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3-{2-[2-(3,5-Dinitro-2-oxidophenyl)ethyl]-3,3-dimethyl-3*H*-indol-1-ium-1-yl}propanoic acid bis(dimethylformamide) solvate

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The crystal structure of the title compound, $C_{21}H_{19}N_3O_7\cdot 2C_3H_7NO$, has been prepared, for the first time in the dark, as the permanent merocyanine mode of the open form. It has a zwitterionic *trans–transoid* structure and is solvated with two *N*,*N*-dimethylformamide (DMF) molecules, forming O—H···O and C—H···O hydrogen bonds. The crystal structure is further stabilized by a variety of weak C—H···O hydrogen bonds.

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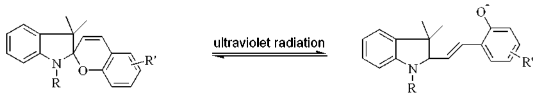
Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.005 Å
R factor = 0.063
wR factor = 0.153
Data-to-parameter ratio = 13.2

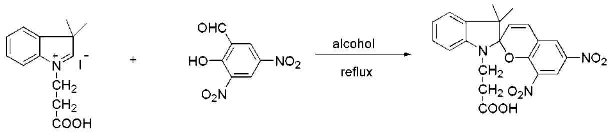
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

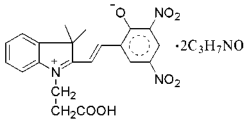
Comment

Photochromic materials based on different classes of spiropyrans are widely used in various fields of science and technology (see Scheme below; the principle of photochromic compounds based on spiropyrans) (Bertelson, 1971; Guglielmetti, 1990).



Recently, our group has studied the synthesis and the photochromic properties of certain spiropyrans and spirooxazines containing various functional groups (Li *et al.*, 1999; Li, Li, Wang, Matsuura & Meng, 2000; Li, Wang, Matsuura & Meng, 2000; Chang *et al.*, 2002). Since the lifetime of the open merocyanine forms is one of the important characteristics of photochromic systems based on spiropyrans, it is necessary to carry out a detailed study of the structure of the merocyanine.





(I)

Crystals with the open forms of indolinospiropyrans have been isolated from ethanol by recrystallization under UV irradiation (Aldoshin *et al.*, 1981; Aldoshin & Atovmyan, 1985; Aldoshin, 1990). Here, for the first time, the open form of the title compound, (I), was obtained in the dark and was studied by X-ray crystallography.

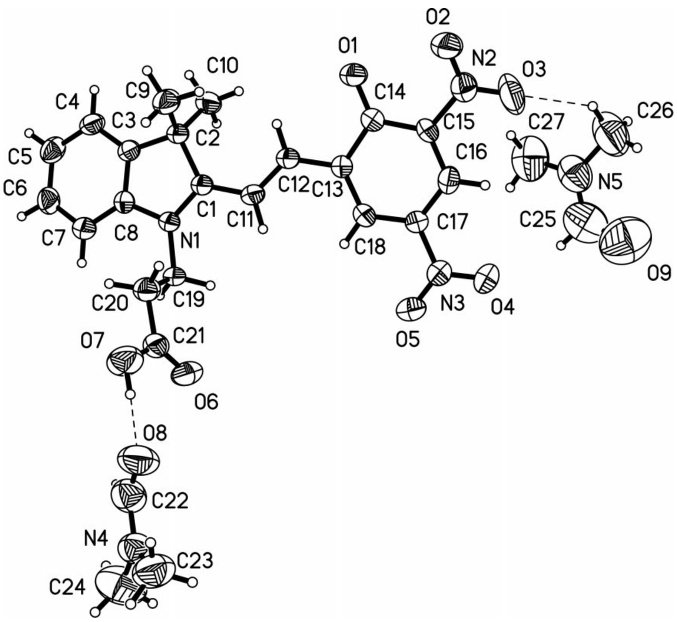


Figure 1
A view of the title compound solvated with two DMF molecules, with the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

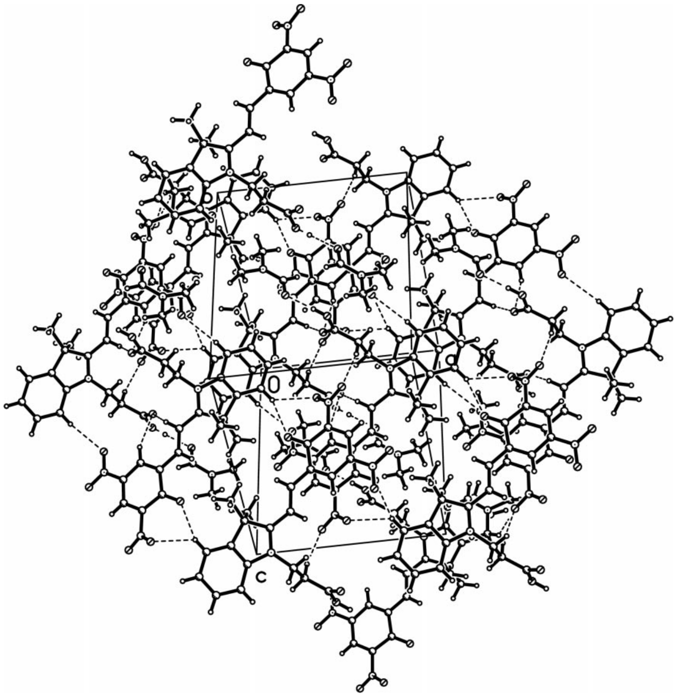


Figure 2
Packing of molecules in the structure of the title compound.

A perspective view of (I) with the atom-labeling scheme is shown in Fig. 1 and the molecular packing in Fig. 2. It can be seen that the molecule has a zwitterionic *trans–transoid* structure and is nearly planar. The indoline moiety has the conformation of a flattened envelope, bending along the N1—C2 vector with a small dihedral angle of 6.1 (5)°. The C11—C12 bond length is 1.342 (4) Å, typical for a C═C bond. The C1—C11—C12—C13 torsion angle is −176.4 (3)°. The C14—O1 bond length is 1.238 (4) Å, which suggests it is of full double-bond character. The N1—C1 bond length is 1.322 (4) Å, which suggests its complete double-bond nature and localization of its positive charge mainly on atom N1.

In the crystalline state, compound (I) is solvated with two DMF molecules, forming O—H···O and C—H···O hydrogen bonds; this contrasts with the solvation of the phenolate O atom by water molecules, which is evidently typical for merocyanine molecules in polar solvents (Aldoshin *et al.*, 1981). This may be due to the fact that the solvent molecule has no strong hydrogen donor and thus O—H···O hydrogen bonds can not be formed, with the phenolate O atom acting as hydrogen acceptor. However, the formation of O—H···O hydrogen bonds between the carboxyl group and DMF molecule, and even the formation of weak C—H···O hydrogen bonds, facilitates the solvation of (I).

The N3/O4/O5 nitro group is very nearly coplanar with the attached benzene ring, the dihedral angle being only 1.0 (5)°, while the N2/O2/O3 nitro group is twisted by 24.7 (5)°, facilitating the formation of C26—H26*A*···O3 hydrogen bonds and possibly also because of steric hindrance by the phenolate O atom. The deviations of N1 from C1/C8/C19 and C1 from C11/N1/C2 are 0.024 (3) and 0.005 (4) Å, respectively, which are much less than in the corresponding systems of the closed forms (Aldoshin *et al.*, 1981; Chuev *et al.*, 1994), indicating that atoms N1 and C1 are of the sp^2 hybridized type.

In addition, the crystal structure is further stabilized by a variety of C—H···O interactions that may be classified as weak-donor–strong-acceptor hydrogen bonds (Desiraju & Steiner, 1999). All of these interactions are intermolecular hydrogen bonds (Table 2), which play an important role in deciding the packing mode.

In conclusion, the crystal structure of (I) is stable enough for the introduction of an additional nitro group into the position *ortho* to the atom O1 (Kholmanskii & Dyumaev, 1981), and is easily obtained in the absence of UV irradiation. Its transition to the open forms is accompanied by extensive modification of bond lengths, which is indicative of the bipolar structure. It is solvated, for the first time, with two different DMF molecules by O—H···O hydrogen bonds and weak C—H···O hydrogen bonds.

Experimental

The title compound, (I), was synthesized as described earlier (see reaction scheme) (Li *et al.*, 1999). Single crystals suitable for X-ray crystallography were obtained from the mixed solvent DMF/CH_2Cl_2 by slow evaporation at room temperature in the dark.

Crystal data

$C_{21}H_{19}N_3O_7 \cdot 2C_3H_7NO$
$M_r = 571.58$
Triclinic, $P\overline{1}$
$a = 10.633$ (4) Å
$b = 12.078$ (4) Å
$c = 12.262$ (4) Å
$\alpha = 113.266$ (6)°
$\beta = 95.167$ (6)°
$\gamma = 95.326$ (6)°
$V = 1426.6$ (9) Å^3
$Z = 2$
$D_x = 1.331$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 636 reflections
$\theta = 2.8$–22.4°
$\mu = 0.10$ mm^{-1}
$T = 293$ (2) K
Plate, red
0.24 × 0.22 × 0.16 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.958$, $T_{\max} = 1.000$
7300 measured reflections
4991 independent reflections
2331 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.039$
$\theta_{\max} = 25.0°$
$h = -12 \rightarrow 12$
$k = -13 \rightarrow 14$
$l = -13 \rightarrow 14$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.063$
$wR(F^2) = 0.153$
$S = 1.00$
4991 reflections
378 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0559P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.17$ e Å^{-3}
$\Delta\rho_{\min} = -0.18$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: none

Table 1
Selected geometric parameters (Å, °).

N1—C1	1.322 (4)	C1—C2	1.522 (4)
O1—C14	1.238 (4)	C11—C12	1.342 (4)
O7—H7*A*	0.8536		
C1—N1—C8	111.0 (3)	C11—C12—C13	126.9 (3)
N1—C1—C11	122.3 (3)	C18—C13—C12	122.5 (3)
N1—C1—C2	109.8 (3)	C12—C13—C14	116.3 (3)
C11—C1—C2	127.9 (3)	O1—C14—C15	124.1 (3)
C3—C2—C1	101.0 (2)	O1—C14—C13	122.0 (3)
C12—C11—C1	125.1 (3)		
C8—N1—C1—C11	−174.4 (3)	C2—C1—C11—C12	4.6 (6)
C8—N1—C1—C2	5.0 (4)	C1—C11—C12—C13	−176.4 (3)
C19—N1—C1—C2	−171.6 (3)	C11—C12—C13—C18	5.6 (6)
N1—C1—C2—C3	−6.7 (4)	C11—C12—C13—C14	−176.0 (4)
C6—C7—C8—N1	−175.9 (3)	C18—C13—C14—O1	175.1 (3)
C1—N1—C8—C3	−1.0 (4)	C12—C13—C14—O1	−3.4 (5)
C1—N1—C8—C7	176.3 (4)	C12—C13—C14—C15	177.8 (3)
N1—C1—C11—C12	−176.2 (3)	O1—C14—C15—C16	−174.2 (3)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O7—H7*A*···O8	0.85	1.71	2.560 (5)	173
C4—H4···O1$^{\rm i}$	0.93	2.46	3.348 (5)	159
C4—H4···O2$^{\rm i}$	0.93	2.47	3.175 (5)	133
C20—H20*A*···O3$^{\rm ii}$	0.97	2.40	3.345 (5)	166
C7—H7···O5$^{\rm iii}$	0.93	2.58	3.501 (5)	173
C11—H11···O6$^{\rm iii}$	0.93	2.55	3.305 (4)	139
C18—H18···O6$^{\rm iii}$	0.93	2.55	3.401 (4)	152
C26—H26*A*···O3	0.96	2.54	3.319 (8)	138

Symmetry codes: (i) $2 - x, 1 - y, 2 - z$; (ii) $1 - x, 1 - y, 2 - z$; (iii) $1 - x, 1 - y, 1 - z$.

H atoms were located geometrically and included in the structure factor calculations.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1998); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1997); software used to prepare material for publication: *SHELXTL*.

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