Gerkin, R. E., Lundstedt, A. P. & Reppart, W. J. (1984). *Acta Cryst.* C**40**, 1892–1894.
Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Molecular Structure Corporation (1989). *TEXSAN. TEXRAY Structure Analysis Package.* MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
Molecular Structure Corporation (1991). *MSC/AFC Diffractometer Control Software.* MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
Sheldrick, G. M. (1985). *SHELXS*86. *Program for the Solution of Crystal Structures.* University of Göttingen, Germany.
Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3174–3187.
Zachariasen, W. H. (1963). *Acta Cryst.* **16**, 1139–1144.
Zachariasen, W. H. (1968). *Acta Cryst.* A**24**, 212–216.

Acta Cryst. (1996). C**52**, 1486–1488

Xanthene-9-carboxylic Acid

ANTHONY C. BLACKBURN, ALLISON J. DOBSON AND
ROGER E. GERKIN*

Department of Chemistry, The Ohio State University, Columbus, Ohio 43210, USA. E-mail: rgerkin@magnus.acs.ohio-state.edu

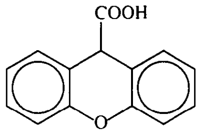
(Received 6 October 1995; accepted 30 November 1995)

Abstract

In xanthene-9-carboxylic acid, $C_{14}H_{10}O_3$, hydrogen bonding is of the cyclic dimer type but involves two crystallographically inequivalent molecules and does not occur about a center of symmetry. The carboxylic H atoms are ordered. The dihedral angle (fold angle) of the xanthene core is 14.2 (1)° for molecule *A* and 11.3 (2)° for molecule *B*. The planes of the carboxyl groups are almost perpendicular to the xanthene cores.

Comment

In the title structure, (I), hydrogen bonding is of the cyclic dimer type but it involves two crystallographically inequivalent molecules and does not occur about a center of symmetry. There are, therefore, two inequivalent hydrogen bonds involving the O1*A* and O1*B* atoms as donors and the O2*B* and O2*A* atoms as acceptors. The donor–acceptor distances of 2.647 (4) and 2.650 (4) Å are somewhat below the average for organic O···O hydrogen bonds (2.77 Å; Ceccarelli, Jeffrey & Taylor, 1981) and indicate strong hydrogen bonds. The interatomic distances in the carboxyl groups (Table 2) are entirely consistent with ordered carboxyl H atoms.



(I)

The xanthene cores show pseudo-mirror symmetry; for the eight pairs of core bond distances that would be identical under mirror symmetry, the r.m.s. difference within pairs is 0.011 (8) Å for molecule *A* and 0.010 (8) Å for molecule *B*. Moreover, the averages of these pairs of values for the *A* and *B* molecules have an r.m.s. difference of only 0.006 (8) Å. The calculation of grand means is therefore justified. For comparison, the xanthene core values obtained for methyl 9-xanthenyl ketone (Rochlin & Rappoport, 1992) have been chosen and will be cited in square brackets. The grand mean of the ring bond lengths involving the C9 atom is 1.507 (7) Å [1.516 (4) Å], of those involving O10 is 1.377 (6) Å [1.392 (3) Å] and of the aromatic (outer ring) bonds is 1.380 (10) Å [1.391 (4) Å]. The mean values for the central ring angles, C12—C9—C13 and C11—O10—C14, are 111.5 (3) [109.4 (2)] and 118.5 (3)° [116.4 (2)°], respectively.

The central ring of the xanthene core of each molecule is in a boat conformation (Fig. 1), with atoms C9 and O10 on the same side of the plane defined by atoms C11, C12, C13 and C14. The angle between this latter plane and the carboxyl group plane is 86.3 (6)° for molecule *A* and 84.8 (7)° for molecule *B*.

Overall, the xanthene core of each molecule is V-shaped with atoms C1–C4, C13, C14, C9 and O10 defining one plane and atoms C5–C8, C11, C12, C9 and O10 defining the other, with C9 and O10 lying on the line of intersection. The mean distances of the respective atoms from these least-squares best-fit planes are 0.016 and 0.016 Å for molecule *A*, and 0.017 and 0.021 Å for molecule *B*. The dihedral angle (folding angle) is 14.2 (1)° for *A* and 11.3 (2)° for *B*; for methyl 9-xanthenyl ketone (Rochlin & Rappoport, 1992), this value was found to be 30.1°, while for 9-isopropylxanthene (Chu & Yang, 1977) it was 21.9°.

In the present structure, all of the closest intermolecular approaches of atoms, excluding those participating in hydrogen bonding, involve H and O atoms or H and C atoms. With respect to the sums of the van der Waals radii (Bondi, 1964) of the involved atoms, only four interatomic approaches show deficits, the maximum deficit being 0.11 Å for the atom pair C14*A*···H3*B*$^{\mathrm{i}}$ [symmetry code: (i) $1-x$, $1-y$, $-\frac{1}{2}+z$].

A point of particular interest is that with respect to a pair of hydrogen-bonded partners, the 'midpoint' of the cyclic portion is a pseudo-center of symmetry. There is, however, no pseudo-center which relates such a hydrogen-bonded dimer to another hydrogen-bonded dimer. A somewhat similar occurrence was

Acta Crystallographica Section C
ISSN 0108-2701 © 1996

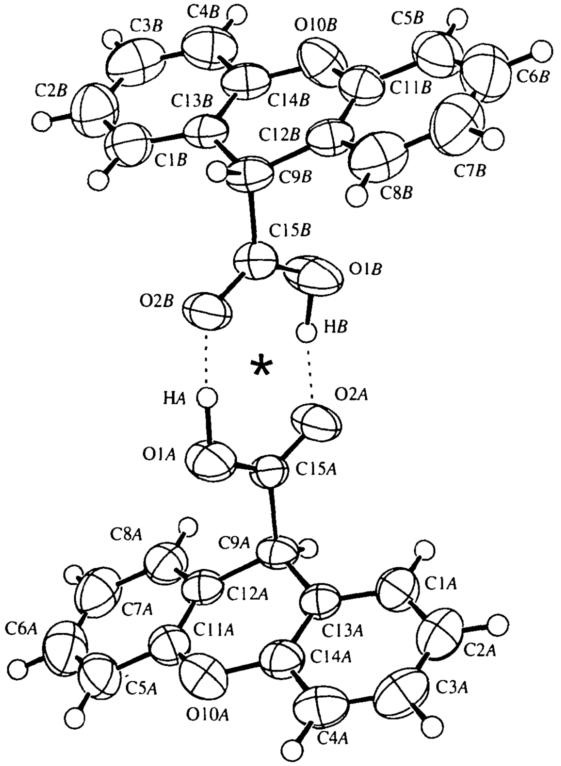


Fig. 1. An *ORTEP*II drawing (Johnson, 1976) of the *A* and *B* molecules of the dimer of xanthene-9-carboxylic acid, showing the atomic numbering scheme. The pseudo-center of symmetry and the hydrogen bonds are also displayed, and displacement ellipsoids are drawn at the 50% probability level for all atoms, except the H atoms for which they have been set artificially small.

seen in the structure of the β phase of fluorene-4-carboxylic acid (Blackburn, Dobson & Gerkin, 1996), where the 'midpoint' of the cyclic portion of that cyclic hydrogen-bonded dimer was also not a center of symmetry, though the space group in that instance was centrosymmetric. In order to exclude any (rigorous) further symmetry beyond that reported here, the program *MISSYM* (Le Page, 1987, 1988) was employed, with negative results. Moreover, axial photographs clearly exhibited *mmm* symmetry and thus obviate potential alternative assignments in the monoclinic system.

Experimental

Xanthene-9-carboxylic acid (Aldrich Chemical Company) was dissolved in trichloroethylene and the solution treated with Norit-A decolorizing carbon. The resulting mixture was filtered and the filtrate evaporated slowly at room temperature to yield colorless columns. A cut column was mounted with epoxy cement on a glass fiber for analysis.

Crystal data

$C_{14}H_{10}O_3$
$M_r = 226.23$
Orthorhombic
$Pna2_1$
$a = 16.139$ (1) Å
$b = 5.117$ (1) Å
$c = 26.887$ (2) Å
$V = 2220.4$ (6) Å^3
$Z = 8$
$D_x = 1.353$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 12.6$–$13.8°$
$\mu = 0.089$ mm^{-1}
$T = 296$ K
Cut column
0.46 × 0.27 × 0.27 mm
Colorless

Data collection

Rigaku AFC-5*S* diffractometer
ω scans
Absorption correction: none
3011 measured reflections
3011 independent reflections
1946 observed reflections [$I > 0.5\sigma(I)$]

$\theta_{\max} = 27.50°$
$h = 0 \rightarrow 20$
$k = 0 \rightarrow 6$
$l = -34 \rightarrow 0$
6 standard reflections monitored every 150 reflections intensity decay: 5.6%

Refinement

Refinement on F
$R = 0.058$
$wR = 0.046$
$S = 1.32$
1946 reflections
315 parameters
H atoms: C—H 0.98 Å, $B = 1.2B_{\rm eq}$ of attached atom; for O—H, all H-atom parameters refined
$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{\max} = <0.01$

$\Delta\rho_{\max} = 0.18$ e Å^{-3}
$\Delta\rho_{\min} = -0.18$ e Å^{-3}
Extinction correction: Zachariasen (1963, 1968)
Extinction coefficient: 7 (1) × 10^{-7}
Atomic scattering factors from Stewart, Davidson & Simpson (1965) for H atoms and from Cromer & Waber (1974) for C and O atoms

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

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

	x	y	z	$U_{\rm eq}$
Molecule *A*				
O1*A*	0.5629 (2)	0.3366 (6)	0.2398	0.079 (1)
O2*A*	0.6004 (2)	0.7415 (5)	0.2559 (2)	0.0692 (10)
O10*A*	0.4845 (2)	0.2705 (6)	0.1131 (2)	0.0664 (10)
C1*A*	0.6261 (3)	0.8154 (8)	0.1334 (2)	0.060 (1)
C2*A*	0.6774 (3)	0.7872 (10)	0.0926 (2)	0.071 (2)
C3*A*	0.6637 (3)	0.5859 (11)	0.0600 (2)	0.073 (2)
C4*A*	0.5986 (3)	0.4171 (10)	0.0672 (2)	0.068 (1)
C5*A*	0.3523 (3)	0.1661 (9)	0.1435 (3)	0.070 (2)
C6*A*	0.2885 (3)	0.2053 (12)	0.1761 (3)	0.087 (2)
C7*A*	0.2930 (3)	0.3952 (12)	0.2124 (3)	0.082 (2)
C8*A*	0.3631 (3)	0.5519 (9)	0.2157 (2)	0.064 (1)
C9*A*	0.5081 (2)	0.6700 (7)	0.1880 (2)	0.046 (1)
C11*A*	0.4223 (3)	0.3218 (8)	0.1473 (2)	0.056 (1)
C12*A*	0.4299 (2)	0.5122 (7)	0.1832 (2)	0.049 (1)
C13*A*	0.5612 (2)	0.6456 (7)	0.1419 (2)	0.045 (1)
C14*A*	0.5482 (3)	0.4485 (8)	0.1086 (2)	0.053 (1)
C15*A*	0.5609 (2)	0.5832 (7)	0.2320 (2)	0.043 (1)
H*A*	0.593 (4)	0.310 (14)	0.275 (3)	0.18 (3)
Molecule *B*				
O1*B*	0.6978 (2)	0.6229 (6)	0.3318 (2)	0.088 (1)
O2*B*	0.6627 (2)	0.2178 (5)	0.3147 (2)	0.0664 (10)
O10*B*	0.7844 (2)	0.6811 (6)	0.4582 (2)	0.074 (1)
C1*B*	0.6399 (3)	0.1383 (10)	0.4381 (2)	0.068 (2)
C2*B*	0.5906 (3)	0.1636 (12)	0.4793 (3)	0.088 (2)
C3*B*	0.6076 (3)	0.3599 (13)	0.5128 (2)	0.085 (2)
C4*B*	0.6717 (3)	0.5319 (11)	0.5053 (2)	0.075 (2)
C5*B*	0.9114 (3)	0.8030 (10)	0.4232 (3)	0.079 (2)
C6*B*	0.9724 (3)	0.7786 (12)	0.3885 (3)	0.093 (2)

C7*B*	0.9663 (3)	0.5911 (13)	0.3524 (3)	0.093 (2)
C8*B*	0.8973 (3)	0.4304 (10)	0.3505 (2)	0.079 (2)
C9*B*	0.7566 (3)	0.2915 (7)	0.3819 (2)	0.050 (1)
C11*B*	0.8425 (3)	0.6412 (9)	0.4215 (2)	0.058 (1)
C12*B*	0.8338 (2)	0.4529 (8)	0.3851 (2)	0.053 (1)
C13*B*	0.7056 (2)	0.3088 (8)	0.4290 (2)	0.050 (1)
C14*B*	0.7210 (3)	0.5055 (8)	0.4631 (2)	0.056 (1)
C15*B*	0.7019 (2)	0.3757 (7)	0.3392 (2)	0.047 (1)
H*B*	0.647 (4)	0.671 (12)	0.307 (2)	0.15 (2)

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

Molecule *A*		Molecule *B*	
C9*A*—C12*A*	1.504 (5)	C9*B*—C12*B*	1.497 (5)
C9*A*—C13*A*	1.512 (5)	C9*B*—C13*B*	1.514 (5)
C11*A*—C12*A*	1.377 (5)	C11*B*—C12*B*	1.381 (6)
C13*A*—C14*A*	1.367 (5)	C13*B*—C14*B*	1.384 (5)
C11*A*—O10*A*	1.385 (5)	C11*B*—O10*B*	1.377 (6)
C14*A*—O10*A*	1.379 (5)	C14*B*—O10*B*	1.368 (5)
C9*A*—C15*A*	1.524 (5)	C9*B*—C15*B*	1.509 (5)
C15*A*—O1*A*	1.280 (4)	C15*B*—O1*B*	1.283 (4)
C15*A*—O2*A*	1.214 (4)	C15*B*—O2*B*	1.220 (4)
O1*A*—H*A*	1.09 (8)	O1*B*—H*B*	1.09 (6)
C12*A*—C9*A*—C13*A*	111.2 (3)	C12*B*—C9*B*—C13*B*	111.8 (3)
O10*A*—C11*A*—C12*A*	122.3 (4)	O10*B*—C11*B*—C12*B*	122.9 (4)
C9*A*—C12*A*—C11*A*	121.0 (4)	C9*B*—C12*B*—C11*B*	120.7 (4)
C9*A*—C13*A*—C14*A*	120.8 (4)	C9*B*—C13*B*—C14*B*	120.0 (4)
O10*A*—C14*A*—C13*A*	122.9 (4)	O10*B*—C14*B*—C13*B*	123.2 (4)
C11*A*—O10*A*—C14*A*	118.3 (3)	C11*B*—O10*B*—C14*B*	118.7 (3)
C12*A*—C9*A*—C15*A*	112.3 (3)	C12*B*—C9*B*—C15*B*	111.9 (3)
C13*A*—C9*A*—C15*A*	107.1 (3)	C13*B*—C9*B*—C15*B*	107.5 (3)
C9*A*—C15*A*—O1*A*	115.3 (3)	C9*B*—C15*B*—O1*B*	115.5 (4)
C9*A*—C15*A*—O2*A*	120.7 (3)	C9*B*—C15*B*—O2*B*	121.7 (3)
O1*A*—C15*A*—O2*A*	123.9 (4)	O1*B*—C15*B*—O2*B*	122.8 (4)

Table 3. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*A*—H*A*···O2*B*	1.09 (8)	1.61 (8)	2.650 (4)	158 (6)
O1*B*—H*B*···O2*A*	1.09 (6)	1.60 (6)	2.647 (4)	160 (5)

The Laue symmetry and the observed reflection-limiting conditions indicated the space group to be either *Pnma* (centrosymmetric) or *Pna*2_1. The centrosymmetric option was explored without success, but the direct-methods program *SHELXS*86 (Sheldrick, 1985) yielded acceptable initial positions of the C and O atoms in space group *Pna*2_1 (No. 33), which was adopted. Refinement proceeded well and the space group was retained.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1989). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *TEXSAN*. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *TEXSAN*.

We acknowledge the partial support provided to AJD by a National Needs Fellowship. We thank Dr J. C. Gallucci for help of various sorts. The diffractometer was purchased with funds provided in part by an NIH grant.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and least-squares-planes data, together with a stereoview of the unit cell, have been deposited with the IUCr (Reference: FG1134). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Blackburn, A. C., Dobson, A. J. & Gerkin, R. E. (1996). *Acta Cryst.* **C52**, 1482–1486.
Bondi, A. (1964). *J. Phys. Chem.* **68**, 441–451.
Ceccarelli, C., Jeffrey, G. A. & Taylor, R. J. (1981). *J. Mol. Struct.* **70**, 255–271.
Chu, S. S. C. & Yang, H. T. (1977). *Acta Cryst.* B**33**, 2291–2293
Cromer, D. T. & Waber, J. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, Tables 2.2A, 2.3.1. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Le Page, Y. (1987). *J. Appl. Cryst.* **20**, 264–269.
Le Page, Y. (1988). *J. Appl. Cryst.* **21**, 983–984.
Molecular Structure Corporation (1988). *MSC/AFC Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
Molecular Structure Corporation (1989). *TEXSAN. Single Crystal Structure Analysis Software*. Version 5.0. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
Rochlin, E. & Rappoport, Z. (1992). *J. Am. Chem. Soc.* **114**, 230–241.
Sheldrick, G. M. (1985). *SHELXS*86. *Crystallographic Computing* 3, edited by G. M. Sheldrick, C. Krüger & R. Goddard, pp. 175–189. Oxford University Press.
Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3174–3187.
Zachariasen, W. H. (1963). *Acta Cryst.* **16**, 1139–1144.
Zachariasen, W. H. (1968). *Acta Cryst.* A**24**, 212–216.

Acta Cryst. (1996). **C52**, 1488–1490

Accurate Redetermination of Diiodobis(phenylsulfonyl)methane, $(PhSO_2)_2CI_2$

CHRISTOPHER GLIDEWELL,[a] GEORGE FERGUSON,[b] SPYROS NIKAS[c] AND ANASTASIOS VARVOGLIS[c]

[a]*School of Chemistry, University of St Andrews, St Andrews, Fife KY16 9ST, Scotland,* [b]*Department of Chemistry and Biochemistry, University of Guelph, Guelph, Ontario, Canada N1G 2W1, and* [c]*Laboratory of Organic Chemistry, Aristotelian University of Thessaloniki, 540 06 Thessaloniki, Greece. E-mail: cg@st-andrews.ac.uk*

(*Received 29 November 1995; accepted 8 December 1995*)

Abstract

The structure of the title compound, $C_{13}H_{10}I_2O_4S_2$, has been redetermined, with proper treatment of both anomalous dispersion and absorption. The unusual structural features reported in an earlier determination [Stergioudis, Bozopoulos, Kavounis & Rentzeperis (1989). *Z. Kristallogr.* **189**, 57–63] are not reproduced by the present analysis; the structure and conformation of the title compound are now found to be very similar to those of $(PhSO_2)_2CBr_2$; the molecules are joined into chains along the *a* direction by very short I···O interactions [I···O 2.927 (7) Å].

Acta Crystallographica Section C
ISSN 0108-2701 © 1996