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(*S*),(*E*)-5-Methoxycarbonyl-2-triphenylmethylaminohex-4-en-4-olide†

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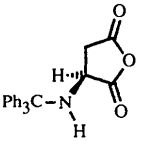
Abstract

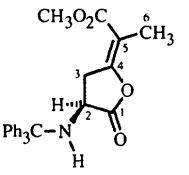
The title compound, $C_{27}H_{25}NO_4$, is the major product of the Wittig reaction of (*S*)-*N*-triphenylmethylaspartic anhydride with the stabilized ylide $Ph_3P{=}C(Me)CO_2Me$. The crystal structure determination unambiguously confirms the *E* configuration of the C4=C5 double bond and shows that the molecule, with the exception of the triphenylmethylamino moiety, adopts an overall planar conformation.

Comment

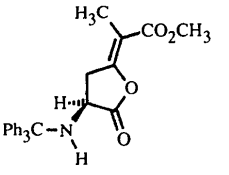
We have recently shown that the readily available (*S*)-*N*-triphenylmethylaspartic anhydride, (1), can be applied in the asymmetric synthesis of amino acid and peptide derivatives through its reactions with a variety of nucleophiles (Athanassopoulos, Tzavara, Papaioannou, Sindona & Maia, 1995). In particular, Wittig reaction of the anhydride (1) with the stabilized ylide $Ph_3P{=}C(Me)CO_2Me$ produces a mixture of the isomeric enollactones (2) and (3) in the ratio 6:1.7. The assignment of the configuration of their C=C double bond was based solely on the magnitude of the homoallylic couplings between the H(C3) and H(C6) protons. In this paper, we describe the crystal structure of the title enollactone, (2), which shows unambiguously that the C4=C5 double bond of the major product of the above-mentioned Wittig reaction has the *E* configura-



(1)



(2)



(3)

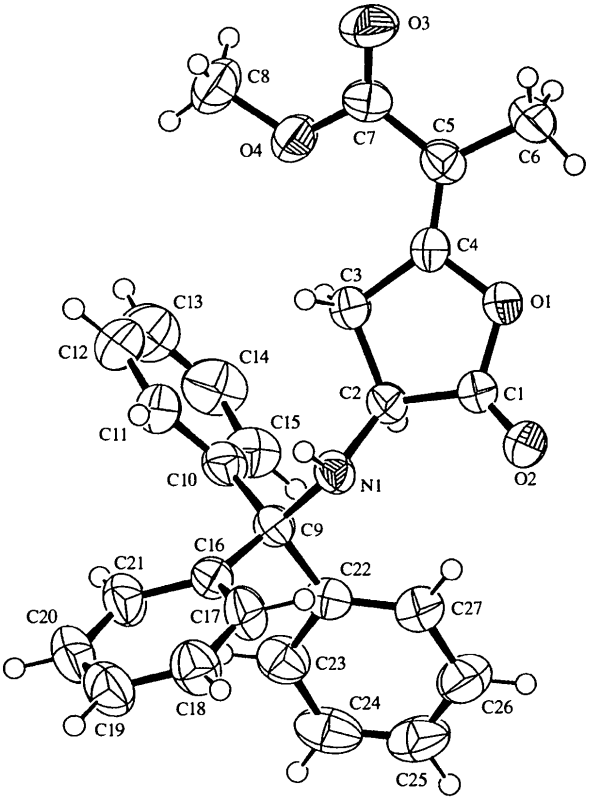


Fig. 1. Molecular structure with atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are represented by spheres of arbitrary size.

† Alternative nomenclature: methyl 2-[2-oxo-3-(triphenylmethylamino)-tetrahydrofuran-5-ylidene]propanoate.

tion, in agreement with previously reported proton NMR data.

The distances and angles of the core enollactone moiety are comparable to those reported for a similar molecule (Begley, Gedge, Knight & Pattenden, 1979). With the exception of the triphenylmethylamino moiety, the molecule shows overall planarity as expected for such a conjugated system. The triphenylmethyl moiety adopts the propeller-like conformation which is the established way of reducing steric interaction between the phenyl rings in this group (Destro, Pilati & Simonetta, 1980). There are no hydrogen bonds. Fig. 1 depicts the correct absolute configuration of the molecule which was assigned to agree with the known chirality of (*S*)-*N*-triphenylmethylaspartic anhydride from which (2) was synthesized. As collected, the X-ray data did not allow the determination of the absolute configuration.

Experimental

The Wittig reagent $Ph_3P{=}C(Me)CO_2Me$ (1.11g, 3.2 mmol) was added to a solution of anhydride (1) (1.00g, 2.8 mmol) in dichloromethane (10 ml) and the resulting solution was kept at ambient temperature for 20 h. The solvent was removed under reduced pressure and the resulting oily residue was taken up in ethyl acetate and washed sequentially with 5% aqueous $NaHCO_3$ and water. The organic phase was dried (Na_2SO_4) and the solvent removed to leave a residue which was subjected to flash column chromatography, using the solvent system petroleum ether 40–60°/ethyl acetate (8.5:1.5) as the eluant. The fractions with R_f 0.49 for the same solvent system were pooled and gave crystalline enollactone (2) (0.72 g, 60%) on evaporation of the solvents. Crystals suitable for X-ray analysis were obtained by recrystallization from diethyl ether/hexane.

Crystal data

$C_{27}H_{25}NO_4$
M_r = 427.48
Orthorhombic
$P2_12_12_1$
a = 10.806 (1) Å
b = 21.947 (4) Å
c = 9.614 (4) Å
V = 2280.0 (11) Å^3
Z = 4
D_x = 1.245 Mg m^{-3}
D_m not measured

Cu $K\alpha$ radiation
λ = 1.5418 Å
Cell parameters from 25 reflections
θ = 15.4–24.4°
μ = 0.672 mm^{-1}
T = 293 (2) K
Prism
0.32 × 0.27 × 0.16 mm
Colourless

Data collection

Rigaku AFC-5*R* diffractometer
ω–2θ scans
Absorption correction: none
2069 measured reflections
2069 independent reflections
1925 observed reflections [$I > 2\sigma(I)$]

θ_{max} = 62.08°
$h = 0 \rightarrow 12$
$k = 0 \rightarrow 25$
$l = 0 \rightarrow 11$
3 standard reflections monitored every 147 reflections
intensity decay: 8.3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.0347
$wR(F^2)$ = 0.0977
S = 1.045
2069 reflections
298 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0488P)^2 + 0.3013P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = −0.001
$\Delta\rho_{max}$ = 0.13 e Å^{-3}
$\Delta\rho_{min}$ = −0.13 e Å^{-3}

Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0080 (5)
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)
Absolute configuration: Flack (1983)
Flack parameter = 0.5 (4)

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

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

	x	y	z	U_{eq}
C1	0.2494 (2)	0.87783 (12)	0.8303 (3)	0.0480 (6)
C2	0.3717 (2)	0.86548 (11)	0.8999 (3)	0.0424 (6)
C3	0.3549 (2)	0.89287 (12)	1.0453 (3)	0.0456 (6)
C4	0.2178 (2)	0.90238 (11)	1.0589 (3)	0.0428 (6)
O1	0.1619 (2)	0.88950 (9)	0.9314 (2)	0.0511 (5)
O2	0.2211 (2)	0.87788 (11)	0.7111 (2)	0.0660 (6)
C5	0.1453 (2)	0.92178 (11)	1.1612 (3)	0.0469 (6)
C6	0.0066 (3)	0.9251 (2)	1.1488 (3)	0.0644 (8)
C7	0.1978 (3)	0.94558 (12)	1.2907 (3)	0.0488 (6)
O3	0.1431 (2)	0.97763 (10)	1.3707 (2)	0.0757 (7)
O4	0.3155 (2)	0.92932 (9)	1.3097 (2)	0.0585 (5)
C8	0.3779 (3)	0.9497 (2)	1.4328 (3)	0.0756 (10)
N1	0.4749 (2)	0.88568 (10)	0.8152 (2)	0.0428 (5)
C9	0.5906 (2)	0.84913 (11)	0.8212 (3)	0.0429 (6)
C10	0.6184 (2)	0.83265 (12)	0.9738 (3)	0.0488 (6)
C11	0.6601 (3)	0.8775 (2)	1.0646 (3)	0.0596 (7)
C12	0.6716 (3)	0.8661 (2)	1.2056 (3)	0.0786 (11)
C13	0.6395 (4)	0.8099 (2)	1.2595 (4)	0.0889 (12)
C14	0.5984 (4)	0.7652 (2)	1.1710 (4)	0.0806 (11)
C15	0.5885 (3)	0.77609 (14)	1.0296 (3)	0.0629 (8)
C16	0.6924 (2)	0.88774 (11)	0.7522 (3)	0.0442 (6)
C17	0.6643 (2)	0.92185 (12)	0.6352 (3)	0.0543 (7)
C18	0.7539 (3)	0.95237 (15)	0.5617 (3)	0.0646 (8)
C19	0.8756 (3)	0.94934 (15)	0.6034 (4)	0.0682 (9)
C20	0.9055 (3)	0.91604 (15)	0.7189 (4)	0.0680 (9)
C21	0.8154 (2)	0.88548 (14)	0.7929 (3)	0.0573 (7)
C22	0.5772 (3)	0.79220 (11)	0.7280 (3)	0.0464 (6)
C23	0.6781 (3)	0.75346 (12)	0.7138 (3)	0.0581 (7)
C24	0.6732 (4)	0.70419 (13)	0.6229 (4)	0.0706 (10)
C25	0.5681 (4)	0.69187 (15)	0.5502 (3)	0.0705 (9)
C26	0.4679 (4)	0.7296 (2)	0.5638 (3)	0.0718 (9)
C27	0.4724 (3)	0.78001 (13)	0.6511 (3)	0.0554 (7)

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

C1—O2	1.186 (3)	C4—C5	1.328 (4)
C1—O1	1.380 (3)	C4—O1	1.395 (3)
C1—C2	1.506 (4)	C5—C7	1.465 (4)
C2—N1	1.450 (3)	C5—C6	1.506 (4)
C2—C3	1.532 (4)	C7—O3	1.198 (3)
C3—C4	1.502 (3)		
O1—C1—C2	108.7 (2)	C1—O1—C4	111.1 (2)
C1—C2—C3	103.4 (2)	C4—C5—C7	121.0 (2)
C4—C3—C2	104.5 (2)	C4—C5—C6	123.0 (3)
C5—C4—O1	117.4 (2)	C7—C5—C6	115.8 (2)
C5—C4—C3	133.8 (2)	C2—N1—C9	117.4 (2)
O1—C4—C3	108.8 (2)		
O2—C1—C2—N1	33.1 (4)	O1—C4—C5—C6	5.4 (4)
N1—C2—C3—C4	139.4 (2)	C3—C4—C5—C6	−177.8 (3)
C1—C2—C3—C4	15.0 (3)	C4—C5—C7—O3	159.9 (3)
C5—C4—O1—C1	171.9 (2)		

H atoms were placed geometrically and thereafter allowed to ride on their parent atoms with common isotropic displacement parameters (U_{iso} = 0.08 Å^2). For the H atoms of the C6 methyl group, the torsion angle was also refined (U_{iso} = 0.13 Å^2). The H atom on N1 was located from a difference map and refined isotropically. Programs used include *PARST* (Nardelli, 1983).

Data collection: *TEXSAN* (Molecular Structure Corporation, 1985). Cell refinement: *TEXSAN*. Data reduction: *TEXSAN*. Program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *PLATON* (Spek, 1990). Software used to prepare material for publication: *SHELXL*93.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BM1098). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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2,4,6-Tri-*O*-benzyl-*myo*-inositol 1,3,5-Tris-(dibenzylphosphate)

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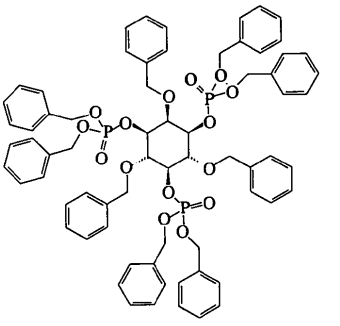
Abstract

This paper reports the crystal structure of 2,4,6-tri-*O*-benzyl-*myo*-inositol 1,3,5-tris(dibenzylphosphate), $C_{69}H_{69}O_{15}P_3$. The X-ray analysis reveals a cyclohexyl ring in a chair conformation with five substituents in equatorial orientations and one in an axial orientation.

Comment

The title compound, (I), was investigated as part of a study on the regioselective phosphorylation of *myo*-inositol and of intramolecular interactions in this series of compounds related to biological intracellular carriers. Structural data are very scarce on these analogues (*i.e.* on *myo*-inositol hexaphosphate or tri- and tetraphosphates) (Blank, Pletcher & Sax, 1985). These interactions induce conformation and inter-site hydrogen-bond changes which are pH dependent. We reported recently



(I)

on NMR investigations of conformational variations with pH (Brigando, Mossoyan, Favier & Benlian, 1995) and on the influence of intramolecular labile hydrogen bonds (Brigando & Mossoyan, 1996). It appears that certain chemical shifts occur when the pH is raised, by the H1–H6 protons of the *myo*-inositol ring C atoms, which could be assigned to the direct through-space interaction with the vicinal phosphate-O atom. This is observed in aqueous and mixed-solvent solution. It appears that, even in the case of esters, the phosphorylation on the 1, 3 and 5 positions has a noticeable but non-uniform influence on the vicinal C2, C4 and C6 centres. This is sustained by comparison with the structure of the non-phosphorylated molecule (Graingeot, Brigando & Benlian, 1996). The phosphorylation is the crucial step of the synthesis of *myo*-inositol trisphosphates. The structure of (I) was determined by X-ray diffraction. An *ORTEP*II (Johnson, 1976) view is shown in Fig. 1.

The molecule assumes a chair conformation with three dibenzyl phosphate groups at the C1, C3 and C5 positions. The three other substituents on the central ring are benzyloxy groups (at the C2, C4 and C6 positions). The only substituent in an axial position is the benzyloxy group on C2, the others are in equatorial positions. The stereochemistry of the central ring is shown in Fig. 2.

The adoption of these orientations by the substituents appears to have been determined by the requirement of minimum steric interactions. Two remarkable features of this structure are worth a closer look. One is the relative mobility of the outer rims of the benzyl groups in the structure as shown by the U_{eq} values (>0.12)