C2	0.38406 (15)	−0.3931 (3)	1.26054 (12)	0.0470 (5)
C3	0.32939 (14)	−0.3408 (3)	1.18107 (10)	0.0432 (4)
C4	0.27458 (13)	−0.1270 (3)	1.16806 (10)	0.0376 (4)
C5	0.27231 (15)	0.0285 (3)	1.23787 (11)	0.0438 (4)
C6	0.32584 (15)	−0.0263 (3)	1.31783 (11)	0.0476 (5)
C7	0.22228 (13)	−0.0651 (3)	1.08119 (10)	0.0374 (4)
C8	0.16821 (13)	−0.2139 (3)	1.01730 (10)	0.0394 (4)
C9	0.13807 (13)	−0.0699 (3)	0.95103 (10)	0.0394 (4)
C10	0.08036 (15)	−0.0987 (3)	0.86229 (11)	0.0456 (5)
C11	0.03111 (15)	−0.3314 (3)	0.84962 (10)	0.0449 (5)
C12	0.4452 (2)	−0.2944 (4)	1.41627 (13)	0.0620 (6)

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

O1—C9	1.349 (2)	C1—C12	1.498 (2)
O1—N1	1.408 (2)	C7—C8	1.420 (2)
N1—C7	1.307 (2)	C8—C9	1.340 (2)
N2—C11	1.140 (3)		
C9—O1—N1	108.08 (12)	C9—C8—C7	104.2 (2)
C7—N1—O1	105.54 (13)	C8—C9—O1	110.52 (14)
N1—C7—C8	111.71 (14)	N2—C11—C10	179.2 (2)
C8—C7—C4	128.72 (15)		
C3—C4—C7—C8	33.6 (2)	C8—C9—C10—C11	10.4 (3)

Refinement was on F^2 for all reflections except for three flagged by the user for potential systematic errors. The temperature of the crystal was controlled using the Oxford Cryosystem Cryostream Cooler (Cosier & Glazer, 1986). H atoms were added at calculated positions and refined using a riding model. Anisotropic displacement parameters were used for all non-H atoms, while H atoms were given isotropic displacement parameters equal to 1.2 (or 1.5 for methyl H atoms) times the equivalent isotropic displacement parameter of their attached atom.

Data collection: Siemens *P3R3* system. Cell refinement: Siemens *P3R3* system. Data reduction: *SHELXTL-Plus* (Sheldrick, 1990). Program(s) used to solve structure: *SHELXTL-Plus*. Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *SHELXTL-Plus*. Software used to prepare material for publication: *SHELXL93*.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and torsion angles have been deposited with the IUCr (Reference: BM1078). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Bis[5,5-bis(4-methoxyphenyl)-3,3-dimethyl-2-tetrahydrofuranyl] Ether

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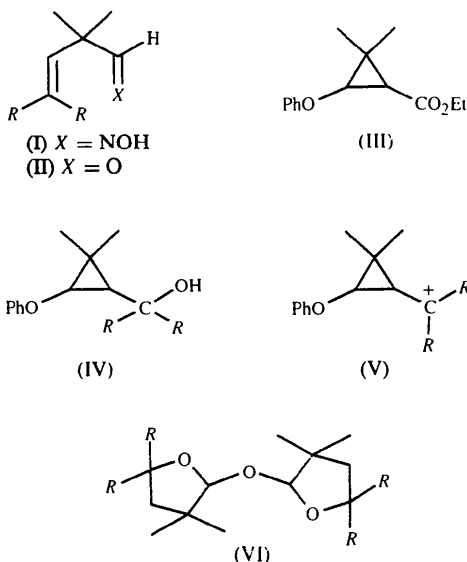
Abstract

(2,2-Dimethyl-3-phenoxycyclopropanyl)bis(*p*-methoxyphenyl)methanol gave the title compound, $C_{40}H_{46}O_7$, an oxygen-bridged dimer, under conditions which yielded monomeric aldehydes from alcohols containing other substituents.

Comment

We are currently investigating the photochemical reactivity of a number of β,γ-unsaturated oxime derivatives, (I), under sensitized conditions using an electron-accepting sensitizer. The starting materials for this study are β,γ-unsaturated aldehydes, (II), readily made from cyclopropane esters, (III) (Julia & Baillarge, 1966; Zimmerman & Pratt, 1970). The use of a Grignard reagent converts the esters to the alcohols, (IV), which are then subjected to acid-induced ring opening. With the $R = C_6H_5$, *p*-$^tBuC_6H_4$, *p*-BrC_6H_4, *p*-ClC_6H_4 and *p*-$CH(CH_3)_2C_6H_4$ derivatives of (IV), this ring opening occurs readily. When *p*-cyanophenyl groups are the substituents [(IV); $R = p$-CNC_6H_4], the ring opening, carried out using a mixture of acetone, concentrated hydrochloric acid and water (6:3:1) at reflux for 12 h, is an extremely slow process, presumably because conversion to the cation (V) is unfavourable. The *p*-methoxyphenyl derivative [(IV); $R = p$-$MeOC_6H_4$], however, under the usual conditions (mixture of acetone, con-

(I) X = NOH
(II) X = O

(III)

(IV)

(V)

(VI)

centrated hydrochloric acid and water in a 4:2:1 ratio stirred at room temperature for 3 h) gave a white crystalline compound which was deposited rapidly on the sides of the flask.

It was clear from the NMR spectra that this compound was not the expected aldehyde [(II); $R = p$-MeOC$_6$H$_4$]. The identity of this product was difficult to establish from conventional techniques and even the mass spectrum provided no assistance. The crystal structure showed the product to be an oxygen-bridged dimer, (VI).

Fig. 1 shows that compound (VI) has an approximate molecular twofold axis through the O24 atom. The greatest deviation from twofold symmetry is in the methoxy groups at C11 and C41. The methoxy C15 atom is in the plane of its attached phenyl group and on the same side as C10, whereas the C45 atom is
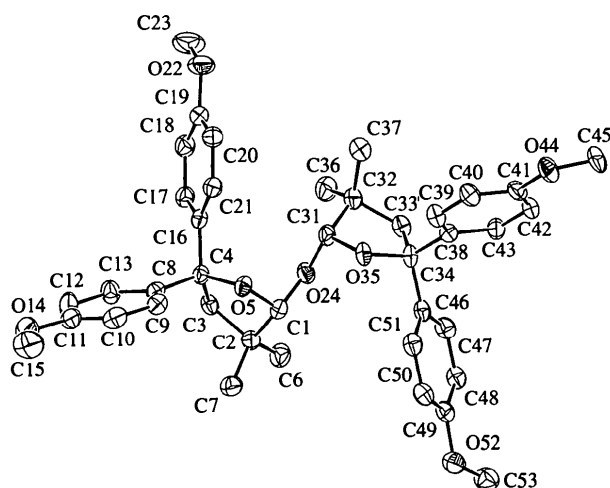
0.151 (5) Å out of its corresponding plane and faces the C42 atom. In the five-membered rings, atoms C1 and C31 are 0.571 (3) and 0.519 (3) Å, respectively, out of the planes defined by C2–C4, O5 and C32–C34, O35. There are no unusual interatomic distances or angles and no short intermolecular contacts.

Experimental

After conventional work-up and chromatography, the microcrystalline compound was dissolved in diethyl ether/hexane (1:1) at room temperature. The solvent was then allowed to evaporate slowly over a period of about a week. This yielded the product as white needles which were removed by filtration and washed with hexane. ^{1}H NMR (CDCl$_3$): δ 7.10–6.70 (16H, *m*, aromatic), 5.15 (2H, *s*, HCO), 3.75 (6H, *s*, OCH$_3$), 3.70 (6H, *s*, OCH$_3$), 2.50 (4H, *dd*, J_{AB} = 10.70 Hz, CH$_2$), 0.70 (6H, *s*, CH$_3$), 0.50 (6H, *s*, CH$_3$); ^{13}C NMR (CDCl$_3$): δ 157.0–126.1 (aromatic), 113.3 (OCH$_3$), 113.1 (OCH$_3$), 104.2 (OCO), 87.7 (CPh$_2$), 51.2 (CH$_2$), 44.2 [C(CH$_3$)$_2$], 26.0 (CH$_3$), 22.0 (CH$_3$); MS [EM, *m/z* (%)]: 327 (22), 311 (95), 281 (100), 267 (18), 243 (28), 227 (50).

Crystal data

C$_{40}$H$_{46}$O$_7$	Mo $K\alpha$ radiation
M_r = 638.77	λ = 0.71069 Å
Monoclinic	Cell parameters from 250
$P2_1/n$	reflections
a = 15.2841 (11) Å	θ = 2–25°
b = 8.3869 (13) Å	μ = 0.081 mm^{-1}
c = 28.3216 (9) Å	T = 150 (2) K
β = 102.104 (14)°	Block
V = 3549.7 (6) Å^3	0.32 × 0.28 × 0.26 mm
Z = 4	Colourless
D_x = 1.195 Mg m^{-3}	
D_m not measured	

Data collection

Enraf–Nonius CAD-4 FAST diffractometer	R_{int} = 0.0686
Area detector scans	θ_{max} = 25.11°
Absorption correction: none	h = −15 → 16
	k = −6 → 9
11 437 measured reflections	l = −29 → 31
5376 independent reflections	Standard reflections: see text
3159 observed reflections	
[$I > 2\sigma(I)$]	

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max}$ = 0.006
$R(F)$ = 0.0449	$\Delta\rho_{max}$ = 0.230 e Å^{-3}
$wR(F^2)$ = 0.1066	$\Delta\rho_{min}$ = −0.214 e Å^{-3}
S = 0.822	Extinction correction: none
5367 reflections	Atomic scattering factors
458 parameters	from *International Tables*
H atoms refined as riding model	*for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)
$w = 1/[\sigma^2(F_o^2) + (0.038P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$	

Fig. 1. A perspective view of (VI) with displacement ellipsoids plotted at the 50% probability level.

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}
C1	0.9658 (2)	0.8151 (3)	0.21391 (9)	0.0291 (6)
C2	1.0374 (2)	0.9023 (3)	0.24987 (9)	0.0287 (6)
C3	1.1166 (2)	0.7921 (2)	0.24889 (9)	0.0280 (6)
C4	1.0756 (2)	0.6231 (2)	0.24006 (8)	0.0251 (6)
O5	0.97959 (10)	0.6514 (2)	0.22509 (6)	0.0278 (4)
C6	1.0527 (2)	1.0723 (3)	0.23548 (10)	0.0398 (7)
C7	1.0120 (2)	0.8997 (3)	0.29962 (9)	0.0383 (7)
C8	1.0907 (2)	0.5195 (2)	0.28544 (9)	0.0266 (6)
C9	1.0212 (2)	0.4450 (2)	0.30093 (9)	0.0321 (6)
C10	1.0364 (2)	0.3472 (3)	0.34192 (10)	0.0381 (7)
C11	1.1220 (2)	0.3251 (3)	0.36762 (10)	0.0379 (7)
C12	1.1927 (2)	0.3993 (3)	0.35295 (10)	0.0447 (7)
C13	1.1769 (2)	0.4944 (3)	0.31226 (9)	0.0350 (7)
O14	1.14479 (15)	0.2321 (2)	0.40857 (7)	0.0593 (6)
C15	1.0736 (2)	0.1551 (3)	0.42497 (11)	0.0668 (11)
C16	1.1064 (2)	0.5327 (2)	0.19951 (9)	0.0257 (6)
C17	1.1872 (2)	0.5587 (3)	0.18668 (9)	0.0309 (6)
C18	1.2122 (2)	0.4769 (3)	0.14900 (9)	0.0349 (7)
C19	1.1554 (2)	0.3648 (3)	0.12364 (9)	0.0338 (7)
C20	1.0741 (2)	0.3335 (3)	0.13656 (9)	0.0340 (7)
C21	1.0504 (2)	0.4159 (3)	0.17368 (9)	0.0290 (6)
O22	1.17201 (13)	0.2783 (2)	0.08525 (7)	0.0498 (5)
C23	1.2537 (2)	0.3098 (4)	0.07091 (12)	0.0690 (10)
O24	0.97876 (11)	0.8500 (2)	0.16651 (6)	0.0317 (4)
C31	0.9277 (2)	0.7562 (3)	0.12933 (9)	0.0309 (6)
C32	0.9510 (2)	0.8017 (3)	0.08102 (9)	0.0337 (6)
C33	0.8913 (2)	0.9490 (3)	0.06825 (9)	0.0332 (7)
C34	0.8092 (2)	0.9209 (3)	0.09106 (9)	0.0284 (6)
O35	0.83503 (11)	0.7860 (2)	0.12377 (6)	0.0318 (4)
C36	1.0500 (2)	0.8381 (3)	0.08446 (10)	0.0469 (8)
C37	0.9223 (2)	0.6645 (3)	0.04481 (10)	0.0455 (8)
C38	0.7251 (2)	0.8709 (3)	0.05465 (9)	0.0283 (6)
C39	0.6860 (2)	0.7209 (3)	0.05677 (9)	0.0337 (7)
C40	0.6110 (2)	0.6755 (3)	0.02406 (9)	0.0348 (7)
C41	0.5715 (2)	0.7781 (3)	−0.01245 (9)	0.0315 (6)
C42	0.6080 (2)	0.9273 (3)	−0.01514 (9)	0.0338 (7)
C43	0.6843 (2)	0.9716 (3)	0.01813 (9)	0.0322 (7)
O44	0.49594 (12)	0.7214 (2)	−0.04301 (6)	0.0441 (5)
C45	0.4594 (2)	0.8158 (3)	−0.08425 (10)	0.0505 (8)
C46	0.7871 (2)	1.0605 (3)	0.12145 (9)	0.0270 (6)
C47	0.8071 (2)	1.2178 (3)	0.11305 (9)	0.0337 (7)
C48	0.7847 (2)	1.3420 (3)	0.14122 (9)	0.0325 (6)
C49	0.7409 (2)	1.3095 (3)	0.17776 (9)	0.0307 (6)
C50	0.7178 (2)	1.1530 (3)	0.18583 (9)	0.0339 (7)
C51	0.7407 (2)	1.0319 (3)	0.15792 (9)	0.0330 (7)
O52	0.71592 (12)	1.4218 (2)	0.20798 (6)	0.0393 (5)
C53	0.7177 (2)	1.5846 (3)	0.19314 (10)	0.0465 (8)

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

C1—O5	1.415 (3)	O24—C31	1.411 (3)
C1—O24	1.428 (3)	C31—O35	1.415 (3)
C1—C2	1.517 (3)	C31—C32	1.532 (3)
C2—C3	1.529 (3)	C32—C33	1.534 (3)
C3—C4	1.549 (3)	C33—C34	1.545 (3)
C4—O5	1.459 (3)	C34—O35	1.463 (3)
O5—C1—O24	111.4 (2)	O24—C31—O35	111.6 (2)
O5—C1—C2	105.4 (2)	O24—C31—C32	109.4 (2)
O24—C1—C2	108.1 (2)	O35—C31—C32	105.8 (2)
C1—C2—C3	99.1 (2)	C31—C32—C33	99.9 (2)
C2—C3—C4	105.1 (2)	C32—C33—C34	105.9 (2)
O5—C4—C3	104.3 (2)	O35—C34—C33	104.3 (2)
C1—O5—C4	108.4 (2)	C31—O35—C34	109.8 (2)
C31—O24—C1	115.1 (2)		

Conventional diffraction standards were not used. The consistency was checked from successive frames of the area detector and no decay was noted.

Data collection: *MADNES* (Enraf–Nonius, 1990). Cell refinement: *MADNES*. Data reduction: *MADNES*. Program(s)

used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *PLATON*92 (Spek, 1992a) and *PLUTON*92 (Spek, 1992b). Software used to prepare material for publication: *SHELXL*93.

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2,10-Dichloro-6-(2,4-dimethylphenoxy)-dibenzo[d,g][1,3,6,2]dioxathiaphosphocine 6-Sulfide

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Abstract

In the crystal structure of the title compound, $C_{20}H_{15}Cl_2O_3PS_2$, the dioxathiaphosphocine ring adopts a boat–chair conformation, with the phosphoryl sulfide group axial and the phenoxy group equatorial. The planar chlorobenzene groups fused to the heterocyclic ring form an angle of 67.90 (10)° with one another.