187	-190
6	43	42
7	140	-139
8	136	137
9	68	59
10	146	144
12*	18	-18
13	68	-63
15	34	-34
16	58	-52

rected by the two analyses are less than 0·0015 Å for any bond.) In the second analysis the libration amplitude about the axis of the second moment of inertia is somewhat greater, indicating that the cyano groups are wagging appreciably. The cyano groups can not be regarded as part of a rigid molecule and the C–N distances have been corrected by the method of Busing & Levy (1964), assuming the riding motion.

Molecular structure

Bond lengths and angles with their estimated standard deviations are given in Tables 5 and 6. The details

Table 3 (*cont.*)

L	|FO|	FC
19•	16	-16
20•	31	25
21	75	-77
22	59	-58
23	30	-35
24•	24	-21
27•	19	-20
28	32	-36
29•	20	20
31•	22	24
H,K= 5 3		
1	100	-94
2	49	40
3	97	-92
4	65	55
5	83	-76
6•	28	-23
7	106	100
8	88	-83
9•	30	24
10•	21	16
12	55	-55
14	50	46
16•	17	15
17	109	-109
18	84	75
19	112	-117
20•	25	24
21•	22	-20
22•	23	24
23	45	43
24	37	36
26•	18	-5
27•	13	16
28	40	42
29	44	52
H,K= 6 3		
0	79	75
1	55	-42
2	41	32
3	55	49
4•	16	-8
5	155	164
6	74	-61
7	42	36
8	57	49
9	36	-25
10•	23	16
11	53	44
12	121	-123
13	78	66
14	51	-46
15•	24	-24
16	92	-98
18	67	-65
19	94	100
20	40	42
21	37	40
22	39	-37
23•	30	-29
25•	22	20
27	51	58
28•	13	-16
29•	22	28
H,K= 7 3		
1	186	-198
2	41	37
3	90	83
4	49	-42
5•	26	-23
6	107	98
8•	15	16
9	63	56
10•	13	12
11	57	55
12	36	-33
13	49	47
14	44	-43
15•	16	11
16	42	-35
17	71	-70
18	55	52
19•	24	-20
20	35	-33
21	35	-34
22	58	-62
23•	20	14
24	47	-55
25	51	55
26	44	-50
28	35	40
H,K= 8 3		
0	34	31
1•	24	24
2	64	-58
3	56	56
4	87	84
5	99	100
6	111	110
7	43	38
9	107	-106
11	42	-40
12	40	-33
13	33	23
14•	28	20
15	88	-87
16	40	37
17•	17	14
19	87	86
20•	27	-21
21•	11	7
22•	26	-24
23	31	29
24•	13	-13
25	35	34
26•	18	-20
27•	12	10
H,K= 9 3		
2	58	-60
3	125	133
4	132	140
5	99	96
6	57	-54
7•	21	-19
8	108	-104
9•	26	29
10	134	135
11	122	133
12	58	-55
14	58	58
15•	28	-17
16	69	68
18	58	-51
19•	27	-25
20	68	62
21•	28	-26
22•	29	27
23•	27	24
24	39	-44
25•	18	17
26•	30	34
H,K= 10 3		
0	83	86
1	39	-32
2•	29	-23
3	84	87
4	67	65
5	115	121
6	75	76
8	47	-41
9•	17	16
11	58	-62
12•	29	-28
13	92	-92
14	38	-36
16•	29	-26
18•	19	-16
19•	14	-16
H,K= 11 3		
2	101	101
3	64	62
4	34	-38
5•	25	-24
6	69	70
7•	28	-21
8•	31	31
9•	26	23
11•	12	24
12	90	100
14	47	48
15	35	37
16•	26	-19
17•	23	20
18	31	29
20•	26	-29
21•	19	-17
22•	25	-25
H,K= 12 3		
1	42	-33
2	60	-58
4•	21	-22
5	56	51
6•	14	2
7•	20	21
9	47	-42
10•	30	30
11	74	-81
13•	26	-20
16•	21	-20
17•	15	-14
20•	25	33
H,K= 13 3		
1•	15	-17
2	31	-33
4	38	-35
6•	30	29
7	53	-57
8•	17	-15
9	49	-53
12•	20	-14
13	44	-48
15	34	-34
16•	19	18
17•	18	13
H,K= 14 3		
2•	25	-22
3•	8	18
4	34	39
5•	17	13
6	46	49
9•	10	16
10•	23	23
13•	7	-11
14•	9	-9
15•	10	11
H,K= 15 3		
3	35	-38
4•	24	-27
5•	19	-22
6	48	57
7•	25	27
8	35	40
9•	10	13
10•	13	18
11•	12	-15
H,K= 0 4		
0	45	-47
1	215	-225
2	37	-20
3	32	-35
4	146	-155
5	105	-100
6	110	109
7†	440	-488
8	94	90
9•	31	25
10	158	-162
11	37	22
12	126	-114
13	64	-59
14	155	155
15	165	169
16	112	-106
17	160	-172
18	233	-254
19	162	-168
20	46	45
22	32	-31
24•	16	-16
25•	16	18
28	46	51
29	68	-83
30•	23	35
H,K= 1 4		
1	153	157
2	155	-156
4	190	203
5	135	-132
6	102	98
7•	17	-13
8	116	-108
9	95	87
11	31	21
12	51	-45
13	56	-45
14•	23	20
15	116	-110
16•	24	-15
17	116	-111
18	107	-105
20	41	41
21•	30	21
24	65	-64
26•	20	24
27	37	-37
28•	24	-23
29•	17	23
30	38	-49
H,K= 2 4		
0	73	79
1	52	50
2	72	67
3	219	-241
4	32	28
5	142	-135
6	106	109
7	198	204
9	62	57
10	62	59
11	75	68
12	64	54
13	88	80
14	84	85
15	47	-39
16	73	-72
17•	20	15
18	122	-123
19•	26	23
20	66	61
21	101	-98
22	68	-71
24•	29	-29
25•	26	-35
29	55	62
H,K= 3 4		
1	154	-158
2•	30	-24
3	156	-156
4	73	65
5	55	-52
6	176	183
8	39	31
9•	22	-8
12•	16	9
16	64	61
17	37	26
18	45	41
19	43	-35
20	47	40
21	51	-51
22	42	39
26	31	28
27•	30	26
28•	19	-23
29•	17	16
30•	22	-30
H,K= 4 4		
0	79	76
1	70	-62
2	71	71
3	94	-95
5	68	-66
6	47	44
7	106	-104
8	61	-60
9	32	26
10•	25	17
11	41	31
15	78	72
18	34	-25
19•	20	21
21•	17	21
22	64	-62
23	43	42
25	35	30
27•	28	27
28•	17	17
29•	10	16
H,K= 5 4		
1	75	69
2	40	36
4	81	77
5	75	72
6	106	100
8	59	53
9	33	27
10	55	47
11	56	53
12	47	-43
13•	15	-16
16	88	88
17	37	-31
18	34	-32
19	55	-58
20	36	-33
21•	18	-22
22•	19	20
24•	25	-20
25	31	32
27•	25	27
28•	30	-35
H,K= 6 4		
0	106	108
1•	16	18
2•	23	26
3•	22	-25
4	110	-109
5•	26	-25
7•	26	21
8	46	-41
9	80	76
11	55	51
14•	26	26
16	58	61
17	35	-27
19•	31	30
22	39	-39
24•	14	4
27•	13	-16
H,K= 7 4		
1	45	40
2•	26	19
3	40	31
4	41	-39
5	67	60
6	38	33
7	46	46
8•	17	16
9•	31	32
10•	18	15
11	40	34
12	37	-34
13	61	59
15	64	67
16	57	58
17	49	53
18	64	-68
20•	18	-26
21	51	-52
24	49	-61
26•	26	-30
H,K= 8 4		
0	88	86
1•	28	23
3•	22	20
4	66	-63
5	38	-31
6	62	62
7	91	-87
8	43	-41
9	38	-34
11	32	28
12	41	34
13	54	53
15•	25	21
16	35	33
17	61	-56
18•	30	28
19•	17	-13
22	37	-35
23•	24	25
24•	19	-16
25•	8	7
H,K= 9 4		
1	75	72
2	118	121
3•	21	19
4•	22	-20
5	89	-89
6	35	-26
7	94	-96
8	41	45
9	43	41
10	85	87
11	50	45
12•	28	27
13•	19	18
14	47	44
15•	21	-22
16	78	80
17	55	-53
19•	27	26
20•	24	-24
21•	17	16
23•	28	-27
24•	10	10
H,K= 10 4		
0	44	32
1•	18	23
2	75	-75
3	103	-105
4	157	-182
5	79	-84
7	67	68
8	34	28
10	40	-40
13	40	-42
14	32	31
15	62	-64
17•	28	28
18	43	-40
20	32	29
21	58	-72
22•	28	34
23•	24	-35
H,K= 11 4		
1	38	-38
2	56	52
4	65	-69
5	42	36
6	35	38
7•	30	-31
8•	14	-17
9	53	-55
10	43	-42
11•	27	-29
12	49	49
15	50	51
16	32	-33
17•	15	9
18•	22	28
19	46	-55
21	33	-44
H,K= 12 4		
0	41	-50
1	32	-29
2•	19	9
3•	19	19
4•	19	-15
5•	13	11
6•	28	29
7	65	-71
8	55	53
9	44	38
11	49	48
12•	20	22
13•	25	26
14	40	37
15	71	82
17•	22	-18
18•	21	-12
19•	18	-18
H,K= 13 4		
2•	31	33
3•	28	-28
4•	28	33
5•	23	-24
6•	23	18
7	37	-41
8•	13	-21
11•	20	15
13•	22	19
H,K= 14 4		
0	62	-73
12•	16	38
13•	21	27
H,K= 15 4		
2	49	58
3•	21	27
H,K= 1 5		
2	62	52
3•	18	13
4•	18	-12
5	32	31
6	68	62
7	45	-36
8	33	18
9	37	-33
10	68	66
11	94	91
12	72	68
13	158	-162
14	58	-49
15	63	-48
16	54	47
17	80	77
18	43	42
20	75	70
23•	21	28
24•	24	-28
27	59	-74
H,K= 2 5		
0	44	36
1	58	51
4	85	78
5	37	-39
6	83	79
7	110	114
8	66	-67
9	40	36
10	53	-45
12	39	40
13	68	60
14	59	55
16	89	91
17	49	48
18•	24	18
19	47	48
22	39	37
23	35	39
27•	14	8
H,K= 3 5		
1	90	-87
3	105	96
4	40	35
5	31	25
6•	18	0
7•	20	-17
8	46	-48
9	38	-37
10	73	64
12	74	78
13	83	-84
14	41	35
16•	25	19
17•	25	20
18	70	-73
19	44	50
20	40	38
22•	22	-17
23•	20	-13
24	31	-35
25	35	41
27•	31	-32
28•	31	-48
H,K= 4 5		
0	70	-68
1	73	69
3•	20	20
5	92	-85
6	61	-57
7	34	-27
8	67	-61
9	50	44
10	38	-35
12	82	84
14	48	44
18	60	62
19	31	-30
20	36	31
21•	31	-32
22•	28	28
23•	20	13
26	33	-35
27•	29	-34
H,K= 5 5		
1	83	72
2	59	-50
3	55	52
4	113	-108
5	56	54
6	59	-52
7	123	122
8	50	-48
9•	31	24
12	37	35
13•	21	-25
15	71	72
16	32	36
18	41	-42
20	40	-40
21	41	45
22	38	-41
25•	29	-33
26•	8	-10
H,K= 6 5		
0	66	-63
3	46	-44
4	61	-55
5	40	33
6	62	-58
9	52	-47
10	36	-31
11	67	69
13	86	91
15•	26	-27
16•	27	-35
17•	30	-28
19	33	34
22•	29	37
H,K= 7 5		
1	56	-47
2	62	-51
3•	26	31
4	131	-132
5	36	-38
6	61	56
7	61	-53
8	62	56
10•	25	-31
11•	25	14
12	59	60
13	60	-60
14•	22	15
15•	20	-11
16•	20	21
18•	19	26
19•	30	36
20	33	-35
21	31	34
22	45	-49
H,K= 8 5		
0	105	-104
1	34	-34
2	107	-110
3	95	-91
4	64	-60
6	37	34
7•	27	25
9	39	-35
11	31	29
12	48	44
15	60	-67
16	41	38
17•	19	-16
20	46	-47
21	32	-32
22	34	41
23	34	-36
H,K= 9 5		
1	98	-91
2	82	-82
3	98	95
5	33	-33
6	41	-37
7	52	-51
8	53	-48
12•	27	-25
13	35	-38
14	34	34
16	43	39
18	41	-36
19	34	33
20	34	38
21•	21	-22
22•	17	24
H,K= 0 6		
0	44	-34
2	81	75
3	74	63
4	86	-82
7•	26	-21
8	115	115
10	204	-212
12	74	-64
13•	17	18
14	169	179
15	109	108
16	106	103
17	55	58
18•	17	24
19•	17	-20
20	70	73
21	41	38
24•	17	-12
25	37	45
H,K= 1 6		
2	40	-34
3	52	43
4	55	48
5	121	-111
6	59	-56
8	146	-143
9	83	81
10	54	-46
11	85	-76
12	50	37
14	38	32
15•	29	-24
16	68	-65
17	80	-78
18	79	-81
19	36	38
24•	15	-18
25•	28	30
H,K= 2 6		
0	140	132
2	57	57
4	80	-74
7	124	127
8•	28	-29
9	51	-52
11	42	-39
12	65	62
16•	26	20
17	45	47
18•	31	25
20	62	60
21	36	-38
22	39	41
23•	29	-26
24	40	-46
25•	22	-21
H,K= 3 6		
1•	25	-24
2	61	-57
3•	21	-20
4	44	-41
6	52	-47
7	55	52
8•	31	-32
9	60	59
16•	31	-33
17•	30	28
22	36	-40
24	31	-36
H,K= 4 6		
0	96	-94
3	53	50
4	67	-64
6	46	-41
8	36	-27
9	47	-44
10	62	-62
11•	30	-32
13	41	-46
14	37	-38
15•	20	18
17	45	44
20•	19	20
21	40	41
23•	12	-12
24•	9	-7
H,K= 5 6		
6	88	-93
9	34	30
11•	21	-23
12•	26	-31
13	36	-40
14•	17	12
15•	18	-10
H,K= 6 6		
0	34	-36
1	31	30
3	92	90
4	43	-42
5	37	33
10	41	-41
13	38	-43
14•	23	-21
16•	21	-23
17•	12	16
18•	28	-32
21•	29	32
22•	14	17
23•	13	-23
H,K= 7 6		
1	57	-55
3•	17	-18
5	39	-37
6	35	-36
8•	24	25
11	47	-44
12	55	-56
17•	28	27
19•	27	29
20•	20	21
H,K= 8 6		
2•	24	27
3	65	66
4	61	61
5•	15	19
6	96	107
7	59	-64
9	32	-32
10	45	-42
12	33	34
13	34	-36
H,K= 9 6		
2	91	94
3	45	46
4•	28	26
6	60	-60
12•	17	-19
14•	28	34
15•	29	-37
H,K= 1 7		
1	56	-46
2	58	-51
3	40	33
4	32	28
5	35	-30
6	59	-55
7	62	-59
10	43	-34
11	72	67
12•	27	-31
14	55	-53
15	44	-42
16	38	-37
18	32	-32
19	38	-39
20•	21	-18
H,K= 2 7		
0	48	49
2	40	-37
6	39	38
7	43	46
8	43	-47
11	65	-73
13	57	-57
14	43	-45
17•	18	19
18•	26	-29
20	34	-37
21•	13	17
H,K= 3 7		
1	45	-45
2•	21	-24
3	83	85
4	47	45
7	38	-32
8•	29	25
9•	28	-29
12•	20	22
13	36	39
17•	19	23
20•	25	32
21•	22	-29
H,K= 4 7		
1	34	24
2•	23	-20
3	54	48
8	40	-37
11	47	-49
13	44	-43
14•	23	-24
15•	16	16
16	31	-35
17•	14	13
19•	19	-19
H,K= 5 7		
1	59	60
4•	29	25
5	43	-41
6•	17	-18
9•	23	-23
10•	16	-19
11•	27	-25
12•	14	-15
13•	25	19
14•	28	-32
15	40	45
17	36	41
19•	17	-25
H,K= 6 7		
0	98	105
1•	13	-25
2	65	63
4	54	51
5	35	39
6	52	51
7•	19	-20
8•	30	30
9	66	-74
10•	16	23
11•	23	-26
13	35	38
14•	15	19
17•	20	-24
18•	13	-16
H,K= 7 7		
1	71	72
2•	26	25
5	44	-45
6	44	43
7	47	-53
8	50	52
9•	19	-6
10	32	-35
11	37	39
12	34	36
13•	29	-28
15•	27	-28
16•	14	-19
17	32	44
H,K= 8 7		
0	73	84
1	50	-55
3•	29	-30
5•	29	24
6•	27	34
8	36	-35
H,K= 9 7		
1•	26	-27
3	50	51
5•	27	-27
7	32	-29
9•	18	21
10•	27	-28
H,K= 0 8		
2	32	-38
3•	19	25
4•	19	-18
5•	18	-23
6	63	62
7	31	27
8	69	65
9	57	65
10	79	-80
11•	15	-11
12	61	-63
13•	29	-30
14	56	65
15•	29	-34
H,K= 1 8		
2	40	35
3	45	45
6•	28	17
8	40	-39
10	35	-31
11	61	-68
12	80	94
14	42	45
15	34	41
16•	25	-29
H,K= 2 8		
0	82	93
2•	23	-32
3•	23	28
4•	23	-30
6•	28	26
14	43	-50
15	36	-46
16	37	-45
H,K= 3 8		
1	50	54
3	35	34
5•	19	25
6•	19	23
7•	19	-19
8•	18	14
9•	18	-16
10•	29	36
11•	14	20
12	35	46
13•	22	27
15•	23	29
H,K= 4 8		
1	32	-30
3•	13	-15
4	33	30
5•	28	-30
6•	22	26
8	40	43
9•	16	22
10•	28	33
H,K= 5 8		
1•	16	16
2•	23	21
3•	26	25
7•	28	-34
8•	15	19
9•	20	-25
10•	18	22
11•	10	-6
H,K= 6 8		
1•	22	-21
3•	11	-17
4•	13	24
5•	22	-30
6•	11	21
8•	28	34
9•	22	27
H,K= 7 8		
4•	14	-21
5•	14	-21
6•	11	21
7•	19	-26
8•	29	37
H,K= 8 8		
0	57	-74
1•	29	-46
2	31	-42
3•	23	-30
H,K= 1 9		
3•	28	35
4•	17	6
5•	13	18
6•	14	16
H,K= 2 9		
0•	17	15
1•	14	-27
3•	14	-21
4•	11	-24
H,K= 3 9		
1•	22	-30
3•	15	22

of the molecule are shown in Fig. 3. As expected, the intramolecular overcrowding affects the planarity of the molecule. Least-squares planes through various groups of atoms in the structure are presented in Table 7 and the deviations from some of these planes are shown in Fig. 4. The six atoms of the benzenoid ring C(5)–C(10) (plane I) are almost planar. Four atoms C(2), C(3), C(9) and C(10) in the quinonoid ring are almost in one plane II, while C(1), C(4), C(11) and C(12) have significant deviations from this plane. The two C–C(CN)$_2$ groups are entirely on the same side of plane II and this clearly shows that the quinonoid ring is distorted into the shape of a boat. Planes I and II are folded up by 15·3° (shown diagrammatically in Fig. 4). Plane III through the four atoms, $\begin{matrix}\mathrm{C(2)}\\\mathrm{C(9)}\end{matrix}\!>\!\mathrm{C(1)}{=}\mathrm{C(11)}$, and plane IV through $\begin{matrix}\mathrm{C(3)}\\\mathrm{C(10)}\end{matrix}\!>\!\mathrm{C(4)}{=}\mathrm{C(12)}$ are tilted from plane II by 16·7° and 21·6°, respectively. The angle between planes III and IV is 38·3°. C(13)–N(1) and C(14)–N(2) lie on the opposite side of plane III by 0·158, 0·304 Å and −0·044, −0·054 Å, respectively. C(15), N(3), C(16) and N(4) lie 0·194, 0·365, −0·067 and −0·129 Å away from plane IV. Therefore, the two

Table 4. *Rigid-body thermal parameters*

(*a*) 12 innermost atoms C(1) ~ C(12) (*b*) 20 atoms C(1) ~ N(4)

Principal axes of the molecule relative to the crystal axes (*a*, *b*, *c*)

(a) Moment of inertia (atomic weight Å^2)	Direction cosines			(b) Moment of inertia (atomic weight Å^2)	Direction cosines		
316·0	0·898	−0·228	−0·376	907·5	0·426	0·378	0·822
409·8	−0·437	−0·360	−0·824	1862·8	−0·902	0·248	0·354
704·6	0·053	−0·905	0·423	2584·7	−0·070	−0·892	0·446

Molecular vibrational tensors

(*a*)

Translation **T** (× 10^{-2} Å^2) σ(**T**) (× 10^{-2} Å^2)

$$\begin{pmatrix}3{\cdot}00 & 0{\cdot}14 & -0{\cdot}08\\ & 3{\cdot}15 & -0{\cdot}01\\ & & 2{\cdot}54\end{pmatrix}\qquad\begin{pmatrix}0{\cdot}10 & 0{\cdot}09 & 0{\cdot}11\\ & 0{\cdot}11 & 0{\cdot}12\\ & & 0{\cdot}18\end{pmatrix}$$

Rotation **ω**(deg^2) σ(**ω**) (deg^2)

$$\begin{pmatrix}2{\cdot}6 & 0{\cdot}4 & -2{\cdot}5\\ & 7{\cdot}8 & -0{\cdot}6\\ & & 2{\cdot}7\end{pmatrix}\qquad\begin{pmatrix}1{\cdot}3 & 0{\cdot}8 & 0{\cdot}9\\ & 1{\cdot}3 & 0{\cdot}9\\ & & 0{\cdot}8\end{pmatrix}$$

(*b*)

Translation **T** (× 10^{-2} Å^2) σ(**T**) (× 10^{-2} Å^2)

$$\begin{pmatrix}3{\cdot}22 & 0{\cdot}30 & 0{\cdot}18\\ & 2{\cdot}81 & 0{\cdot}05\\ & & 2{\cdot}15\end{pmatrix}\qquad\begin{pmatrix}0{\cdot}16 & 0{\cdot}15 & 0{\cdot}17\\ & 0{\cdot}20 & 0{\cdot}20\\ & & 0{\cdot}27\end{pmatrix}$$

Rotation **ω**(deg^2) σ(**ω**) (deg^2)

$$\begin{pmatrix}6{\cdot}1 & 0{\cdot}6 & 0{\cdot}8\\ & 8{\cdot}9 & 0{\cdot}5\\ & & 4{\cdot}3\end{pmatrix}\qquad\begin{pmatrix}1{\cdot}4 & 0{\cdot}5 & 0{\cdot}7\\ & 0{\cdot}8 & 0{\cdot}6\\ & & 0{\cdot}6\end{pmatrix}$$

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

(a) R.m.s. amplitude	Direction cosines			(b) R.m.s. amplitude	Direction cosines		
0·159 Å	0·177	−0·017	0·984	0·145 Å	−0·002	−0·002	0·987
0·171	−0·833	0·530	0·159	0·163	0·443	−0·894	0·071
0·180	0·524	0·848	−0·079	0·185	0·882	0·448	0·146
0·36°	0·710	0·015	0·704	1·99°	−0·346	−0·057	0·937
2·22	0·684	−0·249	−0·686	2·50	−0·910	0·262	−0·320
2·83	0·165	0·968	−0·187	3·02	0·228	0·963	0·142

Table 5. *Bond lengths* (Å)

The e.s.d.'s given in parentheses refer to the least significant digits in the bond lengths.

	Uncorrected	Corrected		Uncorrected	Corrected
C(1)—C(2)	1·459 (5)	1·461	C(13)—N(1)	1·140 (5)	1·148
C(2)—C(3)	1·348 (5)	1·348	C(14)—N(2)	1·135 (5)	1·142
C(3)—C(4)	1·452 (5)	1·454	C(15)—N(3)	1·155 (6)	1·165
C(4)—C(10)	1·469 (5)	1·471	C(16)—N(4)	1·148 (5)	1·159
C(5)—C(10)	1·393 (5)	1·394			
C(5)—C(6)	1·387 (5)	1·389	C(2)—H(1)	1·05 (4)	
C(6)—C(7)	1·383 (5)	1·384	C(3)—H(2)	1·09 (4)	
C(7)—C(8)	1·388 (5)	1·389	C(5)—H(3)	0·98 (3)	
C(8)—C(9)	1·392 (5)	1·394	C(6)—H(4)	0·99 (4)	
C(1)—C(9)	1·459 (5)	1·461	C(7)—H(5)	0·93 (4)	
C(9)—C(10)	1·423 (5)	1·424	C(8)—H(6)	1·04 (4)	
C(1)—C(11)	1·383 (5)	1·384			
C(4)—C(12)	1·382 (5)	1·383	C(13)···C(8)	2·969 (5)	
C(11)-C(13)	1·427 (5)	1·428	C(15)···C(5)	2·963 (5)	
C(11)-C(14)	1·433 (5)	1·434	C(13)···H(6)	2·32 (4)	
C(12)-C(15)	1·422 (5)	1·423	C(15)···H(3)	2·46 (4)	
C(12)-C(16)	1·428 (5)	1·429			

$=\mathrm{C}{<}\substack{\mathrm{CN}\\ \mathrm{CN}}$ groups are twisted about the C=C axes so that C(13) and C(15) are away from C(8) and C(5), respectively. The angle between planes III and V, $\mathrm{C(1)=C(11)}{<}\substack{\mathrm{C(13)}\\ \mathrm{C(14)}}$, is 5·0° and that between planes IV and VI, $\mathrm{C(4)=C(12)}{<}\substack{\mathrm{C(15)}\\ \mathrm{C(16)}}$, is 6·6°. Such distortion of mol-

Table 6. *Bond angles* (°)

The e.s.d.'s given in parentheses refer to the least significant digits in the bond angles.

C(2)—C(1)—C(9)	117·3 (3)	C(4)—C(12)-C(15)	124·3 (3)
C(2)—C(1)—C(11)	117·4 (3)	C(4)—C(12)-C(16)	121·5 (3)
C(9)—C(1)—C(11)	125·3 (3)	C(15)-C(12)-C(16)	114·1 (3)
C(1)—C(2)—C(3)	120·9 (3)	C(11)-C(13)-N(1)	177·3 (4)
C(2)—C(3)—C(4)	120·2 (3)	C(11)-C(14)-N(2)	178·5 (4)
C(3)—C(4)—C(10)	117·2 (3)	C(12)-C(15)-N(3)	177·0 (4)
C(3)—C(4)—C(12)	118·2 (3)	C(12)-C(16)-N(4)	179·1 (5)
C(10)-C(4)—C(12)	124·5 (3)		
C(4)—C(10)-C(5)	121·8 (3)	C(1)—C(2)—H(1)	119 (2)
C(4)—C(10)-C(9)	118·2 (3)	C(3)—C(2)—H(1)	119 (2)
C(5)—C(10)-C(9)	119·9 (3)	C(2)—C(3)—H(2)	116 (2)
C(10)-C(5)—C(6)	120·1 (3)	C(4)—C(3)—H(2)	123 (2)
C(5)—C(6)—C(7)	120·1 (3)	C(10)-C(5)—H(3)	125 (2)
C(6)—C(7)—C(8)	120·7 (3)	C(6)—C(5)—H(3)	115 (2)
C(7)—C(8)—C(9)	120·4 (3)	C(5)—C(6)—H(4)	120 (2)
C(1)—C(9)—C(8)	121·9 (3)	C(7)—C(6)—H(4)	119 (2)
C(1)—C(9)—C(10)	119·1 (3)	C(6)—C(7)—H(5)	118 (2)
C(8)—C(9)—C(10)	118·8 (3)	C(8)—C(7)—H(5)	121 (2)
C(1)—C(11)-C(13)	125·8 (3)	C(7)—C(8)—H(6)	122 (2)
C(1)—C(11)-C(14)	120·5 (3)	C(9)—C(8)—H(6)	117 (2)
C(13)-C(11)-C(14)	113·6 (3)		

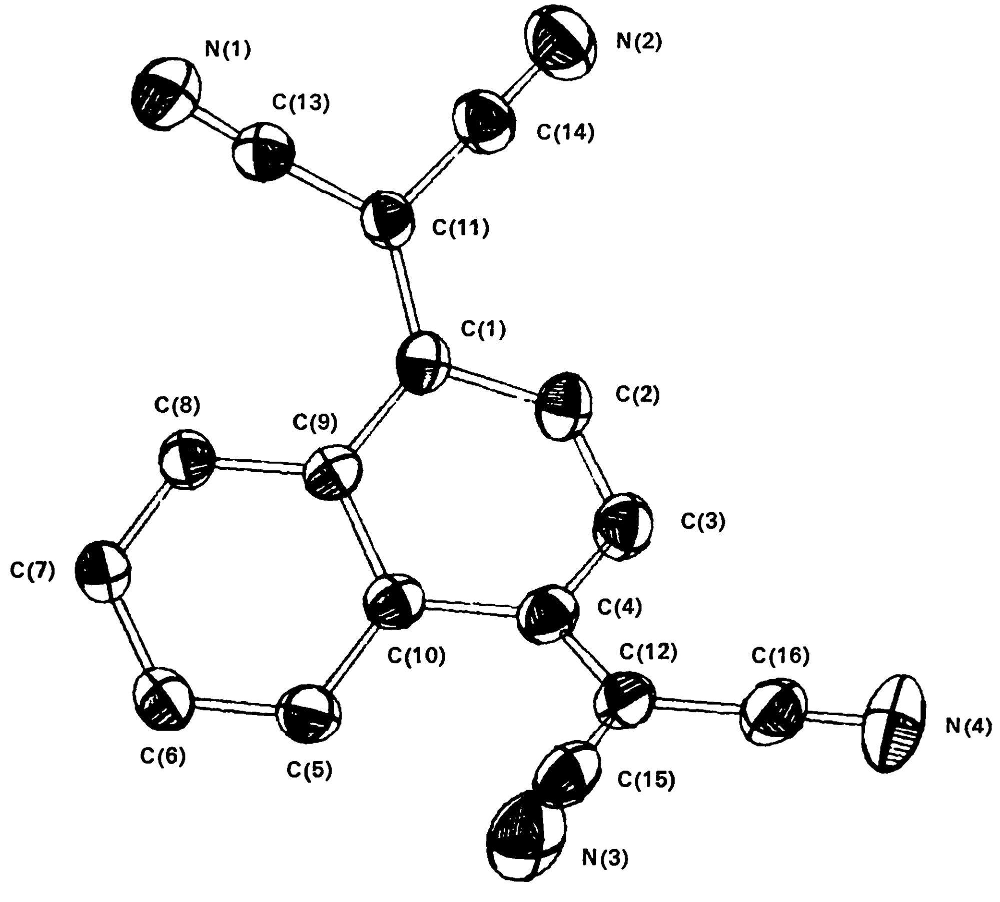


Fig. 2. Perspective drawing of the molecule showing the ellipsoids of thermal motion with a probability of 50%.

ecules as a result of intramolecular overcrowding is already reported for 10-dicyanomethyleneanthrone (Silverman & Yannoni, 1967), in contrast to 1,4-naphthoquinone and its related substances (Gaultier & Hauw, 1965, 1966, 1969) where no intramolecular overcrowding is found and hence the molecules are almost planar.

The average C–C bond distance in the benzoid ring (1·390 Å) except the fused ring bond, C(9)–C(10), is close to the value found in benzene, 1·392 Å (Cox, Cruickshank & Smith, 1958). The mean value of the C–C single bonds of the quinonoid ring, C(1)–C(2), C(3)–C(4), C(4)–C(10) and C(1)–C(9), is 1·462 Å. The length of C(2)–C(3), 1·348 Å, is compatible with the corresponding bond length of 2,2′-di-(1,4-naphthoquinone), 1·340 Å (Ammon, Sundaralingam & Stewart, 1969) and of TCNQ, 1·347 Å (Long, Sparks & Trueblood, 1965). For bond distances in dicyanomethylene groups, double bonds C(1)–C(11) and C(4)–C(12) (mean value 1·384 Å) are longer than the expected value for an ethylenic double bond (1·34 Å), while single bonds C(11)–C(13), C(11)–C(14), C(12)–C(15) and C(12)–C(16) (mean value 1·428 Å) are shorter than values for a single bond between *sp*- and sp^2-carbon atoms (1·45 Å) (Stoicheff, 1962). The mean value of the $C{\equiv}N$ bond distances is 1·154 Å. The bond lengths obtained in the TCNQ moiety are in reasonable agreement with the corresponding values found in TCNQ and its complexes (Williams & Wallwork, 1968; Hanson, 1968; Goldstein, Seff & Trueblood, 1968). The bond length, C(9)–C(10), of the fused ring, 1·424 Å, is close to the corresponding bond length in 10-dicyanomethyleneanthrone (1·43 Å) (Silverman & Yannoni, 1967), naphthalene (1·418 Å) and anthracene (1·428 Å) (Cruickshank, 1957, 1956*b*).

The bond angles related to dicyanomethylene groups are different from the corresponding values obtained in TCNQ and its related substances. This can be interpreted as relieving intramolecular overcrowding between C(8) and C(13) and between C(5) and C(15). The bond angles, C(2) C(1) C(9), C(3) C(4) C(10) (mean value, 117·3°) and C(13) C(11) C(14), C(15) C(12) C(16) (mean value, 113·9°) are narrower than the corresponding values in TCNQ (118·3 and 116·1°, respectively). The bond angles, C(9) C(1) C(11), C(10) C(4) C(12) (mean value 124·9°) and C(1) C(11) C(13), C(4) C(12) C(15) (mean value 125·1°) are significantly opened.

The non-bonded distances C(8)···C(13), C(5)···C(15) and H(6)···C(13), H(3)···C(15) are close to the

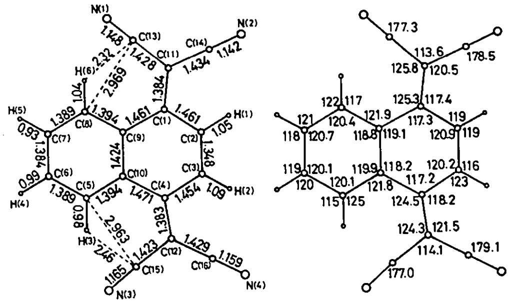


Fig. 3. Bond lengths (Å) and angles (°).

Table 7. *Least-squares planes*

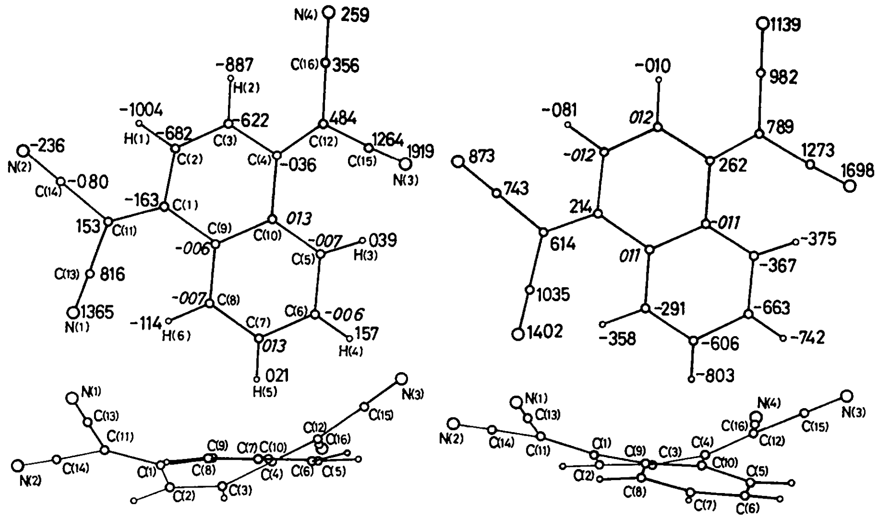
Equation of the plane: $AX+BY+CZ=D$, where X, Y and Z are the coordinates in Å referred to the crystal axes a, b and c. D is the plane-to-origin distance in Å.

		A	B	C	D
I	[C(5) ~ C(10)], benzenoid ring	0·0098	0·9325	−0·3610	−1·3597
II	C(2), C(3), C(9) and C(10) in quinonoid ring	0·2357	0·8477	−0·4753	−0·5780
III	$\left.\begin{matrix}C(2)\\C(9)\end{matrix}\right>C(1)=C(11)$	0·3515	0·9109	−0·2163	0·6171
IV	$\left.\begin{matrix}C(3)\\C(10)\end{matrix}\right>C(4)=C(12)$	0·0508	0·6650	−0·7451	−2·5926
V	$C(1)=C(11)\left<\begin{matrix}C(13)\\C(14)\end{matrix}\right.$	0·4323	0·8786	−0·2029	1·1056
VI	$C(4)=C(12)\left<\begin{matrix}C(15)\\C(16)\end{matrix}\right.$	0·1212	0·5907	−0·7977	−2·3433

Displacements (Å × 10^3) of atoms from mean planes.*
Boldface deviations indicate the atoms used to define the least-squares plane.

	III	V		IV	VI
C(1)	**−003**	**010**	C(3)	**005**	192
C(2)	**001**	141	C(4)	**−015**	**009**
C(9)	**001**	−059	C(10)	**005**	−072
C(11)	**001**	**−027**	C(12)	**005**	**−024**
C(13)	158	**009**	C(15)	194	**008**
C(14)	−044	**008**	C(16)	−067	**008**
N(1)	304	060	N(3)	365	053
N(2)	−054	061	N(4)	−129	028

* Displacements of atoms from planes I and II are shown in Fig. 4.



(*a*) (*b*)

Fig. 4. Deviations (Å × 10^3) from the least-squares planes and projections parallel to these planes, (*a*) plane I and (*b*) plane II.

typical values of 3·0 and 2·4 Å, respectively, for non-bonded interaction of this type.

Although the molecule has none of the symmetry elements, the bond lengths and angles of the chemically equivalent bonds agree well with each other. The angle between planes II and III is slightly different from that between planes II and IV, and this is attributed to the difference between the molecular environments of the two dicyanomethylene groups.

Molecular packing

The arrangement of the molecule is shown in Figs. 5 and 6 and intermolecular distances less than 3·6 Å are listed in Table 8. The molecules, I and VII, related by a glide plane perpendicular to the *a* axis stack each other along the *b* axis. The plane of the benzenoid ring makes an angle of 69° with the *b* axis. The shortest C···C contact is 3·377 Å [C(7)···C(9) in VII], which is slightly shorter than the van der Waals contact. All other contacts are of the van der Waals type. The shortest intermolecular approach, 3·183 Å, occurs between N(3)···C(12) in IV, which is close to the sum of the van der Waals radii.

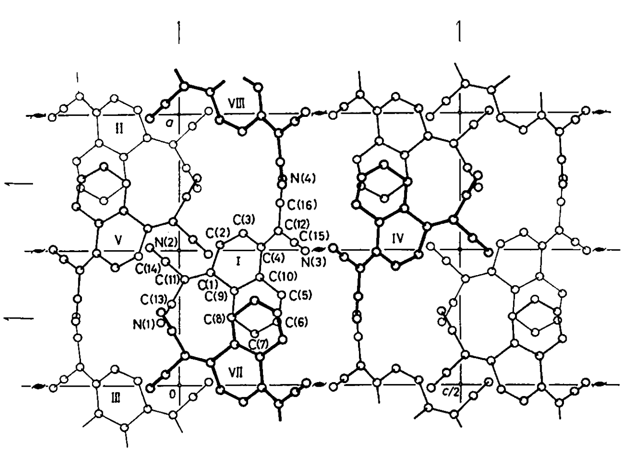


Fig. 5. Projection of the structure along the *b* axis.

Table 8. *Intermolecular distances less than* 3·6 Å

I	x	y	z	V	$1-x$	$-y$	$-z$
II	$\frac{1}{2}+x$	$-\frac{1}{2}-y$	$-z$	VI	$1-x$	$-1-y$	$-z$
III	$-\frac{1}{2}+x$	$-\frac{1}{2}-y$	$-z$	VII	$\frac{1}{2}-x$	$\frac{1}{2}+y$	z
IV	$1-x$	$\frac{1}{2}+y$	$\frac{1}{2}-z$	VIII	$\frac{3}{2}-x$	$\frac{1}{2}+y$	z

Atom [in molecule (I)]	to atom	in molecule	*d*
C(2)	N(1)	II	3·448 (5) Å
C(7)	N(2)	III	3·395 (5)
C(8)	N(2)	III	3·383 (5)
N(3)	C(4)	IV	3·503 (5)
N(3)	C(5)	IV	3·473 (5)
N(3)	C(12)	IV	3·183 (5)
N(3)	C(15)	IV	3·318 (6)
C(1)	C(14)	V	3·491 (5)
C(1)	N(2)	V	3·539 (5)
C(4)	N(2)	V	3·460 (5)
C(10)	N(2)	V	3·555 (5)
C(9)	N(2)	V	3·547 (5)
C(2)	N(2)	VI	3·444 (5)
C(5)	C(7)	VII	3·421 (5)
C(6)	C(7)	VII	3·536 (5)
C(6)	C(8)	VII	3·542 (5)
C(7)	C(8)	VII	3·438 (5)
C(7)	C(9)	VII	3·377 (5)
C(7)	C(1)	VII	3·581 (5)
N(3)	C(6)	VII	3·467 (5)
N(3)	C(7)	VII	3·500 (5)
N(1)	C(11)	VII	3·350 (5)
N(1)	C(13)	VII	3·279 (6)
N(1)	C(14)	VII	3·264 (5)
N(4)	C(3)	VIII	3·553 (6)

All crystallographic computations were performed on the HITAC 5020E computer of the Computer Centre of the University of Tokyo using the Universal Crystallographic Computation Program System 5020

UNICS (Crystallographic Society of Japan, 1967). Fig. 2 was drawn using *ORTEP* (Johnson, 1965).

The authoress expresses her thanks to Professor Ariyuki Aihara and Yasumasa Ihaya of this University for their encouragement. She is indebted to Mr Noboru Suzuki for supplying samples and to Mr Seiich Ueda for experimental assistance. This research was supported in part by a Scientific Research Grant of the Ministry of Education.

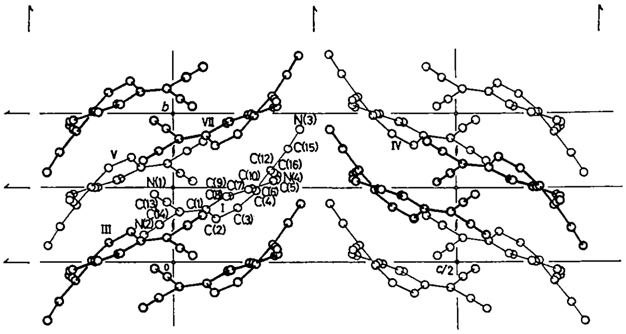


Fig. 6. Projection of the structure along the *a* axis.

References

Ammon, H. L., Sundaralingam, M. & Stewart, J. M. (1969). *Acta Cryst.* **B25**, 336.
Busing, W. R. & Levy, H. A. (1964). *Acta Cryst.* **17**, 142.
Chatterjee, S. (1967). *J. Chem. Soc.* (*B*), p. 1170.
Cox, E. G., Cruickshank, D. W. J. & Smith, J. A. S. (1958). *Proc. Roy. Soc.* A**247**, 1.
Cruickshank, D. W. J. (1956*a*). *Acta Cryst.* **9**, 747, 754.
Cruickshank, D. W. J. (1956*b*). *Acta Cryst.* **9**, 915.
Cruickshank, D. W. J. (1957). *Acta Cryst.* **10**, 504.
Cruickshank, D. W. J. (1961). *Acta Cryst.* **14**, 896.
Crystallographic Society of Japan (1967). 5020 *UNICS, The Universal Crystallographic Computation Program System.*
Gaultier, J. & Hauw, C. (1965). *Acta Cryst.* **18**, 179.
Gaultier, J. & Hauw, C. (1966). *Acta Cryst.* **20**, 620.
Gaultier, J. & Hauw, C. (1969). *Acta Cryst.* B**25**, 419.
Goldstein, P., Seff, K. & Trueblood, K. N. (1968). *Acta Cryst.* B**24**, 778.
Hanson, A. W. (1968). *Acta Cryst.* B**24**, 768.
International Tables for X-ray Crystallography (1962). Vol. III, p. 202. Birmingham: Kynoch Press.
Johnson, C. K. (1965). *ORTEP*. USAEC Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tennessee.
Karle, I. L. & Karle, J. (1963). *Acta Cryst.* **16**, 969.
Long, R. E., Sparks, R. A. & Trueblood, K. N. (1965). *Acta Cryst.* **18**, 932.
Silverman, J. & Yannoni, N. F. (1967). *J. Chem. Soc.* (*B*), p. 194.
Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3175.
Stoicheff, B. P. (1962). *Tetrahedron*, **17**, 135.
Williams, R. M. & Wallwork, S. C. (1968). *Acta Cryst.* B**24**, 168.

Acta Cryst. (1971). B**27**, 1368

The Crystal Structures of Dichlorobis-(2,3-dimethylpyridine)copper(II) and Dibromobis-(2,3-dimethylpyridine)copper(II)

By Walter Stählin and Hans R. Oswald

Institut für anorganische Chemie, Universität Zürich, Rämistrasse 76, 8001 *Zürich, Switzerland*

(*Received* 12 *September* 1970)

Dichlorobis-(2,3-dimethylpyridine)copper(II) [$=\mathrm{CuL_2Cl_2}$] and dibromobis-(2,3-dimethylpyridine)copper(II) [$=\mathrm{CuL_2Br_2}$] are isotypic with the following monoclinic unit-cell dimensions: $\mathrm{CuL_2Cl_2}$: $a=7{\cdot}461$ (4), $b=14{\cdot}80$ (1), $c=7{\cdot}879$ (6) Å, $\beta=110{\cdot}11$ (5)°; $\mathrm{CuL_2Br_2}$: $a=7{\cdot}566$ (5), $b=15{\cdot}33$ (2), $c=7{\cdot}899$ (6) Å, $\beta=109{\cdot}72$ (6)°. The space group is $P2_1/c$. The structure determination from Patterson and Fourier syntheses was followed by a full-matrix least-squares refinement including anisotropic thermal parameters. For $\mathrm{CuL_2Cl_2}$ the final R value for 961 observed Weissenberg reflexions was 6·8%, whereas for 831 observed Weissenberg reflexions of $\mathrm{CuL_2Br_2}$ a R value of 7·6% was obtained. The structures consist of isolated $\mathrm{CuL_2Cl_2}$ ($\mathrm{CuL_2Br_2}$) units with exactly planar, *trans* square coordination of the copper atom. The Cu-Cl distance is 2·25 Å, the Cu-Br distance is 2·39 Å and the Cu–N distance is 1·98 Å. The fact that there are no further ligands in the neighbourhood of the copper atom which would lead to its common distorted octahedral coordination is attributed to the steric influence of the methyl groups in the α position to the nitrogen atoms.

Introduction

Ludwig & Gasser (1969) reported on the preparation and on spectroscopical investigations on copper(II) complexes of the general formula $\mathrm{CuL_2X_2}$ and $\mathrm{CuL_4X_2}$ where L stands for a unidendate substituted pyridine or piperidine base and X for a halide.

For complexes containing unsubstituted pyridine they found a microsymmetry of D_{2h} with a distorted octahedron consisting of two pyridine, two equatorial