organic compounds

An azo dye molecule having a pyridine-2,6-dione backbone

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The title azo dye, 2-(2-methoxyethoxy)ethyl 4-[(5-cyano-1-ethyl-4-methyl-2,6-dioxo-1,2,3,6-tetrahydropyridin-3-ylidene)-hydrazino]benzoate, $C_{21}H_{24}N_4O_6$, with a 1-ethyl-5-cyano-2-hydroxy-4-methyl-6-pyridone component, crystallizes in the hydrazone form. Hydrogen bonding mediates the formation of four-molecule aggregates, which are further grouped into an extended structure by $\pi-\pi$ stacking interactions between the aromatic rings of adjacent molecules, with a centroid–centroid separation of 3.697 (2) Å.

Comment

Azo dyes have found widespread application in the textile and food industries, and elsewhere. Those having 1-alkyl-5-cyano-2-hydroxy-4-methyl-6-pyridone components have good coloration properties and give bright green–yellow hues. More importantly, they have excellent colour fastness to washing. This type of molecule has two enantiotropic isomers, i.e. the 2-hydroxy-6-pyridone form and the pyridine-2,6-dione form. To date, there is only one structural report on these two types of backbones (Black et al., 1992). In this communication, we report the single-crystal structure of a yellow azo dye, (I), using 1-ethyl-5-cyano-2-hydroxy-4-methyl-6-pyridone as the coupling component.

(I)
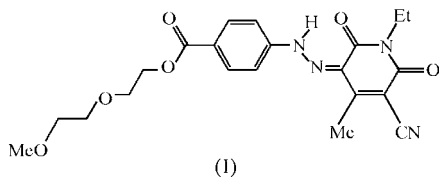
The molecular structure of (I) with the atom-numbering scheme is shown in Fig. 1, while selected bond distances and angles are given in Table 1. The bond distances and angles of the benzene ring, the pyridine-2,6-dione ring and the 2-(2-methoxyethoxy)ethyl ester moiety in this structure are in the normal ranges (Black et al., 1992).

The dye exists in the hydrazone form, which can be deduced by the relevant bond lengths [C1—O2 = 1.234 (2), C2—N2 = 1.320 (2), C1—C2 = 1.471 (3), C2—C3 = 1.441 (2) and N1—N2 = 1.307 (2) Å]; the first two exhibit partial double-bond character, while the other three display predominantly single-bond character. Furthermore, higher R_1 and wR_2 values are obtained if a H atom is added to atom O2 to model a hydroxyl group. The whole molecule, except for the ethyl and methoxyethoxyethyl ester groups, is essentially planar. The dihedral angle between the two aromatic rings is 0.7 (2)°. The ethyl and methoxyethoxyethyl ester groups of this molecule adopt cis configurations with respect to the molecular plane.

In the crystal packing of (I), $\pi-\pi$ stacking and hydrogen-bonding interactions are observed between neighbouring molecules. As illustrated in Fig. 2, every four contiguous molecules can be classified as one group, with a centroid–centroid separation of 3.697 (2) Å between the aromatic rings. Weak C—H···O hydrogen bonds also connect the packed molecules (Table 2). The ethyl and methoxyethoxyethyl ester groups of these four molecules point to the outside of each aggregate, minimizing the internal steric hindrance and, at the same time, deterring adjacent groups from further stacking.
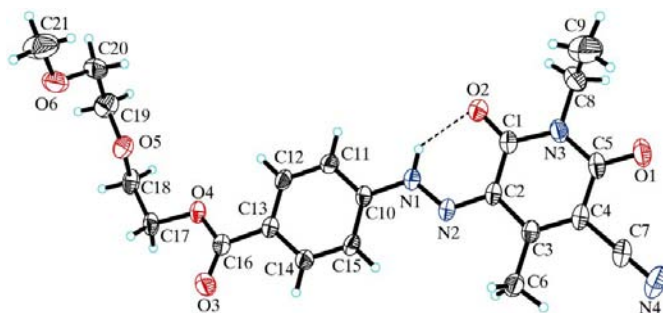

Figure 1
A drawing of (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. The intramolecular N—H···O hydrogen bond is shown as a dashed line.
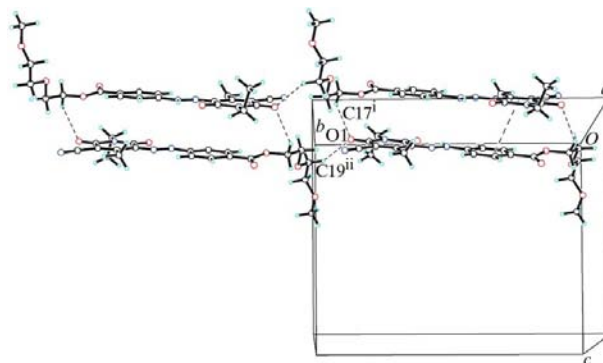

Figure 2
A perspective view of four adjacent molecules of (I) joined by hydrogen bonds and $\pi-\pi$ stacking interactions between the aromatic rings. For clarity, labels are given only once for the hydrogen-bond contacts. Hydrogen bonds and centroid–centroid $\pi-\pi$ stacking separations are indicated by dashed lines. [Symmetry codes: (i) $1 - x, 1 - y, -z$; (ii) $x, -1 + y, z$.]

(FAB, m/z): positive-ion, 429.3 (50%) $[M]^+$, 879.1 (100%) $[M_2Na]^+$; negative-ion, 427.6 (100%) $[M - H]^-$, 877.5 (74%) $[M_2Na - 2H]^-$. Orange single crystals of (I) suitable for X-ray analysis were grown from a mixture of methanol and acetone in a 2:1 (v/v) ratio by slow evaporation at room temperature in air.

Crystal data

$C_{21}H_{24}N_4O_6$	$D_x = 1.351$ Mg m^{-3}
$M_r = 428.44$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 8347
$a = 8.7074$ (17) Å	reflections
$b = 17.749$ (4) Å	$\theta = 3.2$–$27.5°$
$c = 14.081$ (3) Å	$\mu = 0.10$ mm^{-1}
$\beta = 104.53$ (3)°	$T = 120$ (2) K
$V = 2106.6$ (8) Å^3	Block, orange
$Z = 4$	$0.20 \times 0.20 \times 0.10$ mm

Data collection

Rigaku Mercury CCD area-detector diffractometer	3648 independent reflections
	3434 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{int} = 0.098$
Absorption correction: multi-scan	$\theta_{max} = 25.0°$
(*REQAB*; Jacobson, 1998)	$h = -10 \rightarrow 10$
$T_{min} = 0.978$, $T_{max} = 0.988$	$k = -21 \rightarrow 19$
17551 measured reflections	$l = -16 \rightarrow 16$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o{}^2) + (0.0632P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.054$	$+ 0.9136P]$
$wR(F^2) = 0.142$	where $P = (F_o{}^2 + 2F_c{}^2)/3$
$S = 1.16$	$(\Delta/\sigma)_{max} < 0.001$
3648 reflections	$\Delta\rho_{max} = 0.34$ e Å^{-3}
283 parameters	$\Delta\rho_{min} = -0.21$ e Å^{-3}
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

C1—O2	1.234 (2)	C16—O3	1.208 (2)
C1—N3	1.380 (2)	C16—O4	1.337 (2)
C2—N2	1.320 (2)	C17—O4	1.452 (2)
C5—O1	1.221 (2)	C18—O5	1.424 (2)
C5—N3	1.395 (2)	C19—O5	1.417 (2)
C7—N4	1.147 (3)	C20—O6	1.407 (2)
C8—N3	1.474 (2)	N1—N2	1.307 (2)
C10—N1	1.403 (2)		
N4—C7—C4	179.3 (2)	C1—N3—C5	123.83 (16)
N3—C8—C9	111.23 (18)	C1—N3—C8	119.52 (15)
N1—N2—C2	121.20 (15)	C5—N3—C8	116.53 (15)

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1A···O2	0.88	1.94	2.612 (2)	132
C6—H6C···O5^i	0.98	2.31	3.254 (2)	163
C15—H15···O6^i	0.95	2.35	3.141 (2)	141
C17—H17B···O1^{ii}	0.99	2.53	3.271 (2)	132
C19—H19A···O1^{iii}	0.99	2.56	3.424 (2)	146

Symmetry codes: (i) $-x + 1, y + \frac{1}{2}, -z + \frac{1}{2}$; (ii) $-x + 1, -y + 1, -z$; (iii) $x, y - 1, z$.

H atoms were placed in geometrically idealized positions, with C—H = 0.95–0.99 Å and N—H = 0.88 Å, and refined as riding atoms, with $U_{iso}(H) = 1.5_{eq}$(N and methyl C) or 1.2_{eq}(C) for the other C atoms.

Data collection: *CrystalClear* (Molecular Structure Corporation & Rigaku, 2001); cell refinement: *CrystalClear*; data reduction:
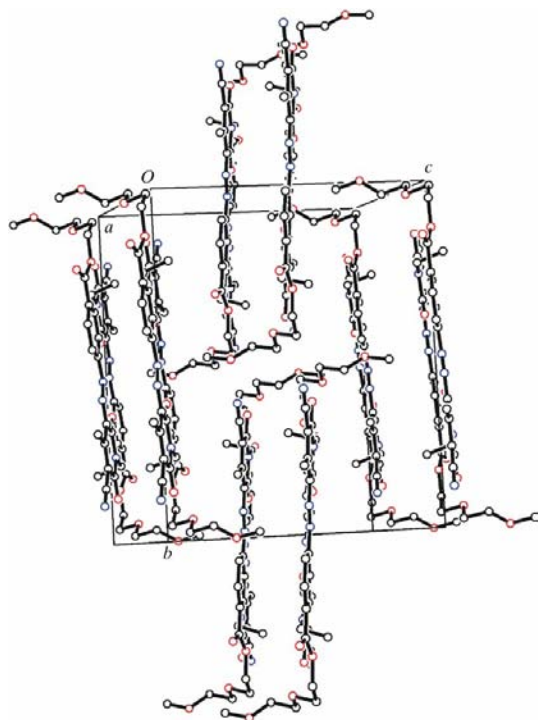

Figure 3
A packing diagram for (I), viewed along the common plane of the benzene rings.

Instead, all the groups of molecules are parallel to one another with van der Waals interactions between adjacent pairs (Fig. 3). This separation is larger than that found in a similar structure in which *n*-butyl and Cl groups replace the ethyl and methoxyethoxyethyl ester groups, respectively (Black *et al.*, 1992), where an interlayer contact of 3.3 Å was observed among all the phenyl rings due to the less pronounced spatial crowding. In addition, a strong intramolecular N—H···O hydrogen bond (Table 2) is present between atoms N1 and O2, forming a six-membered ring.

Electrospray ionization mass spectrometry (ESI–MS), a soft ionization technique, is a powerful tool to analyze the structures of azo dyes (Lemr *et al.*, 2000). Both positive-ion ESI–MS and negative-ion ESI–MS have been carried out, giving peaks corresponding to the molecular ions as well as the dimeric sodium(I) salts in different abundances for different ESI–MS.

Experimental

Compound (I) was prepared as a yellow powder *via* the method described by Horakova & Lycka (1988), by coupling of diazotized 2-(2-methoxyethoxy)ethyl 4-aminobenzoate with 5-cyano-1-ethyl-2-hydroxy-4-methyl-6-pyridone. ^{1}H NMR (500 MHz, CDCl$_3$, 298 K, TMS, p.p.m.): 14.98 (*s*, 1H), 8.18 (*d*, $J = 8.5$ Hz, 2H), 7.54 (*d*, $J = 9.0$ Hz, 2H), 4.53 (*t*, 2H), 4.07 (*t*, 2H), 3.88 (*t*, 2H), 3.73 (*t*, 2H), 3.60 (*t*, 2H), 2.65 (*s*, 3H), 1.62 (*s*, 3H), 1.28 (*t*, 3H); ^{13}C NMR (125 MHz, CDCl$_3$, 298 K, TMS, p.p.m.): 165.55, 161.45, 159.56, 158.40, 144.24, 131.73, 128.38, 124.15, 116.51, 114.09, 103.33, 71.96, 70.61, 69.26, 64.38, 59.12, 35.32, 16.63, 12.97. Elemental analysis calculated for C$_{21}$H$_{24}$N$_4$O$_6$: C 58.87, H 5.65, N 13.08%; found: C 58.89, H 5.62, N 13.16%. ESI–MS

organic compounds

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FA1171). Services for accessing these data are described at the back of the journal.

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