C6	0.2062 (8)	0.3668 (2)	1.0776 (7)	0.0409 (13)
C7	0.1308 (8)	0.3646 (2)	1.2453 (8)	0.0459 (14)
C8	0.2395 (8)	0.3544 (2)	1.3815 (8)	0.0465 (14)
C9	0.5286 (8)	0.3187 (2)	1.5108 (8)	0.0482 (15)
C10	0.4283 (9)	0.2784 (2)	1.5518 (8)	0.056 (2)
C11	0.3260 (8)	0.2572 (2)	1.4016 (7)	0.0432 (14)
C12	0.3293 (7)	0.2754 (2)	1.2439 (7)	0.0395 (13)
C13	0.4336 (7)	0.3139 (2)	1.2037 (7)	0.0400 (13)
C14	0.4325 (8)	0.3423 (2)	1.3582 (7)	0.0430 (13)
C15	0.6345 (8)	0.3044 (2)	1.1707 (8)	0.051 (2)
C16	0.7406 (9)	0.2874 (2)	1.3296 (9)	0.061 (2)
N17	0.7217 (7)	0.3132 (2)	1.4757 (7)	0.0571 (14)
C17	0.8356 (11)	0.2977 (3)	1.6263 (11)	0.080 (2)
C18	0.0323 (11)	0.1934 (2)	0.8645 (8)	0.064 (2)
C19	−0.1182 (13)	0.1772 (3)	0.7433 (10)	0.091 (3)
C20	0.0987 (10)	0.3953 (2)	0.8098 (8)	0.053 (2)
C21	−0.0673 (11)	0.4060 (2)	0.6958 (9)	0.072 (2)
O1A	0.4553 (6)	0.12531 (14)	0.3081 (6)	0.0705 (14)
C1A	0.4015 (9)	0.0917 (2)	0.7494 (10)	0.063 (2)
O2A	0.6238 (7)	0.04226 (14)	0.3357 (5)	0.0609 (12)
C2A	0.3962 (10)	0.1155 (2)	0.6042 (11)	0.066 (2)
C3A	0.4626 (9)	0.1011 (2)	0.4572 (9)	0.056 (2)
O3A	0.7157 (11)	0.1536 (3)	0.3845 (9)	0.152 (4)
O4A	0.9753 (7)	0.0568 (2)	0.3785 (7)	0.079 (2)
C4A	0.5313 (8)	0.0614 (2)	0.4585 (8)	0.0483 (15)
C5A	0.7266 (10)	0.0078 (2)	0.4197 (8)	0.060 (2)
O5A	1.0664 (12)	0.0147 (2)	0.1841 (8)	0.120 (3)
C6A	0.9246 (9)	0.0221 (2)	0.4799 (11)	0.066 (2)
C7A	0.9569 (9)	0.0325 (3)	0.6602 (10)	0.069 (2)
C8A	0.8745 (9)	0.0140 (2)	0.7789 (10)	0.064 (2)
C9A	0.5878 (8)	−0.0191 (2)	0.8755 (7)	0.0465 (14)
C10A	0.4995 (10)	0.0238 (2)	0.9062 (8)	0.057 (2)
C11A	0.4682 (8)	0.0511 (2)	0.7516 (7)	0.0442 (13)
C12A	0.5261 (7)	0.0367 (2)	0.6004 (7)	0.0381 (13)
C13A	0.6145 (8)	−0.0045 (2)	0.5714 (7)	0.0409 (13)
C14A	0.7261 (8)	−0.0165 (2)	0.7379 (7)	0.0468 (14)
C15A	0.4745 (9)	−0.0383 (2)	0.5241 (8)	0.0503 (15)
C16A	0.3548 (8)	−0.0467 (2)	0.6681 (8)	0.0509 (15)
N17A	0.4639 (7)	−0.05363 (14)	0.8276 (6)	0.0464 (12)
C17A	0.3504 (10)	−0.0640 (2)	0.9653 (9)	0.063 (2)
C18A	0.5904 (9)	0.1510 (2)	0.2855 (9)	0.058 (2)
C19A	0.5651 (10)	0.1735 (2)	0.1226 (9)	0.071 (2)
C20A	1.0375 (10)	0.0493 (3)	0.2297 (9)	0.065 (2)
C21A	1.0651 (13)	0.0878 (3)	0.1328 (11)	0.094 (3)

Table 2. *Selected geometric parameters (Å, °)*

O1—C18	1.349 (8)	O1A—C18A	1.319 (8)
O1—C3	1.403 (7)	O1A—C3A	1.406 (8)
C2—C3	1.389 (9)	C2A—C3A	1.376 (10)
C3—C4	1.371 (8)	C3A—C4A	1.372 (9)
O3—C18	1.180 (9)	O3A—C18A	1.161 (8)
O4—C20	1.338 (8)	O4A—C20A	1.319 (9)
O4—C6	1.447 (6)	O4A—C6A	1.440 (8)
C5—C6	1.536 (8)	C5A—C6A	1.566 (10)
O5—C20	1.192 (8)	O5A—C20A	1.191 (10)
C6—C7	1.480 (8)	C6A—C7A	1.460 (11)
C18—C19	1.496 (11)	C18A—C19A	1.471 (9)
C20—C21	1.496 (10)	C20A—C21A	1.478 (11)
C18—O1—C3	117.0 (5)	C18A—O1A—C3A	118.9 (5)
C4—C3—C2	117.4 (6)	C4A—C3A—C2A	117.6 (6)
C4—C3—O1	123.4 (6)	C4A—C3A—O1A	120.4 (6)
C2—C3—O1	119.0 (5)	C2A—C3A—O1A	121.9 (6)
C20—O4—C6	116.8 (5)	C20A—O4A—C6A	118.6 (6)
O4—C6—C7	108.7 (5)	O4A—C6A—C7A	109.5 (6)
O4—C6—C5	112.5 (4)	O4A—C6A—C5A	109.8 (6)
C7—C6—C5	113.3 (4)	C7A—C6A—C5A	115.6 (5)
O3—C18—O1	121.6 (6)	O3A—C18A—O1A	121.5 (7)
O3—C18—C19	125.9 (7)	O3A—C18A—C19A	125.9 (7)
O1—C18—C19	112.4 (7)	O1A—C18A—C19A	112.6 (6)
O5—C20—O4	123.6 (6)	O5A—C20A—O4A	121.6 (7)
O5—C20—C21	124.1 (6)	O5A—C20A—C21A	126.0 (8)
O4—C20—C21	112.2 (6)	O4A—C20A—C21A	112.4 (8)

SHELXL (Sheldrick & Schneider, 1995) was used for the structure refinement and *SHELXTL-Plus* (Sheldrick, 1991) was used for data collection, cell refinement, data reduction, structure solution, molecular graphics and the preparation of material for publication.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry, together with a packing diagram, have been deposited with the IUCr (Reference: AB1311). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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6′-Diethylamino-2′-methylaminospiro-[isobenzofuran-1(3*H*),9′-[9*H*]xanthen]-3-one

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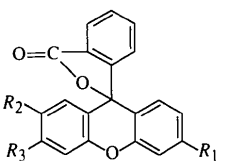
Abstract

The title compound, $C_{25}H_{24}N_2O_3$, is one of the fluoran derivatives. The molecule has a Y-style structure which is composed of a half-chair xanthene moiety and an almost planar isobenzofuran fragment. The C—O single-bond distance of 1.528 (6) Å in the lactone ring is longer than those normally found in both lactone and 2′-nitrofluoran.

Comment

During the study of 6′-diethylamino-2′-substituted fluoran derivatives (Liu, Wang, Liu & Miao, 1995), we obtained the title compound, (I) (where R_1 = Et_2N, R_2 = $NHCH_3$, R_3 = H), and determined its crystal structure. The structure analysis shows that the molecule has a Y-like shape, with the isobenzofuran moiety, which

has a high degree of planarity, nearly perpendicular to the two parts of the xanthene ring; the dihedral angles are 87.53 (13) and 94.76 (12)°, with the dihedral angle between the two parts of the xanthene system being 7.3 (7)°. These values are comparable to the values found in $C_{24}H_{20}N_2O_5$ (where R_1 = Et_2N, R_2 = NO_2, R_3 = H) of 87.97 (11), 93.86 (14) and 6.6 (5)°, respectively (Liu, Wang, Liu & Miao, 1995), and in $C_{24}H_{20}NCl$ (where R_1 = Et_2N, R_2 = Cl, R_3 = H) of 93.30 (10), 96.8 (2) and 3.7 (4)°, respectively (Liu, Zhou, Liu & Miao, 1995).



(I)

The gross molecular conformation around the spiro C atom (C1) of the title compound is similar to that found in $C_{20}H_{12}O_5.(CH_3)_2O$, (II) (where R_1 = R_3 = OH, R_2 = H; Osborn & Rogers, 1975), and $C_{32}H_{32}O_7$, (III) (where R_1 = R_3 = hexylcarbonyloxy, R_2 = H; Wang *et al.*, 1991). The comparable bond lengths and some of the valence angles around the spiro C atoms are shown in Fig. 2. The C1—C31 distance of 1.480 (8) Å is typical of C_{sp^2}—C_{sp^3} bonds [1.482 (11) Å; Kimura, 1985] and does not show comparable weakness of the bond. But in the lactone ring, the C1—O2 distance [1.526 (6) Å] is longer than the normal lactone ring value [1.463 (7) Å] (Cameron, Jochem, Linden, Morris & Shepherd, 1989) and indicates severe weakness in the bond. When the title compound reacts with acetic acid, this weak bond cleaves and yields the fluorescent form of the molecule, with a colour change to green.

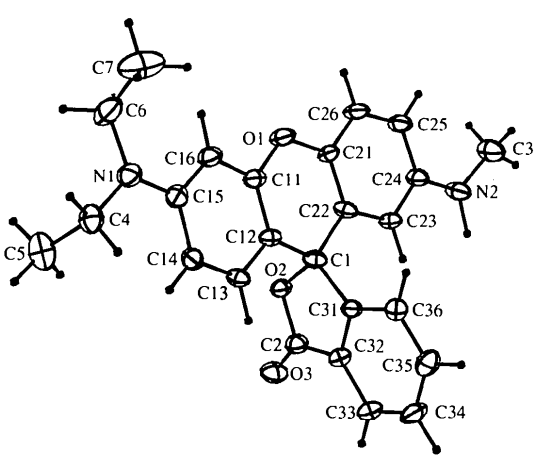


Fig. 1. A perspective drawing of the title compound with the atomic numbering scheme. The displacement ellipsoids are at 30% probability.

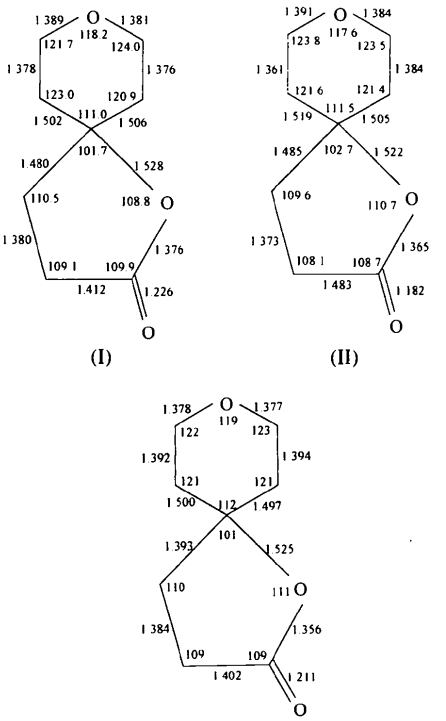


Fig. 2. The comparable bond lengths and some of the valence angles around the spiro C atoms of related compounds. [(I) $C_{25}H_{24}N_2O_3$: R_1 = Et_2N, R_2 = MeNH, R_3 = H; (II) $C_{20}H_{12}O_5.(CH_3)_2O$: R_1 = R_3 = OH, R_2 = H; (III) $C_{32}H_{32}O_7$: R_1 = R_3 = hexylcarbonyloxy, R_2 = H.]

Experimental

A mixture of 2′-carboxy-4-diethylamino-2-hydroxybenzophenone and 4-methylaminophenol sulfate (molar ratio 1:1) was heated under stirring for 3 h at 393 K, then cooled and extracted with benzene. After condensing the solvent extract, a light-yellow powder was obtained. Crystals for analysis were obtained on recrystallization from ethanol.

Crystal data

$C_{25}H_{24}N_2O_3$
M_r = 400.48
Monoclinic
$C2/c$
a = 30.973 (8) Å
b = 8.040 (5) Å
c = 21.268 (6) Å
β = 127.04 (4)°
V = 4226.4 (2) Å^3
Z = 8
D_x = 1.259 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 10–15°
μ = 0.089 mm^{-1}
T = 295 K
Prism
0.30 × 0.25 × 0.25 mm
Light yellow

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none

R_{int} = 0.003
θ_{max} = 23°
h = 0 → 30
k = 0 → 8
l = −24 → 24

2772 measured reflections
2754 independent reflections
1472 observed reflections
$[|F_o| > 3\sigma(|F_o|)]$

3 standard reflections
frequency: 60 min
intensity decay: 0.1%

Refinement

Refinement on F
$R = 0.052$
$wR = 0.060$
$S = 1.45$
1472 reflections
271 parameters
Unit weights applied

$(\Delta/\sigma)_{max} = 0.08$
$\Delta\rho_{max} = 0.237$ e Å^{-3}
$\Delta\rho_{min} = -0.113$ e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

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

$B_{eq} = (4/3)\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	B_{eq}
O1	0.7401 (1)	−0.1397 (6)	0.2266 (2)	4.1 (1)
O2	0.6016 (1)	−0.1107 (5)	0.0294 (2)	3.0 (1)
O3	0.5218 (1)	−0.1076 (6)	−0.0897 (2)	4.7 (1)
N1	0.8343 (2)	−0.0484 (8)	0.1179 (2)	4.0 (1)
N2	0.5710 (2)	−0.0506 (8)	0.2461 (2)	4.5 (1)
C1	0.6405 (2)	0.0148 (8)	0.0928 (3)	2.8 (1)
C2	0.5571 (2)	−0.0268 (8)	−0.0323 (3)	3.4 (2)
C3	0.5767 (2)	−0.077 (1)	0.3175 (3)	5.9 (2)
C4	0.8366 (2)	0.0112 (9)	0.0556 (3)	4.2 (2)
C5	0.8113 (2)	−0.107 (1)	−0.0133 (3)	6.2 (2)
C6	0.8797 (2)	−0.148 (1)	0.1798 (4)	5.6 (2)
C7	0.9193 (3)	−0.055 (1)	0.2532 (5)	8.9 (3)
C11	0.7378 (2)	−0.0757 (8)	0.1639 (3)	3.1 (1)
C12	0.6920 (2)	0.0019 (8)	0.1010 (3)	2.8 (1)
C13	0.6961 (2)	0.0623 (8)	0.0431 (3)	3.0 (1)
C14	0.7417 (2)	0.0455 (8)	0.0475 (3)	3.2 (1)
C15	0.7876 (2)	−0.0345 (8)	0.1123 (3)	3.3 (2)
C16	0.7846 (2)	−0.0959 (9)	0.1709 (3)	3.5 (2)
C21	0.6969 (2)	−0.1108 (8)	0.2283 (3)	2.9 (1)
C22	0.6490 (2)	−0.0383 (8)	0.1676 (3)	2.9 (1)
C23	0.6078 (2)	−0.0164 (8)	0.1747 (3)	3.1 (1)
C24	0.6140 (2)	−0.0685 (9)	0.2424 (3)	3.4 (2)
C25	0.6631 (2)	−0.1404 (9)	0.3033 (3)	3.8 (2)
C26	0.7039 (2)	−0.1602 (9)	0.2958 (3)	3.9 (2)
C31	0.6106 (2)	0.1728 (8)	0.0579 (2)	2.9 (1)
C32	0.5620 (2)	0.1447 (8)	−0.0149 (3)	3.0 (1)
C33	0.5271 (2)	0.2791 (9)	−0.0597 (3)	4.3 (2)
C34	0.5421 (2)	0.437 (1)	−0.0282 (3)	5.0 (2)
C35	0.5906 (2)	0.4652 (9)	0.0454 (3)	4.4 (2)
C36	0.6255 (2)	0.3340 (9)	0.0896 (3)	3.5 (2)

Table 2. *Selected geometric parameters (Å, °)*

O1—C11	1.389 (8)	C23—C24	1.396 (9)
O1—C21	1.381 (8)	N2—C24	1.389 (9)
O2—C1	1.528 (6)	C1—C12	1.502 (9)
O2—C2	1.376 (5)	C1—C22	1.506 (8)
O3—C2	1.226 (6)	C1—C31	1.480 (8)
N1—C4	1.450 (9)	C2—C32	1.412 (9)
N1—C6	1.457 (7)	C4—C5	1.51 (1)
N1—C15	1.381 (8)	C6—C7	1.48 (1)
N2—C3	1.436 (9)	C11—C12	1.378 (6)
C11—C16	1.374 (9)	C24—C25	1.395 (6)
C12—C13	1.398 (9)	C25—C26	1.38 (1)
C13—C14	1.364 (9)	C31—C32	1.380 (5)
C14—C15	1.403 (6)	C31—C36	1.405 (9)
C15—C16	1.39 (1)	C32—C33	1.415 (8)
C21—C22	1.376 (6)	C33—C34	1.38 (1)
C21—C26	1.375 (9)	C34—C35	1.388 (6)
C22—C23	1.387 (9)	C35—C36	1.393 (8)
C11—O1—C21	118.2 (4)	C11—C16—C15	119.8 (4)
C1—O2—C2	108.8 (4)	O1—C21—C22	124.0 (5)
C4—N1—C6	117.0 (6)	O1—C21—C26	115.7 (4)
C4—N1—C15	121.3 (4)	C22—C21—C26	120.3 (6)
C6—N1—C15	120.9 (6)	C1—C22—C21	120.9 (6)
C3—N2—C24	122.3 (4)	C1—C22—C23	119.5 (4)
O2—C1—C12	105.9 (5)	C21—C22—C23	119.6 (5)
O2—C1—C22	106.8 (5)	C22—C23—C24	120.7 (4)
O2—C1—C31	101.7 (3)	N2—C24—C23	119.0 (4)
C12—C1—C22	111.0 (4)	N2—C24—C25	122.4 (6)
C12—C1—C31	114.6 (5)	C23—C24—C25	118.5 (6)
C22—C1—C31	115.5 (6)	C24—C25—C26	120.2 (6)
O2—C2—O3	118.0 (6)	C21—C26—C25	120.7 (4)
O2—C2—C32	109.9 (4)	C1—C31—C32	110.5 (5)
O3—C2—C32	132.1 (5)	C1—C12—C11	123.0 (6)
N1—C4—C5	113.3 (6)	C1—C12—C13	121.9 (4)
N1—C6—C7	114.0 (7)	C2—C32—C31	109.1 (5)
O1—C11—C12	121.7 (6)	C2—C32—C33	130.6 (4)
O1—C11—C16	114.3 (4)	C31—C32—C33	120.3 (6)
C12—C11—C16	124.0 (6)	C32—C33—C34	118.6 (4)
C11—C12—C13	115.1 (1)	C1—C31—C36	128.7 (3)
C12—C13—C14	123.0 (4)	C32—C31—C36	120.8 (5)
C13—C14—C15	120.5 (6)	C33—C34—C35	121.2 (6)
N1—C15—C14	120.7 (6)	C34—C35—C36	120.6 (6)
N1—C15—C16	121.6 (4)	C31—C36—C35	118.5 (4)
C14—C15—C16	117.7 (6)		

The H atoms were located from difference syntheses. Non-H atoms were refined anisotropically and all H atoms were fixed. Calculations were carried out on a VAX3100 computer.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *MULTAN*11/82 (Main *et al.*, 1982) and *MolEN*. Program(s) used to refine structure: *MolEN*. Molecular graphics: *ORTEP* (Johnson, 1965). Software used to prepare material for publication: *MolEN*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: DE1014). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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