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Two Crystal Structures Towards the Discotic Columnar Mesophase of (1,4,8,11,15,18,22,25-Octahexylphthalocyaninato)nickel

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Abstract

(1,4,8,11,15,18,22,25-Octahexylphthalocyaninato)-nickel is a thermotropic liquid crystal, undergoing a transition to a discotic columnar mesophase at 418 K. Its crystals are weakly diffracting needles. Single-crystal X-ray diffraction studies at 103 K, using intense synchrotron radiation of wavelength 0.504 Å at Station F2, CHESS and the 'Princeton 1k' CCD area detector, and at 295 K using a Cu $K\alpha$ rotating anode diffractometer, have respectively shown that the symmetry of the crystals is increased from primitive monoclinic (space group $P2_1/n$) to C-centred monoclinic (space group $C2/c$) when the temperature is raised. Solution of the structure at each temperature shows that the increase in symmetry at 295 K arises from slight movement of the molecules, as well as increased thermal motion of the hexyl groups, and small conformational changes in these groups, indicating the first stage of the transition to the discotic columnar mesophase, when the hexyl groups are thought to become completely mobile. The quality of the refinement of the structure is indicative of what can now be realized by employing multipole wiggler synchrotron radiation and a CCD area detector, as well as cryocooling, for difficult small molecule samples. The temperature of the space group transition was determined at the Daresbury SRS, on Station 7.2, using a CCD detector to monitor an area of the diffraction pattern, whilst varying the temperature systematically. A gradual appearance of spots for $h+k=2n+1$ occurred between 205 and 195 K. Tests were also made using an image plate system at 195 and 293 K, which confirmed the transition from primitive to C-centred lattice symmetry with temperature. No other changes were apparent on the CCD or IP detectors.

1. Introduction

Phthalocyanines are important commercial pigments and catalysts (Moser & Thomas, 1983*b*). They also exhibit interesting semiconductor and electro-optical properties in the solid state, which render them important materials for applications in advanced technologies (see, for example, Leznoff & Lever, 1989; Gregory, 1991; Ao, Kümmert & Haarer, 1995; Wright, 1989; Wöhrle & Meissner, 1991; Frampton, O'Connor, Peterson & Silver, 1988). Such properties are critically dependent upon molecular packing and this can vary significantly from one polymorphic form to another. While there are numerous structure determinations of unsubstituted phthalocyanines, especially of the parent and its transition metal derivatives in the more common α and β forms (for compilations see, for example, Moser & Thomas, 1983*a*; Snow & Barger, 1989; Cook, 1993), much less is known about derivatives bearing substituents at the ring sites. Among the latter, phthalocyanines highly substituted with aliphatic chains are of particular interest, since many of these materials undergo a transition at elevated temperatures to a liquid crystal discotic columnar mesophase (Simon & Bassoul, 1993; Cherodian *et al.*, 1991). In addition, such substituents are likely to promote new types of molecular assemblies of the macrocycle in the crystalline state.

The first crystal structure determination of one of these materials was carried out on 1,4,8,11,15,18,22,25-octahexylphthalocyanine (Chambrier, Cook, Helliwell & Powell, 1992). As with other members of this series, crystals of this material were weakly diffracting, necessitating data collection using a rotating anode Cu $K\alpha$ source and an AFC-5*R* diffractometer. Determination of the structure showed that six of the hexyl groups attached to the aromatic core are positioned approximately in its plane. The other two are approximately perpendicular to the aromatic plane and thus act as spacers between the phthalocyanine cores, such that the minimum distance is 8.5 Å. It was suggested that at elevated temperatures the hexyl groups would become mobile, allowing the distance between aromatic cores to reduce to ~4.4 Å and explaining the transition to the liquid crystal phase. However, spectroscopic evidence from thin films suggested that different modes of packing exist for other homologues and indeed also for compounds with the same length chains, but with metal(II) ions substituted in the central cavity

Table 1. *Experimental details*

	Cu $K\alpha$	CHESS
Crystal data		
Chemical formula	$C_{80}H_{112}N_8Ni$	$C_{80}H_{112}N_8Ni$
Chemical formula weight	1244.52	1244.52
Cell setting	Monoclinic	Monoclinic
Space group	$C2/c$	$P2_1/n$
a (Å)	22.55 (2)	22.347
b (Å)	37.14 (1)	37.246
c (Å)	18.994 (7)	18.834
β (°)	114.60 (5)	115.185
V (Å^3)	14 463 (29)	14 186
Z	8	8
D_x (Mg m^{-3})	1.143	1.165
Radiation type	Cu $K\alpha$	Synchrotron
Wavelength (Å)	1.5418	0.504
No. of reflections for cell parameters	25	All data
θ range (°)	10.5–25.4	1.15–30.60
μ (mm^{-1})	0.713	0.322
Temperature (K)	295.2	103 (2)
Crystal form	Needle	Needle
Crystal size (mm)	0.55 × 0.07 × 0.03	0.50 × 0.03 × 0.01
Crystal colour	Green	Green
Data collection		
Diffractometer	Rigaku AFC-5*R*	Station *F*2 at CHESS
Data collection method	ω–2θ scans	φ oscillations
Absorption correction	ψ scans (North, Phillips & Mathews, 1968)	None
T_{min}	0.939	–
T_{max}	1.000	–
No. of measured reflections	12 794	85 873
No. of independent reflections	10 972	26 811
No. of observed reflections	3715	16 769
Criterion for observed reflections	$I > 2.50\sigma(I)$	$I > 2\sigma(I)$
R_{int}	0.136	0.055
θ_{max} (°)	60.13	30.60
Range of h, k, l	$-7 \rightarrow h \rightarrow 25$ $-19 \rightarrow k \rightarrow 41$ $-21 \rightarrow l \rightarrow 21$	$-21 \rightarrow h \rightarrow 29$ $-52 \rightarrow k \rightarrow 0$ $-21 \rightarrow l \rightarrow 26$
No. of standard reflections	3	–
Frequency of standard reflections	Every 150 reflections	–
Intensity decay (%)	0.39	–
Refinement		
Refinement on	F	F^2
R	0.1650	0.0687
wR	0.1347	0.2117
S	3.294	1.103
No. of reflections used in refinement	3715	16 769
No. of parameters used	682	1685
H-atom treatment	H-atom parameters not refined	H-atom parameters not refined
Weighting scheme	$w = 1/[\sigma^2(F_o) + 0.00004\lvert F_o\rvert^2]$	$w = 1/[\sigma^2(F_o^2) + (0.0690P)^2 + 15.7879P]$, where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$	0.2140	0.29
$\Delta\rho_{max}$ (e Å^{-3})	1.26	0.723
$\Delta\rho_{min}$ (e Å^{-3})	−0.83	−0.958
Extinction method	None	None
Source of atomic scattering factors	*International Tables for Crystallography* (1992, Vol. C, Table 6.1.1.2)	*International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)
Computer programs		
Data collection	*MSC/AFC* (MSC, 1988)	–
Cell refinement	*MSC/AFC* (MSC, 1988)	*DENZO* and *SCALEPACK* (Otwinowski, 1988)
Data reduction	*TEXSAN* (MSC, 1985)	*DENZO* and *SCALEPACK* (Otwinowski, 1988)
Structure solution	*SHELXS*86 (Sheldrick, 1985)	*SHELXS*86 (Sheldrick, 1985)
Structure refinement	*TEXSAN* (MSC, 1985)	*SHELXL*93 (Sheldrick, 1993)
Preparation of material for publication	*TEXSAN* (MSC, 1989)	*SHELXL*93 (Sheldrick, 1993) and *TEXSAN* (MSC, 1989)

(Critchley, Willis, Cook, McMurdo & Maruyama, 1992; Critchley *et al.*, 1993; Cook, 1994).

The present investigation of (1,4,8,11,15,18,22,25-octahexylphthalocyaninato)nickel (1) was undertaken to explore the effect of the nickel ion on both ring geometry and packing, as well as to obtain further information about possible pathways for transitions to the liquid crystal phase. The crystal structures of (1) at 295 and 103 K are reported and prove to be quite different to that of the metal-free analogue, but bear remarkable similarities to proposed structures of the mesophases. In addition, it was discovered that a lowering of space group symmetry occurs on reducing the temperature. Moreover, this paper provides a technical description of the use of multipole wiggler synchrotron radiation of wavelength 0.504 Å in conjunction with a CCD area detector, which is of considerable interest in terms of methodology. Finally, CCD and IP area detectors were used to confirm the nature of the phase transition and to find the space group transition temperature.

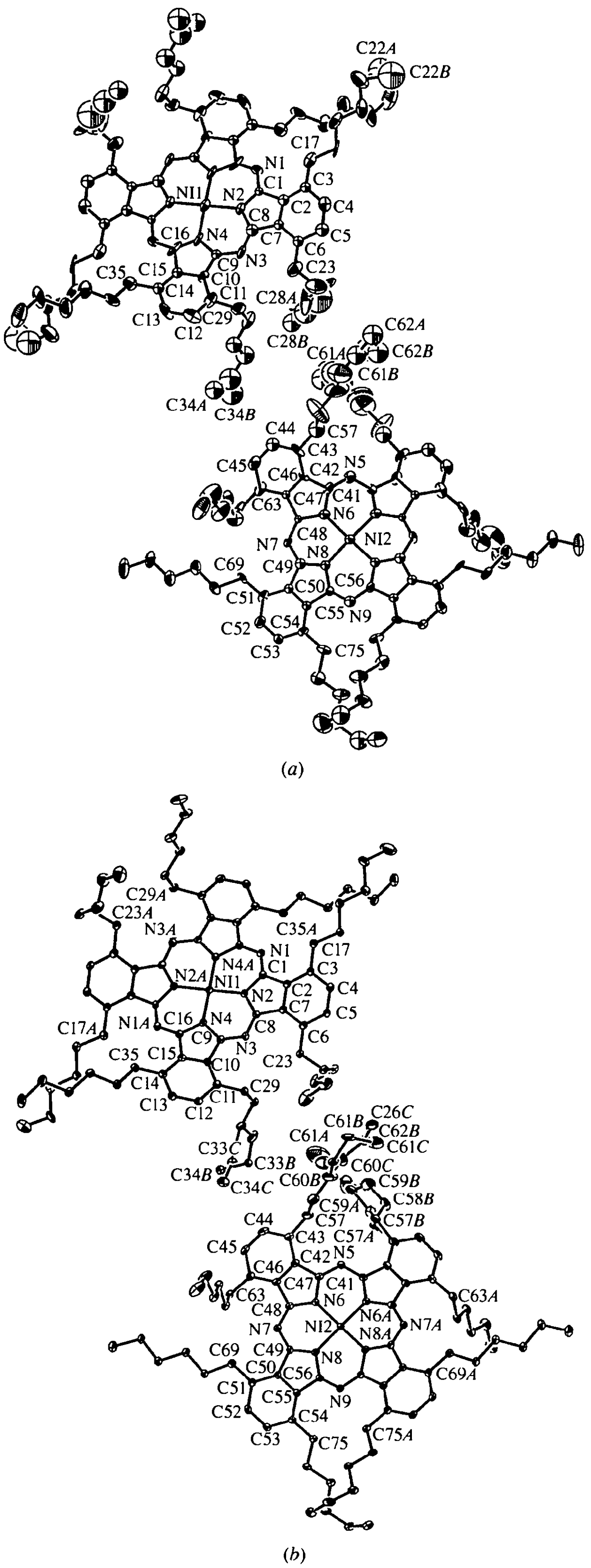

Fig. 1. *ORTEP* (Johnson, 1965) plot of the crystal structure of (1) using 30% probability thermal ellipsoids at: (*a*) 295 and (*b*) 103 K.

2. Experimental

2.1. *Preparation and crystallization*

1,4,8,11,15,18,22,25-Octahexylphthalocyanine (36 mg, 0.03 mmol) in pentan-1-ol (5 ml) was heated under reflux and excess nickel acetate (0.15 mmol) was introduced. Reflux was maintained for a further 40 min. The solution was left to cool to room temperature and then acetone (20 ml) was added. Filtration to remove inorganic salts, followed by concentration of the filtrate, yielded the crude metallophthalocyanine. Elution over silica (eluant: petrol) and recrystallization from THF: acetone (1:1) afforded (**1**) (yield 77%). Found: C, 77.01; H, 9.26; N, 8.93. $C_{80}H_{112}N_8Ni$ requires: C, 77.21; H, 9.07; N, 9.00%. λ_{max} (cyclohexane): 701, 665, 632, 340 nm. Crystals suitable for X-ray diffraction studies were grown by slow evaporation of a solution of the compound in THF.

2.2. *Cu Kα rotating anode data collection at 295 K*

Room-temperature data collection was carried out first, using the Manchester AFC-5*R* diffractometer, with a 12 kW Cu *K*α source. Data collection and refinement procedures are summarized in Table 1. Although data were collected to 0.89 Å resolution, of the 10 972 unique reflections that were recorded, only 3715 reflections had $I > 2.5\sigma(I)$ and, beyond 1.2 Å resolution, the data were very weak (*i.e.* 64% of the observed reflections were obtained in the data collected to 1.2 Å).

2.3. *Structure solution and refinement at 295 K*

The structure was solved by Patterson methods using *SHELXS*86 (Sheldrick, 1985), developed using *DIRDIF* (Beurskens, 1984) and refined by full-matrix least-squares using *TEXSAN* (Molecular Structure Corporation, 1985). The asymmetric unit contains two half molecules; for molecule (1), Ni1 lies on a centre of symmetry and for molecule (2), Ni2, N5 and N9 lie on a twofold axis (Fig. 1*a*). Although the phthalocyanine cores are well ordered, thermal motion of the hexyl groups is high, particularly towards the extremities of these groups; in four cases, for C22, C28, C34 and

C61–C62, the atoms were resolved into two disordered fragments, *A* and *B*. The occupancies for each fragment were fixed, respectively, at 0.6:0.4, 0.6:0.4, 0.3:0.7 and 0.5:0.5; these values leading to similar displacement parameters for the atoms of each part of the particular disordered fragment. The non-H atoms were refined either anisotropically or isotropically and H atoms were included in calculated positions (C—H = 0.95 Å) with isotropic thermal parameters which were 20% greater than the equivalent *B* value of the atom to which they were bonded.

2.4. *CHESS data collection at 103 K*

Data collection was carried out using 25 keV X-rays (0.504 Å wavelength) at the tuneable station, F2, fed by a 24 pole multipole wiggler. The short wavelength was selected in order to compress the diffraction pattern, thereby increasing the recordable resolution. A Princeton 1 k CCD detector of aperture 50 × 50 mm (Tate *et al.*, 1995) was used to collect the data. This was moved as close as possible to the crystal, to a distance of 43 mm, and also translated so that the direct beam impinged at the edge of the detector rather than the centre, in order to maximize the resolution at the other edge of the detector. The sample was mounted on a fibre and cooled to 103 K using an MSC liquid nitrogen gas system. The data were collected in 99 2° oscillations, using 90 s exposures, with a further two stationary dark images being recorded to correct for the detector dark current. The data were subsequently processed using *DENZO* and *SCALEPACK* (Otwinowski, 1988). 85 873 reflections were recorded to a resolution of 0.7 Å, which merged to give a total of 27 025 unique reflections, the overall merging *R* factor on *I* being 0.055. However, the merging *R* factor rose rapidly from 0.18 in the 0.88–0.83 Å shell, to 0.38 in the 0.73–0.7 Å shell, indicating that the highest resolution data were weak. Interestingly, it was found that the lattice symmetry had changed from C-centred monoclinic, space group $C2/c$, to primitive monoclinic, space group $P2_1/n$, although the unit-cell parameters were very similar at each temperature (see Table 1); 6455 reflections violated the systematic absence conditions for the space group $C2/c$. The reduction in unit cell volume was approximately 2%.

2.5. *Structure solution and refinement*

The structure was solved by the Patterson method using *SHELXS*86 (Sheldrick, 1985) and developed using difference-Fourier methods. Values for f', f'' and μ at 0.504 Å wavelength were taken from Sasaki (1989). Refinement was carried out using *SHELXL* (Sheldrick, 1993). The asymmetric unit consists of two crystallographically non-equivalent molecules. The numbering scheme employed was consistent with the room-temperature structure (see Fig. 1*b*), with *A* suffixes being used for the atoms which are crystallographically equivalent at room temperature (except in cases where there was disorder), but crystallographically non-equivalent at 103 K. Generally, the non-H atoms show much lower thermal motion than at room temperature, including the atoms of the hexyl groups. However, in three cases some atoms of these groups show disorder. Each of the disordered groups of atoms was resolved into two fragments, as follows: C33—C34, with occupancies of 0.639 (9) and 0.361 (9), C60—C61—C62, with occupancies of 0.499 (8) and 0.501 (8), and C57*A*—C58*A*—C59*A*, with occupancies of 0.571 (7) and 0.429 (7). All non-H atoms were refined anisotropically, except for C33*C*. H atoms were included in calculated positions, using the riding model. The full data collection and refinement details are shown in Table 1.

2.6. *Determination of the transition temperature*

In view of the observed space group change, experiments were undertaken to confirm its nature and to determine the temperature of the space group transition. Measurements were carried out at SRS, Daresbury, on Station 7.2. X radiation of 1.488 Å was used and crystal cooling was achieved with an Oxford Instruments Cryostream. A CCD detector (Moon, Allinson & Helliwell, 1994), which had an aperture of 25 × 25 mm, was employed to record the diffraction patterns. At this wavelength, it was necessary to use a 16° oscillation diffraction pattern, recorded in 16 min, to yield a number of diffraction spots sensitive to temperature. It then was found that the transition temperature lay between 185 and 230 K. Within the 16° oscillation, it was found that a 4° oscillation allowed the recording of some of the temperature-sensitive spots and by lowering the temperature stepwise from 230 K, whilst monitoring this 4° diffraction pattern (recorded in 4 min), a gradual appearance of spots due to $h + k = 2n + 1$ was observed between 205 and 195 K (Fig. 2).

Also recorded were oscillation diffraction patterns at 195 and 293 K, using a Mar image plate and a wavelength of 1.488 Å. Due to the larger aperture of the Mar image plate, which has a diameter of 180 mm, an oscillation of 4°, which was recorded in 8 min, clearly showed that the differences are confined to a change in lattice symmetry between the two temperatures (see Fig. 3). No other changes, away from the lattice points, such as the appearance of diffuse scattering, were observed.

3. Description of the structures

At 295 K, the asymmetric unit contains two half molecules, with the other halves being generated by an inversion centre for molecule (1) and by a twofold axis for molecule (2). At 103 K, the asymmetric unit consists of two complete crystallographically non-equivalent molecules. However, the structures at each temperature are similar to one another, particularly the core bond lengths and angles. The latter are also similar to those in 1,4,8,11,15,18,22,25-octahexylphthalocyanine (Chambrier, Cook, Helliwell & Powell, 1992). Bond lengths and angles about the Ni atoms are shown in Table 2.* For molecule (1), the N—Ni1—N angles are close to 90 and 180°, for adjacent and opposite N atoms, respectively. However, the N6—Ni2—N8 angles are 172.5 (4)° at 295 and 174.14 (12) and 174.01 (12)° at 103 K, showing a small distortion towards tetrahedral geometry about Ni2. Metallation has the effect of reducing the distance between opposite N atoms from 4.191 and 3.897 Å in 1,4,8,11,15,18,22,25-octahexylphthalocyanine (Chambrier, Cook, Helliwell & Powell, 1992) to between 3.80 (2) and 3.88 (3) Å at 295 K and 3.808 (5) and 3.843 (5) Å at 103 K. Similar effects are seen in the unsubstituted phthalocyanines (Mason, Williams & Fielding, 1979). In both the 295 and 103 K structure, six of the hexyl groups lie approximately in the phthalocyanine plane, for molecule (1), whilst two are approximately perpendicular to it, lying above and below the plane (Fig. 4). For molecule (2), four of the hexyl groups are approximately in the plane of the phthalocyanine moiety, whilst the other four form an angle to it, directly above and below the plane (Fig. 4).

The two different molecules interleave each other in stacks. Their lobes are staggered with respect to one another and the Ni atoms are translated (see Fig. 5), so that the stacks are tilted, the angle of tilt being defined by the unit-cell angle β, *i.e.* 114.60° at 295 K and 115.19° at 103 K (Fig. 6). The phthalocyanine cores are not planar, particularly in the case of molecule (2). The angles between the least-squares planes through the core atoms of the molecules are 14.2 and 12.8° at 295 and

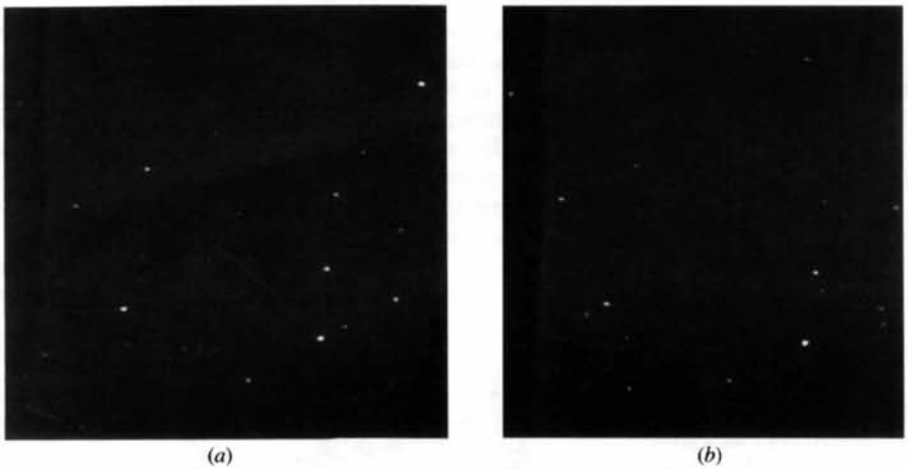
(*a*) (*b*)

Fig. 2. 4° oscillation images recorded using a CCD at SRS at: (*a*) 293 and (*b*) 103 K.

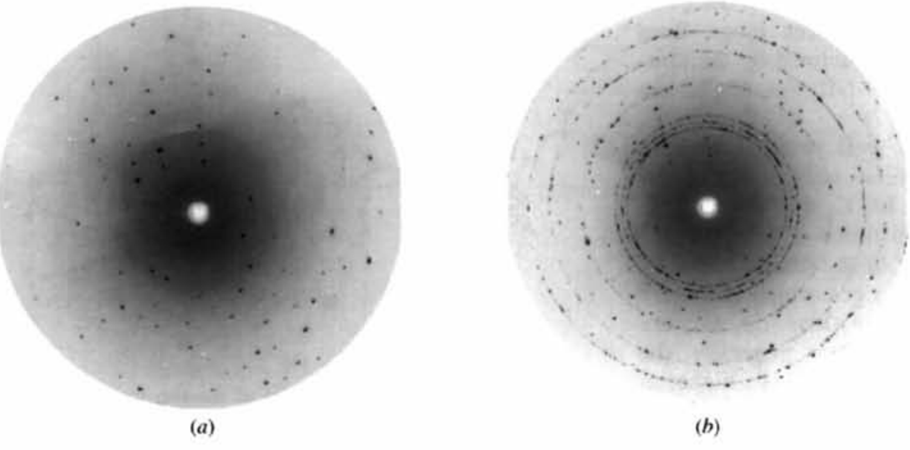
(*a*) (*b*)

Fig. 3. Mar IP 4° oscillation images recorded at: (*a*) 293 and (*b*) 195 K (the rings on the image are due to ice diffraction).

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* Lists of structure factors, atomic coordinates, anisotropic displacement parameters and complete geometry have been deposited with the IUCr (Reference: AN0534). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Bond lengths (Å) and angles (°) about the N atoms*

	295 K	103 K
Ni1—N2	1.91 (1)	1.920 (3)
Ni1—N2*A*	1.91 (1)	1.924 (3)
Ni1—N4	1.94 (1)	1.917 (3)
Ni1—N4*A*	1.94 (1)	1.913 (3)
N2—N2*A*	3.82 (2)	3.843 (5)
N4—N4*A*	3.88 (3)	3.831 (5)
Ni2—N6	1.91 (1)	1.907 (3)
Ni2—N6*A*	1.91 (1)	1.907 (3)
Ni2—N8	1.89 (1)	1.906 (3)
Ni2—N8*A*	1.89 (1)	1.913 (3)
N6—N8*A*	3.80 (2)	3.808 (5)
N6*A*—N8	3.80 (2)	3.815 (5)
N2—Ni1—N2*A*	180.00	179.93 (15)
N2—Ni1—N4	90.1 (5)	89.43 (12)
N2—Ni1—N4*A*	89.9 (5)	90.63 (12)
N4—Ni1—N4*A*	180.00	179.9 (2)
N2*A*—Ni1—N4*A*	90.1 (5)	89.31 (12)
N4—Ni1—N2*A*	89.9 (5)	90.63 (12)
N6—Ni2—N8*A*	172.5 (4)	174.14 (12)
N8—Ni2—N6	89.6 (5)	89.64 (12)
N6—Ni2—N6*A*	90.8 (5)	90.58 (12)
N8—Ni2—N6*A*	172.5 (4)	174.01 (12)
N6*A*—Ni2—N8*A*	89.6 (5)	89.56 (12)
N8—Ni2—N8*A*	91.1 (7)	90.84 (12)

103 K, respectively. The shortest intermolecular contacts between one phthalocyanine core and the next are: at 295 K: 3.31 (2) Å (between C5 and C48); at 103 K: 3.340 (5) and 3.301 (5) Å (for C5-C48 and C5*A*-C48*A*, respectively). At 295 K, the aromatic cores of adjacent molecules lie approximately in the xy planes, with the Ni atoms at $z = 0, 0.5$ for Ni1 and at $z = 0.25, 0.75$ for Ni2. At 103 K, the Ni1 atoms lie 0.232 Å above or below the planes at $z = 0$ and 0.5, whilst the Ni2 atoms lie 0.236 Å above or below the planes at $z = 0.25$ and 0.75. Thus, the average spacing between the cores is $0.25c$, *i.e.* 4.728 and 4.709 Å at 295 and 103 K, respectively. Within these planes, the Ni atoms show pseudo-hexagonal cross-sectional symmetry; at 295 K, the distances between Ni atoms within the layers are 21.725 or 22.548 Å (the latter being defined by the unit cell dimension a), with Ni—Ni—Ni angles of 58.74 or 62.52°; at 103 K, the Ni—Ni distances range from 21.317 to 22.34 Å (the latter being defined by the unit-cell dimension a) and the Ni—Ni—Ni angles lie between 57.73 and 61.89° (Fig. 7).

The core atoms of (1) are well ordered at both temperatures. In contrast, whilst only three hexyl groups show slight disorder at 103 K, the hexyl atoms exhibit high thermal mobility/disorder at 295 K, particularly towards the extremities of the chains. In fact, there is an indication of U_{eq} changes which are more than can be attributed to temperature alone, *i.e.* they are due in part to the space group change; generally, the U_{eq}'s for the aromatic core are up to 2.5 times higher at 295 K compared with those at 103 K, but for some of the hexyl atoms they are up to five times the size.

4. Discussion

4.1. *Data collection*

Crystals of (1) are extremely fine weakly diffracting needles. Initially the structure was determined using data collected from a Cu $K\alpha$ rotating anode diffractometer at ambient temperature. However, the diffraction pattern was very weak beyond 1.2 Å, so that although it was possible to solve and refine the structure, the precision of the derived parameters was low. Moreover, the thermal motion of the long hexyl chains was large. To improve the precision of the structure, further data collection was carried out using synchrotron radiation from a multipole wiggler at CHESS, to substantially increase the intensity of the radiation. A wavelength of 0.504 Å was selected to reduce systematic errors due to absorption as well as to compress the diffraction pattern so that the recordable resolution was maximized. Finally, liquid nitrogen cooling was used to reduce thermal motion, particularly in the hexyl groups. This led to much improved structural precision, due to the higher resolution limits and number of observed data: R values are 0.0687 and 0.165 at 103 and 295 K, respectively, and average e.s.d.'s are reduced by a factor of between 3 and 10 at 103 K. The data/parameter ratio at 103 K is also much improved to 9.95 *versus* 5.44 at 295 K, even though quite a number of the non-H atoms could only be refined isotropically at 295 K. Moreover, it was found that a change in space group from $C2/c$ to $P2_1n$ occurs when the temperature is lowered, whilst the unit-cell dimensions at each temperature are only slightly different.

Ideally, to compare the different methods of data collection directly, it would be best to use the same

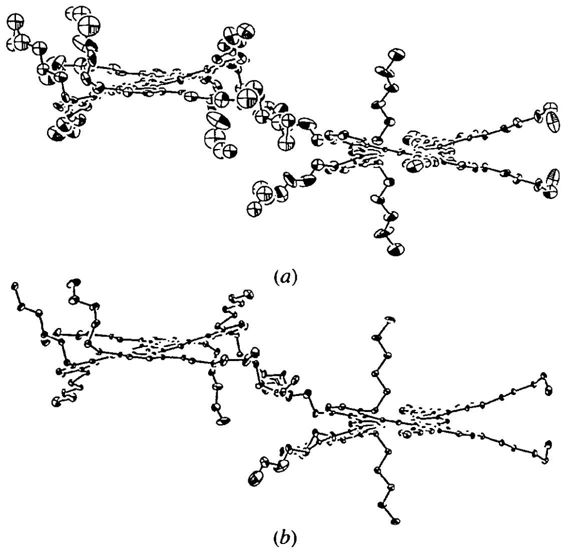


Fig. 4. *ORTEP* (Johnson, 1965) plot of the two molecules of (1) viewed approximately parallel to the planes of the aromatic cores, with 30% probability thermal ellipsoids at: (*a*) 295 and (*b*) 103 K.

crystal throughout. This was not possible because the crystallinity of the samples reduces substantially with time. Nevertheless, we can dissect the component parts of the measurement methods employed, to facilitate comparison between the different technologies (*i.e.* the use of low-temperature *versus* room-temperature synchrotron radiation *versus* rotating anode and the CCD detector *versus* the scintillation counter).

The impact of cryocooling can be calculated from the atomic displacement parameters. At 1 Å resolution, for the Ni atoms, which constitute approximately a quarter of the scattering power, the average intensity would be improved by a factor of *ca* 3, whilst using the average *B* factors for the whole structure, the improvement would be by a factor of *ca* 15. The effect of the use of synchrotron radiation can be estimated from the ratio of the beam intensities at the sample for a wavelength of

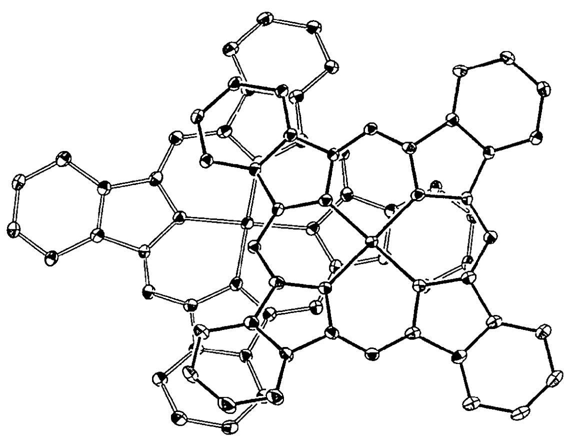
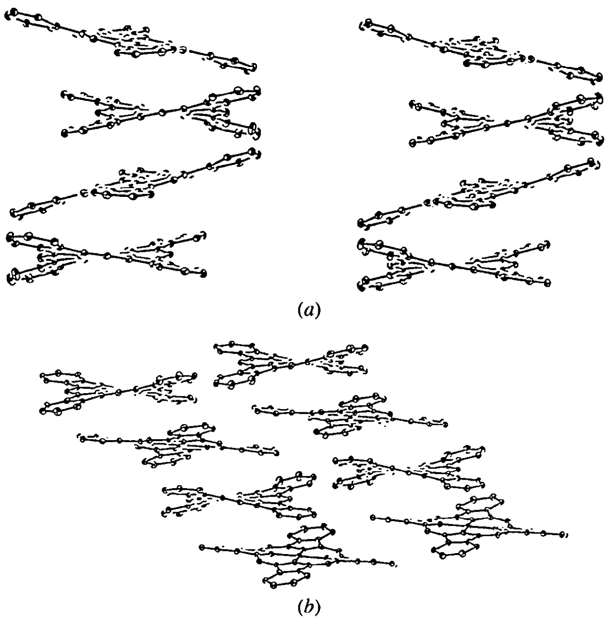


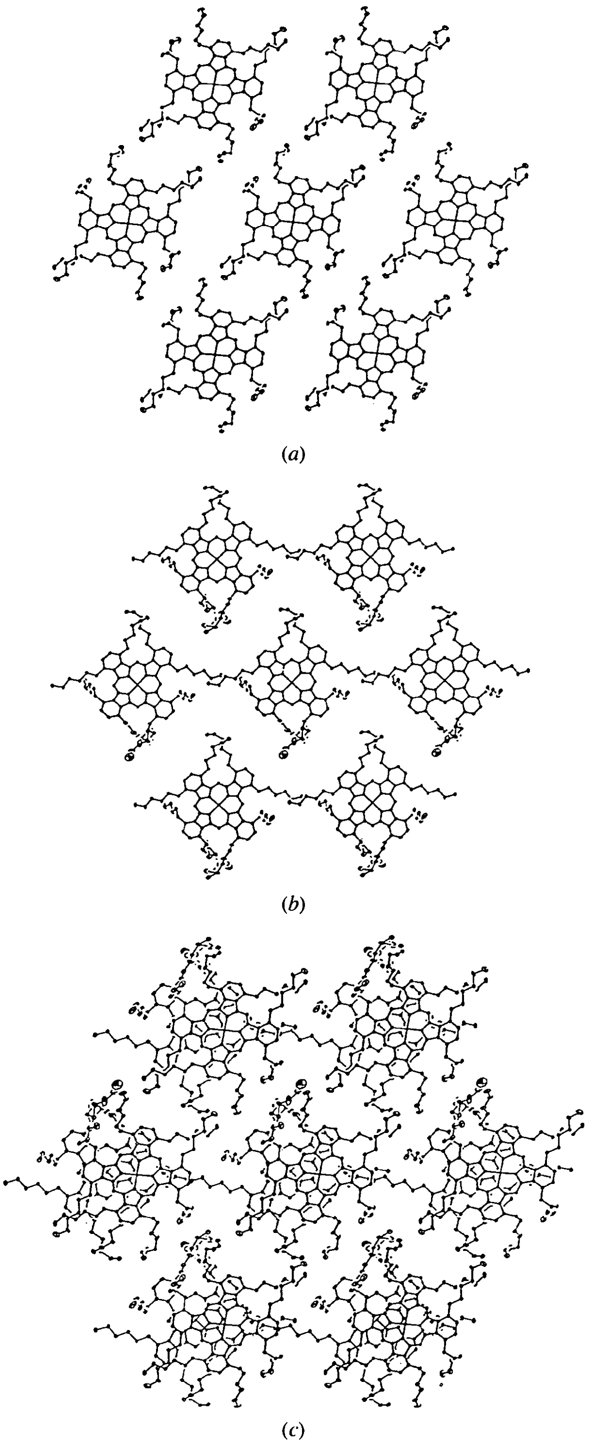
Fig. 5. *ORTEP* (Johnson, 1965) plot of two adjacent phthalocyanine cores at 103 K, using 30% probability thermal ellipsoids.



(*a*)

(*b*)

FIg. 6. Packing of (1) at 103 K: (*a*) with the hexyl groups omitted for clarity, viewed down the *x* axis, using 30% probability thermal ellipsoids; (*b*) with the hexyl groups omitted for clarity, viewed down the *y* axis, using 30% probaility thermal ellipsoids.



(*a*)

(*b*)

(*c*)

Fig. 7. View of (1) at 103 K showing the pseudo-hexagonal packing in the *xy* planes for: (*a*) molecule (1); (*b*) molecule (2); (*c*) molecules (1) and (2) in two adjacent layers.

0.504 Å and a current of 50 mA at Station F2, CHESS, *versus* a Cu $K\alpha$ rotating anode, which is approximately 30×10^9 to 10^9 ph s^{-1} mm^{-2}, *i.e.* a gain of 30-fold (Helliwell, Ealick, Doing, Irving & Szebenyi, 1993). The impact of the CCD area detector revolves around the number of 'simultaneous' measurements that can be made, compared with one measurement at a time on the single counter based diffractometer; in this study, a 2° rotation of the crystal for each CCD image yielded about 850 spots on average, clearly indicating a major gain in measurement efficiency.

Overall, for the determination of crystal structures of samples with low scattering efficiency, these techniques have proved extremely effective (Helliwell & Helliwell, 1996). Clearly, much can be done in the home laboratory with the rotating anode and longer wavelengths (Helliwell, Gallois, Kariuki, Kaucic & Helliwell, 1993), together with cryocooling. However, the role of the synchrotron becomes more important as the sample scattering efficiency progressively decreases and higher resolution data are required.

4.2. *Molecular packing and the relationship of the crystal structures to the mesophases*

In both crystal structures of (1) the two crystallographically non-equivalent molecules form interleaving stacks, with alternate layers of molecules (1) and (2) spaced on average by 4.749 and 4.709 Å at 295 and 103 K, respectively, although the shortest contact between the aromatic cores is considerably shorter at approximately 3.3 Å (Fig. 6). Within these planes, the molecules have pseudo-hexagonal cross-sectional symmetry (Fig. 7). The short intermolecular contacts between the phthalocyanine cores indicate π-stacking interactions (Hunter & Sanders, 1990). In unsubstituted phthalocyanines, π-stacking occurs such that the phthalocyanine planes are approximately 3.4 Å apart and not rotated with respect to one another. Their centres are offset, so that the π-cloud of one molecule lies over the cavity of the next. In the other dimension the molecules are perpendicular to one another, maximizing π–π interactions, thus giving rise to the characteristic herringbone packing. In the present study the almost parallel aromatic cores are rotated so that the lobes of the phthalocyanine cores are staggered with respect to one another, presumably to minimize steric hindrance between the hexyl chains. The Ni atoms in adjacent phthalocyanines are offset (see Fig. 5), so that the stacks are tilted (Fig. 6). Moreover, the herringbone formation is not seen and instead the stacks are side by side in two dimensions, since the hexyl groups prevent the perpendicular π–π interactions. This in turn is in contrast to the unmetallated 1,4,8,11,15,18,22,25-octahexylphthalocyanine, where again the herringbone structure is not seen (Chambrier, Cook, Helliwell & Powell, 1992). This time, however, the phthalocyanine cores are not rotated with respect to one another and two hexyl groups which are almost perpendicular to the aromatic planes cause the planes to lie at a distance of 8.5 Å from one another, suggesting that there is very little interaction between them. The tilted columnar stacks are side by side in two dimensions. In (1) the presence of the positively charged nickel ion has the effect of increasing the attractive interactions with the π-clouds of molecules lying above and below (Hunter & Sanders, 1990), and the staggering of the lobes reduces steric hindrance between the hexyl chains, allowing the close approach of the aromatic centres.

For the unmetallated 1,4,8,11,15,18,22,25-octahexylphthalocyanine, it was suggested that an increase in temperature would cause the hexyl groups to become mobile, allowing the distance between the aromatic cores to reduce and leading to the formation of the liquid crystal phase at 432 K (Chambrier, Cook, Helliwell & Powell, 1992).

The mesophase behaviour of (1) has been investigated optically by microscopy and by differential scanning calorimetry (Cook, Cracknell & Harrison, 1992). These experiments have shown that K to D_{hd}, D_{hd} to D_{hd} and D_{hd} to I transitions are at 418, 437 and 442 K, respectively, where K is the crystalline phase, I is the isotropic liquid phase and the two D_{hd} phases are mesophases with differing textures; the lower temperature mesophase has a needle texture and that at higher temperature has a fan texture (Cook, Cracknell & Harrison, 1992). Diffraction studies on the mesophases of related compounds (*e.g.* 1,4,8,11,15,18,22,25-octaoctylphthalocyanine) show that for both D_{hd} mesophases, and using a rectangular lattice, then $a = b \times 3^{1/2}$, indicating that the lattice has two-dimensional hexagonal lattice symmetry. For the needle texture mesophase, this is found to be more ordered (Cherodian *et al.*, 1991). There is also a diffuse peak, unrelated to the hexagonal lattice, indicating a spacing of 4.8 Å, which was assigned to the spacing between layers of molecules in the columns. The broadness of the peak suggests a variation in this distance so that the D_{hd} assignment denotes discotic disordered hexagonal (Cherodian *et al.*, 1991). The crystal structures of (1) at 103 and 295 K have pseudo-hexagonal cross-sectional symmetry with the unit-cell dimension $b \simeq a \times 3^{1/2}$ (Fig. 7). In the other dimension the molecules are formed into tilted columnar stacks, with an average spacing of ~4.7 Å (similar to that of the D_{hd} mesophase of 1,4,8,11,15,18,22,25-octaoctylphthalocyanine), although this spacing varies substantially, because the aromatic cores are not parallel to one another (see Fig. 6). Thus, there is a striking resemblance of the crystalline phases to the mesophases. At liquid nitrogen temperatures, the molecules are generally well ordered, even (for the most-part) to the ends of the hexyl groups. The aromatic cores are locked rotationally by the long hexyl chains. The change of lattice symmetry which occurs at *ca* 200 K arises because the layers of molecules adjust slightly so that the Ni atoms which were lying *ca* 0.23 Å above or below the planes at $z = 0, 0.25, 0.5$ and 0.75, become coincident with these planes. Accompanying this movement is an increase in thermal motion, which is particularly marked in the hexyl chains, and also some small changes in conformation in these groups. This space group transition probably represents the first stage towards the transition to the discotic columnar mesophase. Presumably, at 418 K, the thermal motion of the hexyl groups becomes so large that free relative rotation of the molecules can take place, to give the discotic columnar mesophase, with average hexagonal symmetry, due to the random rotational orientation of the molecules.

5. Conclusions

The use of advanced technologies (synchrotron radiation with a wavelength of 0.5 Å and a CCD detector) as well as cryocooling have allowed the crystal structure of (1) to be determined to high precision. This crystal structure together with that determined at 295 K show remarkable similarities to the discotic columnar mesophases into which (1) melts. It is probable that the increased mobility of the hexyl groups at elevated temperatures allows free relative rotation of the phthalocyanine cores in the mesophases, which in the crystalline phases are locked together by the ordering of these groups.

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References

Ao, R., Kümmert, L. & Haarer, D. (1995). *Adv. Mater.* **5**, 495–499.

Beurskens, P. T. (1984). *DIRDIF. Direct Methods for Difference Structures – an Automatic Procedure for Phase Extension and Refinement of Difference Structure Factors.* Technical Report 1984/1. Crystallography Laboratory, Toernooiveld, 6525 ED Nijmegen, The Netherlands.

Chambrier, I., Cook, M. J., Helliwell, M. & Powell, A. K. (1992). *J. Chem. Soc. Chem. Commun.* pp. 444–445.

Cherodian, A. S., Davies, A. N., Richardson, R. M., Cook, M. J., McKeown, N. B., Thomson, A. J., Feijoo, J., Ungar, G. & Harrison, K. J. (1991). *Mol. Cryst. Liq. Cryst.* **196**, 103–114.

Cook, M. J. (1993). *Advances in Spectroscopy*, Vol. 22, *Spectroscopy of New Materials*, edited by R. J. H. Clark & R. E. Hester, pp. 87–150. Chichester: Wiley.

Cook, M. J. (1994). *J. Mater. Sci. Mater. Electron.* **5**, 117–128.

Cook, M. J., Cracknell, S. J. & Harrison, K. J. (1992). *J. Mater. Chem.* **1**, 703–704.

Critchley, S. M., Willis, M. R., Cook, M. J., McMurdo, J. & Maruyama, Y. (1992). *J. Mater. Chem.* **2**, 157–159.

Critchley, S. M., Willis, M. R., Maruyama, Y., Bandow, S., Cook, M. J. & McMurdo, J. (1993). *Mol. Cryst. Liq. Cryst.* **229**, 47–51.

Frampton, C. S., O'Connor, J. M., Peterson, J. & Silver, J. (1988). *Displays*, pp. 174–178.

Gregory, P. (1991). *High-Technology Applications of Organic Colorants*, ch. 7, p. 59. New York: Plenum Press.

Helliwell, J. R. & Helliwell, M. (1996). *J. Chem. Soc. Chem. Commun.* pp. 1595–1602.

Helliwell, J. R., Ealick, S., Doing, P., Irving, T. & Szebenyi, M. (1993). *Acta Cryst.* D**49**, 120–128.

Helliwell, M., Gallois, B., Kariuki, B., Kaucic, V. & Helliwell, J. R. (1993). *Acta Cryst.* B**49**, 420–428.

Hunter, C. A. & Sanders, J. K. M. (1990). *J. Am. Chem. Soc.* **112**, 5525–5534.

Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.

Leznoff, C. C. & Lever, A. B. P. (1989). Editors. *Phthalocyanines – Properties and Applications.* New York: VCH Publishers.

Mason, R., Williams, G. A. & Fielding, P. E. (1979). *J. Chem. Soc. Dalton Trans.* pp. 676–683.

Molecular Structure Corporation (1985). *TEXSAN. TEXRAY Structure Analysis Package.* MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Molecular Structure Corporation (1988). *MSC/AFC Diffractometer Control Software.* MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Molecular Structure Corporation (1989). *TEXSAN. Single Crystal Structure Analysis Software.* MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Moon, K. J., Allinson, N. M. & Helliwell, J. R. (1994). *Nucl. Instrum. Meth. Phys. Res. A*, **348**, 631–634.

Moser, F. H. & Thomas, A. L. (1983*a*). *The Phthalocyanines*, Vol. 1, *Properties*. Boca Raton, Florida: CRC Press.

Moser, F. H. & Thomas, A. L. (1983*b*). *The Phthalocyanines*, Vol. 2, *Manufacture and Applications*. Boca Raton, Florida: CRC Press.

North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.

Otwinowski, Z. (1988). *DENZO. A Program for Automatic Evaluation of Film Densities.* Department of Molecular Biophysics and Biochemistry, Yale University, New Haven, Connecticut.

Sasaki, S. (1989). *KEK*. Report 88-14. National Laboratory for High Energy Physics, Tsukuba, Japan.

Sheldrick, G. M. (1985). *SHELXS86. Program for the Solution of Crystal Structures.* University of Göttingen, Germany.

Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.

Simon, J. & Bassoul, P. (1993). *Phthalocyanines – Properties and Applications*, Vol. 2, edited by C. C. Leznoff & A. B. P. Lever, pp. 223–299. New York: VCH Publishers.

Snow, A. W. & Barger, W. R. (1989). *Phthalocyanines – Properties and Applications*, Vol. 2, edited by C. C. Leznoff and A. B. P. Lever, pp. 341–392. New York: VCH Publishers.

Tate, M. R., Eikenberry, E. F., Barma, S. L., Wall, M. E., Lawrence, J. L. & Gruner, S. M. (1995). *J. Appl. Cryst.* **28**, 196–205.

Wöhrle, D. & Meissner, D. (1991). *Adv. Mater.* **3**, 129–138.

Wright, J. D. (1989). *Prog. Surf. Sci.* **31**, 1–60.