

A synchrotron-radiation study of the lactone form of rhodamine B at 120 K

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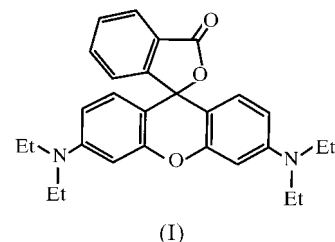
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The structure of the lactone form of rhodamine B, 3,6-bis(diethylamino)-1',3'-dihydrospiro[xanthene-9,3'-isobenzofuran]-1'-one, C₂₈H₃₀N₂O₃, has been determined at 120 K using synchrotron radiation at a wavelength of 0.496 Å. The structure contains two independent rhodamine B molecules with virtually identical geometry. The xanthene main planes of the molecules are inclined at an angle of 41.6 (2)° to one another. Molecule 2 has a statistically disordered ethyl group, with 71% in one orientation and 29% in a second orientation. The lactone C—O bonds are 1.497 (1) and 1.495 (1) Å. There are no classical hydrogen bonds, but the structure is stabilized by two short C···O interactions. The crystals of the lactone form were produced by a novel hydrothermal reaction.

Comment

In an attempt to create a new zeolite with rhodamine as the template molecule, purple crystals of up to millimetre sizes have been produced. Two room-temperature X-ray studies in Shanghai and Grenoble have proved that the crystals were of the lactone form of rhodamine B, (I) (A. Kvik & Y. Long, 1999, unpublished results). These studies, however, failed to resolve the disorder of one of the ethyl groups, and the present low-temperature study (120 K), using high-resolution synchrotron radiation out to a resolution of 0.58 Å, was carried out in order to resolve this disorder.



The present work shows that the disorder in (I) is a statistical splitting between two orientations [*A* 71 (1)% and *B* 29 (1)%; Fig. 1]. All bond distances have been determined with a precision of about 0.002 Å, except for those involving H atoms.

The structure of (I) contains two independent rhodamine B molecules, both having virtually identical geometry with a central planar section and planar groups bonded to C7 and C35. The two major planes of the molecules are perpendicular to each other [89.17 (4)°] in the two molecules. The major central planes of the molecules are inclined to each other at an angle of 41.6 (2)°.

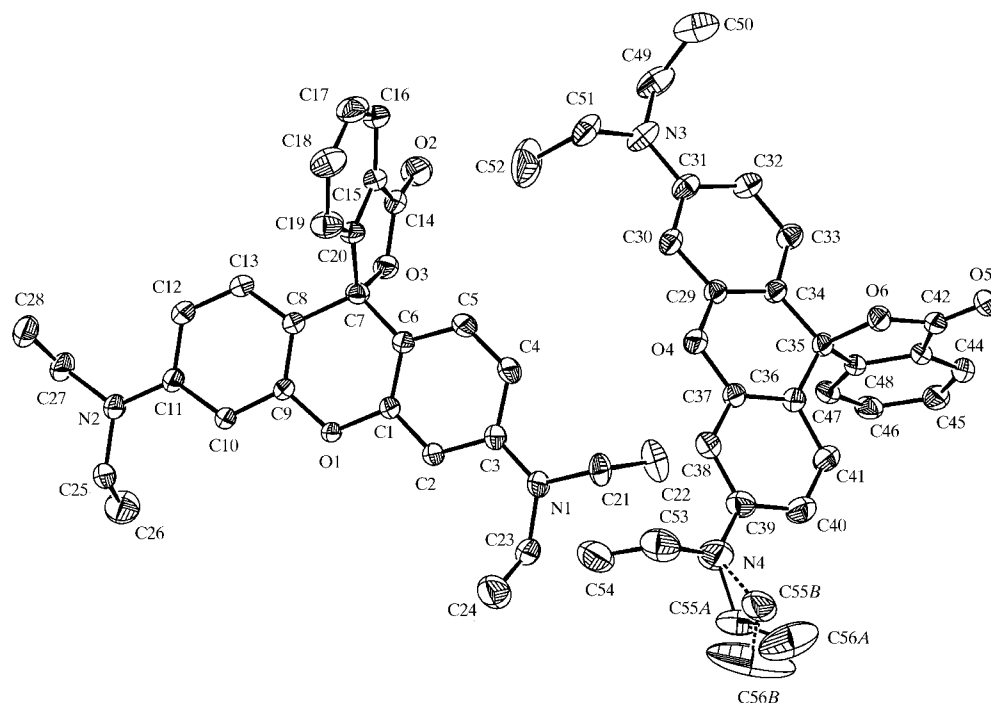


Figure 1

The molecular structure of (I), with 50% probability displacement ellipsoids. H atoms have been omitted for clarity. The bonds in the minor component of the disordered ethyl group have been illustrated with dashed lines.

There are no classical hydrogen bonds in the structure, but one weak C—H...O interaction links the two molecules in the asymmetric unit [C44—H44...O2ⁱ 3.096 (2) Å and 123.4 (13)°; symmetry code: (i) $\frac{1}{2} + x, \frac{1}{2} - y, z - \frac{1}{2}$]. The lactone C—O bonds are rather long C—O single bonds: C7—O3 1.4972 (12) and C35—O6 1.4949 (12) Å. All other bonds are normal.

To our knowledge, no other structure determination of the lactone form of rhodamine B has been published, although Abrahams *et al.* (1986) reported a determination of the zwitterionic form in a platinum complex.

Experimental

A hydrothermal method was used to grow large single crystals of rhodamine B lactone from the sol–gel system of rhodamine B–Na₂O–SiO₂–glycerol–H₂O. The molecular composition of this sol–gel was in the ratio 0.2:0.18:1.0:10:40. Silica sol (21.4 wt% Si₂O and 0.2 wt% Na₂O) was mixed with an aqueous solution of sodium hydroxide to form a uniform mixture. A homogeneous sol was obtained after vigorous stirring for 1 h at ambient temperature. The sol was then transferred and sealed into a stainless steel autoclave lined with Teflon and heated under autogenous pressure at 373 K. A gel was formed from the sol after heating for several hours at this temperature. Single crystals of the lactone, (I), with largest dimensions 7.0 × 4.0 × 1.4 mm, grew under these hydrothermal conditions over 1–2 d. Crystals were easily isolated from the gel and were washed, filtered and dried at 333 K for 2 h.

Crystal data

C ₂₈ H ₃₀ N ₂ O ₃	Synchrotron radiation
<i>M_r</i> = 442.54	λ = 0.496 Å
Monoclinic, <i>P</i> _{2₁} / <i>n</i>	Cell parameters from 512 reflections
<i>a</i> = 16.224 (2) Å	θ = 2.4–25.0°
<i>b</i> = 15.523 (3) Å	μ = 0.052 mm ^{−1}
<i>c</i> = 19.061 (4) Å	<i>T</i> = 120 (2) K
β = 99.250 (10)°	Triangular prism, purple
<i>V</i> = 4738.0 (15) Å ³	0.3 × 0.1 × 0.1 mm
<i>Z</i> = 8	
<i>D_x</i> = 1.241 Mg m ^{−3}	

Table 1
Selected geometric parameters (Å).

O1—C1	1.3674 (12)	O4—C29	1.3698 (13)
O1—C9	1.3696 (12)	O5—C42	1.2024 (13)
O2—C14	1.2038 (13)	O6—C42	1.3474 (13)
O3—C14	1.3484 (13)	O6—C35	1.4949 (12)
O3—C7	1.4972 (12)	N3—C31	1.3641 (14)
N1—C3	1.3604 (14)	N3—C51	1.4522 (16)
N1—C21	1.4494 (14)	N3—C49	1.4528 (17)
N1—C23	1.4521 (16)	N4—C39	1.3641 (16)
N2—C11	1.3623 (13)	N4—C53	1.463 (2)
N2—C25	1.4393 (15)	N4—C55A	1.477 (3)
N2—C27	1.4553 (14)	N4—C55B	1.511 (5)
O4—C37	1.3666 (13)		

Data collection

Bruker SMART CCD area-detector diffractometer with Oxford Cryosystems Cryostream cooler (Cosier & Glazer, 1986)	13 193 reflections with <i>I</i> > 2σ(<i>I</i>)
φ scans, 0.1° interval	<i>R</i> _{int} = 0.052
49 459 measured reflections	θ _{max} = 25°
21 735 independent reflections	<i>h</i> = −16 → 27
	<i>k</i> = −20 → 25
	<i>l</i> = −32 → 24

Refinement

Refinement on <i>F</i> ²	All H-atom parameters refined
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)] = 0.058	<i>w</i> = 1/[σ ² (<i>F_o</i> ²) + (0.0878 <i>P</i>) ²]
<i>wR</i> (<i>F</i> ²) = 0.151	where <i>P</i> = (<i>F_o</i> ² + 2 <i>F_c</i> ²)/3
<i>S</i> = 0.880	(Δ/σ) _{max} = 0.001
21 667 reflections	Δρ _{max} = 0.72 e Å ^{−3}
842 parameters	Δρ _{min} = −0.30 e Å ^{−3}

The structural data were collected at the European Synchrotron Radiation Facility in Grenoble on the ID11 beamline (Kvick & Wulff, 1992; Krumrey *et al.*, 1995) using an undulator source. The ethyl group bonded to N4 was statistically disordered. The occupancies of the two orientations together had full occupancy [C55A, C56A 0.711 (6); C55B, C56B 0.289 (6)]. All H atoms, except for a few on the disordered ethyl group, could be located and refined isotropically with an average C—H distance of 0.975 Å.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SMART*; data reduction: *SAINT* (Siemens, 1996); program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 1990).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1410). An additional figure is also available. Services for accessing these data are described at the back of the journal.

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