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The Crystal Structure of an Analogue of Nickel Phthalocyanine

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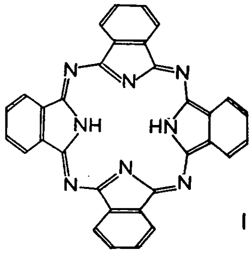
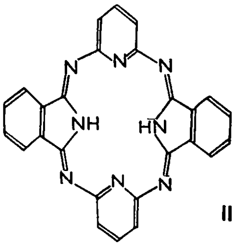
The un-named analogue of nickel phthalocyanine of structure III crystallizes in the monoclinic system with $a = 23{\cdot}5_5$, $b = 3{\cdot}78_1$, $c = 21{\cdot}9_7$ Å and $\beta = 92{\cdot}8°$, with space group $C^6_{2h}\text{–}I2/a$, and with four molecules of $NiC_{26}H_{14}N_8$ in the unit cell. The heavy-atom method of phase determination applied to $F(h0l)$ data enabled a good projection of the structure to be derived, and reliable x and z coordinates to be assigned to the atoms. There was more difficulty over the y coordinates, since only $F(hll)$ data, of lower accuracy, were available. They suggested, however, that the molecule, unlike those of the phthalocyanines, was non-planar; and this was confirmed by a generalized projection. A twofold symmetry axis passes through the nickel atom, and the *iso*indole and pyridine rings are tilted by about 25° out of the plane normal to this axis, and in opposite directions. The stereochemical reasons for this distortion are discussed.

Introduction

The analyses of the crystal structures of phthalocyanine (I) and its metallic derivatives (Robertson, 1935, 1936) are classics in the evolution of X-ray crystallography. Several circumstances combined to render these substances a very favourable case for the application of X-ray methods: they crystallized well, their molecules proved to be planar and highly symmetrical and their unit cells to possess one very short axis (~ 4 Å), and—in particular—the parent compound and its metal derivatives were found to be isomorphous, or very nearly so. The heavy-atom method, and the still more powerful method of isomorphous replacement, could therefore be developed, and their application led to the first direct solutions of the phase problem for organic substances.


I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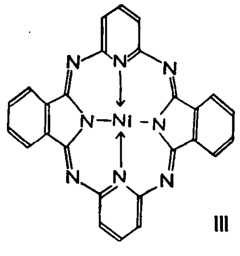
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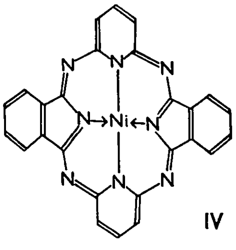
IV

Linstead and his co-workers (cf. Elvidge & Linstead, 1952) have recently described a new series of compounds* of a related type, of which the compound of formula II forms metal derivatives such as III. (An alternative valency-bond structure is shown at IV.) It was of obvious interest to examine these compounds by crystallographic methods; and through the kindness of Prof. Linstead specimens of the parent compound and of its lead and nickel derivatives were made available for X-ray examination. A detailed study of the last of these substances has been made, and the results now reported show important differences between its structure and that of the corresponding phthalocyanine.

Experimental

Preliminary examination by rotation photographs suggested that the nickel and lead compounds were probably isomorphous with each other, but not with the metal-free compound. Attention was therefore concentrated on the nickel compound (III), with the heavy-atom method of phase determination in view. It seemed likely that the nickel atom would be 'heavy' enough for this purpose, whilst avoiding the disadvantages attendant on the presence of so very heavy an atom as lead.

The substance consisted of fairly long, but extremely fine, needles. The crystals were elongated in the direction of [b], and the faces {100} were most prominently developed, with {101} and {$10\bar{1}$} also

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* At the present phase of the organic chemical research work it is difficult to decide on the most suitable system of nomenclature for these compounds. Two names have been tentatively proposed for II: symm-*cyclo*bis-1-iminyl-3-2′-pyrid-6′-yliminoi*so*indoline, and [αγ-di*iso*indoline] [βδ-dipyridine] tetra-azaporphin. Neither name appears to be free from objection. As no trivial name has been given, the compounds II and III will be referred to in this paper by these roman numerals.

appearing. There was some tendency for twinning about (001) to occur. The crystals had been grown from hot nitrobenzene solutions, and attempts to obtain more massive crystals from this solvent had only limited success. The research was therefore carried out on crystals with dimensions of which the following are typical: up to 1 mm. in length, cross-section $0{\cdot}02\times0{\cdot}05$ mm.^{2}, weight $1{\cdot}7\ \mu g$. The difficulties arising from this slenderness of habit will be referred to later.

Rotation, oscillation, and moving-film photographs, using Cu $K\alpha$ radiation, indicated the Laue symmetry to be $2/m$, and led to the following unit-cell data:

$NiC_{26}H_{14}N_8$. Formula weight $= 497{\cdot}1$.

Monoclinic prismatic.

$$a = 23{\cdot}5_5,\ b = 3{\cdot}78_1,\ c = 21{\cdot}9_7\ \text{Å},\ (\text{each} \pm 0{\cdot}2\%),\ \beta = 92{\cdot}8^\circ\ .$$

$$U = 1954\ \text{Å}^3.\ D_m = 1{\cdot}677,\ Z = 4,\ D_x = 1{\cdot}690.\ F(000) = 1016.$$

Absorption coefficient for Cu $K\alpha$ radiation $= 18{\cdot}8$ cm.$^{-1}$.

Absent reflexions are $h0l$ when either h or l is odd, and hll when $h+l$ is even. (Body-centring is also shown in a [111] rotation photograph, which indicated an axial translation of 16·5 Å.) The space group is thus either C_s^4–Ia or C_{2h}^6–$I2/a$ (equivalent to $C2/c$ of *International Tables* with a change of z axis). The latter was provisionally adopted, and it appears to be borne out by the subsequent analysis. It implies that the molecule of III possesses either a centre, or a twofold axis, of symmetry, with the nickel atoms in special positions. With the above choice of axes the general positions are $(0, 0, 0;\ \frac{1}{2}, \frac{1}{2}, \frac{1}{2})\pm|x, y, z;\ x, \bar{y}, \frac{1}{2}+z|$.

Intensity measurements were made visually on moving-film photographs, using the multiple-film technique. The analysis has been principally based on the b-axis projection, and some 204 $h0l$ reflexions were recorded—about 60% of those theoretically accessible. Because of the crystal habit, it was difficult to record the weaker reflexions, and the intensity data (covering a range of 1000:1) cannot be regarded as very accurate. On the other hand, absorption was small (never more than 10%), and no attempt to correct for it was thought necessary. After applying the other usual corrections, the derived relative structure amplitudes were placed on an approximately absolute scale by comparing their average value with a corresponding average for nickel phthalocyanine (Robertson & Woodward, 1937). Later, a more exact scaling was possible by reference to the calculated structure factors.

Determination of the structure

In the $h0l$-zone of nickel phthalocyanine the nickel atom determines the phases (i.e. the signs) of all but 23 of the 161 observed structure factors, and of all but 5 of the strongest 87. A similar situation being presumed with III, a preliminary b-axis electron-density projection was calculated, using 91 terms, all with positive signs. (The origin was taken at the nickel atom at this stage.) It subsequently transpired that 7 of these signs were wrong. Despite this, and the fact that the $F(h0l)$ values used in this synthesis, which had been obtained using a twinned crystal, involved some minor errors that were subsequently corrected, the resulting electron-density map (Fig. 1) clearly revealed the general plan of the molecule, and thus confirmed the structure postulated to account for the

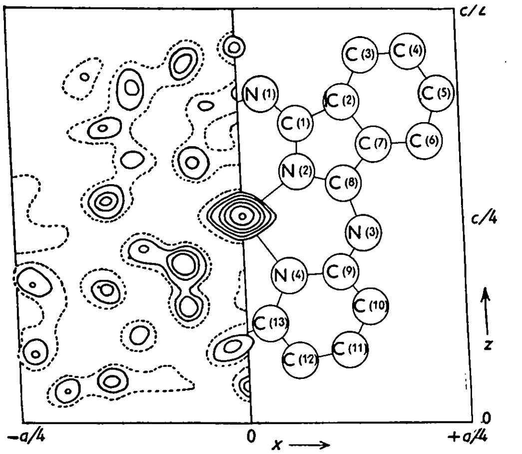

Fig. 1. Composite diagram: left-hand side showing first electron-density projection on (010), with arbitrary contour-line scale; right-hand side showing numbering of atoms. (Atoms referred to in the text by primed numbers are those in the other half of the molecule, produced by inversion through the nickel atom at its centre.)

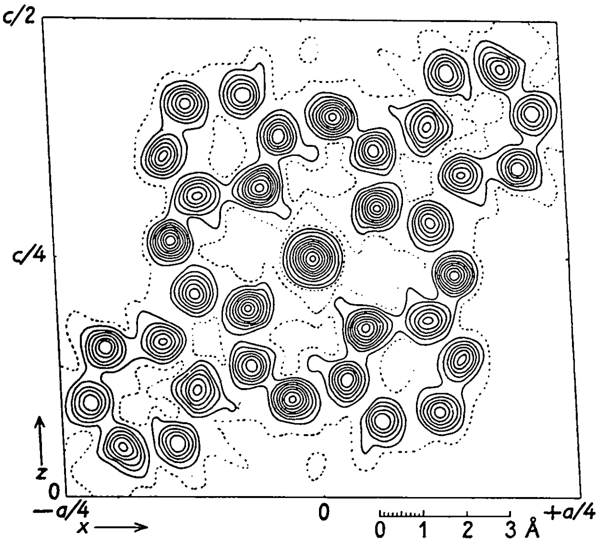

Fig. 2. Final electron-density map projected on (010). Contour-line scale: 1 e.Å^{-2}, with first line broken. For the nickel atom, only the 1st, 2nd, 4th, and thereafter every fourth, lines are shown.

Table 1. *Atomic coordinates, with respect to an origin at a centre of symmetry on the c glide plane*

x, y and z as fractions of the primitive translations; X, Y, Z, X' and Z' in Ångström units, the last two referred to orthogonal axes, with $[Z']$ parallel to $[z]$

Atom	x	y	z	X	Y	Z	X'	Z'
Ni	0·0000	0·18	0·2500	0·000	0·68	5·493	0·000	$5{\cdot}492_5$
N(1)	0·0265	0·26	0·3978	$0{\cdot}624_5$	0·98	8·739	0·624	$8{\cdot}708_5$
N(2)	0·0653	0·20	0·3044	$1{\cdot}536_5$	$0{\cdot}75_5$	$6{\cdot}688_5$	1·535	$6{\cdot}613_5$
N(3)	0·1371	0·10	0·2328	$3{\cdot}229_5$	0·38	5·115	$3{\cdot}225_5$	$4{\cdot}957_5$
N(4)	0·0502	0·16	0·1800	1·182	$0{\cdot}60_5$	$3{\cdot}954_5$	1·181	3·897
C(1)	0·0652	0·15	0·3630	$1{\cdot}535_5$	$0{\cdot}56_5$	7·975	1·534	7·900
C(2)	0·1179	−0·02	0·3885	2·776	$-0{\cdot}07_5$	$8{\cdot}535_5$	2·773	8·400
C(3)	0·1397	−0·12	0·4445	3·289	$-0{\cdot}45_5$	$9{\cdot}764_5$	3·285	9·604
C(4)	0·1927	−0·27	0·4491	4·539	−1·02	$9{\cdot}867_5$	$4{\cdot}533_5$	9·646
C(5)	0·2250	−0·31	0·3992	5·299	−1·17	8·769	$5{\cdot}292_5$	8·511
C(6)	0·2066	−0·21	0·3434	$4{\cdot}864_5$	$-0{\cdot}79_5$	7·544	4·859	7·307
C(7)	0·1515	−0·06	0·3385	3·568	$-0{\cdot}22_5$	7·436	$3{\cdot}563_5$	7·262
C(8)	0·1164	0·08	0·2882	2·741	0·30	6·331	$2{\cdot}737_5$	6·197
C(9)	0·1096	0·22	0·1855	2·580	0·83	4·075	2·577	3·949
C(10)	0·1405	0·37	0·1448	3·309	1·40	$3{\cdot}180_5$	3·305	3·019
C(11)	0·1167	0·50	0·0897	2·747	1·89	1·970	2·744	1·836
C(12)	0·0612	0·46	0·0807	1·442	1·74	$1{\cdot}773_5$	1·440	1·703
C(13)	0·0276	0·30	0·1224	0·649	$1{\cdot}13_5$	2·689	0·648	2·657

chemical evidence. The analysis then proceeded by successive syntheses until the final electron-density map shown in Fig. 2 was reached. All the atoms (except hydrogen) are well resolved, and the nitrogen atoms are easily distinguished from the carbons by the greater height of their peaks. Thus far the structure determination is absolute.

The final x and z coordinates given in Table 1 were derived from this map, with some minor changes suggested by an (F_o-F_c)-synthesis. (The numbering of the atoms is shown in Fig. 1; primed numbers refer to corresponding atoms in the other half of the molecule.) In determining coordinates from the electron-density data, use was made of a least-squares method which had been described to the author by Dr J. D. Dunitz and attributed by him to Dr V. Schomaker. No termination-of-series corrections have been applied, as the accuracy was not thought sufficient to justify such refinement. In Table 1 atomic positions are also given with respect to orthogonal axes, X' and Z'.

Structure factors calculated from these x and z coordinates are compared with the observed structure amplitudes in Table 2. The atomic scattering functions used initially were those of James & Brindley (*Internationale Tabellen*) for nickel, and of McWeeny (1951) for carbon and nitrogen, each with a suitable temperature factor. It was subsequently found desirable to modify these functions. The problem was to vary the three scattering curves independently so as to attain the best possible agreement between observed and calculated structure factors; and this was done by applying the least-squares method to groups of structure factors covering various limited ranges of sin θ—a method essentially similar to that recently described by Luzzati (1953). The scattering functions adopted were as follows:

$\sin\theta$	f_{Ni}	f_{N}	f_{C}
0·0	26·0	(7·5)	6·0
0·1	24·0	$6{\cdot}3_5$	$5{\cdot}0_5$
0·2	19·9	4·9	4·0
0·3	16·1	$3{\cdot}8_5$	$2{\cdot}9_5$
0·4	12·9	3·2	$2{\cdot}2_5$
0·5	10·2	$2{\cdot}4_5$	$1{\cdot}6_5$
0·6	8·5	1·9	$1{\cdot}2_5$
0·7	6·9	$1{\cdot}4_5$	$0{\cdot}9_5$
0·8	5·3	1·1	$0{\cdot}7_5$
0·9	3·8	$0{\cdot}9_5$	$0{\cdot}6_5$
1·0	2·5	$0{\cdot}8_5$	0·6

The values for nickel are somewhat anomalous, and a similar effect can be detected with the phthalocyanine (Robertson & Woodward, 1937, p. 226). The agreement between observed and calculated amplitudes is fairly good for a structure of this kind, the value of $R\ (=\Sigma||F_o|-|F_c||\div\Sigma|F_o|)$ being 11·8%. A detailed statistical consideration of errors has not been attempted, but the x and z coordinates are probably reliable to ±0·02 Å, though the position of C(5) may be less certain.

In approaching the y coordinates, the molecule was at first expected to be planar, as are those of the phthalocyanines. Evidence against this supposition soon appeared. For instance, the projected aspect of the molecule in Fig. 2 could not be produced by merely tilting a planar molecule with normal dimensions. The crystal habit made it impracticable to obtain intensity measurements in either of the other two principal zones. The y values had therefore to be inferred from the intensities of the $h1l$-series, only the first layer line about the b axis being conveniently accessible. 108 such reflexions were recorded, and, though the resulting amplitudes are not of high accuracy, they were adequate to indicate the general pattern of the structure in the third dimension.

The space group $I2/a$ provides special positions of

Table 2. *Observed structure amplitudes and calculated structure factors for $h0l$*

$h0l$	F_o	F_c
200	166	211
400	63	−62
600	72	60
800	106	99
10,0,0	17	−20
12,0,0	103	−85
14,0,0	78	81
16,0,0	70	75
18,0,0	38	38
20,0,0	25	22
22,0,0	$<$ 18	3
24,0,0	$<$ 17	−18
26,0,0	$<$ 15	17
28,0,0	17	25
$\overline{28}$,0,2	28	−24
$\overline{26}$,0,2	$<$ 15	−2
$\overline{24}$,0,2	$<$ 17	−2
$\overline{22}$,0,2	$<$ 18	−18
$\overline{20}$,0,2	57	−58
$\overline{18}$,0,2	63	−63
$\overline{16}$,0,2	87	−87
$\overline{14}$,0,2	80	−82
$\overline{12}$,0,2	19	−16
$\overline{10}$,0,2	26	−26
$\overline{8}$02	26	−42
$\overline{6}$02	114	−107
$\overline{4}$02	80	83
$\overline{2}$02	186	−204
002	165	−199
202	87	−82
402	78	−93
602	11	16
802	129	−125
10,0,2	13	−12
12,0,2	61	−50
14,0,2	48	−49
16,0,2	$<$ 16	−17
18,0 2	33	−40
20,0,2	19	−27
22,0,2	$<$ 18	−28
24,0,2	43	−46
26,0,2	$<$ 16	−28
28,0,2	23	−24
$\overline{22}$,0,4	40	49
$\overline{20}$,0,4	94	98
$\overline{18}$,0,4	38	44
$\overline{16}$,0,4	58	71
$\overline{14}$,0,4	43	45
$\overline{12}$,0,4	56	39
$\overline{10}$,0,4	15	7
$\overline{8}$04	27	25
$\overline{6}$04	91	92
$\overline{4}$04	76	83
$\overline{2}$04	$<$ 18	11
004	129	−121
204	35	54
404	22	−20
604	75	72
804	101	105
10,0,4	130	140
12,0,4	126	110
14,0,4	52	53
16,0,4	52	57
18,0,4	$<$ 17	5
20,0,4	$<$ 18	−4
22,0,4	54	61
24,0,4	54	57
$\overline{22}$,0,6	23	−35
$\overline{20}$,0,6	21	30
$\overline{18}$,0,6	38	−24
$\overline{16}$,0,6	65	−70
$\overline{14}$,0,6	18	−15
$\overline{12}$,0,6	36	−35
$\overline{10}$,0,6	48	−52
$\overline{8}$06	176	−149
$\overline{6}$06	43	−52
$\overline{4}$06	30	−43
$\overline{2}$06	99	−91
006	95	−104
206	69	−68
406	97	−101
606	82	−88
806	113	−99
10,0,6	60	−88
12,0,6	18	−16
14,0,6	38	−34
16,0,6	19	−22
18,0,6	$<$ 17	−6
20,0,6	$<$ 17	1
22,0,6	24	−23
$\overline{28}$,0,8	25	27
$\overline{26}$,0,8	$<$ 15	4
$\overline{24}$,0,8	$<$ 16	25
$\overline{22}$,0,8	$<$ 17	8
$\overline{20}$,0,8	$<$ 18	−9
$\overline{18}$,0,8	$<$ 17	0
$\overline{16}$,0,8	20	−34
$\overline{14}$,0,8	61	64
$\overline{12}$,0,8	64	73
$\overline{10}$,0,8	117	95
$\overline{8}$08	118	114
$\overline{6}$08	112	105
$\overline{4}$08	160	144
$\overline{2}$08	25	30
008	20	20
208	95	96
408	22	50
608	91	85
808	112	114
10,0,8	17	11
12,0,8	21	20
14,0,8	20	13
16,0,8	41	31
18,0,8	21	−14
20,0,8	$<$ 18	−6
22,0,8	38	37
24,0,8	22	25
$\overline{28}$,0,10	34	−38
$\overline{26}$,0,10	$<$ 13	−11
$\overline{24}$,0,10	$<$ 15	−5
$\overline{22}$,0,10	58	−56
$\overline{20}$,0,10	114	−107
$\overline{18}$,0,10	$<$ 18	6
$\overline{16}$,0,10	22	32
$\overline{14}$,0,10	36	−53
$\overline{12}$,0,10	68	−70
$\overline{10}$,0,10	$<$ 15	−16
$\overline{8}$,0,10	25	17
$\overline{6}$,0,10	145	−138
$\overline{4}$,0,10	109	−103
$\overline{2}$,0,10	20	−1
0,0,10	27	−23
2,0,10	52	52
4,0,10	54	57
6,0,10	129	−110
8,0,10	62	−71
10,0,10	35	−37
12,0,10	34	−39
14,0,10	142	−128
16,0,10	82	−85
18,0,10	43	38
20,0,10	33	−26
22,0,10	42	−44
24,0,10	26	−28
$\overline{26}$,0,12	27	27
$\overline{24}$,0,12	$<$ 17	16
$\overline{22}$,0,12	31	43
$\overline{20}$,0,12	66	57
$\overline{18}$,0,12	$<$ 18	17
$\overline{16}$,0,12	$<$ 18	−7
$\overline{14}$,0,12	20	21
$\overline{12}$,0,12	56	57
$\overline{10}$,0,12	$<$ 16	−8
$\overline{8}$,0,12	$<$ 15	11
$\overline{6}$,0,12	50	56
$\overline{4}$,0,12	59	47
$\overline{2}$,0,12	32	35
0,0,12	44	48
2,0,12	31	32
4,0,12	49	55
6,0,12	43	36
8,0,12	60	58
10,0,12	47	48
12,0,12	$<$ 17	9
14,0,12	69	68
16,0,12	20	35
18,0,12	61	62
20,0,12	23	19
22,0,12	$<$ 15	13
24,0,12	30	30
$\overline{26}$,0,14	27	−28
$\overline{24}$,0,14	$<$ 14	21
$\overline{22}$,0,14	$<$ 15	−8
$\overline{20}$,0,14	$<$ 17	−19
$\overline{18}$,0,14	$<$ 18	4
$\overline{16}$,0,14	$<$ 17	−6
$\overline{14}$,0,14	43	−45
$\overline{12}$,0,14	58	−51
$\overline{10}$,0,14	71	−64
$\overline{8}$,0,14	56	−51
$\overline{6}$,0,14	70	−80
$\overline{4}$,0,14	50	−53
$\overline{2}$,0,14	19	−18
0,0,14	68	−70
2,0,14	110	−109
4,0,14	79	−89
6,0,14	$<$ 16	−2
8,0,14	44	−40
10,0,14	$<$ 17	−18
12,0,14	$<$ 17	18
14,0,14	50	54
16,0,14	$<$ 18	−17
18,0,14	52	−62
20,0,14	$<$ 15	−10
22,0,14	37	−32
24,0,14	29	−22
$\overline{16}$,0,16	51	47
$\overline{14}$,0,16	26	33
$\overline{12}$,0,16	59	56
$\overline{10}$,0,16	45	40
$\overline{8}$,0,16	$<$ 17	2
$\overline{6}$,0,16	$<$ 17	25
$\overline{4}$,0,16	$<$ 17	5
$\overline{2}$,0,16	73	80
0,0,16	29	32

Table 2 (*cont.*)

$h0l$	F_o	F_c
2,0,16	57	62
4,0,16	66	72
6,0,16	41	24
8,0,16	< 17	6
10,0,16	< 17	− 4
12,0,16	< 18	16
14,0,16	< 18	3
16,0,16	23	30
18,0,16	21	22
20,0,16	28	29
$\overline{18}$,0,18	52	−53
$\overline{16}$,0,18	36	−46
$\overline{14}$,0,18	41	−37
$\overline{12}$,0,18	40	−39
$\overline{10}$,0,18	< 18	16
$\bar{8}$,0,18	< 18	10
$\bar{6}$,0,18	41	40
$\bar{4}$,0,18	24	−20
$\bar{2}$,0,18	< 15	−11
0,0,18	25	−22
2,0,18	112	−104
4,0,18	46	−40
6,0,18	32	−22
8,0,18	< 18	−14
10,0,18	49	−47
12,0,18	49	−41
14,0,18	23	−27
16,0,18	46	−40
18,0,18	30	−34
$\overline{14}$,0,20	57	54
$\overline{12}$,0,20	< 17	16
$\overline{10}$,0,20	< 17	− 6
$\bar{8}$,0,20	< 18	22
$\bar{6}$,0,20	76	72
$\bar{4}$,0,20	44	40
$\bar{2}$.0,20	50	−51
0,0,20	46	52
2,0,20	50	58
4,0,20	< 18	12
6,0,20	< 18	− 4
8,0,20	24	31
10,0,20	79	70
$\overline{12}$,0,22	26	−25
$\overline{10}$,0,22	19	−31
$\bar{8}$,0,22	20	−30
$\bar{6}$,0,22	76	−75
$\bar{4}$,0,22	44	−50
$\bar{4}$,0,24	26	32
$\bar{2}$,0,24	21	25
0,0,24	< 15	− 1
2,0,24	< 15	13
4,0,24	< 15	13
6,0,24	< 15	17
8,0,24	< 14	10
10,0,24	19	19
$\bar{2}$,0,26	21	−23
0,0,26	< 13	−14
2,0,26	< 13	− 5
4,0,26	27	−33
6,0,26	< 13	−17
8,0,26	18	−15
10,0,26	22	−27
$\bar{4}$,0,28	29	34
$\bar{2}$,0,28	23	35

two kinds, *a–d* and *e* of *International Tables*. In the *b*-axis ($h0l$) projection these appear as centres of inversion, and are indistinguishable. However, in the $h1l$-series of reflexions a heavy atom in the first kind of position would contribute only to alternate spectra (in *a* or *b* only to those even in l; in *c* or *d* only to those odd in l). A statistical examination of the $F(h1l)$ values did indeed show an alternation in favour of the odd terms, but the averages differed by only 18%. Whilst this is certainly significant, it is much less than would be expected for positions *c* or *d*, as is seen by an elementary application of the methods for predicting average values of the structure factor, or by comparison of corresponding values for phthalocyanine and its nickel derivative (~ 30%). It follows that the nickel atoms of III occupy positions of type *e* ($0, y, \frac{1}{4}$; $0, \bar{y}, \frac{3}{4}$), and furthermore that y_{Ni} is probably in the range $0{\cdot}16b-0{\cdot}19b$. It also follows that the molecule possesses a digonal axis of symmetry, and not a centre. Trial-and-error methods then led to a structure like that suggested in Fig. 3. The atoms N(2), N(4), N(2′) and N(4′) are approximately coplanar with the nickel atom; the *iso*indole residues are tilted out of this plane through about 25° in one direction, and the pyridine residues through a similar angle in the opposite direction.

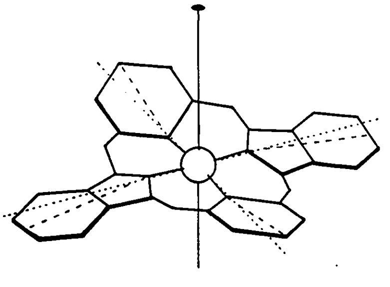

Fig. 3. Approximate perspective drawing, suggesting the manner of molecular distortion.

This type of non-planarity was unambiguously confirmed by a generalized projection (Cochran & Dyer, 1952). In this synthesis $F(h1l)$ terms were used, instead $F(h0l)$ as in an ordinary two-dimensional synthesis. Whilst, for a centrosymmetrical crystal, $F(h0l) = F(\bar{h}0\bar{l})$, the analogous proposition for $F(h1l)$ is not necessarily true. In the present space group, $F(h1l) = \pm F(\bar{h}1\bar{l})$, according as l is even or odd. Therefore only the 43 even terms could be used for the generalized projection, and these are the terms of lower average magnitude, and hence of less certain signs. However, by a suitable transfer of origin (to $\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$) the above rule can be reversed, and the syn-

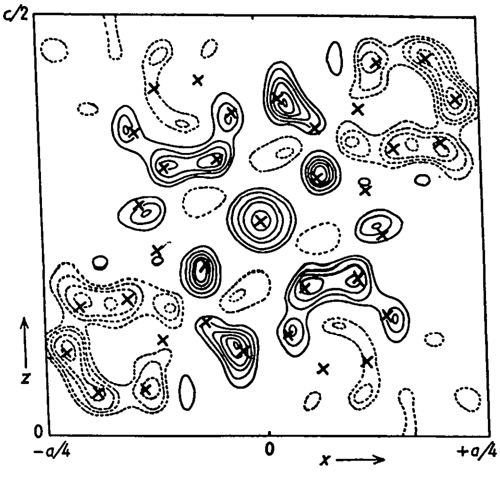

Fig. 4. Generalized projection with respect to the plane, $y = \frac{1}{4}b$, calculated from $h1l$ data. Contour-line scale arbitrary; negative contours represented by broken lines. The atomic positions given by Fig. 2 are indicated by crosses.

Table 3. *Observed structure amplitudes and calculated structure factors for* $h1l$

$h1l$	F_o	F_c
013	127	128
015	< 10	9
017	79	75
019	< 13	−10
0,1,11	26	−21
0,1,13	50	−44
0,1,15	50	54
0,1,17	86	−72
11$\bar{8}$	21	6
11$\bar{6}$	18	29
11$\bar{4}$	62	55
11$\bar{2}$	158	−206
112	25	−14
114	44	60
116	12	− 3
118	47	30
21$\bar{9}$	76	80
21$\bar{7}$	60	−58
21$\bar{5}$	16	15
21$\bar{3}$	81	59
21$\bar{1}$	125	144
211	205	−292
213	31	10
215	44	−25
217	24	49
219	42	32
2,1,11	34	31
2,1,13	66	−71
2,1,15	74	83
31$\bar{8}$	72	56
31$\bar{6}$	< 12	24
31$\bar{4}$	46	−37
31$\bar{2}$	133	−118
312	140	102
314	24	57
316	26	−30
4,1,$\overline{11}$	63	−56
41$\bar{9}$	47	49
41$\bar{7}$	68	−79
41$\bar{5}$	39	50
41$\bar{3}$	< 11	−28
41$\bar{1}$	107	102
411	29	41
413	18	−27
415	81	−78
417	66	66
419	50	−42
5,1,$\overline{12}$	57	75
5,1,$\overline{10}$	45	−49
51$\bar{8}$	50	43
51$\bar{6}$	62	−48
51$\bar{4}$	< 11	4
51$\bar{2}$	31	50
510	33	−17
512	26	−46
514	< 13	32
516	< 13	−19
518	23	−20
6,1,$\overline{11}$	26	−27
61$\bar{9}$	87	89
61$\bar{7}$	142	−143
61$\bar{5}$	60	53
61$\bar{3}$	37	−46
61$\bar{1}$	24	18
611	42	−30
613	18	23
615	58	−44
617	110	107
619	26	−42
7,1,$\overline{12}$	52	50
7,1,$\overline{10}$	< 20	−24
71$\bar{8}$	< 17	−22
71$\bar{6}$	78	−72
71$\bar{4}$	67	60
71$\bar{2}$	< 13	13
710	67	68
712	18	−46
714	57	55
716	86	−82
718	26	45
81$\bar{9}$	94	86
81$\bar{7}$	78	−72
81$\bar{5}$	44	54
81$\bar{3}$	58	−49
81$\bar{1}$	58	67
811	21	−44
813	70	68
815	89	−124
817	37	48
819	47	−60
8,1,11	89	91
91$\bar{6}$	34	−34
91$\bar{4}$	23	24
91$\bar{2}$	72	−58
910	< 14	18
912	21	6
914	69	56
916	77	−64
918	34	52
10,1,$\bar{5}$	57	52
10,1,$\bar{3}$	< 16	−11
10,1,$\bar{1}$	29	−30
10,1,1	23	−16
10,1,3	110	106
10,1,5	76	−85
11,1,4	23	− 5
12,1,$\bar{1}$	32	35
12,1,1	< 18	− 7
12,1,3	< 19	25
12,1,5	89	−81
12,1,7	< 21	18
12,1,9	< 23	−25
12,1,11	65	54
13,1,2	49	−38
14,1,$\bar{1}$	29	43
14,1,1	< 19	− 4
14,1,3	78	66
14,1,5	< 20	−40
14,1,7	< 23	25
14,1,9	73	−64
15,1,0	37	44
15,1,2	72	−40
15,1,4	< 22	− 1
15,1,6	< 23	−17
15,1,8	90	71
16,1,$\bar{3}$	89	−78
16,1,$\bar{1}$	< 21	45
16,1,1	45	−61
17,1,$\bar{2}$	47	−46
18,1,$\bar{3}$	102	−86

thesis represented in Fig. 4 was based on 65 terms odd in l. This projection should ideally resemble Fig. 2, except that each atomic peak is now *modulated* by a factor $\cos 2\pi(ky/b)$, where y is the coordinate of that atom with respect to the origin plane chosen ($y = \frac{1}{4}b$ in the present case). The signs, and approximate heights, of the peaks confirm the structure sketched in Fig. 3. And incidentally the general resemblance between Figs. 2 and 4 confirms the original projected structure, and does so on the basis of quite independent experimental data.

As was suggested by its originators, it is in principle possible to use such a projection to refine the y coordinates. Since only first-layer-line data were available (and only 65 structure factors), the degree of refinement to be expected would not be considerable. Some amendment of the original coordinates was however attempted; in particular Fig. 4 suggested that the *iso*indole and pyridine rings are slightly twisted ($\sim 8°$) about axes running, respectively, through Ni–N(2) and Ni–N(4), as is also represented in Fig. 3. With these various inclinations in view, the final y coordinates were chosen which (to the nearest $0{\cdot}01b$) kept the atoms of the pyridine and *iso*indole rings, respectively, co-planar. These y values are given in Table 1.

These coordinates were used in calculating the structure factors which are compared with the observed amplitudes in Table 3. Agreement was improved compared with that given by the original trial structure; the quantity R is about 19·6% for all 108 terms; it falls to 18·5% if 11$\bar{2}$ and 211, which are likely to be affected by extinction errors, are omitted; and it has the value 16·2% if the odd terms in *l*, with the larger contribution from the heavy atom, are considered alone. No great accuracy is claimed for the *y* coordinates, but this measure of agreement is held to be adequate to support the general pattern of distortion described. The atomic scattering curves used were those already tabulated.

Molecular dimensions and discussion

The principal interatomic distances are given in Table 4. The distances as projected on (010), which are much more accurately known, are added in parentheses. The latter are probably reliable to ±0·03 Å; the former may be in error by as much as ±0·05 Å. The shortest intermolecular contacts appear to be 3·6 Å between C(3) and C(11) of a second molecule related to the first by the *c* glide plane, and $3{\cdot}7_5$ Å between C(5) and C(10′) of the molecule resulting from the *a* glide plane. All other such distances exceed 3·8 Å. With a *b* axial length of 3·78 Å, and the heterocyclic rings tilted as described above, the perpendicular distance between rings in successive unit cells will have the usual value of about 3·4 Å.

Table 4. *Bond lengths and bond angles*

Lengths are given in Ångström units; the values in parentheses are the lengths projected on (010)

N(1)–C(1)	1·29 (1·22)	C(8)–N(3)	1·33 (1·33)
C(1)–C(2)	1·48 (1·34)	N(3)–C(9)	1·30 (1·20)
C(2)–C(3)	1·36 (1·31)	C(9)–C(10)	1·31 (1·18)
C(3)–C(4)	1·37 (1·29)	C(10)–C(11)	1·40 (1·31)
C(4)–C(5)	1·37 (1·25)	C(11)–C(12)	1·32 (1·31)
C(5)–C(6)	1·33 (1·28)	C(12)–C(13)	1·38 (1·24)
C(6)–C(7)	1·41 (1·30)	N(4)–C(9)	1·42 (1·40)
C(7)–C(2)	1·39 (1·39)	N(4)–C(13)	1·45 (1·31)
C(7)–C(8)	1·45 (1·35)	C(13)–N(1′)	1·34 (1·33)
N(2)–C(1)	1·30 (1·29)	Ni–N(2)	1·90 (1·90)
N(2)–C(8)	1·35 (1·27)	Ni–N(4)	$1{\cdot}98_5$ (1·98)

C(13′)–N(1)–C(1)	122°
C(8)–N(3)–C(9)	124°
N(2)–Ni–N(4)	$89{\cdot}_7{}^{\circ}$
N(4)–Ni–N(2′)	$90{\cdot}_3{}^{\circ}$

The chief point of interest in this structure is its non-planarity. The planar phthalocyanine molecule is one of great stability and is hardly affected by the introduction of the metal atom. The structure may therefore be regarded as a norm, exemplifying a set of molecular dimensions that are peculiarly free from strain. The distortion of molecule III can then reasonably be related to any failure of the dimensions characteristic of I to fit into it. In phthalocyanine the C–N bonds radiating from the *iso*indole rings (corresponding to C(1)–N(1) and C(8)–N(3) of III) subtend an angle of about 153°. Four such *iso*indole systems can therefore be linked together in one plane, so as to give a nitrogen valency angle of about 117°—a value appropriate to bonds possessing about 50% of double-bond character—, and so as to bring the other four nitrogen atoms to within 1·8–1·9 Å of the molecular centre—a distance convenient for the formation of Ni–N bonds. In compound III two of the *iso*indole residues are replaced by pyridines. The natural angle between the bonds radiating from the 2- and 6-positions of pyridine should be about 120°. Were the molecule to remain planar and otherwise undistorted, the consequences would be that the valency angles at N(1) and N(3) would rise to about 134°, and that the atoms N(4) and N(4′) would be about 2·4 Å from the centre. The observed distortion can be interpreted as tending to counter these two consequences.

This counter-effect can occur in two ways: by the widening of the angle between the pyridine bonds; and by the buckling of the whole macrocycle—a process quite analogous to that whereby the cyclohexane molecule achieves a ring of six atoms (with 120° as its natural angle) whilst maintaining an angle of 110° at each carbon atom. Both kinds of distortion occur. The widening of the angle between C(9)–N(3) and C(13)–N(1′), to about 143°, can easily be seen in Fig. 2. The buckling takes two forms: (i) the tilting of the *iso*indole rings about a line parallel to C(1) · · · C(8), and of the pyridines in the opposite sense about a line parallel to C(9) · · · C(13); and (ii) the twisting of each ring system about the lines Ni–N(2) and Ni–N(4) respectively. Experiments with models suggest that (i) has the effect of diminishing the valency angle at N(1) and N(3), and (ii) that of bringing N(4) closer to Ni.

These distortions will be opposed by several factors, of which two require comment. First, the resonance stabilization of these large ring systems depends on maintaining a nearly planar arrangement of their atoms (e.g. Coulson, 1952). The resonance energy will be diminished, though not perhaps very greatly, by a 25° departure from the planar. Secondly, the nickel atoms will make use of hybridized dsp^2 orbitals to accommodate the electron-pairs provided by N(2) and N(4). Such hybridized orbitals require a planar distribution of bonds. The deviation implied by the coordinates of Table 1 is slight, amounting to about 2° only; and it seems to be indicated by Fig. 4, which shows a small, but probably significant, difference between the heights of the atomic peaks in question.

In the phthalocyanines the sixteen alternate carbon and nitrogen atoms constitute an inner resonating system that is conjugated to the benzenoid rings only to a lesser extent (cf. Robertson, 1936, p. 1205). The situation in III seems to be different. The bonds N(4)–C(9) and N(4)–C(13) are lengthened, no doubt in order to allow N(4) to approach the more closely to Ni. They can therefore have less double-bond character than N(2)–C(1) and N(2)–C(8), or than the corresponding bonds in phthalocyanine (~ 1·34 Å). On the other hand the C–C bonds of the pyridine appear to be rather short on the average. The obvious interpretation is that the conjugation is mostly directed round by way of these carbon atoms, giving a 20-atom conjugated ring: N(1)–C(1)–N(2)–C(8)–N(3)–C(9)–C(10)–C(11)–C(12)–C(13)–N(1′)– etc. Elvidge & Linstead (1952) suggested that this canonical form might contribute appreciably to the stabilization of III. The bond-lengths now reported support this suggestion, and amplify it by making it appear possible that this form is predominant.

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The Structures of Molecular Compounds Exhibiting Polarization Bonding. I. General Introduction and the Crystal Structure of Phenoquinone

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'Polarization bonding' is the term which has been introduced to describe the interaction between polarizing and polarizable molecules. In crystalline molecular compounds formed by nitro-compounds and quinones, such interaction is revealed by the unusual plane-to-plane stacking of the molecules rather than by a shortening of the van der Waals separations.

Crystals of phenoquinone, $(C_6H_5OH)_2.C_6H_4O_2$, are monoclinic, space group $P2_1/c$, with two formula units in each cell of dimensions $a_0 = 11{\cdot}16$, $b_0 = 5{\cdot}97$, $c_0 = 11{\cdot}48$ Å, $\beta = 100°$. By two-dimensional Fourier methods it is found that each quinone molecule is sandwiched between two centro-symmetrically related phenol molecules arranged parallel to the quinone with perpendicular separations of 3·33 Å. Such groups of three molecules are stacked in columns parallel to [201] and the columns are linked by hydrogen bonds of length 2·64 Å between phenolic OH groups and quinone oxygen atoms.

It is suggested that the polarization bonding in complexes of this type might be interpreted as the formation of partial molecular π-bonds.

Introduction: polarization bonding

The term 'polarization bonding' has recently been introduced (McKeown, Ubbelohde & Woodward, 1951) to describe the interaction between a polarizing molecule and a polarizable molecule, as found, for example, in molecular compounds formed by nitro compounds, quinones, etc. with aromatic hydrocarbons, amines and phenols. Although such bonding does not necessarily result in an unusually close approach of the two molecules, they regard the interaction between adjacent molecules in crystalline *p*-nitroaniline as being an extreme case of polarization bonding on the grounds of a close approach of 2·66 Å observed (Abrahams & Robertson, 1948) between an oxygen atom of the NO_2 group and the CH group *ortho* to the NH_2 group. A study of the thermal expansion of *p*-nitroaniline (McKeown *et al.*, 1951) reveals that the short intermolecular distance of the 'polarization bond' is associated with the direction of maximum coefficient of expansion and it is tentatively proposed that this may be accounted for by the overlap of two potential energy curves corresponding to resonance between the two structures