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Structure of a Triazaoxabicyclodecatriene Derivative

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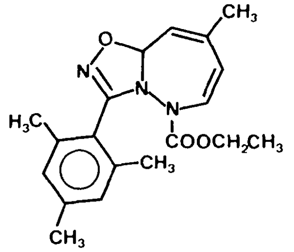
Abstract

The structure of ethyl 5-methyl-10-(2,4,6-trimethylphenyl)-8-oxa-1,2,9-triazabicyclo[5.3.0]deca-3,5,9-triene-2-carboxylate (I) has been determined. The 1,2-diazepine ring has a twisted-sofa form and the 1,2,4-oxadiazole ring has an envelope conformation, with the bridgehead C7 atom out of the plane of the ring. The terminal methyl group of the side chain is disordered, being split over two different positions.

Comment

Compound (I) has been obtained as the main adduct, along with two minor products, from the cycloaddition reaction between 2,4,6-trimethylphenylnitrile oxide and ethyl 5-methyl-1,2-diazepine-1-carboxylate (Beltrame, Cadoni, Carnasciali, Gelli, Lai, Mugnoli & Pani, 1992). The crystal structure determination of (I) has been performed to confirm the C=N diazepine bond as the preferred reaction site (in the competition between one C=N and two C=C bonds) and to define the regioselectivity of the cycloaddition reaction.



Apart from the disordered end of the ethoxycarbonyl chain, the bond lengths are in good agreement with the average literature values (Allen, Kennard, Watson, Brammer, Orpen & Taylor, 1987); the only significant differences concern the observed bond distances N2—C3 [1.409 (6) Å] and N9=C10 [1.267 (6) Å]. However, these values compare well with the corresponding bond distances found in a 1,2-diazepine derivative similar to (I) [1.408 (3) Å; Allmann & Debaerdemaeker (1974)] and in recent structure determinations of 1,2,4-oxadiazoles retrieved from the Cambridge Structural Database, version 4.6 [1.280 (9) Å, sample e.s.d.; Allen, Kennard & Taylor (1983)]. In the disordered part of the molecule the bond lengths O13—C14, and C14—C15 and C14—C15′ refine to long and short distances, respectively, while the bond angles O13—C14—C15 and O13—C14—C15′ have fairly normal values. The puckering parameters (Cremer & Pople, 1975) calculated for the seven- and five-membered rings [q_2 = 0.415 (4), q_3 = 0.285 (4) Å, φ_2 = −149.0 (6), φ_3 = −175 (1)°; q_2 = 0.269 (4) Å, φ_2 = 35.7 (9)°, respectively] correspond to an approximate twisted sofa (Boessenkool & Boeyens, 1980) and an envelope conformation, respectively. In the oxadiazole ring, the N1, O8, N9 and C10 atoms are coplanar within 0.005 (4) Å, with a deviation of 0.429 (5) Å for the C7 atom. Intermolecular distances are in the normal range. There is just one contact appreciably shorter than the sum of the van der Waals radii (Pauling, 1960): C14···C15($1-x, -\frac{1}{2}+y, \frac{1}{2}-z$) 3.64 (2) Å.

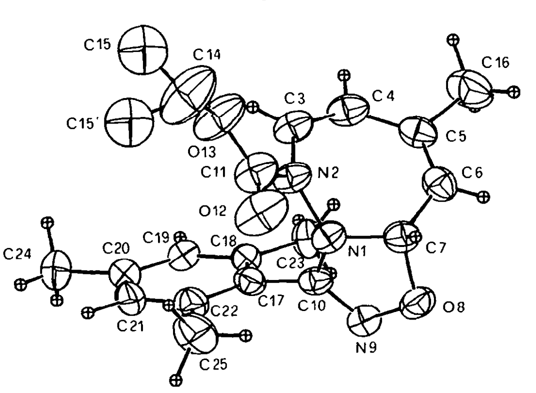


Fig. 1. Thermal ellipsoids are drawn at the 40% probability level and the disordered atoms C15 and C15′ are treated isotropically. H atoms are on an arbitrary scale.

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Experimental

Crystal data

$C_{19}H_{23}N_3O_3$
$M_r = 341.41$
M.p. = 406 K
Orthorhombic
$P2_12_12_1$
$a = 7.671\ (3)$ Å
$b = 8.621\ (2)$ Å
$c = 28.191\ (8)$ Å
$V = 1864\ (1)$ Å^3
$Z = 4.00$
$D_x = 1.216$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 25 reflections
$\theta = 16.0\text{–}19.2°$
$\mu = 0.078$ mm^{-1}
$T = 293$ K
Prism
0.54 × 0.40 × 0.32 mm
Colourless

Data collection

Enraf–Nonius CAD-4F diffractometer
ω-θ scans
Absorption correction: none
2450 measured reflections
2450 independent reflections
1628 observed reflections $[F > 4\sigma(F)]$

$\theta_{\max} = 27.5°$
$h = 0 \rightarrow 9$
$k = 0 \rightarrow 11$
$l = 0 \rightarrow 36$
2 standard reflections
frequency: 180 min
intensity variation: 5%

Refinement

Refinement on F
Final $R = 0.0618$
$wR = 0.0841$
$S = 1.667$
1628 reflections
227 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F) + 0.0015F^2]$

$(\Delta/\sigma)_{\max} = 0.06$
$\Delta\rho_{\max} = 0.37$ e Å^{-3}
$\Delta\rho_{\min} = -0.20$ e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Tables 2.2A, 2.3.1 for C, N and O; Table 2.2C for H)

To deal with the disordered end of the side chain, during the refinement the sum of the s.o.f.'s of C15 and C15′ was tied to unity and the bond distances C14—C15 and C14—C15′ were constrained to the same variable value. The final values of the s.o.f.'s of C15 and C15′ are 0.47 (2) and 0.53 (2), respectively.

Data collection: Enraf–Nonius CAD-4 software. Cell refinement: Enraf–Nonius CAD-4 software. Data reduction: *NRCVAX* (Gabe, Le Page, Charland, Lee & White, 1989) and *CADABS* (local software). Program(s) used to solve structure: *NRCVAX*. Program(s) used to refine structure: *NRCVAX* and *SHELX76* (Sheldrick, 1976). Program(s) used for geometrical calculations: *PARST* (Nardelli, 1983). Molecular graphics: *ORTEP* (Johnson, 1976). Preparation of CIF: *PARSTCIF* (Nardelli, 1992).

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2)

$$U_{\rm eq} = \tfrac{1}{3}\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
N1	0.0451 (5)	0.3427 (5)	0.1544 (1)	0.0541 (12)
N2	0.1975 (5)	0.4221 (5)	0.1645 (1)	0.0582 (13)
C3	0.3461 (7)	0.4041 (6)	0.1356 (2)	0.0633 (16)
C4	0.3951 (7)	0.2703 (7)	0.1178 (2)	0.0653 (18)
C5	0.3257 (6)	0.1145 (6)	0.1259 (1)	0.0579 (17)
C6	0.1760 (7)	0.0783 (5)	0.1476 (2)	0.0602 (16)
C7	0.0325 (6)	0.1778 (6)	0.1653 (2)	0.0580 (15)
O8	−0.1277 (4)	0.1426 (4)	0.1404 (1)	0.0645 (11)
N9	−0.1451 (5)	0.2541 (4)	0.1017 (1)	0.0592 (14)
C10	−0.0424 (5)	0.3646 (5)	0.1115 (1)	0.0483 (14)
C11	0.1908 (8)	0.5173 (8)	0.2042 (2)	0.0797 (20)
O12	0.0699 (6)	0.5197 (6)	0.2314 (1)	0.1060 (19)
O13	0.3364 (6)	0.5971 (6)	0.2074 (2)	0.1092 (20)
C14	0.3688 (16)	0.6815 (12)	0.2540 (3)	0.1489 (44)
C16	0.4424 (8)	−0.0155 (8)	0.1085 (3)	0.0991 (25)
C17	−0.0196 (5)	0.5071 (5)	0.0832 (2)	0.0492 (13)
C18	0.0672 (6)	0.4987 (5)	0.0394 (2)	0.0485 (13)
C19	0.0963 (6)	0.6340 (5)	0.0145 (2)	0.0566 (15)
C20	0.0423 (7)	0.7772 (5)	0.0319 (2)	0.0673 (18)
C21	−0.0466 (7)	0.7822 (5)	0.0739 (2)	0.0694 (19)
C22	−0.0809 (6)	0.6495 (6)	0.0994 (2)	0.0617 (14)
C23	0.1248 (7)	0.3470 (5)	0.0185 (2)	0.0619 (16)
C24	0.0768 (9)	0.9250 (7)	0.0030 (3)	0.0972 (27)
C25	−0.1883 (8)	0.6590 (8)	0.1455 (2)	0.0925 (23)
C15	0.4942 (26)	0.7775 (19)	0.2482 (8)	0.1245 (85)
C15′	0.3086 (24)	0.8180 (19)	0.2469 (6)	0.1224 (72)

Table 2. *Geometric parameters* (Å, °)

N1—N2	1.384 (5)	C7—O8	1.447 (5)
N1—C7	1.457 (6)	O8—N9	1.461 (5)
N1—C10	1.396 (5)	N9—C10	1.267 (6)
N2—C3	1.409 (6)	C10—C17	1.476 (6)
N2—C11	1.388 (6)	C11—O12	1.206 (7)
C3—C4	1.313 (7)	C11—O13	1.315 (7)
C4—C5	1.463 (7)	O13—C14	1.52 (1)
C5—C6	1.338 (6)	C14—C15	1.28 (2)
C5—C16	1.516 (8)	C14—C15′	1.28 (2)
C6—C7	1.482 (6)		
C7—N1—C10	106.4 (4)	N1—C7—O8	99.1 (4)
N2—N1—C10	121.1 (4)	C7—O8—N9	107.6 (3)
N2—N1—C7	119.7 (4)	O8—N9—C10	105.9 (4)
N1—N2—C11	115.2 (4)	N1—C10—N9	112.7 (4)
N1—N2—C3	120.7 (4)	N9—C10—C17	125.5 (4)
C3—N2—C11	124.1 (4)	N1—C10—C17	121.7 (4)
N2—C3—C4	123.3 (5)	N2—C11—O13	109.5 (5)
C3—C4—C5	130.0 (5)	N2—C11—O12	123.6 (5)
C4—C5—C6	126.7 (5)	O12—C11—O13	126.9 (5)
C5—C6—C7	131.0 (5)	C11—O13—C14	116.6 (5)
N1—C7—C6	116.4 (4)	O13—C14—C15′	104 (1)
C6—C7—O8	110.3 (4)	O13—C14—C15	109 (1)
C7—N1—C10—N9	18.7 (5)	C5—C6—C7—N1	5.9 (8)
N2—N1—C10—N9	160.0 (4)	C5—C6—C7—O8	117.7 (6)
N2—N1—C7—C6	−50.8 (6)	C6—C7—O8—N9	−95.9 (4)
C7—N1—N2—C3	75.6 (5)	N1—C7—O8—N9	26.7 (4)
C10—N1—N2—C3	−60.7 (6)	C7—O8—N9—C10	−17.5 (5)
C10—N1—C7—O8	−26.9 (4)	O8—N9—C10—N1	−0.9 (5)
N1—N2—C11—O12	8.0 (8)	N1—C10—C17—C18	111.3 (5)
N1—N2—C3—C4	−39.9 (7)	N2—C11—O13—C14	−167.4 (6)
C3—N2—C11—O13	6.1 (7)	O12—C11—O13—C14	10.5 (10)
N2—C3—C4—C5	−6.2 (9)	C11—O13—C14—C15	−166.8 (11)
C3—C4—C5—C6	12.3 (9)	C11—O13—C14—C15′	−93.6 (11)
C4—C5—C6—C7	6.3 (9)		

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Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55949 (22 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: NA1025]

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Structure of Photochromic Spiroxazines. II. 1′,3′,3′-Trimethylspiro{anthra[2,1-*f*][1,4]benzoxazine-2,2′-indoline}-7,12-dione

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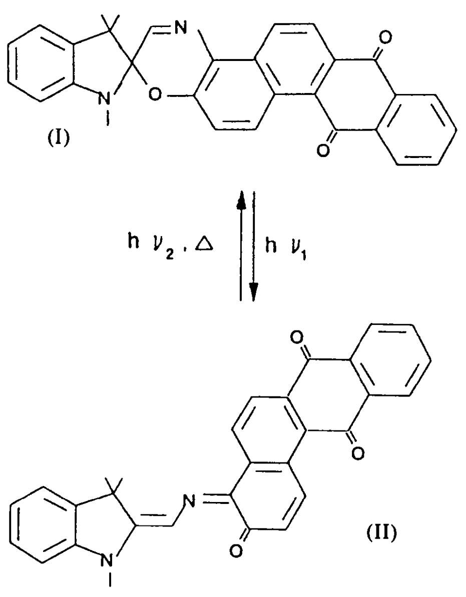
Abstract

The asymmetric unit comprises two crystallographically independent molecules. The molecule consists of a substituted indoline ring orthogonally linked to an anthraquinone–benzo–oxazine moiety through a spiro C atom having regular sp^3 hybridization. The length of the $C_{\rm spiro}$—O bond, that undergoes cleavage upon photoexcitation, is larger than that normally observed for other spiroxazines having lower photocolourability than the title compound.

Comment

The title compound (I), as for all other spiroindolinonaphthoxazines, exhibits photochromism. Upon UV irradiation it undergoes a ring-opening reaction leading to a red-absorbing merocyanine-like structure (II). The reaction is reversible, (I) being restored by either thermal or photochemical bleaching.



The electrocyclic ring-opening reaction of spirobenzopyrans or spironaphthoxazines, leading to coloured merocyanines, has been extensively studied with a host of different spectroscopic techniques. There is now a general consensus on the reactive excited-state multiplicity, which has been identified as a singlet, that leads to the ring opening, and it is likely that the photocolouration is based on a charge-transfer process from the indoline N-atom lone pair, $n_{\rm N}$, into the antibonding orbital of the $C_{\rm spiro}$—O bond, $\sigma^*_{C\,{\rm spiro}—O}$, of the oxazine moiety. This process should be maximized when the $n_{\rm N}$ is antiperiplanar to the $C_{\rm spiro}$—O bond. The length of the latter bond should increase with the extent of the $n_{\rm N}$–σ^* interaction and the N—$C_{\rm spiro}$ bond length should concomitantly decrease. The efficiency of the photocolouration reaction may then correlate, among other things, to $C_{\rm spiro}$—O bond distance. To verify this hypothesis we have carried out the X-ray structure analysis of the anthraquinone-based spiroxazine (I).

Two crystallographically independent molecules exist in the asymmetric unit. The significant difference between them may reflect the extent to which the conformation of (I) is affected by crystal packing, but we found no significant differences for the bond involved in the ring-opening reaction.

On the other hand, the $C_{\rm spiro}$—O bond is much longer (1.473–1.475 Å) than those typically observed in oxygen-containing six-membered heterocycles [1.41–1.43 Å (Kennard, Watson & Town, 1973)]. These bonds are also longer than those observed in spiroindolinenaphthoxazines [1.454 Å (Millini, Del

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