H(secondary CH$_2$ group) 0.97 Å or C—H(aromatic) 0.93 Å. The disordered phenyl rings were refined as a rigid group applying the geometry of a regular hexagon with isotropic displacement parameters for the C atoms. The site occupancy factor of each of the two rings was refined as one additional variable by constraining the sum of the two values to 1.

Program(s) used to solve structure: SHELXS86 (Sheldrick, 1985). Program(s) used to refine structure: SHELXL93 (Sheldrick, 1993).

I thank Professor Dr H. W. Roesky, University of Göttingen, for providing the sample.

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3-(4-Butoxycarbonylphenyloxycarbonyl)-xanthen-9-one

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Abstract

The title compound, butyl 4-[(9-oxoxanthen-3-yl)-carbonyloxy]benzoate, C$_{25}$H$_{20}$O$_6$, has been obtained as a product of the intramolecular cyclization of 2-phenoxyterephthaloyl dichloride in the presence of butyl 4-hydroxybenzoate. The crystal and molecular structures

are reported. The xanthone group is planar to within 0.084 (1) Å. Molecules in the crystal are packed with planes of xanthone groups parallel to one another.

Comment

The title compound, (I), was obtained as a product (60% yield) of the reaction between 2-phenoxyterephthaloyl dichloride and butyl 4-hydroxybenzoate (mole ratio 2:1) in hot pyridine (2-phenoxyterephthaloyl dichloride was obtained by refluxing 2-phenoxyterephthalic acid with thionyl chloride and removing the excess thionyl chloride by distillation under reduced pressure; butyl 4-hydroxybenzoate was obtained by Fischer esterification of 4-hydroxybenzoic acid and n-butanol). The raw product, obtained after pouring the reaction mixture into an excess of ethanol, was purified by silica-gel chromatography, using chloroform as eluent, and finally recrystallized from chloroform–hexane solution (m.p. 403 K).

(I)
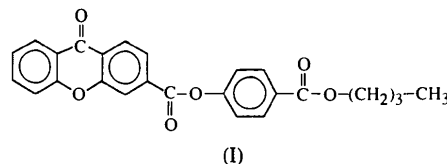
The proton NMR spectrum was not consistent with the structure of the expected product, i.e. bis(4-butoxycarbonylphenyl)-2-phenoxyterephthalate, indicating the formation of a different compound. This seemingly unusual behaviour is actually consistent with previous observations (Kricheldorf, Schwarz & Ruhser, 1988). It was shown, in fact, that intramolecular cyclization of 2-phenoxyterephthaloyl dichloride (via Friedel–Crafts acylation) may also occur under rather mild conditions giving xanthone-3-carboxylic acid chloride. In our case, the formation of the title compound may be accounted for by intramolecular cyclization of 2-phenoxyterephthaloyl dichloride followed by esterification with butyl 4-hydroxybenzoate. The X-ray analysis was undertaken for the definitive assignment of the molecular structure.

Bond lengths and angles in the molecule are all close to expected values. In particular, as far as the geometry of the xanthone moiety is concerned, the observed bond lengths and angles are in fair agreement with those previously reported for xanthone (Onuma, Iijima & Oonishi, 1990). A small, but probably statistically significant, spread of the bond lengths in the benzenoid rings of the xanthone group was observed, the shortest C—C distances being C17—C18 and C24—C25 [1.375 (1) and 1.377 (1) Å, respectively] and C13—C14 and C22—C23 [1.381 (1) and 1.380 (1) Å, respectively]. This is consistent with the central pyranoid ring having partial aromatic character (Lumbroso, Curé & Evers, 1986).

The two benzenoid rings are planar to within 0.009 (1) Å and the central pyranoid ring, including the carbonyl atom O5, is planar to within 0.032 (1) Å. The whole xanthone group is planar to within 0.084 (1) Å. The dihedral angle between the average planes of the xanthone group and the phenylene group (C6–C11) is 54.42 (3)° and is essentially due to the torsion around the O3—C9 bond. The terminal aliphatic chain has a *trans*-planar conformation. The crystal packing (Fig. 2) shows that the xanthone rings, as well as the phenylene rings, are packed with their planes parallel to one another. The average planes of the xanthone rings are stacked at distances of about 3.4 Å.
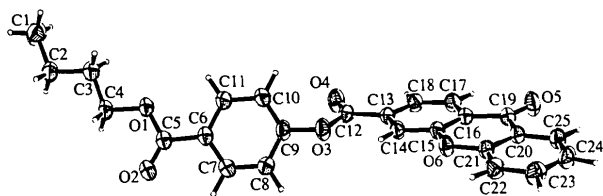

Fig. 1. A view of the molecule showing the labelling of the non-H atoms. Displacement ellipsoids are shown at the 50% probability level.
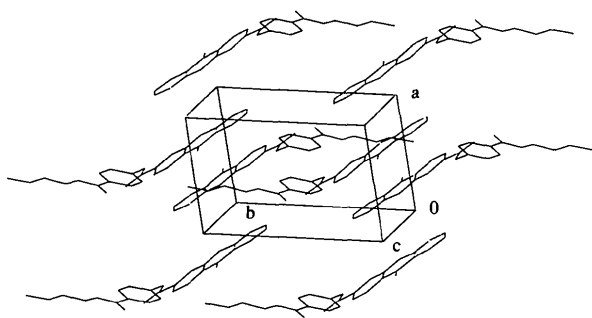

Fig. 2. Crystal packing of the title compound. H atoms are omitted for clarity.

Experimental

Crystal data

C$_{25}$H$_{20}$O$_6$
$M_r = 416.43$
Triclinic
$P\bar{1}$
$a = 7.590\,(1)$ Å
$b = 11.640\,(1)$ Å
$c = 11.748\,(3)$ Å
$\alpha = 88.00\,(1)°$
$\beta = 88.08\,(1)°$
$\gamma = 80.02\,(1)°$
$V = 1021\,(2)$ Å^3
$Z = 2$
$D_x = 1.354$ Mg m^{-3}
$D_m = 1.34\,(1)$ Mg m^{-3}
D_m measured by flotation in CCl$_4$–heptane

Cu $K\alpha$ radiation
$\lambda = 1.54178$ Å
Cell parameters from 25 reflections
$\theta = 13.4$–$27.0°$
$\mu = 0.759$ mm^{-1}
$T = 295$ K
Prism
$0.71 \times 0.16 \times 0.13$ mm
Colorless

Data collection

Enraf–Nonius diffractometer
ω/θ scans
Absorption correction: none
4206 measured reflections
4206 independent reflections
3780 observed reflections
[$I > 3.0\sigma(I)$]

$\theta_{max} = 75.0°$
$h = -9 \rightarrow 9$
$k = -14 \rightarrow 14$
$l = 0 \rightarrow 14$
2 standard reflections frequency: 120 min intensity decay: 1.4%

Refinement

Refinement on F
$R = 0.044$
$wR = 0.067$
$S = 3.021$
3780 reflections
361 parameters
All H-atom parameters refined
$w = 4F_o^2/[\sigma^2(F_o^2) + (0.03F_o^2)^2]$
$(\Delta/\sigma)_{max} = 0.03$

$\Delta\rho_{max} = 0.337$ e Å^{-3}
$\Delta\rho_{min} = -0.177$ e Å^{-3}
Extinction correction: Stout & Jensen (1989)
Extinction coefficient: $3.7\,(4) \times 10^{-6}$
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)

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

	x	y	z	U_{eq}
O1	0.7279 (1)	-0.76053 (8)	0.49544 (8)	0.0501 (3)
O2	0.8505 (2)	-0.6330 (1)	0.59065 (9)	0.0730 (4)
O3	0.5099 (1)	-0.30803 (8)	0.18237 (8)	0.0467 (3)
O4	0.6286 (2)	-0.39855 (8)	0.02368 (9)	0.0530 (3)
O5	0.2084 (2)	0.10123 (9)	-0.28217 (8)	0.0592 (3)
O6	0.1615 (1)	0.06297 (7)	0.06533 (7)	0.0397 (2)
C1	0.7650 (3)	-1.1769 (1)	0.5971 (2)	0.0661 (5)
C2	0.8046 (2)	-1.0609 (1)	0.6333 (1)	0.0563 (4)
C3	0.7339 (2)	-0.9607 (1)	0.5514 (1)	0.0546 (4)
C4	0.7858 (2)	-0.8482 (1)	0.5840 (1)	0.0508 (4)
C5	0.7690 (2)	-0.6554 (1)	0.5104 (1)	0.0450 (4)
C6	0.7027 (2)	-0.5686 (1)	0.4190 (1)	0.0408 (4)
C7	0.7341 (2)	-0.4556 (1)	0.4282 (1)	0.0503 (4)
C8	0.6724 (2)	-0.3705 (1)	0.3467 (1)	0.0485 (4)
C9	0.5798 (2)	-0.4006 (1)	0.2568 (1)	0.0405 (3)
C10	0.5467 (2)	-0.5118 (1)	0.2448 (1)	0.0511 (4)
C11	0.6090 (2)	-0.5963 (1)	0.3274 (1)	0.0494 (4)
C12	0.5413 (2)	-0.3164 (1)	0.0686 (1)	0.0383 (3)
C13	0.4535 (2)	-0.2082 (1)	0.0073 (1)	0.0350 (3)
C14	0.3459 (2)	-0.1195 (1)	0.0648 (1)	0.0353 (3)
C15	0.2635 (2)	-0.0217 (1)	0.0026 (1)	0.0333 (3)
C16	0.2855 (2)	-0.0129 (1)	-0.1152 (1)	0.0348 (3)
C17	0.3959 (2)	-0.1037 (1)	-0.1710 (1)	0.0410 (3)
C18	0.4803 (2)	-0.2000 (1)	-0.1108 (1)	0.0403 (3)
C19	0.1948 (2)	0.0915 (1)	-0.1785 (1)	0.0400 (3)
C20	0.0926 (2)	0.1815 (1)	-0.1069 (1)	0.0382 (3)
C21	0.0830 (2)	0.1647 (1)	0.0109 (1)	0.0369 (3)
C22	-0.0085 (2)	0.2499 (1)	0.0813 (1)	0.0462 (4)
C23	-0.0913 (2)	0.3540 (1)	0.0325 (1)	0.0527 (4)
C24	-0.0866 (2)	0.3724 (1)	-0.0848 (1)	0.0523 (4)
C25	0.0032 (2)	0.2875 (1)	-0.1545 (1)	0.0464 (4)

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

O1—C4	1.455 (1)	C12—C13	1.492 (1)
O1—C5	1.332 (1)	C2—C3	1.520 (1)
C5—C6	1.487 (1)	C13—C14	1.381 (1)
O2—C5	1.205 (1)	C13—C18	1.398 (1)
C6—C7	1.385 (1)	C14—C15	1.395 (1)
O3—C9	1.404 (1)	C3—C4	1.497 (1)
C6—C11	1.387 (1)	C15—C16	1.391 (1)
O3—C12	1.353 (1)	C16—C17	1.398 (1)
C7—C8	1.386 (1)	C16—C19	1.478 (1)

O4—C12	1.193 (1)	C17—C18	1.375 (1)
O5—C19	1.222 (1)	C19—C20	1.464 (1)
C8—C9	1.376 (1)	C20—C21	1.393 (1)
O6—C15	1.364 (1)	C20—C25	1.408 (1)
O6—C21	1.376 (1)	C21—C22	1.388 (1)
C9—C10	1.374 (1)	C22—C23	1.380 (1)
C1—C2	1.511 (1)	C23—C24	1.388 (1)
C10—C11	1.391 (1)	C24—C25	1.377 (1)

C4—O1—C5	115.65 (6)	C14—C13—C18	120.67 (7)
C9—O3—C12	120.31 (6)	C13—C14—C15	118.77 (7)
C15—O6—C21	118.89 (6)	O6—C15—C14	115.42 (6)
C1—C2—C3	112.92 (9)	O6—C15—C16	123.17 (6)
C2—C3—C4	112.18 (8)	C14—C15—C16	121.41 (7)
O1—C4—C3	108.26 (7)	C15—C16—C17	118.57 (6)
O1—C5—O2	123.13 (7)	C15—C16—C19	119.99 (6)
O1—C5—C6	113.37 (7)	C17—C16—C19	121.43 (7)
O2—C5—C6	123.50 (8)	C16—C17—C18	120.73 (7)
C5—C6—C7	117.92 (7)	C13—C18—C17	119.82 (7)
C5—C6—C11	122.51 (7)	O5—C19—C16	121.81 (7)
C7—C6—C11	119.56 (7)	O5—C19—C20	123.51 (7)
C6—C7—C8	120.40 (8)	C16—C19—C20	114.66 (6)
C7—C8—C9	118.73 (8)	C19—C20—C21	120.49 (6)
O3—C9—C8	115.45 (7)	C19—C20—C25	121.35 (7)
O3—C9—C10	122.01 (7)	C21—C20—C25	118.16 (7)
C8—C9—C10	122.38 (7)	O6—C21—C20	122.61 (7)
C9—C10—C11	118.31 (7)	O6—C21—C22	115.57 (7)
C6—C11—C10	120.61 (8)	C20—C21—C22	121.82 (7)
O3—C12—O4	124.66 (7)	C21—C22—C23	118.76 (8)
O3—C12—C13	110.64 (6)	C22—C23—C24	120.64 (8)
O4—C12—C13	124.70 (7)	C23—C24—C25	120.48 (8)
C12—C13—C14	121.27 (7)	C20—C25—C24	120.10 (8)
C12—C13—C18	118.05 (6)		

C4—O1—C5—C6	−178.6 (1)	C15—C16—C19—C20	2.8 (2)
C12—O3—C9—C8	129.1 (1)	O1—C5—C6—C7	178.2 (1)
C12—O3—C9—C10	−55.4 (2)	O1—C5—C6—C11	−0.6 (2)
C9—O3—C12—C13	179.8 (1)	C16—C19—C20—C21	−1.3 (2)
C21—O6—C15—C16	−3.3 (2)	O3—C12—C13—C14	−4.4 (2)
C15—O6—C21—C20	4.8 (2)	O3—C12—C13—C18	176.8 (1)

Data collection: *SDP* package (Enraf–Nonius, 1985). Cell refinement: *SDP* package. Data reduction: *SDP* package. Program(s) used to solve structure: *SIR*88 (Burla *et al.*, 1989). Program(s) used to refine structure: *SDP* package. Molecular graphics: *ORTEP*II (Johnson, 1976) and *PLUTO* (Motherwell & Clegg, 1978).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: NA1123). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Bis(*para*-phénolammonium) Diphosphate Monohydrate

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Abstract

The structure of the title compound, bis(4-hydroxy-phenylammonium) dihydrogen diphosphate monohydrate, $2C_6H_8NO^+.H_2P_2O_7^{2-}.H_2O$, consists of alternately stacked organic and inorganic sheets connected by a three-dimensional network of hydrogen bonds. N—H$\cdots$O and O—H$\cdots$O hydrogen bonds are responsible for the cohesion in the inorganic sheets.

Commentaire

De nombreux mono- ou cyclophosphates de différents cations organiques sont actuellement connus. En revanche très peu de diphosphates ont été étudiés (Averbuch-Pouchot & Durif, 1992*a,b*, 1993; Adams & Ramdas, 1976, 1977, 1978; Kammoun, Jouini & Daoud, 1992; Kammoun, Jouini, Debbabi & Daoud, 1990). Nous décrivons dans ce travail la préparation et la structure cristalline du diphosphate (1,4-HO—C$_6$H$_4$—NH$_3$)$_2$H$_2$P$_2$O$_7$,H$_2$O, (I). La Fig. 2 représente la projection de l'ensemble de l'arrangement atomique de ce sel sur le plan *ac*. On y observe des couches alternées inorganiques et organiques perpendiculaires à la direction [100].

$$\left(HO - \!\!\!\!\bigcirc\!\!\!\! - \overset{+}{NH_3} \right)_2 \quad H_2P_2O_7^{2-} \quad H_2O$$

(I)
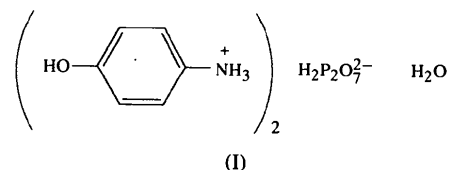
Groupement dihydrogénodiphosphate: les valeurs extrêmes des liaisons P—O, 1,606 (1) et 1,485 (2) Å, sont voisines de celles observées pour des composés analogues connus (Averbuch-Pouchot & Durif, 1992*a*, 1993). La plus longue distance (1,606 Å) correspond à l'atome d'O liant P—O(L), la distance intermédiaire [1,563 (2) Å] à celui porteur d'hydrogène P—OH et les deux courtes (1,493 et 1,485 Å) aux deux atomes d'O externes P—O(E). L'angle P—O—P est de 129,9 (2)°. Les valeurs moyennes calculées des indices de distorsion des différents angles et liaisons dans les tétraèdres PO$_4$ selon la méthode décrite par Baur (1974) sont ID(PO) = 0,031, ID(OPO) = 0,038, ID(OO) = 0,015.