THE CRYSTAL AND MOLECULAR STRUCTURE OF CHARGE-TRANSFER COMPLEX OF AZO DYESTUFF 5-(4-CHLORO-2-NITROPHENYL)-AZO-6-HYDROXY-1-ETHYL-3-CYANO-4-METHYL-2-PYRIDONE WITH NAPHTHALENE

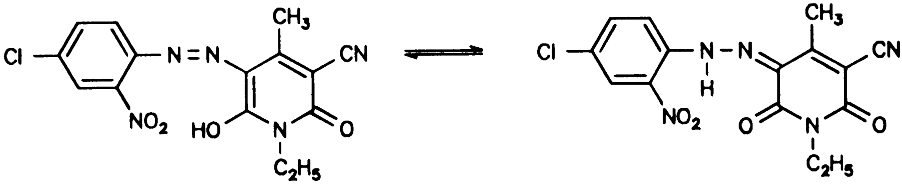
Josef PŘIKRYL[a], Bohumil KRATOCHVÍL[b], Jan ONDRÁČEK[b],
Jaroslav MAIXNER[c], Jiří KLICNAR[a] and Karel HUML[d]

[a] *Department of Chemical Technology of Fibrous Materials,*
University of Chemical Technology, 532 10 Pardubice, The Czech Republic
[b] *Department of Solid State Chemistry,*
Prague Institute of Chemical Technology, 166 28 Prague 6, The Czech Republic
[c] *Central Laboratories,*
Prague Institute of Chemical Technology, 166 28 Prague 6, The Czech Republic
[d] *Institute of Macromolecular Chemistry,*
Academy of Sciences of the Czech Republic, 162 06 Prague 6, The Czech Republic

Received October 6,1992
Accepted December 10, 1992

The title charge-transfer complex crystallizes in the ratio of two molecules of azo dyestuff to one molecule of naphthalene. The crystals are triclinic, space group $P\bar{1}$, lattice parameters a = 7.953(1), b = 11.608(2), c = 11.717(2) Å, α = 101.89(2), β = 94.27(2), γ = 109.91(2)°, Z = 2. The structure was solved by direct methods and refined anisotropically to R = 0.054 for 1 768 unique observed reflections. Crystal packing is stabilized by van der Waals forces and partly by π–π stacking interaction among naphthalene, phenyl and pyridine rings of pyridon azo dyestuff.

5-(4-Chloro-2-nitrophenyl)-azo-6-hydroxy-1-ethyl-3-cyano-4-methyl-2-pyridone, the constitution of which may be formulated in tautomeric forms *Ia* and *Ib* (Scheme 1, ref.[1]), was used as a yellow dispersion dyestuff for synthetic fibers. When applying this dyestuff it was found that it forms crystalline molecular complexes of charge transfer



Ia *Ib*

SCHEME 1

type (CT-complexes) with various aromatic compounds as simple aromatic hydrocarbons (naphthalene, biphenyl, anthracene) as well as variously substituted aromatic compounds (1- or 2-naphthol, 2- or 4-hydroxybiphenyl, *p*-dichlorobenzene, 4-nitroaniline, 4-cresylbenzoate, *N*-phenylanthranilic acid and other). These complexes are stable in crystalline form but in solution of organic solvents they decompose into their components. The free azo dyestuff of the formula *Ia*, *Ib* forms brilliant yellow crystals. The corresponding CT-complexes exhibit a bathochrome colour effect. For example, CT-complexes with naphthalene and biphenyl are orange, those with 1- or 2-naphthol are red violet, while those with 4,4'-dihydroxybiphenyl are blue violet. CT-complexes crystallize easily from solutions of organic solvents (e.g. from acetone) and from mixtures of aqueous dispersions of the dyestuff and aromatic compounds (the dyeing process). They can be also formed by co-sublimation of the components at higher temperatures.

The reported structure determination was undertaken in order to explain in more details a packing arrangement between pyridon azo dyestuff and aromatic hydrocarbone. CT-complexes of pyridon azo dyestuff type have not been described so far.

EXPERIMENTAL

Preparation

The CT-complex of the azo dyestuff (see *Ia*, *Ib*) with naphthalene was prepared by crystallization from solution of acetone using the following procedure: 5 g dyestuff and 1.7 g naphthalene was dissolved by refluxing in minimal quantity of acetone (ca 140 ml) and the resulting solution was slowly cooled to room temperature. Orange crystals of CT-complex were collected by filtration and dried in air at room temperature to a constant weight, the yield was 4.42 g (75.1%). The elemental analysis confirms the stoichiometric ratio of 2 mol dyestuff to 1 mol naphthalene in the complex. For $C_{40}H_{32}Cl_2N_{10}O_8$ (851.7) calculated: 56.41% C, 3.79% H, 8.33% Cl, 16.45% N; found: 55.92% C, 4.03% H, 8.08% Cl, 16.21% N. The dyestuff was prepared by copulation of diazoted 4-chloro-2-ni-

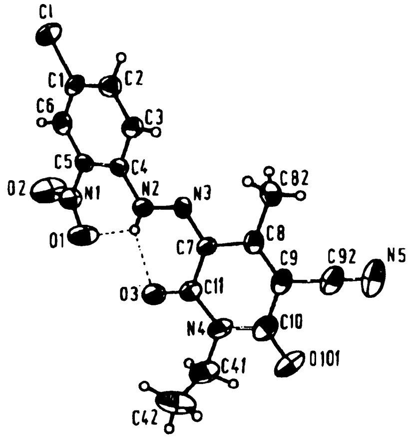


FIG. 1
View of the pyridon azo dyestuff molecule. Thermal ellipsoids are drawn at the 50% probability

troaniline with 1-ethyl-3-cyano-4-methyl-6-hydroxy-2-pyridone (according to the procedure described in ref.[2]) and recrystallized from ethanol.

Crystal Structure Determination

The phase problem was solved by direct methods and the structure refined anisotropically by full-matrix least-squares. The H atom positions were localized from the difference Fourier synthesis and refined isotropically. No peaks of chemical significance appeared in the final difference map. Absorption and extinction effects were ignored. Basic crystallographic data, measurement and refinement details are summarized in Table I.

TABLE I
Basic crystallographic data, measurement and refinement parameters

a = 7.953(1) Å	V = 982.8(3) Å^3
b = 11.608(2) Å	Z = 2
c = 11.717(2) Å	D(calc) = 1.480 g cm^{-3}
α = 101.89(2)°	Space group $P\bar{1}$
β = 94.27(2)°	μ(MoKα) = 2.31 cm^{-1}
γ = 109.91 (2)°	F(000) = 452
Crystal dimensions	0.2 × 0.2 × 0.4 mm
Diffractometer and radiation used	Enraf–Nonius CAD4, MoKα, λ = 0.71073 Å
Scan technique and temperature	$\omega/2\Theta$; 296 K
No. and Θ range of reflections for lattice parameter refinement	18; 19 – 21°
Range of h, k and l	$-10 \rightarrow 10$, $-13 \rightarrow 13$, $-13 \rightarrow 13$
Standard reflections	-3 3 -9, 2 -1 3
Standard reflections monitored in interval; intensity fluctuation	60 min; -0.6%
Total number of reflections measured; 2Θ range	2 053; 0 – 42°
Value of R_{int}	0.020
Number of unique observed reflections	1 768
Criterion for observed reflections	$I \geq 1.96\ \sigma(I)$
Function minimized	$\sum w (\lvert F_o \rvert - \lvert F_c \rvert)^2$
Weighting scheme	$w = [\ \sigma^2 (F) + 0.0009F^2\ ]^{-1}$
Parameters refined	335
Value of R, wR and S	0.054, 0.048, 1.78
Ratio of max. least-squares shift to e.s.d. in the last cycle	0.001
Max. and min. heights in final $\Delta\rho$ map	0.34; -0.66 eÅ^{-3}
Source of atomic scattering factors	SHELX76[3]
Programs used	SHELX86[4], SDP[5], SHELX76[3], PARST[6], MOLDRAW[7]
Computer used	PDP 11/73, PC AT

TABLE II

Atomic coordinates (. 10^4) for non-H atoms and their equivalent isotropic thermal parameters (. 10^4)[a]. E.s.d's in parentheses. $U_{eq} = [\sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j]/3$

Atom	x	y	z	U_{eq}, Å^2
		Dyestuff		
Cl	4369(1)	5249.7(9)	8745.5(8)	496(4)
O1	9005(3)	7342(3)	5079(3)	733(14)
O2	9613(4)	6477(4)	6390(3)	918(17)
O3	7557(3)	8076(2)	2927(2)	466(10)
O101	4569(4)	8284(3)	−431(2)	643(13)
N1	8574(4)	6818(3)	5861(3)	464(13)
N2	5622(4)	7055(3)	4404(3)	319(11)
N3	4187(3)	6908(2)	3667(2)	295(10)
N4	6089(4)	8157(3)	1237(2)	397(11)
N5	−92(5)	6734(4)	−610(3)	759(17)
C1	4780(5)	5811(3)	7488(3)	333(14)
C2	3359(5)	5899(3)	6788(3)	388(15)
C3	3661(5)	6310(3)	5786(3)	347(14)
C4	5369(4)	6649(3)	5437(3)	279(12)
C5	6762(4)	6544(3)	6162(3)	304(12)
C6	6472(5)	6135(3)	7187(3)	363(14)
C7	4363(4)	7267(3)	2684(3)	294(12)
C8	2684(4)	6997(3)	1920(3)	340(13)
C9	2802(5)	7308(3)	875(3)	387(14)
C10	4505(5)	7951(3)	479(3)	444(14)
C11	6128(5)	7862(3)	2310(3)	352(13)
C41	7847(6)	8755(5)	849(4)	572(20)
C42	8574(9)	10166(6)	1298(7)	851(29)
C82	921(5)	6382(5)	2316(4)	475(17)
C92	1196(6)	7005(4)	45(3)	502(15)
		Naphthalene		
C21	5378(14)	9480(5)	6945(6)	962(34)
C22	4142(6)	9750(4)	5153(4)	571(18)
C23	2577(8)	9636(5)	4341(7)	844(27)
C24	3952(10)	9373(5)	6187(6)	864(27)
C25	2908(13)	10028(6)	3302(7)	966(33)

[a] Supplementary materials (lists of structure factors, anisotropic thermal parameters, H-atom coordinates) are available on request from authors.

TABLE III
Bond distances (in Å), angles (in °). Numbers in parentheses are e.s.d.

Bond	Distance	Bond	Distance
Cl–C1	1.739(4)	C2–C3	1.363(5)
O1–N1	1.209(5)	C3–C4	1.397(5)
O2–N1	1.213(6)	C4–C5	1.399(5)
O3–C11	1.220(4)	C5–C6	1.387(5)
O101–C10	1.206(5)	C7–C8	1.451(5)
N1–C5	1.453(5)	C7–C11	1.482(5)
N2–N3	1.318(4)	C8–C9	1.347(5)
N2–C4	1.391(5)	C8–C82	1.497(5)
N3–C7	1.305(5)	C9–C10	1.468(5)
N4–C10	1.405(5)	C9–C92	1.438(6)
N4–C11	1.370(5)	C21–C24	1.341(12)
N4–C41	1.486(5)	C22–C23	1.460(9)
N5–C92	1.141(6)	C22–C24	1.372(9)
C1–C2	1.391(6)	C23–C25	1.397(12)
C1–C6	1.363(6)	C41–C42	1.499(8)

Atoms	Angle	Atoms	Angle
O1–N1–O2	121.3(4)	N3–C7–C11	124.1(3)
O2–N1–C5	118.3(4)	N3–C7–C8	115.5(3)
O1–N1–C5	120.3(3)	C8–C7–C11	120.3(3)
N3–N2–C4	118.7(3)	C7–C8–C82	119.1(3)
N2–N3–C7	120.7(3)	C7–C8–C9	117.6(3)
C11–N4–C41	117.9(3)	C9–C8–C82	123.3(4)
C10–N4–C41	117.3(3)	C8–C9–C92	120.6(4)
C10–N4–C11	124.8(3)	C8–C9–C10	124.6(3)
Cl–C1–C6	119.9(3)	C10–C9–C92	114.8(3)
Cl–C1–C2	119.2(3)	N4–C10–C9	115.3(3)
C2–C1–C6	120.8(3)	O101–C10–C9	123.3(4)
C1–C2–C3	119.6(4)	O101–C10–N4	121.4(4)
C2–C3–C4	121.8(4)	N4–C11–C7	117.2(3)
N2–C4–C3	120.1(3)	O3–C11–C7	121.5(3)
C3–C4–C5	117.0(3)	O3–C11–N4	121.3(4)
N2–C4–C5	122.9(3)	C23–C22–C24	121.6(6)
N1–C5–C4	121.8(3)	C22–C23–C25	117.3(6)
C4–C5–C6	121.8(3)	C21–C24–C22	122.3(7)
N1–C5–C6	116.4(3)	N4–C41–C42	112.0(5)
C1–C6–C5	119.1(4)	N5–C92–C9	178.3(5)

RESULTS AND DISCUSSION

The final atomic parameters are given in Table II, bond distances and angles in Table III. Figure 1 shows the perspective view of the pyridon azo dyestuff molecule, crystal packing is depicted in Fig. 2. The atom numbering system used is arbitrary and does not correspond to the organic chemistry nomenclature.

The largest displacement from the plane of the substituted phenyl ring (C1, C2, C3, C4, C5, C6; $\chi^2 = 2.759$) is at C5 (0.004(3) Å). The atoms N1 and O2 are situated above this plane (0.061(4) and 0.326(4) Å) and O1 below it (−0.115(4) Å). The pyridine moiety (C7, C8, C9, C10, N4, C11) is also planar with deviations varying from −0.023(4) Å (for C10) to 0.020(4) Å (for C9). Multiple bond character was found for C8–C9 (the bond order is 1.82). The phenyl and pyridine ring planes are mutually tilt by 13.8(1)°. The planar arrangement of the naphthalene ring system was confirmed by the χ^2 test value of 2.639.

Possible intramolecular hydrogen bonds were found between the N2...O1 and N2...O3 atoms with N2 acting as double proton donor. The donor–acceptor distances and the donor–hydrogen–acceptor angles are as follows: 2.634(4) Å and 126(3)° for N2–HN2...O1 and 2.601(4) Å and 136(4)° for N2–HN2...O3.

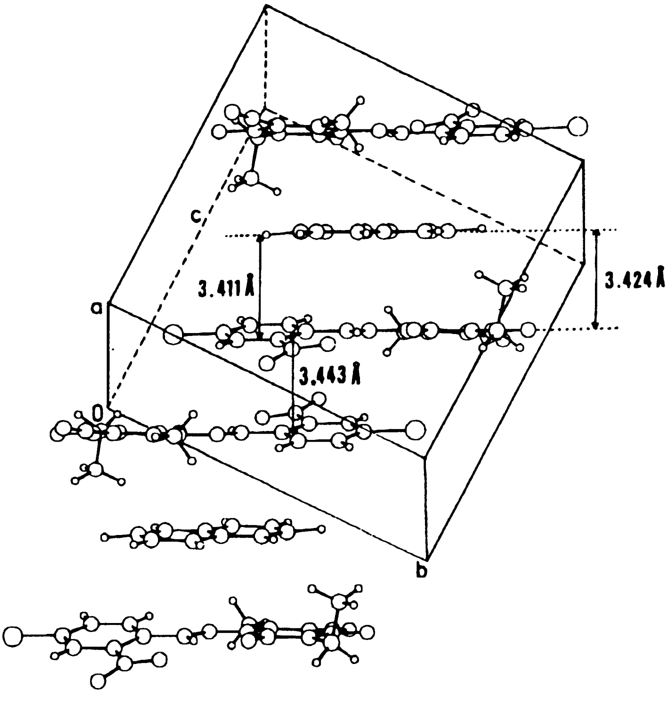


FIG. 2
Crystal packing

No intermolecular hydrogen bond contacts appear to be present, the crystal structure is stabilized by van der Waals forces and partly by the π–π stacking interactions among the naphthalene, phenyl and pyridine rings. As may be seen from Fig. 2, the packing arrangement consists of ...dyestuff – dyestuff – naphthalene – dyestuff – dyestuff – naphthalene... layer sequence. Two stacked phenyl rings (C1, C2, C3, C4, C5, C6 and C1^{i}, C2^{i}, C3^{i}, C4^{i}, C5^{i}, C6^{i}) are related to each other by the translation symmetry operation (i: 1 – x, 1 – y, 1 – z). The corresponding mean interplanar spacing is 3.443(4) Å. As follows from the dihedral angle (4.3(2)°) between pyridine (C7, C8, C9, C10, N4, C11) and naphthalene rings (C21, C22, C22^{ii}, C23, C24, C25; ii: 1 – x, 2 – y, 1 – z), they are nearly coplanar with the mean interplanar distance of 3.424(4) Å. Finally, the stacking interaction between phenyl (C1, C2, C3, C4, C5, C6) and the second naphthalene rings (C21^{ii}, C22, C22^{ii}, C23^{ii}, C24^{ii}, C25^{ii}) is 3.411(4) Å and their dihedral angle equals 9.4(2)°.

REFERENCES

1. Cee A., Horáková B., Lyčka A.: Dyes and Pigments 9, 357 (1988).
2. Ciba-Geigy: Eur. 0 083 313 (1982); Chem. Abstr. 99, 177 443 (1983).
3. Sheldrick G. M.: *SHELX 76. Program for Crystal Structure Determination.* University of Cambridge, Cambridge 1976.
4. Sheldrick G. M.: *SHELXS 86. Program for Crystal Structure Solution.* University of Götingen, Götingen 1986.
5. Frenz B. A., Associates Inc.: *SDP. Structure Determination Package.* College Station, Texas 77840 and Enraf–Nonius, Delft 1985.
6. Nardelli M.: Comput. Chem. 7, 95 (1983).
7. Ugliengo P., Borzani G., Viterbo D.: J. Appl. Crystallogr. *21* ,75 (1988).

Translated by the author (B. K.).