

Molecular Complexes. Part XXIII.¹ Crystal and Molecular Structures of α -Naphthol-1,2,4,5-Tetracyanobenzene and β -Naphthol-1,2,4,5-Tetracyanobenzene

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The crystal and molecular structures of the 1 : 1 complexes of α -naphthol and 1,2,4,5-tetracyanobenzene (I) and β -naphthol and 1,2,4,5-tetracyanobenzene (II) have been determined by Fourier methods from diffractometer data and refined by least-squares to R 0.043 for 523 reflections (I), and R 0.104 for 651 reflections (II). Both are monoclinic, space group $C2/m$ with $Z = 2$ in unit cells of dimensions: (I), $a = 9.250(5)$, $b = 13.059(7)$, $c = 6.791(4)$ Å, $\beta = 108.3(1)^\circ$; (II), $a = 9.578(1)$, $b = 12.754(3)$, $c = 6.798(4)$ Å, $\beta = 108.13(2)$. The dimensions of the component molecules have been corrected for rigid-body thermal motion and are in agreement with those from previous work. The mode of donor-acceptor overlap of the molecules in the alternate plane-to-plane stacks parallel to the c axes of the crystals gives near-maximisation of the donor-acceptor charge-transfer interactions. The naphthol molecules in both structures are disordered.

THE crystal structures of the molecular complexes of α -naphthol-1,2,4,5-tetracyanobenzene and β -naphthol-1,2,4,5-tetracyanobenzene have been determined as part of our continuing systematic investigation of the crystal structures of molecular complexes, but specifically to examine the effect of hydrogen-bonding substituents on the donor after complex formation with an acceptor of little hydrogen-bonding potential.

EXPERIMENTAL

1,2,4,5-Tetracyanobenzene was prepared by the method of ref. 2. Small orange needles of the molecular complexes were formed by slow evaporation of equimolar solutions of α -naphthol and 1,2,4,5-tetracyanobenzene (I) and β -naphthol and 1,2,4,5-tetracyanobenzene (II) in diglyme. The crystals selected for intensity measurements were sealed in Lindemann glass capillary tubes.

(i) α -Naphthol-1,2,4,5-Tetracyanobenzene Molecular Complex (I).—Crystal data. $C_{20}H_{10}N_4O$, $M = 322.3$, Monoclinic, $a = 9.250(5)$, $b = 13.059(7)$, $c = 6.791(4)$ Å, $\beta = 108.3(1)^\circ$, $U = 778.7$ Å³. $D_m = 1.38$ (by flotation), $Z = 2$, $D_c = 1.37$. Space group $C2$, Cm , or $C2/m$ from systematic absences: hkl when $h + k = 2n + 1$, $h0l$ when $h = 2n + 1$, and $0k0$ when $k = 2n + 1$; structure determination confirmed space group $C2/m$ (No. 12, C_{2h}^3). Mo- K_α radiation, $\lambda = 0.71069$ Å; $\mu(\text{Mo-}K_\alpha) = 0.83$ cm⁻¹.

Unit-cell dimensions were measured and three-dimensional X-ray intensity data collected on a Hilger and Watts four-circle diffractometer with an ω -2 θ scan, using

a graphite monochromator. There was no significant drift in the intensities of the reference reflections during data collection. Of 1585 independent reflections observed with $\theta < 28^\circ$, 523 were taken as significantly (3σ) above background. Intensities were corrected for Lorentz and polarisation effects, but not for absorption or extinction.

With two molecules of α -naphthol and two molecules of 1,2,4,5-tetracyanobenzene present in the unit cell it is not possible to have an ordered structure of symmetry $C2$, Cm , or $C2/m$. As no diffuse reflections could be detected in the diffraction patterns obtained photographically, a model must be assumed in which there is random occupancy of different sites so that the overall symmetry corresponds to one of the three space groups. If the space group is $C2/m$, the centres of gravity of the molecules must lie on two-fold special positions with symmetry $2/m$, so that the α -naphthol would be expected to be disordered. Further, to obtain stacks of alternate donor and acceptor molecules, the 1,2,4,5-tetracyanobenzene and α -naphthol molecules must be centred at positions such as $2a[(0,0,0)$ and $(\frac{1}{2}, \frac{1}{2}, 0)]$; and $2c[(0,0, \frac{1}{2})$ and $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ respectively].

A partial structure, using the co-ordinates of the carbon and nitrogen atoms of 1,2,4,5-tetracyanobenzene taken from the isomorphous 1 : 1 molecular complex of naphthalene and 1,2,4,5-tetracyanobenzene,³ refined well in space group $C2/m$ with C(1) on the two-fold axis and other atoms in general positions. The subsequent Fourier synthesis showed a planar region of electron density perpendicular to the mirror

² A. S. Bailey, B. R. Henn, and J. M. Langdon, *Tetrahedron*, 1963, **19**, 161.

³ S. Kumakura, F. Iwasaki, and Y. Saito, *Bull. Chem. Soc. Japan*, 1967, **40**, 1826.

¹ Part XXII, K. Prout and I. J. Tickle, *J.C.S. Perkin II*, 1973, 1212.

plane of space group $C2/m$ and with point-symmetry $2/m$. This is consistent with a model with four symmetry-equivalent α -naphthol sites each of occupancy 0.25. Two pairs of sites are related by the mirror plane. For each pair the inversion centre requires that the naphthalene nuclei are exactly superposed.

Refinement was by full-matrix least-squares assuming anisotropic thermal motion with constraints applied to the α -naphthol molecule,^{4,5} and the occupancy of the carbon and oxygen atoms for this molecule were $\frac{1}{2}$ and $\frac{1}{2}$ respectively. The estimated bond lengths for the constrained model were adjusted between each cycle and had an estimated standard deviation of 0.005 Å, and a similar procedure, with σ 0.5°, was adopted for the angles. The difference in mean square displacement along the interatomic vector of two bonded atoms was constrained to be zero with σ 0.005 Å², and each of the atoms was constrained to lie in a plane with σ 0.01 Å. All the hydrogen atoms were located with the aid of a difference-Fourier synthesis and were included in the refinement with fixed isotropic temperature factors (U_{iso} 0.05), those in the α -naphthol being constrained.

Full-matrix least-squares refinement was also carried out in space groups $C2$ and Cm , and the results at convergence for the 523 reflections are shown in Table 1. Hamilton's

TABLE 1

Refinement results for the three space groups

Space group	R	R'	No. of parameters
(a) α -Naphthol-1,2,4,5-Tetracyanobenzene (I)			
$C2/m$	0.059	0.043	103
$C2$	0.044	0.037	205
Cm	0.047	0.038	205
(b) β -Naphthol-1,2,4,5-Tetracyanobenzene (II)			
$C2/m$	0.117	0.104	103
$C2$	0.091	0.089	205
Cm	0.101	0.098	205

test⁶ was not conclusive, and as refinement in $C2$ with constraints led to physically unreasonable values for the anisotropic temperature factors of some of the α -naphthol carbon atoms, $C2/m$ was used in the final analysis.

In the last stages of refinement each reflection was assigned a weight according to the expression $w = 1 / \sum_{r=1}^n A_r T_r^*(X)$ where n is the number of coefficients, A_r for a Chebyshev series, T_r^* is the polynomial function, and X is $F_o/F_o(\text{max.})$. Four coefficients, A_r , were used with values 39.2, 27.8, -27.1, and -25.4,⁷ and the final weighted R' was 0.043. The final difference-Fourier map, with a root-mean-square deviation of electron density of 0.05 eÅ⁻³, had no significant features.

(ii) β -Naphthol-1,2,4,5-Tetracyanobenzene Molecular Complex (II).—Crystal data. $C_{20}H_{10}N_4O$, $M = 322.3$. Monoclinic, $a = 9.578(1)$, $b = 12.754(3)$, $c = 6.798(4)$ Å, $\beta = 108.13(2)^\circ$, $U = 789.2$ Å³. $D_m = 1.35$ (by flotation), $Z = 2$, $D_c = 1.36$. Space group $C2$, Cm , or $C2/m$ from system-

⁴ J. Waser, *Acta Cryst.*, 1963, **16**, 1091.

⁵ J. S. Rollett in 'Crystallographic Computing,' ed. F. R. Ahmed, Munksgaard, Copenhagen, 1969, pp. 169—172.

⁶ W. C. Hamilton, *Acta Cryst.*, 1965, **18**, 502.

⁷ J. S. Rollett in 'Computing Methods in Crystallography,' ed. J. S. Rollett, Pergamon, Oxford, 1965, p. 40.

atic absences [as for (I)]; structure determination confirmed space group $C2/m$ (No. 12, C_{2h}^3). Mo- K_α radiation, $\lambda = 0.71069$ Å, $\mu(\text{Mo-}K_\alpha) = 0.82$ cm⁻¹.

Unit-cell dimensions were measured and three-dimensional X-ray intensity data collected on a Nonius CAD4F four-circle diffractometer with an ω -2 θ scan using a graphite monochromator. Preliminary peak scans showed the crystal to be slightly split, but as no other sample was available the data were collected in the hope that the gross features, at least, of the structure could be determined. Of 876 independent reflections observed with $\theta < 28^\circ$, 651 were taken as significantly (3σ) above background. Intensities were corrected for Lorentz and polarisation effects, but not for absorption or extinction.

A partial structure, using the co-ordinates of the carbon and nitrogen atoms of the α -naphthol-1,2,4,5-tetracyanobenzene molecular complex, refined well in space group $C2/m$ with similar constraints being imposed. The disordered

TABLE 2

Fractional co-ordinates, with estimated standard deviations in parentheses

	x	y	z
(a) α -Naphthol-1,2,4,5-tetracyanobenzene (I)			
C(1)	0.000 0	0.107 7(3)	0.000 0
C(2)	0.136 7(2)	0.053 0(2)	0.057 9(4)
C(3)	0.278 4(3)	0.109 0(2)	0.117 6(4)
N(4)	0.390 4(3)	0.152 9(2)	0.165 5(4)
C(5)	0.468 0(3)	0.450 1(2)	0.484(1)
C(6)	0.306 8(4)	0.439 5(3)	0.414 0(8)
C(7)	0.215 9(4)	0.524 1(4)	0.375 4(7)
C(8)	0.279 7(5)	0.623 1(3)	0.402(1)
C(9)	0.434 1(4)	0.636 3(3)	0.470 9(7)
O(10)	0.245 8(7)	0.345 9(4)	0.385(1)
H(1)	0.000 0	0.183(3)	0.000 0
H(6)	0.260 0(8)	0.369 7(5)	0.392(1)
H(7)	0.102 7(7)	0.515 7(7)	0.324(1)
H(8)	0.211 2(9)	0.684 4(6)	0.373(1)
H(9)	0.478 1(8)	0.706 8(5)	0.491(1)
H(10)	0.150 1(8)	0.355 6(8)	0.344(1)
(b) β -Naphthol-1,2,4,5-tetracyanobenzene (II)			
C(1)	0.000 0	0.110 2(5)	0.000 0
C(2)	0.131 2(5)	0.054 5(3)	0.057 9(6)
C(3)	0.268 1(5)	0.111 2(4)	0.116 2(7)
N(4)	0.378 3(5)	0.152 6(4)	0.163 1(7)
C(5)	0.475 0(3)	0.447 2(2)	0.488(1)
C(6)	0.321 6(5)	0.427 6(4)	0.413(1)
C(7)	0.224 0(5)	0.509 1(6)	0.369 4(9)
C(8)	0.273 8(5)	0.614 2(5)	0.397(1)
C(9)	0.420 5(6)	0.635 5(4)	0.469(1)
O(10)	0.179 2(9)	0.694 9(7)	0.353(1)
H(1)	0.000 0	0.184(7)	0.000 0
H(6)	0.285(1)	0.353 8(6)	0.393(1)
H(7)	0.116 3(7)	0.494 3(9)	0.315(1)
H(8)	0.201 1(9)	0.673 0(7)	0.363(1)
H(9)	0.455(1)	0.710 0(5)	0.488(1)
H(10)	0.094 6(9)	0.667(1)	0.311(1)

oxygen atom and the hydrogen atoms were found from a subsequent difference-Fourier synthesis. Full-matrix least-squares refinement was carried out in all three possible space groups, the results of which are shown in Table 1. As with (I), space group $C2/m$ was used in the final analysis.

Each reflection was assigned a weight as before. Three coefficients, A_r , were used with values⁷ 22.6, 31.2, and 9.9 and the final weighted R' was 0.104.

All calculations for both structures were performed on the Oxford University ICL 1906A computer with the Oxford

CRYSTALS package.⁸ Atomic scattering factors for neutral atoms were taken from ref. 9. Table 2 lists final fractional co-ordinates with their estimated standard deviations, derived from the full variance-covariance matrix. The coefficients in the expression for the anisotropic temperature factor, $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{23}hkb^{*c*} + 2U_{13}hla^{*c*} + 2U_{12}hka^{*b*})]$, together with observed structure amplitudes and structure factors calculated from the atomic parameters in Table 2 are given in Supplementary Publication No. SUP 22155 (19 pp.).*

RESULTS AND DISCUSSION

The overall structures of the two molecular complexes are very similar to each other, and to that of the molecular complex of naphthalene-1,2,4,5-tetracyanobenzene.³ Interatomic distances and interbond angles with estimated standard deviations in parentheses, derived

TABLE 3

Interatomic distances (Å), before and after libration correction, and interbond angles (°), with estimated standard deviations in parentheses, for α -naphthol-1,2,4,5-tetracyanobenzene (I)

C(1)-C(2)	1.397(3)	1.401	
C(2)-C(2 ^{III})	1.384(4)	1.389	
C(2)-C(3)	1.444(3)	1.448	
C(3)-N(4)	1.139(3)	1.142	
C(1)-H(1)	0.99(4)		
C(2)-C(1)-C(2 ^{II})	118.5(3)	C(1)-C(2)-C(2 ^{III})	120.8(2)
H(1)-C(1)-C(2)	120.8(2)	C(2 ^{III})-C(2)-C(3)	120.4(1)
C(1)-C(2)-C(3)	118.8(2)	C(2)-C(3)-N(4)	179.7(3)
C(5)-C(5 ^I)	1.420(4)	1.426	
C(5)-C(6)	1.423(3)	1.428	
C(6)-C(7)	1.363(4)	1.368	
C(7)-C(8)	1.410(4)	1.416	
C(8)-C(9)	1.367(4)	1.372	
C(9)-C(5 ^I)	1.418(3)	1.423	
C(6)-O(10)	1.335(4)	1.341	
C(6)-H(6)	1.000(5)	C(9)-H(9)	0.999(5)
C(7)-H(7)	1.000(5)	O(10)-H(10)	0.850(5)
C(8)-H(8)	1.001(5)		
C(9 ^I)-C(5)-C(6)	121.7(2)	C(6)-O(10)-H(10)	105.1(5)
C(5 ^I)-C(5)-C(6)	118.9(3)	C(5)-C(6)-H(6)	119.9(4)
C(5 ^I)-C(5)-C(9 ^I)	119.3(3)	C(7)-C(6)-H(6)	119.9(4)
C(5)-C(6)-C(7)	120.3(2)	C(6)-C(7)-H(7)	119.6(4)
C(6)-C(7)-C(8)	120.7(2)	C(8)-C(7)-H(7)	119.7(4)
C(7)-C(8)-C(9)	120.6(3)	C(7)-C(8)-H(8)	119.6(4)
C(8)-C(9)-C(5 ^I)	120.1(2)	C(9)-C(8)-H(8)	119.7(4)
C(5)-C(6)-O(10)	119.3(3)	C(8)-C(9)-H(9)	119.9(4)
C(7)-C(6)-O(10)	120.5(3)	C(5 ^I)-C(9)-H(9)	120.0(4)

Roman numeral superscripts denote the following equivalent positions relative to the reference molecule at x, y, z :

$$\begin{array}{ll} \text{I } 1-x, 1-y, 1-z & \text{III } x, \bar{y}, z \\ \text{II } \bar{x}, y, \bar{z} & \end{array}$$

from the parameters in Table 2 are given in Tables 3 and 4, together with bond lengths after correction for rigid-body thermal motion.¹⁰ Equations of important molecular planes are given in Table 5.

* For details see Notice to Authors No. 7 in *J.C.S. Perkin II*, 1977, Index issue.

⁸ J. R. Carruthers in 'Crystals' User Manual, Oxford University Computing Laboratory, Oxford, 1975.

TABLE 4

Interatomic distances (Å), before and after libration correction, and interbond angles (°), with estimated standard deviations in parentheses, for β -naphthol-1,2,4,5-tetracyanobenzene (II)

C(1)-C(2)	1.389(5)	1.393	
C(2)-C(2 ^{III})	1.391(8)	1.395	
C(2)-C(3)	1.441(6)	1.445	
C(3)-C(4)	1.133(5)	1.137	
C(1)-H(1)	0.94(8)		
C(2)-C(1)-C(2 ^{II})	118.6(6)	C(1)-C(2)-C(2 ^{III})	120.7(3)
H(1)-C(1)-C(2)	120.7(3)	C(2 ^{III})-C(2)-C(3)	120.1(3)
C(1)-C(2)-C(3)	119.2(4)	C(2)-C(3)-N(4)	177.6(5)
C(5)-C(5 ^I)	1.421(4)	1.428	
C(5)-C(6)	1.420(4)	1.424	
C(6)-C(7)	1.367(4)	1.372	
C(7)-C(8)	1.415(4)	1.422	
C(8)-C(9)	1.364(4)	1.367	
C(9)-C(5 ^I)	1.421(4)	1.426	
C(8)-O(10)	1.342(5)	1.346	
C(6)-H(6)	1.000(5)	C(9)-H(9)	1.000(5)
C(7)-H(7)	1.000(5)	O(10)-H(10)	0.850(5)
C(8)-H(8)	1.000(5)		
C(9 ^I)-C(5)-C(6)	121.8(2)	C(8)-O(10)-H(10)	105.0(5)
C(5 ^I)-C(5)-C(6)	118.8(3)	C(5)-C(6)-H(6)	119.8(4)
C(5 ^I)-C(5)-C(9 ^I)	119.3(3)	C(7)-C(6)-H(6)	119.8(4)
C(5)-C(6)-C(7)	120.3(3)	C(6)-C(7)-H(7)	119.6(4)
C(6)-C(7)-C(8)	120.8(3)	C(8)-C(7)-H(7)	119.6(4)
C(7)-C(8)-C(9)	120.3(3)	C(7)-C(8)-H(8)	119.9(4)
C(8)-C(9)-C(5 ^I)	120.4(3)	C(9)-C(8)-H(8)	119.9(4)
C(7)-C(8)-O(10)	121.4(3)	C(8)-C(9)-H(9)	119.8(4)
C(9)-C(8)-O(10)	118.4(3)	C(5 ^I)-C(9)-H(9)	119.8(4)

Roman numeral superscripts are defined in the footnotes to Table 3.

TABLE 5

Equations of least-squares best planes, where x, y, z represent fractional co-ordinates with respect to the crystallographic axes. Displacements (Å) of relevant atoms from the plane are given in square brackets

(a) α -Naphthol-1,2,4,5-tetracyanobenzene (I)

Plane (1): 1,2,4,5-tetracyanobenzene

$$-2.875x - 0.003y + 6.791z = -0.000$$

[C(1) 0.000, C(2) 0.001, C(3) -0.002, N(4) 0.001, H(1) -0.000]

Plane (2): α -Naphthol

$$-2.981x - 0.059y + 6.791z = 1.866$$

[C(5) 0.001, C(6) 0.004, C(7) 0.008, C(8) -0.007, C(9) -0.000, O(10) -0.008, H(6) 0.001, H(7) 0.000, H(8) -0.001, H(9) 0.000, H(10) 0.000]

(b) β -Naphthol-1,2,4,5-tetracyanobenzene (II)

Plane (3): 1,2,4,5-tetracyanobenzene

$$-2.932x + 0.071y + 6.798z = 0.011$$

[C(1) -0.003, C(2) 0.002, C(3) 0.001, N(4) -0.001, H(1) 0.002]

Plane (4): β -Naphthol

$$3.312x + 0.239y - 6.792z = -1.640$$

[C(5) 0.003, C(6) -0.001, C(7) -0.005, C(8) -0.003, C(9) 0.002, O(10) 0.003, H(6) 0.000, H(7) 0.002, H(8) -0.000, H(9) -0.002, H(10) 0.001]

For both structures, the centres of libration of the molecules necessarily coincide with their inversion

⁹ 'International Tables for X-Ray Crystallography,' vol. 4, Kynoch Press, Birmingham, 1974.

¹⁰ V. Schomaker and K. N. Trueblood, *Acta Cryst.*, 1968, **B24**, 63.

centres. As is frequently observed,¹¹ the librations of the β -naphthol and 1,2,4,5-tetracyanobenzene (I) molecules

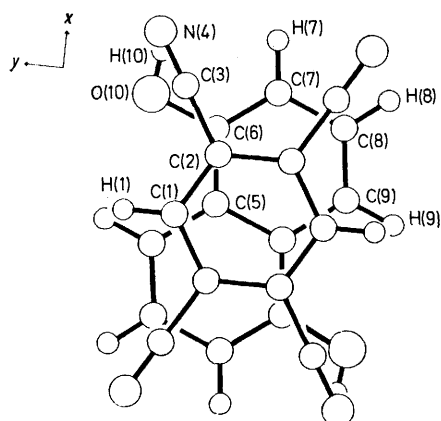


FIGURE 1 Projection of 1,2,4,5-tetracyanobenzene on least-squares best plane of one disordered α -naphthol; O(10) and H(10) have occupancy 0.25

are markedly anisotropic, the axis of greatest libration almost coinciding with the long axis of the molecule. The anisotropy of the librational tensors of the α -naphthol and 1,2,4,5-tetracyanobenzene (II) molecules

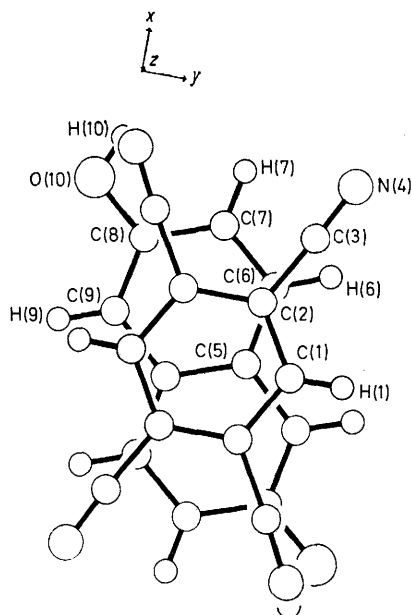


FIGURE 2 Projection of 1,2,4,5-tetracyanobenzene on least-squares best plane of one disordered β -naphthol; O(10) and H(10) have occupancy 0.25

are less marked, but the maximum librational amplitudes are in the molecular planes. The values of $\{\Sigma[U_{ij}$

¹¹ A. Hoekstra, T. Spoelder, and A. Vos, *Acta Cryst.*, 1972, **B28**, 14.

¹² C. K. Prout and I. J. Tickle, *J.C.S. Perkin II*, 1973, 520

¹³ B. Shaanan, U. Shmueli, and D. Rabinovich, *Acta Cryst.*, 1976, **B32**, 2574.

¹⁴ C. K. Prout, T. Morley, I. J. Tickle, and J. D. Wright, *J.C.S. Perkin II*, 1973, 523.

$(\text{obs} - U_{ij}(\text{calc}))^2/N\}^{\frac{1}{2}}$ where N is the number of U_{ij} terms less the number of rigid-body parameters determined were 0.006 for the α -naphthol, 0.004 for the 1,2,4,5-tetracyanobenzene (I), 0.007 for the β -naphthol, and 0.004 Å for the 1,2,4,5-tetracyanobenzene (II), compared with the corresponding $\sigma(U_{ij})$ values of 0.002–0.006, 0.001–0.003, 0.003–0.010, and 0.002–0.004, respectively. The rigid-body approximation therefore gives a reasonable fit to the data. This is not surprising in the cases of the α - and β -naphthol molecules since they were constrained to be rigid bodies in the refinement. The

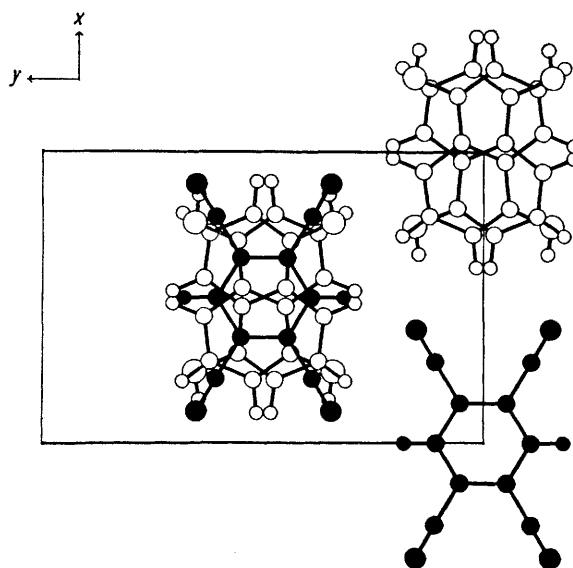


FIGURE 3 Projection viewed approximately normal to the α -naphthol and 1,2,4,5-tetracyanobenzene molecules centred at $(1, 0, \frac{1}{2})$; $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$; and $(0, 0, 0)$; $(\frac{1}{2}, \frac{1}{2}, 0)$ respectively.

Rotation matrix: $\begin{matrix} -0.028 & -1.000 & -0.001 \\ 1.000 & -0.028 & 0.006 \\ -0.006 & -0.001 & 1.000 \end{matrix}$

(Rotation matrix defines transformation from orthogonal axes a, b, c^* to plot co-ordinates)

corrected bond lengths agree reasonably well with those from previous studies.^{12,13}

The dimensions of the 1,2,4,5-tetracyanobenzene molecule in both structures are the same as those observed in the uncomplexed molecule¹² and in other electron-donor-acceptor complexes.^{3,14-16} The bond lengths and bond angles within the naphthalene nucleus of the α - and β -naphthol molecules agree with those in naphthalene itself,¹⁷ but the C–O lengths [1.341 (I) and 1.346 Å (II)] are much shorter than those found in either α -naphthol¹⁸ (1.40 Å) or β -naphthol¹⁹ (1.39 Å). However, C–(OH) length has been correlated with acidic strength, the shorter the bond the stronger

¹⁵ J. D. Wright and P. Murray-Rust, *J. Chem. Soc. (A)*, 1968, 247.

¹⁶ B. Kamenar, C. K. Prout, and J. D. Wright, *J. Chem. Soc. (A)*, 1966, 661.

¹⁷ D. W. J. Cruickshank and R. A. Sparks, *Proc. Roy. Soc.*, 1960, **A258**, 270.

¹⁸ B. Robinson and A. Hargreaves, *Acta Cryst.*, 1964, **17**, 944.

¹⁹ H. C. Watson and A. Hargreaves, *Acta Cryst.*, 1958, **11**, 556.

the acid, and structures of phenols have been determined with C-(OH) lengths of 1.333 Å (2-chloro-4,6-dinitrophenol²⁰) and 1.342 Å (2-nitro-4-chlorophenol²¹). The large angles C(7)-C(6)-O(10) (I) and C(7)-C(8)-O(10) (II)

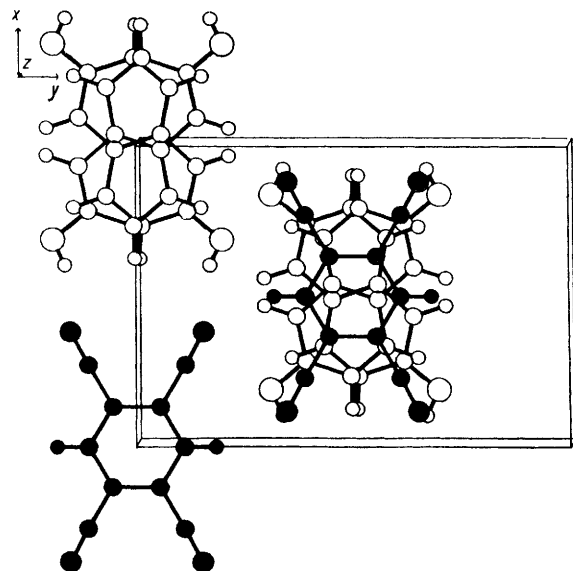


FIGURE 4 Projection viewed approximately normal to the β -naphthol and 1,2,4,5-tetracyanobenzene molecules centred at $(1,0,\frac{1}{2})$; $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$; and $(0,0,0)$; $(\frac{1}{2},\frac{1}{2},0)$ respectively.

Rotation matrix:	0.006	1.000	0.020
	0.999	-0.007	0.038
	0.038	0.020	-0.999

are found on the side where the hydroxy-hydrogen atoms are pointing.

Both structures consist of alternating donor and acceptor components stacked plane-to-plane, the stack

axes being parallel to the crystallographic c axes. Figures 1 and 2 show projections of the acceptor onto the least-squares best plane of one of the disordered donor molecules, and Figures 3 and 4 show the relative orientations of the molecules within the unit cells.

The mean perpendicular distances within the stacks are 3.40 Å for both structures, *i.e.* that expected for an aromatic plane-to-plane van der Waals contact. The inclinations of the plane normals of the donor and acceptor are 0.7° (I) and 2.8° (II). The shortest intermolecular contacts are N(4) \cdots H(10) 2.329, N(4) \cdots O(10) 3.154 Å, N(4) \cdots H(10)-O(10) 164° (I), and N(4) \cdots H(10) 2.009, N(4) \cdots O(10) 2.819 Å, N(4) \cdots H(10)-O(10) 159° (II), indicating the presence of weak O-H \cdots N hydrogen-bonds. Other examples of such hydrogen-bonds occur in pyrazinic acid (O \cdots N 2.669 Å),²² and *m*-aminophenol (O \cdots N 2.75 Å).²³ However, the hydrogen-bonds in the two naphthol-1,2,4,5-tetracyanobenzene structures were unexpected since the electronegativity of the cyanide nitrogen atoms is not great.

In naphthalene-1,2,4,5-tetracyanobenzene³ the overlap integral and hence the charge-transfer energy is maximised when there is a near centre-on-centre orientation, and the observed orientation²⁴ has *ca.* 95% of the maximum charge-transfer stabilisation. Figures 1 and 2 show that the presence of the hydroxy-groups, and their associated hydrogen-bonds, do not much effect this stabilisation.

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