

Experimental

The title compound was synthesized by Stewart N. Thomas under the supervision of Professor A. L. Ternay Jr.

Crystal data

$C_{12}H_6Cl_2S_2$
 $M_r = 285.19$
 Monoclinic
 $I2/a$
 $a = 21.311(4) \text{ \AA}$
 $b = 3.9080(8) \text{ \AA}$
 $c = 27.581(6) \text{ \AA}$
 $\beta = 97.49(3)^\circ$
 $V = 2277.4(8) \text{ \AA}^3$
 $Z = 8$
 $D_x = 1.664 \text{ Mg m}^{-3}$
 D_m not measured

Mo $K\alpha$ radiation
 $\lambda = 0.71073 \text{ \AA}$
 Cell parameters from 45 reflections
 $\theta = 21.6\text{--}29.0^\circ$
 $\mu = 0.900 \text{ mm}^{-1}$
 $T = 163(2) \text{ K}$
 Needle
 $0.25 \times 0.16 \times 0.10 \text{ mm}$
 Colorless

Data collection

Syntex $P2_1$ diffractometer
 ω scans
 Absorption correction:
 analytical from crystal shape
 $T_{\min} = 0.82$, $T_{\max} = 0.91$
 2598 measured reflections
 2598 independent reflections

2146 reflections with
 $I > 2\sigma(I)$
 $\theta_{\max} = 27.51^\circ$
 $h = -26 \rightarrow 27$
 $k = -4 \rightarrow 5$
 $l = -35 \rightarrow 7$
 4 standard reflections
 every 96 reflections
 intensity decay: $< 1\%$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.032$
 $wR(F^2) = 0.085$
 $S = 1.05$
 2597 reflections
 169 parameters
 H atoms: see below
 $w = 1/[\sigma^2(F_o^2) + (0.035P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.39 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.41 \text{ e \AA}^{-3}$
 Extinction correction: none
 Scattering factors from
International Tables for Crystallography (Vol. C)

The C—H distances range from 0.91(2) to 0.95(2) Å, while the C—C—H angles range from 118.4(1) to 121.6(1)°. The U_{iso} values of the H atoms vary from 0.0275(5) to 0.046(7) Å².

Data collection: Syntex $P2_1$ software. Cell refinement: *LSCAL* (Harlow, 1975). Data reduction: *INCON* (Riley & Davis, 1976). Program(s) used to solve structure: *SHELXL93* (Sheldrick, 1993). Program(s) used to refine structure: *SHELXL93*. Molecular graphics: *SHELXL93*. Software used to prepare material for publication: *SHELXL93*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1346). Services for accessing these data are described at the back of the journal.

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(S),(E)-5-Methoxycarbonyl-3-triphenylmethylaminohex-4-en-4-olide†

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Abstract

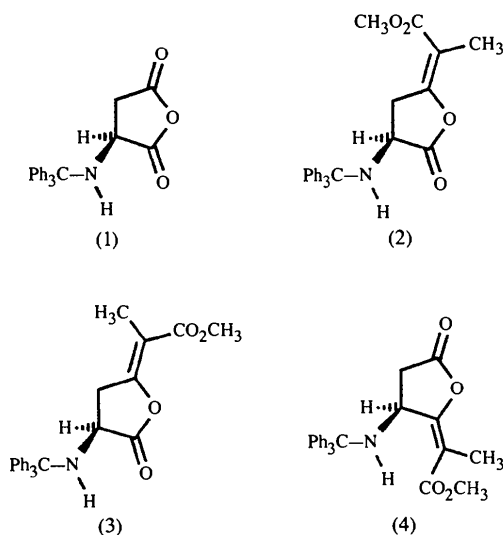
The title compound, $C_{27}H_{25}NO_4$, is the minor product of the Wittig reaction of (S)-N-triphenylmethylaspartic anhydride with the stabilized ylide $\text{Ph}_3\text{P}=\text{C}(\text{Me})\text{CO}_2\text{Me}$. The crystal structure determination unambiguously shows that this product is not the originally proposed Z isomer of the major product (S),(E)-5-methoxycarbonyl-2-triphenylmethylaminohex-4-en-4-olide, but the alternative α -adduct, also with an E configuration at the C4=C5 double bond.

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 (Athanasopoulos *et al.*, 1995). In particular, the Wittig reaction of anhydride (1) with the stabilized ylide $\text{Ph}_3\text{P}=\text{C}(\text{Me})\text{CO}_2\text{Me}$ produced a mixture of two isomeric enol-lactones in the ratio 6:1.7.

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

Although the structure of the major product was unambiguously shown by single-crystal X-ray crystallographic analysis (Nastopoulos *et al.*, 1996) to be the enol-lactone (2), the structure of the minor product was assigned as the enol-lactone (3) based solely on ¹H NMR arguments. As the two compounds gave unexpectedly different products upon reaction with dimethylamine (Papaioannou, 1997), we decided to determine the structure of the minor product by X-ray analysis. In this paper, we describe the crystal structure of the title enol-lactone, (4), which unambiguously shows that the minor product of the reaction is not the alternative geometric isomer (3) of the β -adduct, but indeed the α -adduct (4) of the Wittig reaction, and that the C4=C5 double bond also has an *E* configuration.



A comparison of the crystal structures of enol-lactones (2) and (4) can readily explain the observed multiplicity of the resonances attributed to protons H2 (a triplet with $J = 9.30$ Hz) and H3 (a doublet with $J = 7.35$ Hz) in the ¹H NMR spectra of these compounds. Thus, the dihedral angles H2—C2—C3—H3A and H2—C2—C3—H3B are 21.05 (9) and 142.10 (3)°, respectively in (2), and the corresponding dihedral angles H3—C3—C2—H2A and H3—C3—C2—H2B in (4) are 18.00 (10) and 102.77 (7)°, respectively. The triphenylmethyl moiety adopts a propeller-like conformation in order to minimize steric crowding of the phenyl rings in this group (Destro *et al.*, 1980), while the rest of the molecule shows overall planarity, as expected for such a conjugated system. The distances and angles of the core enol-lactone moiety are comparable to those reported for enol-lactone (2). There are no hydrogen bonds. The absolute configuration of the molecule, which was chosen to agree with the known chirality of (*S*)-*N*-triphenylmethylaspartic anhydride, (1), from which (4) was synthesized, is depicted in Fig. 1.

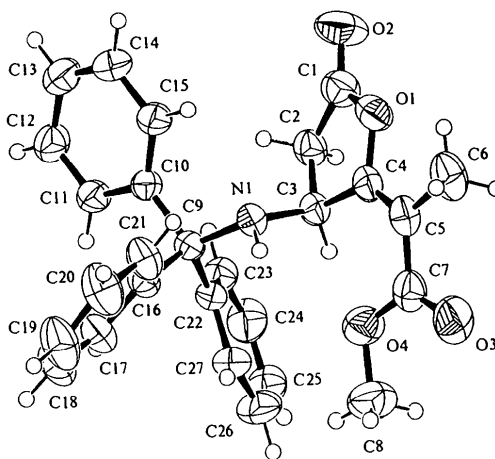


Fig. 1. View of the title molecule with the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are represented by spheres of arbitrary radii.

Experimental

The Wittig reagent Ph₃P=C(Me)CO₂Me (1.11 g, 3.2 mmol) was added to a solution of anhydride (1) (1.00 g, 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 NaHCO₃ and water. The organic phase was dried (Na₂SO₄) and the solvent removed to leave a residue which was subjected to flash column chromatography using the solvent system petroleum ether (313–333 K)/ethyl acetate (8.5:1.5) as the eluant. The fractions with $R_f = 0.60$, for the same solvent system, were pooled and gave crystalline enol-lactone (4) (0.20 g, 17%) on evaporation of the solvents. Crystals suitable for X-ray analysis were obtained by recrystallization from diethyl ether–hexane.

Crystal data

C₂₇H₂₅NO₄

$M_r = 427.48$

Monoclinic

$P2_1$

$a = 10.880$ (4) Å

$b = 8.875$ (3) Å

$c = 11.845$ (5) Å

$\beta = 100.89$ (6)°

$V = 1123.2$ (7) Å³

$Z = 2$

$D_x = 1.266$ Mg m⁻³

D_m not measured

Data collection

Philips PW1100 diffractometer updated by Stoe

ω -2 θ scans

Absorption correction: none

3477 measured reflections

3476 independent reflections

2542 reflections with

$I > 2\sigma(I)$

Mo $K\alpha$ radiation

$\lambda = 0.71069$ Å

Cell parameters from 32 reflections

$\theta = 10.4$ – 19.6 °

$\mu = 0.085$ mm⁻¹

$T = 293$ (2) K

Prism

$0.60 \times 0.40 \times 0.30$ mm

Colourless

$R_{int} = 0.024$

$\theta_{max} = 30.03$ °

$h = -15 \rightarrow 15$

$k = 0 \rightarrow 12$

$l = 0 \rightarrow 16$

3 standard reflections

frequency: 120 min

intensity decay: 2.5%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.061$
 $wR(F^2) = 0.142$
 $S = 1.153$
 3476 reflections
 294 parameters
 H atoms treated by a
 mixture of independent
 and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.1088P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.332 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.487 \text{ e } \text{\AA}^{-3}$
 Extinction correction: none
 Scattering factors from
International Tables for
Crystallography (Vol. C)

Table 1. Selected geometric parameters (\AA , $^\circ$)

C1—O2	1.183 (4)	C3—C4	1.517 (4)
C1—O1	1.380 (4)	C4—C5	1.340 (4)
C1—C2	1.476 (4)	C4—O1	1.382 (3)
C2—C3	1.527 (4)	C5—C7	1.473 (5)
C3—N1	1.484 (3)	C5—C6	1.515 (5)
O2—C1—O1	119.3 (3)	C4—C3—C2	101.9 (2)
O2—C1—C2	131.1 (3)	O1—C4—C3	109.1 (2)
O1—C1—C2	109.5 (3)	C1—O1—C4	110.7 (2)
C1—C2—C3	105.2 (2)	C3—N1—C9	118.5 (2)
C1—C2—C3—N1	94.9 (2)	C3—C4—C5—C6	-173.5 (3)
C1—C2—C3—C4	-17.8 (2)	C4—C5—C7—O3	163.3 (3)
N1—C3—C4—C5	77.0 (4)	C4—C3—N1—C9	-179.4 (2)

The absolute structure Flack (1983) parameter [$\chi = 1.8(17)$] was inconclusive; the absolute configuration was deduced from the known stereochemistry of the synthesis. H atoms were placed in calculated positions and thereafter allowed to ride on their parent atoms with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$, while methyl group H atoms were assigned $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$. For the H atoms of the C6 methyl group, the torsion angle was also refined. The H atom on N1 was located from a difference map and refined isotropically.

Data collection: *DIF4* (Stoe & Cie, 1987a). Cell refinement: *DIF4*. Data reduction: *REDU4* (Stoe & Cie, 1987b). Program used to solve structure: *SHELXS86* (Sheldrick, 1990). Program used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *PLATON* (Spek, 1990). Software used to prepare material for publication: *SHELXL93*. Other programs include *PARST* (Nardelli, 1983).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: AB1492). Services for accessing these data are described at the back of the journal.

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15,17-Di-2-propenylcalix[4]arene-25,26,27,28-tetrol: Self-Complexation and C—H···O Interactions

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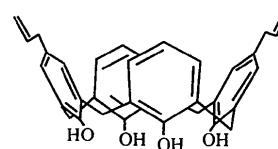
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Abstract

The crystal structure of 15,17-di-2-propenylcalix[4]arene-25,26,27,28-tetrol [systematic name: 15,17-di-2-propenylpentacyclo[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]octacosane-1(25),3,5,7(26),9,11,13(27),15,17,19(28),21,23-dodecaene-25,26,27,28-tetrol], $\text{C}_{34}\text{H}_{32}\text{O}_4$, was determined. The calix[4]arene molecule shows a cone conformation, stabilized by a ring-like hydrogen-bond pattern of the four hydroxyl H atoms. In the crystal structure, complexation of one of the propenyl side chains in the cavity of another calixarene molecule is found. The other side chain shows C—H···O interactions with a neighboring calixarene molecule.

Comment

Calix[4]arenes have received considerable attention in the field of supramolecular chemistry because they can form inclusion complexes with cations, anions or neutral molecules (Gutsche, 1989; Vicens & Böhmer, 1991; Böhmer, 1995). The conformation of calixarenes has been studied both in the solid state (Andreotti & Uguzzoli, 1991) and in solution (Groenen *et al.*, 1991). Four different conformations can be identified.



(I)

The title compound, (I), has a regular cone conformation (Fig. 1), stabilized by four hydrogen bonds connecting the O atoms in a ring-like fashion. Hydrogen-bond data are included in Table 1. The regularity of the conformation is evidenced by the distances between neighboring O atoms [2.661 (3), 2.642 (3), 2.659 (3) and