

2,7-Di-*tert*-butyl-9,9-dimethyl-4,5-bis-(4-tritylanilinocarbonyl)-9*H*-xanthene methanol trisolvate monohydrate**Myroslav O. Vysotsky* and Dieter Schollmeyer**

Fachbereich Chemie, Pharmazie und Geowissenschaften, Johannes Gutenberg Universität, Duesbergweg 10-14, 55128 Mainz, Germany

Correspondence e-mail: vysotsky@uni-mainz.de

The title compound, $C_{75}H_{68}N_2O_3 \cdot 3CH_3OH \cdot H_2O$, was synthesized starting from the corresponding acid and *p*-tritylaniline. Single crystals were obtained from a methanol solution as a solvate, with three methanol molecules and one water molecule. The solid-state structure proves the existence of an intramolecular bifurcated hydrogen bond between one amide H atom and the carbonyl and xanthene O atoms. The packing is stabilized by intermolecular hydrogen bonds.

Received 24 November 2006

Accepted 28 November 2006

Key indicators

Single-crystal X-ray study

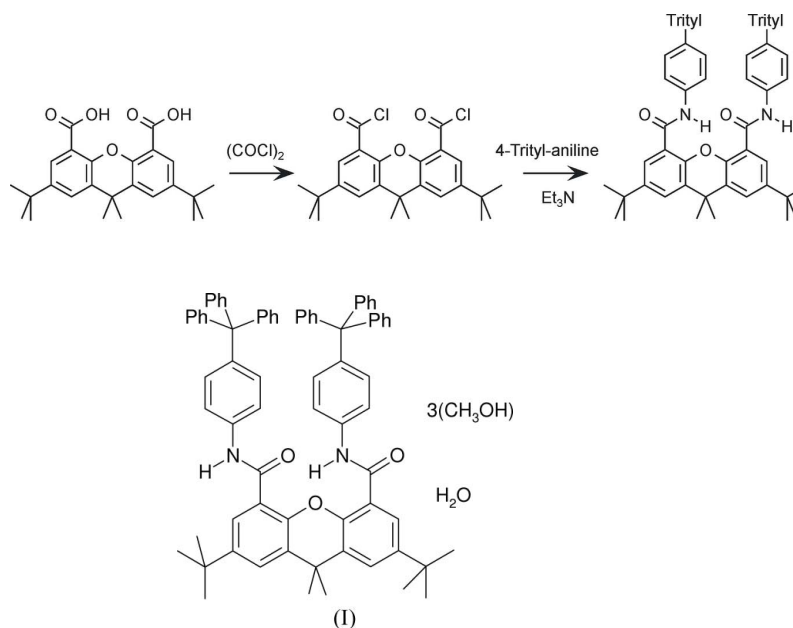
 $T = 173\text{ K}$ Mean $\sigma(C-C) = 0.010\text{ \AA}$ R factor = 0.143 wR factor = 0.391

Data-to-parameter ratio = 15.8

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

Comment

The xanthene building block has been successfully used in the design of artificial receptors for neutral (Nowick *et al.*, 1990) or negatively charged (Meshcheryakov *et al.*, 2006) organic molecules and artificial self-folding structures (Nowick, 2006). The purpose of the present work was to test if bulky groups attached to the aniline groups of a 4,5-diamidoxanthene unit can disrupt the intramolecular bifurcated hydrogen bond which is present in similar diamide derivatives, and thus create a void between the aniline units suitable for the inclusion of small organic molecules.



The title compound, (I) (Fig. 1), was synthesized using a typical procedure. Single crystals suitable for X-ray analysis were grown from a methanol solution. Compound (I) crystallizes as a solvate, containing three methanol molecules and one water molecule.

The X-ray analysis of the structure of (I) reveals the typical intramolecular bifurcated hydrogen bond (Nowick, 2006;

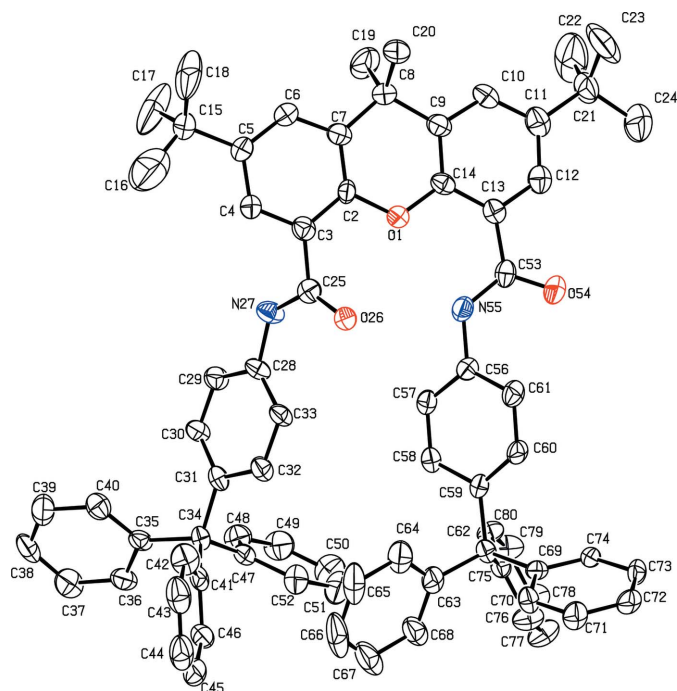


Figure 1
The molecular structure of one molecule of (I). Displacement ellipsoids are drawn at the 50% probability level. H atoms and solvent molecules have been omitted.

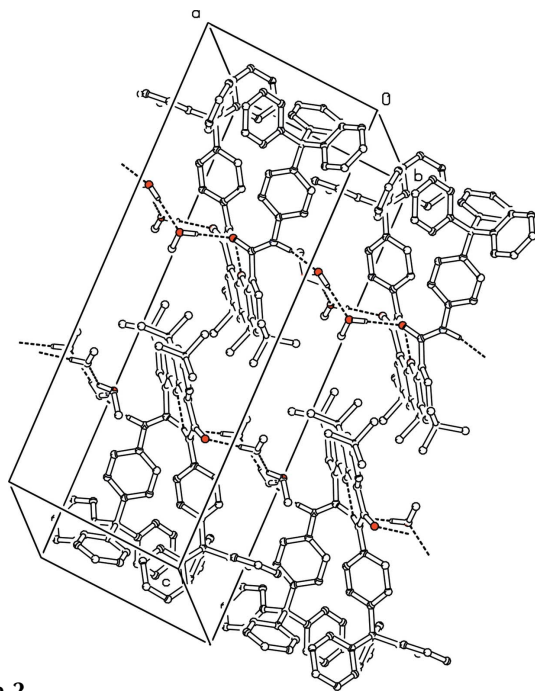


Figure 2
Part of the packing of (I), showing the hydrogen-bond network (dashed lines).

Table 1) and thus proves that simple trityl groups are not large enough to create an inner space between the aniline units suitable for the inclusion of small organic molecules.

The methanol and water molecules are involved in an infinite intermolecular hydrogen-bonding network which holds neighbouring molecules together. The molecules pack in such

a way that the xanthene units display a zipper-like motif (Fig. 2).

Experimental

Oxalyl chloride (1.06 ml, 12.3 mmol) was added in one portion to a stirred suspension of 2,7-di-*tert*-butyl-9,9-dimethylxanthene-4,5-dicarboxylic acid (0.505 g, 1.23 mmol, Fluka) in dichloromethane (20 ml) containing several drops of dimethylformamide. The reaction mixture was stirred at reflux for 2 h and evaporated, the residue was dissolved in chloroform (20 ml), and 4-tritylaniline (0.990 g, 2.95 mmol) and triethylamine (0.85 ml, 5.90 mmol) were added. The reaction mixture was stirred at reflux overnight and concentrated to 5 ml, and methanol (50 ml) was added. After treatment of the resulting mixture in an ultrasonic bath for 10 min, a white precipitate was formed. This was filtered off, washed with methanol (3 × 10 ml) and dried [yield 0.707 g, 55%; m.p. 483–486 K, 468–473 K (phase transition)]. Analysis calculated for C₇₅H₆₈N₂O₃: C 86.17, H 6.56, N 2.68%; found: C 86.20, H 6.36, N 2.67%. Single crystals suitable for X-ray analysis were obtained by slow crystallization from methanol in a tightly closed vial.

Crystal data

C₇₅H₆₈N₂O₃·3CH₄O·H₂O
M_r = 1159.46
 Triclinic, *P* $\bar{1}$
a = 9.970 (4) Å
b = 12.368 (7) Å
c = 27.273 (5) Å
 α = 92.70 (3)°
 β = 95.17 (2)°
 γ = 100.48 (4)°

V = 3287 (2) Å³
Z = 2
D_x = 1.172 Mg m⁻³
 Cu *K*α radiation
 μ = 0.58 mm⁻¹
T = 173 (2) K
 Plate, colourless
 0.20 × 0.20 × 0.07 mm

Data collection

Enraf–Nonius CAD-4
 diffractometer
 $\omega/2\theta$ scans
 Absorption correction: none
 13059 measured reflections
 12444 independent reflections

7152 reflections with *I* > 2σ(*I*)
R_{int} = 0.084
 θ_{\max} = 70.1°
 3 standard reflections
 frequency: 60 min
 intensity decay: 10%

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.143
wR(*F*²) = 0.391
S = 1.07
 12444 reflections
 786 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.1681P)^2 + 10.925P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.72 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.62 \text{ e } \text{Å}^{-3}$

Table 1
Hydrogen-bond geometry (Å, °).

<i>D</i> –H... <i>A</i>	<i>D</i> –H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> –H... <i>A</i>
N27–H27...O5L	0.88	2.05	2.863 (9)	154
N55–H55...O1	0.88	2.00	2.693 (7)	135
N55–H55...O26	0.88	2.38	3.060 (7)	134
O1L–H1L...O26	0.85	1.97	2.816 (9)	179
O3L–H3L...O7L	0.84	2.19	2.827 (17)	133
O5L–H5LA...O3L	0.90	2.12	3.004 (14)	168
O5L–H5LB...O1L ⁱ	0.85	2.13	2.974 (11)	179
O7L–H7L...O54 ⁱ	0.85	1.95	2.800 (13)	179

Symmetry code: (i) *x* – 1, *y*, *z*.

During the time of measurement (4 d), the intensity dropped significantly and the crystal became cloudy. After the measurement, the crystal was warmed to the room temperature. During this time, it cracked in several places which were now completely cloudy. We suppose that the crystal lost significant amount of solvents during the measurement. This decreased the refracting power leading to the high *R* factors. H atoms were placed in calculated positions, with C–H = 0.93 Å (aromatic C) or 0.96–0.98 Å (*Csp*³), O–H = 0.82 Å and N–H = 0.88 Å, and were refined with fixed isotropic displacement parameters using a riding model, with $U_{\text{iso}}(\text{H}) = 1.2\text{--}1.5U_{\text{eq}}(\text{C,N,O})$.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: *CORINC* (Dräger & Gattow, 1971); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976) and *PLATON* (Spek, 2003); software used to prepare material for publication: *publCIF* (Westrip, 2006).

This work was supported by the Deutsche Forschungsgemeinschaft (Vy 6/1).

References

- Altomare, A., Burla, M. C., Camalli, M., Cascarano, G. L., Giacovazzo, C., Guagliardi, A., Moliterni, A. G. G., Polidori, G. & Spagna, R. (1999). *J. Appl. Cryst.* **32**, 115–119.
- Dräger, M. & Gattow, G. (1971). *Acta Chem. Scand.* **25**, 761–762.
- Enraf–Nonius (1989). *CAD-4 Software*. Version 5. Enraf–Nonius, Delft, The Netherlands.
- Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- Meshcheryakov, D., Böhmer, V., Bolte, M., Hubscher-Bruder, V., Arnaud-Neu, F., Herschbach, H., Van Dorsselaer, A., Thondorf, I. & Mögelin, W. (2006). *Angew. Chem. Int. Ed.* **45**, 1648–1652.
- Nowick, J. S. (2006). *Org. Biomol. Chem.* **4**, 3869–3885.
- Nowick, J. S., Ballester, P., Ebmeyer, F. & Rebek, J. Jr (1990). *J. Am. Chem. Soc.* **112**, 8902–8906.
- Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
- Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.
- Westrip, S. P. (2006). *publCIF*. In preparation.