

# A fluoresceinophane: 1<sup>9</sup>,4,16-trioxo-1(2,10)-anthracena-2(1,2)-benzena-cyclohexadecaphane-1<sup>7</sup>,3(1<sup>9</sup>H)-dione

Stéphane Dufresne, Sergio Andrés Pérez Guarín and W. G. Skene\*

Department of Chemistry, University of Montreal, CP 6128, succ. Centre-ville, Montréal, Québec, Canada H3C 3J7  
Correspondence e-mail: w.skene@umontreal.ca

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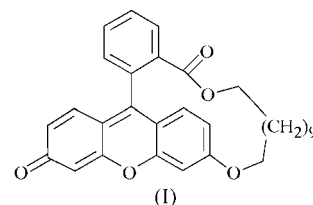
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A novel macrocycle containing fluorescein, the highly fluorescent title compound, C<sub>31</sub>H<sub>32</sub>O<sub>5</sub>, has a xanthene core and a benzyl unit that are planar. The latter is rotated by 72.99 (3)° from the xanthene mean plane. The C<sub>11</sub> alkyl tether and the xanthene group adopt a cage-like structure and the xanthene adopts a quinoid-type configuration. The compound crystallizes as a racemic mixture with one molecule of each isomer per unit cell. Even though the planes described by the xanthene and the benzene rings of different molecules are separated by 3.341 (4) and 3.73 (1) Å, respectively, there is insufficient overlap between the aryl units to promote  $\pi$ -stacking.

## Comment

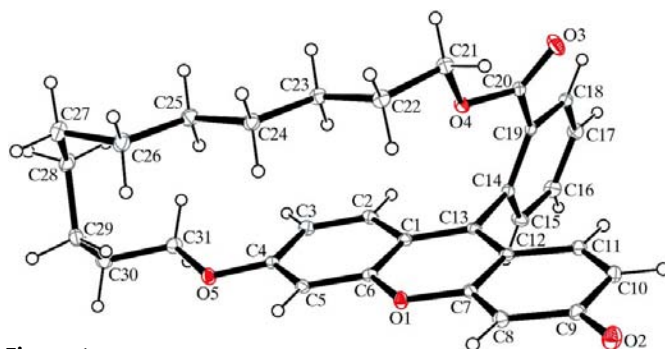
The investigation of macrocycles has been pursued recently along many avenues of science, due to the potential applications of these compounds as nanomolecular machines (Stoddart & Tseng, 2002; Balzani *et al.*, 2000). Many interesting properties can be obtained by incorporating steric elements into the macrocycle that increase activation barriers such as that to rotation (Feringa, 2001; Kelly *et al.*, 1994). These properties are responsible for novel devices such as field-effect transducers, molecular sensors, switches, *etc.* Because of these activation barriers, macrocycles can be used as actuators and are useful for temperature probes or monitors. Macrocytic formation is, however, challenging and numerous difficulties are encountered during the synthesis of such nanoactuators. Consequently, macrocycles have attracted much attention in order to find more efficient protocols for their synthesis and for the preparation of new materials with desired functional properties. We have incorporated fluorescein as a core unit in the title compound, (I), because this fluorescent scaffold ensures that unique photophysical properties can be obtained. The benefits of our approach are the ease and versatility of the macrocyclic synthesis, which can ultimately be used for the synthesis of macrocycles with various ring sizes. The synthesis

of our macrocycle was achieved in three relatively easy steps starting from fluorescein.



The structure of (I) consists of two planar aryl units linked by an undecanyl alkyl tether. The aryl units are twisted with respect to one another because of the steric hindrance between atom H15 and atoms H2 and H11 (all bonded to the C atoms of the same numbers; Fig. 1) that would result from the coplanarity of the two aryl rings. The angle between the two mean planes of the aryl units is 72.99 (3)°. The 17.01° twist from perpendicularity allows the macrocycle to accommodate the long tether chain, as shown in Fig. 1. This is in contrast with linear fluorescein derivatives whose xanthene–benzyl mean planes are rotated by between 85 and 90° (Cody, 1987; Tremayne *et al.*, 1997; Willner *et al.*, 1997; Ajtai & Burghardt, 1995; Wang *et al.*, 2001). The intramolecular C–H... $\pi$  interaction C23–H23A...Cg1, where Cg1 is the centroid of the C1–C6 ring, also contributes to the observed conformation.

The xanthene group consists of three different six-membered rings, namely the central pyran ring and the terminal quinone and benzene rings. These individual rings are generally difficult to identify unequivocally by common techniques such as <sup>1</sup>H NMR. Despite these challenges, the bond distances of the different elements that comprise the three unique rings were expected to be substantially dissimilar, allowing them to be observed in the isolated crystal structure. It is, therefore, not surprising that the isolated xanthene is unsymmetric, with longer bond distances on the side containing the alkyl chain. For example, C2–C3 and C5–C6 are 0.036 (4) and 0.030 (4) Å longer than their respective counterparts C10–C11 and C7–C8, and C1–C13 is also 0.070 (4) Å longer than its corresponding C12–C13 bond. Even though the O1–C7 and O1–C6 bond distances are identical, the C1–C13 and C12–C13 bond distances are considerably different, further contributing to the unsymmetric nature of the molecule.



**Figure 1**  
A drawing of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

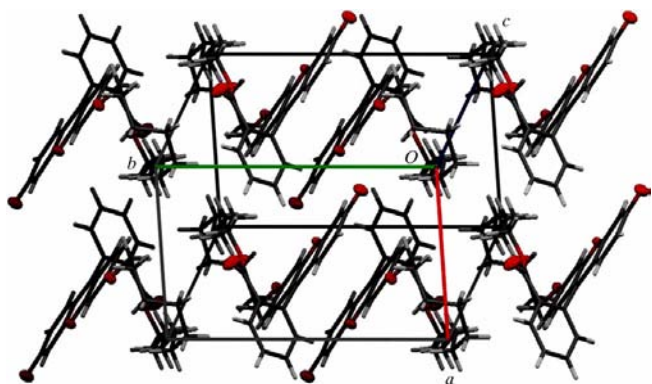
The C12—C13 bond is understood to have greater double-bond character owing to its shorter length relative to C1—C13. This configuration confers an aromatic character on the xanthene. The O2—C9 bond is also 0.112 (4) Å shorter than O5—C4, which is 0.079 (5) Å shorter than the reported value for a similar fluorescein (Yamaguchi *et al.*, 1997). The O2—C9 and O5—C4 bond distances correspond to a ketone and an aryl ether group, respectively, which cannot be readily identified by other standard characterization techniques. The presence of these two different groups further contributes to the unsymmetric nature of the fluorescein. The combined bond distances confirm that the xanthene consists of three different six-membered rings. These different aromatic rings collectively contribute to the high fluorescence exhibited by this compound. Moreover, of the many known conformations of fluorescein, the isolated structure confirms that the highly conjugated quinoid conformation is formed.

Owing to the possible rotation around the C13—C14 bond, the long alkyl chain can potentially lie on either side of the xanthene face. This leads to two possible isomers. The asymmetric molecule has a C12—C3—C14—C19 torsion angle of  $-71.7(2)^\circ$ . Since the compound crystallizes in the  $P\bar{1}$  space group there is an exact inversion-related molecule with the

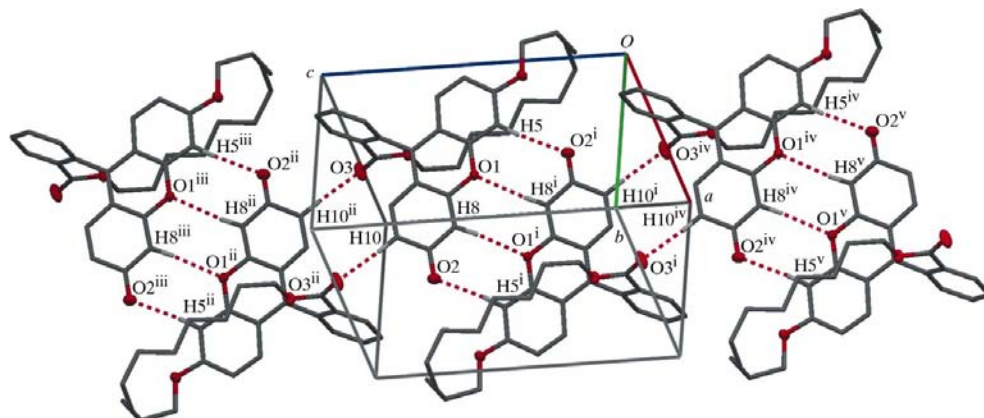
corresponding torsion angle of  $71.7(2)^\circ$ . No disorder was found in the structure, even with the long C<sub>11</sub> tether. Even though the alkyl chain forms a rectangular cage-like structure with the xanthene group, no solvent was found within the structure. The cavity size was the same for both isomers and was calculated to be 7.88 (1) Å wide and 3.762 (6) Å in height. The height was calculated according to the absolute distance between the planes of the xanthene and the alkyl chain, while the width was calculated from the distance between the two average mean planes described by C14/C19/C20 and C27—C29.

The xanthene groups of different isomers adopt an anti-parallel arrangement in the crystal lattice. Conversely, the benzyl units of the two isomers are parallel. The arrangement of the xanthene and the benzyl groups affords a close-packed network that is present in the crystal lattice involving the two inversion-related molecules of (I) (Fig. 2), which extends along the *z* direction. Even though  $\pi$ -stacking is common for such highly conjugated compounds, no such interactions were found for (I). Despite the xanthene—xanthene and benzene—benzene plane distances being ideal for  $\pi$ -interactions at 3.341 (4) and 3.73 (1) Å, respectively, the aryl units do not overlap. In fact, the centroid—centroid distances of xanthene and benzene are much greater, resulting in no apparent intermolecular interactions. However, a van der Waals interaction occurs between the alkyl chains of two molecules separated by 3.89 (1) Å. The observed van der Waals interactions take place between two different isomers.

A total of three unique intermolecular C—H···O hydrogen bonds are present and these are responsible for the supramolecular network represented in Fig. 3. Two such interactions occur between C5—H5···O2 of two separate molecules. There are two additional donor—acceptor bonds involving C8—H8···O1. These two donor—acceptor pairs are separated by 3.355 (2) and 3.4639 (19) Å, respectively, and form a dimer-like structure. Two additional hydrogen bonds occur between two complementary C10—H10···O3 units of two molecules. More specifically, a nontraditional donor—acceptor—donor—acceptor hydrogen-bonding motif was found between the two isolated isomers involving the xanthene unit, leading to a dimer-like arrangement. This is illustrated in Fig. 3,



**Figure 2**  
The three-dimensional network of (I), demonstrating the van der Waals interactions between the alkyl chains.



**Figure 3**  
The supramolecular structure of (I), showing the intramolecular C—H···O bonding giving a dimer-like structure. [Symmetry codes: (i)  $-x + 1, -y + 2, -z + 1$ ; (ii)  $-x + 1, -y + 2, -z + 2$ ; (iii)  $x, y, z + 1$ ; (iv)  $x, y, z - 1$ ; (v)  $-x + 1, -y + 2, -z$ .]

which also shows the interactions between the two isomers involving  $O2 \cdots H5^i - C5^i$ ,  $O1 \cdots H8^i - C8^i$ ,  $O2^i \cdots H5 - C5$  and  $O1^i \cdots H8 - C8$  [details are given in Table 2; symmetry code: (i)  $-x + 1, -y + 2, -z + 1$ ]. Hydrogen bonds between atoms O3 and  $H10^{ii}$  [symmetry code: (ii)  $-x + 1, -y + 2, -z + 2$ ] and the other isomer involving  $O3^i$  and  $H10^{iv}$  [symmetry code: (iv)  $x, y, z - 1$ ] were also observed. All these intermolecular distances are less than 3.5 Å and the  $D-H \cdots A$  angles are ca 150°, so they can therefore be categorized as ideal hydrogen bonds.

### Experimental

Fluorescein (2.73 g) was dissolved in methanol (200 ml) along with a catalytic amount of concentrated sulfuric acid. The orange-red solution was refluxed for 12 h and was then poured into ice-water (100 ml). The resulting precipitate was filtered off to yield the product as an orange solid. This isolated product (1.67 g) was added to dimethylformamide (100 ml) followed by potassium carbonate (1.43 g) and 11-bromoundecan-1-ol (1.28 g), and the mixture was heated at 333 K for 2 d. The resulting red precipitate was filtered off and washed with aqueous sodium hydroxide. The product was solubilized in anhydrous tetrahydrofuran along with sodium hydride. The mixture was subsequently refluxed for 8 h and the title compound, (I), was isolated in 41% yield after column chromatography. Compound (I) was crystallized by slow diffusion of hexanes into a saturated solution of the compound in diisopropyl ether.

#### Crystal data

$C_{31}H_{32}O_5$	$\gamma = 92.167 (3)^\circ$
$M_r = 484.57$	$V = 1276.0 (2) \text{ \AA}^3$
Triclinic, $P\bar{1}$	$Z = 2$
$a = 7.9010 (9) \text{ \AA}$	Cu $K\alpha$ radiation
$b = 12.7844 (13) \text{ \AA}$	$\mu = 0.68 \text{ mm}^{-1}$
$c = 12.9683 (14) \text{ \AA}$	$T = 100 (2) \text{ K}$
$\alpha = 91.895 (2)^\circ$	$0.18 \times 0.16 \times 0.11 \text{ mm}$
$\beta = 102.655 (3)^\circ$	

#### Data collection

Bruker Microstar diffractometer	3392 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	$R_{int} = 0.024$
$T_{min} = 0.804, T_{max} = 0.931$	5 standard reflections
4699 measured reflections	frequency: 1080 min
3831 independent reflections	intensity decay: none

#### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.041$	325 parameters
$wR(F^2) = 0.129$	H-atom parameters constrained
$S = 1.07$	$\Delta\rho_{max} = 0.24 \text{ e \AA}^{-3}$
3831 reflections	$\Delta\rho_{min} = -0.24 \text{ e \AA}^{-3}$

**Table 1**

Selected geometric parameters (Å, °).

O2—C9	1.252 (2)	C5—C6	1.390 (2)
O5—C4	1.3640 (17)	C7—C8	1.360 (2)
O5—C31	1.4542 (17)	C10—C11	1.352 (2)
C1—C13	1.449 (2)	C12—C13	1.379 (2)
C2—C3	1.388 (2)		
C12—C13—C14	120.80 (13)	C1—C13—C14	119.87 (13)

**Table 2**

Hydrogen-bond geometry (Å, °).

$Cg1$  is the centroid of the C1–C6 ring.

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
C5—H5 $\cdots$ O2 <sup>i</sup>	0.95	2.51	3.355 (2)	149 (2)
C8—H8 $\cdots$ O1 <sup>i</sup>	0.95	2.60	3.4639 (19)	151 (3)
C10—H10 $\cdots$ O3 <sup>ii</sup>	0.95	2.47	3.3454 (19)	154 (2)
C23—H23A $\cdots$ Cg1	0.99	2.93	3.82 (2)	150 (2)

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

H atoms were placed in calculated positions, with C—H = 0.93–0.97 Å, and included in the refinement in the riding-model approximation, with  $U_{iso}(H) = 1.2U_{eq}(C)$ .

Data collection: SMART (Bruker, 2003); cell refinement: SMART; data reduction: SAINT (Bruker, 2004); program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: ORTEP-3 (Farrugia, 1997) and SHELXTL (Bruker, 1997); software used to prepare material for publication: UDMX (Marris, 2004).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ3058). Services for accessing these data are described at the back of the journal.

### References

- Ajtai, K. & Burghardt, T. P. (1995). *Biochemistry*, **34**, 15943–15952.
- Balzani, V., Credi, A., Raymo, F. M. & Stoddart, J. F. (2000). *Angew. Chem. Int. Ed.* **39**, 3348–3391.
- Bruker (1997). *SHELXTL*. Version 5.10. Bruker AXS Inc., Madison, Wisconsin, USA.
- Bruker (2003). *SMART*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Bruker (2004). *SAINTE*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Cody, V. (1987). *Acta Cryst.* **C43**, 705–707.
- Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
- Feringa, B. L. (2001). *Acc. Chem. Res.* **34**, 504–513.
- Kelly, T. R., Bowyer, M. C., Bhaskar, K. V., Bebbington, D., Garcia, A., Lang, F., Kim, M. H. & Jette, M. P. (1994). *J. Am. Chem. Soc.* **116**, 3657–3658.
- Marris, T. (2004). *UDMX*. University of Montréal, Québec, Canada.
- Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
- Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
- Stoddart, J. F. & Tseng, H.-R. (2002). *Proc. Natl Acad. Sci. USA*, **99**, 4797–4800.
- Tremayne, M., Kariuki, B. M. & Harris, K. D. M. (1997). *Angew. Chem. Int. Ed.* **36**, 770–772.
- Wang, X., Song, M. & Long, Y. (2001). *J. Solid State Chem.* **156**, 325–330.
- Willner, I., Marx-Tibbon, S., Cohen, S., Eichen, Y. & Kaftori, M. (1997). *J. Phys. Org. Chem.* **10**, 435–444.
- Yamaguchi, K., Tamura, Z. & Maeda, M. (1997). *Acta Cryst.* **C53**, 284–285.