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

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

	x	y	z	U_{eq}
C(1)	0.07667 (18)	0.28196 (21)	0.30805 (15)	0.0414 (12)
C(2)	−0.01163 (17)	0.35408 (23)	0.22759 (15)	0.0497 (13)
C(3)	0.02621 (18)	0.36256 (24)	0.12066 (15)	0.0518 (13)
C(4)	0.14555 (18)	0.42841 (22)	0.12907 (14)	0.0434 (12)
C(5)	0.23452 (16)	0.34215 (20)	0.20246 (13)	0.0360 (11)
C(6)	0.35698 (17)	0.39795 (22)	0.20864 (14)	0.0419 (12)
C(7)	0.38607 (17)	0.52984 (21)	0.27399 (14)	0.0421 (12)
C(8)	0.33332 (17)	0.54353 (20)	0.37030 (14)	0.0355 (11)
C(9)	0.21532 (17)	0.47739 (21)	0.36962 (14)	0.0371 (12)
C(10)	0.20279 (15)	0.32846 (20)	0.31430 (13)	0.0335 (11)
C(11)	0.39058 (18)	0.61375 (22)	0.45178 (15)	0.0486 (13)
C(12)	0.34574 (21)	0.6341 (3)	0.55237 (16)	0.0663 (15)
C(13)	0.21702 (21)	0.6160 (3)	0.53733 (16)	0.0640 (15)
C(14)	0.18003 (20)	0.47775 (25)	0.47833 (16)	0.0578 (14)
C(15)	0.28031 (17)	0.21388 (21)	0.37415 (14)	0.0396 (11)
C(16)	0.33658 (22)	−0.03129 (24)	0.37017 (19)	0.0667 (16)
O(1)	0.04987 (13)	0.19434 (16)	0.36851 (11)	0.0630 (9)
O(2)	0.45437 (14)	0.61848 (17)	0.25206 (12)	0.0719 (10)
O(3)	0.34512 (12)	0.23023 (15)	0.45461 (10)	0.0600 (9)
O(4)	0.26837 (12)	0.08822 (14)	0.32253 (10)	0.0551 (9)

Table 2. *Geometric parameters* (Å, °)

C(1)—C(2)	1.501 (3)	C(8)—C(9)	1.515 (3)
C(1)—C(10)	1.532 (3)	C(8)—C(11)	1.326 (3)
C(1)—O(1)	1.2087 (24)	C(9)—C(10)	1.555 (3)
C(2)—C(3)	1.529 (3)	C(9)—C(14)	1.536 (3)
C(3)—C(4)	1.517 (3)	C(10)—C(15)	1.527 (3)
C(4)—C(5)	1.520 (3)	C(11)—C(12)	1.500 (3)
C(5)—C(6)	1.519 (3)	C(12)—C(13)	1.501 (4)
C(5)—C(10)	1.5635 (25)	C(13)—C(14)	1.522 (3)
C(6)—C(7)	1.497 (3)	C(15)—O(3)	1.1949 (23)
C(7)—C(8)	1.491 (3)	C(15)—O(4)	1.3420 (24)
C(7)—O(2)	1.2164 (24)	C(16)—O(4)	1.447 (3)
C(2)—C(1)—C(10)	117.41 (16)	C(8)—C(9)—C(14)	112.40 (16)
C(2)—C(1)—O(1)	121.86 (18)	C(10)—C(9)—C(14)	114.03 (16)
C(10)—C(1)—O(1)	120.68 (17)	C(1)—C(10)—C(5)	110.63 (14)
C(1)—C(2)—C(3)	112.51 (17)	C(1)—C(10)—C(9)	106.94 (15)
C(2)—C(3)—C(4)	111.16 (15)	C(1)—C(10)—C(15)	108.62 (15)
C(3)—C(4)—C(5)	111.27 (16)	C(5)—C(10)—C(9)	109.74 (15)
C(4)—C(5)—C(6)	113.52 (16)	C(5)—C(10)—C(15)	108.36 (15)
C(4)—C(5)—C(10)	112.30 (15)	C(9)—C(10)—C(15)	112.55 (14)
C(6)—C(5)—C(10)	110.46 (14)	C(8)—C(11)—C(12)	123.47 (20)
C(5)—C(6)—C(7)	115.72 (16)	C(11)—C(12)—C(13)	111.44 (17)
C(6)—C(7)—C(8)	117.23 (16)	C(12)—C(13)—C(14)	110.88 (19)
C(6)—C(7)—O(2)	121.25 (18)	C(9)—C(14)—C(13)	111.48 (18)
C(8)—C(7)—O(2)	121.43 (18)	C(10)—C(15)—O(3)	126.51 (18)
C(7)—C(8)—C(9)	117.95 (15)	C(10)—C(15)—O(4)	110.44 (15)
C(7)—C(8)—C(11)	118.98 (18)	O(3)—C(15)—O(4)	123.04 (18)
C(9)—C(8)—C(11)	123.07 (18)	C(15)—O(4)—C(16)	116.78 (16)
C(8)—C(9)—C(10)	112.31 (15)		

The structure was solved by the application of direct methods and refined using full-matrix least squares on *F*. All H-atom positional parameters were calculated and refined. Atomic scattering factors as stored in the *NRCVAX* program are those of Cromer & Waber (1974).

We thank Professor C. Spino (University of Victoria) for helpful discussions while preparing this manuscript.

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71215 (11 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: CD1041]

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Functionalized Hydrocarbons with Condensed Ring Skeletons. XV. A (Methoxymethoxymethyl)tricyclo-[9.4.0.0^{2,8}]pentadec-9-ene

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Abstract

The tricyclic title compound, (*trans-anti-cis*)-tetramethyl 1-(methoxymethoxymethyl)tricyclo[9.4.0.0^{2,8}]pentadec-9-ene-5,5,13,13-tetracarboxylate, $C_{26}H_{38}O_{10}$, has a *trans-anti-cis* stereochemistry. Ring *A* adopts a chair conformation, ring *B* a half chair and ring *C* a twist chair. The methoxymethoxymethyl substituent adopts a *gauche-gauche* conformation.

Comment

The [6.6.7] tricyclic condensed ring structures, although less frequent than the [6.6.5] and [6.6.6] ones, constitute the skeletons of numerous natural products like the stemodanes, kauranes, stachanes and aphidicolins (Devon & Scott, 1972; Kametani, 1983).

The transannular Diels–Alder (TDA) reaction was used to synthesize a [6.6.7] tricyclic compound (1) starting from a 15-membered ring macrocycle triene with the

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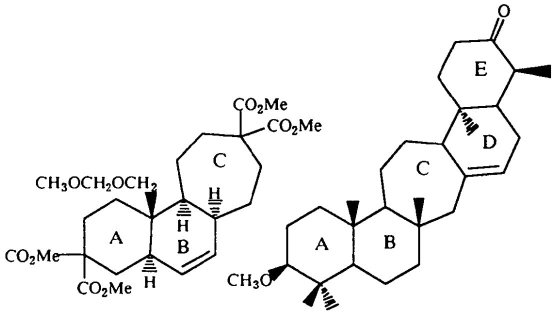
trans-trans-trans (*ttt*) geometry (Hall, Müller & Deslongchamps, 1992). These authors supplied us with a suitable crystal for X-ray diffraction analysis. In the transition-state intermediate, the macrocycle must adopt a boat-like conformation for the TDA reaction to take place.



(1) (2)

The *ttt* macrocycle can adopt two different conformations leading to two different racemic diastereoisomeric tricyclic products with the *trans-anti-cis* (*tac*) or *cis-anti-trans* (*cat*) stereochemistry. From molecular models it is shown that the *cat* (*exo*) transition state experiences steric interactions between the axially oriented methyl ester substituents at C(1) and C(8), and the newly formed double bond $\Delta^{12,13}$. The *tac* (*endo*) transition state does not experience these interactions and is favoured. Different ratios of *tac*/*cat* were obtained depending on the substituents at C(4) and C(5) with *tac* always the major product. We report herein the crystal structure of the major diastereoisomer, obtained from the transannular Diels-Alder reaction of the methoxymethoxymethyl-substituted tricycle, which confirms the *trans-anti-cis* stereochemistry (Fig. 1).

Ring *A* adopts a chair conformation, ring *B* a half chair. The seven-membered ring *C* adopts a slightly twisted chair conformation. This global conformation is similar to the previously reported [6.6.6] tricyclic compound with *tac* stereochemistry (Drouin, Michel, Xu & Deslongchamps, 1990) where *A*, *B* and *C* rings adopt the chair, half-chair and chair conformations, respectively. In the [6.6.7] tricyclic compounds, the *C* ring is usually bridged and frozen into a boat conformation. The title compound is similar to the serratene compound (2) in its non-bridged seven-membered ring *C* and most stable conformation (Haromy & Sundaralingam, 1982). Similarities can be observed only by comparing *A*, *B* and *C* rings of (1) with *E*, *D* and *C* rings of (2), the *trans-anti-trans* stereochemistry of the *ABC* moiety of (2) being non-superimposable to the *trans-anti-cis* stereochemistry of (1). This can be viewed in the stereodiagram of the corresponding molecular superposition of both [6.6.7] rings in Fig 2.

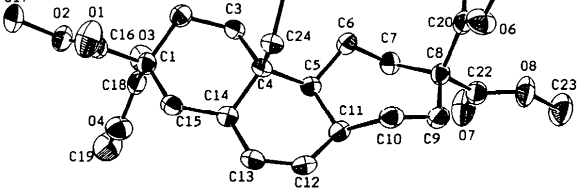


Fig. 1. *ORTEP*II perspective view (Johnson, 1976) of (1) with crystallographic numbering. Thermal ellipsoids are shown at 50% probability levels; H atoms are omitted for clarity.

The least-squares fitting was applied involving all the atoms of the tricyclic skeletons (*SYBYL*; Tripos Associates Inc., 1992). The twist-chair conformation observed for ring *C* is a consequence of steric hindrance by the C(4) substituent. This group is axial to rings *A* and *B*. Its conformation can be described as *trans*, *trans*, *gauche* and *gauche*. The respective torsion angles are: C(14)—C(4)—C(24)—O(9) = −156.5 (4), C(4)—C(24)—O(9)—C(25) = 169.0 (4), C(24)—O(9)—C(25)—O(10) = 70.7 (3) and O(9)—C(25)—O(10)—C(26) = 64.8 (3)°. No abnormally short intermolecular contacts were noted.

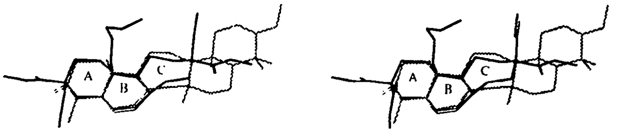


Fig. 2. Stereoview of the superposition of the *ABC*/*EDC* rings for (1) and (2), respectively.

Experimental

Crystal data

$C_{26}H_{38}O_{10}$
M_r = 510.58
Triclinic
$P\bar{1}$
a = 8.2844 (4) Å
b = 11.9757 (10) Å
c = 14.5732 (6) Å
α = 68.929 (5)°
β = 89.855 (4)°
γ = 71.337 (5)°
V = 1267.82 (13) Å^3
Z = 2

D_x = 1.337 Mg m^{-3}
Mo $K\alpha$ radiation
λ = 0.70930 Å
Cell parameters from 24 reflections
θ = 18.00-20.00°
μ = 0.10 mm^{-1}
T = 293 K
Regular shape
0.30 × 0.30 × 0.20 mm
Colorless

Data collection

Enraf-Nonius CAD-4 diffractometer
ω-2θ scans
Absorption correction: none
3516 measured reflections
3289 independent reflections
2179 observed reflections [$I_{\rm net} > 2.5\sigma(I_{\rm net})$]

$R_{\rm int}$ = 0.012
$\theta_{\rm max}$ = 22.42°
$h = -8 \rightarrow 8$
$k = 0 \rightarrow 12$
$l = -14 \rightarrow 15$
3 standard reflections frequency: 60 min intensity variation: none

Refinement

Refinement on F
Final $R = 0.039$
$wR = 0.028$
$S = 1.58$
2179 reflections
326 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F) + 0.0001(F^2)]$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.16$ e Å^{-3}
$\Delta\rho_{\min} = -0.16$ e Å^{-3}
Extinction correction: Larson (1970)
Extinction coefficient: 0.46 (3)

Data collection: *NRCCAD DATCOL* (Le Page, White & Gabe, 1986). Cell refinement: *NRCCAD TRUANG*. Data reduction: *NRCVAX DATRD2* (Gabe, Le Page, Charland, Lee & White, 1989). Program(s) used to solve structure: *NRCVAX SOLVER*. Program(s) used to refine structure: *NRCVAX LSTSQ*. Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *NRCVAX TABLES*.

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

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

	x	y	z	$U_{\rm eq}$
C(1)	0.6653 (4)	0.4703 (3)	0.71086 (20)	0.0314 (21)
C(2)	0.5902 (4)	0.5165 (3)	0.79310 (20)	0.0343 (21)
C(3)	0.6748 (3)	0.4204 (3)	0.89709 (19)	0.0302 (20)
C(4)	0.6607 (3)	0.2886 (3)	0.92098 (19)	0.0273 (20)
C(5)	0.7720 (3)	0.1905 (3)	1.01936 (19)	0.0272 (21)
C(6)	0.7334 (4)	0.2263 (3)	1.10971 (20)	0.0322 (20)
C(7)	0.8557 (4)	0.1325 (3)	1.20393 (19)	0.0335 (22)
C(8)	0.7948 (3)	0.0273 (3)	1.27388 (19)	0.0300 (20)
C(9)	0.7673 (4)	−0.0626 (3)	1.22688 (21)	0.0378 (21)
C(10)	0.6739 (4)	−0.0026 (3)	1.12094 (21)	0.0371 (22)
C(11)	0.7806 (3)	0.0509 (3)	1.04061 (20)	0.0305 (21)
C(12)	0.7487 (4)	0.0289 (3)	0.94863 (22)	0.0341 (23)
C(13)	0.7331 (4)	0.1123 (3)	0.85709 (21)	0.0346 (22)
C(14)	0.7381 (3)	0.2432 (3)	0.83835 (20)	0.0300 (21)
C(15)	0.6602 (3)	0.3363 (3)	0.73269 (20)	0.0331 (21)
C(16)	0.5507 (4)	0.5614 (3)	0.61346 (22)	0.0373 (24)
C(17)	0.5125 (4)	0.7444 (3)	0.46915 (21)	0.0507 (24)
C(18)	0.8468 (4)	0.4756 (3)	0.70287 (22)	0.0383 (23)
C(19)	1.1051 (4)	0.4117 (3)	0.6352 (3)	0.064 (3)
C(20)	0.6380 (4)	0.0898 (3)	1.31678 (21)	0.0360 (23)
C(21)	0.3575 (4)	0.1041 (3)	1.35578 (25)	0.060 (3)
C(22)	0.9344 (4)	−0.0563 (3)	1.36219 (22)	0.0382 (23)
C(23)	1.0014 (5)	−0.2151 (3)	1.52387 (23)	0.066 (3)
C(24)	0.4714 (4)	0.2962 (3)	0.92040 (20)	0.0315 (21)
C(25)	0.2013 (4)	0.4134 (3)	0.95040 (24)	0.048 (3)
C(26)	0.1833 (4)	0.2768 (3)	1.1099 (3)	0.065 (3)
O(1)	0.4150 (3)	0.55770 (21)	0.58961 (15)	0.0582 (17)
O(2)	0.61772 (25)	0.64784 (18)	0.55958 (13)	0.0409 (15)
O(3)	0.9063 (3)	0.53405 (22)	0.73586 (15)	0.0552 (19)
O(4)	0.9332 (3)	0.40789 (19)	0.65085 (15)	0.0494 (17)
O(5)	0.6373 (3)	0.16517 (22)	1.35290 (16)	0.0593 (20)
O(6)	0.5057 (3)	0.05277 (20)	1.31025 (15)	0.0492 (17)
O(7)	1.0804 (3)	−0.06065 (22)	1.36363 (16)	0.0693 (19)
O(8)	0.8763 (3)	−0.12896 (19)	1.43721 (14)	0.0504 (16)
O(9)	0.38043 (23)	0.38339 (18)	0.96452 (14)	0.0375 (15)
O(10)	0.1490 (3)	0.31120 (22)	1.00581 (17)	0.0561 (20)

Table 2. *Geometric parameters* (Å, °)

C(1)—C(2)	1.544 (4)	C(12)—C(13)	1.325 (4)
C(1)—C(15)	1.534 (4)	C(13)—C(14)	1.506 (4)
C(1)—C(16)	1.528 (4)	C(14)—C(15)	1.530 (4)
C(1)—C(18)	1.528 (4)	C(16)—O(1)	1.196 (4)
C(2)—C(3)	1.532 (4)	C(16)—O(2)	1.333 (4)
C(3)—C(4)	1.533 (4)	C(17)—O(2)	1.449 (3)
C(4)—C(5)	1.545 (4)	C(18)—O(3)	1.194 (4)
C(4)—C(14)	1.549 (4)	C(18)—O(4)	1.346 (4)
C(4)—C(24)	1.542 (4)	C(19)—O(4)	1.454 (4)
C(5)—C(6)	1.528 (4)	C(20)—O(5)	1.196 (4)
C(5)—C(11)	1.565 (4)	C(20)—O(6)	1.323 (4)
C(6)—C(7)	1.531 (4)	C(21)—O(6)	1.460 (4)
C(7)—C(8)	1.536 (4)	C(22)—O(7)	1.194 (4)
C(8)—C(9)	1.539 (4)	C(22)—O(8)	1.328 (4)
C(8)—C(20)	1.533 (4)	C(23)—O(8)	1.455 (4)
C(8)—C(22)	1.528 (4)	C(24)—O(9)	1.432 (3)
C(9)—C(10)	1.533 (4)	C(25)—O(9)	1.407 (4)
C(10)—C(11)	1.543 (4)	C(25)—O(10)	1.402 (4)
C(11)—C(12)	1.495 (4)	C(26)—O(10)	1.424 (4)
C(2)—C(1)—C(15)	109.69 (22)	C(5)—C(11)—C(12)	113.09 (22)
C(2)—C(1)—C(16)	107.40 (23)	C(10)—C(11)—C(12)	111.31 (22)
C(2)—C(1)—C(18)	109.22 (24)	C(11)—C(12)—C(13)	124.8 (3)
C(15)—C(1)—C(16)	108.56 (23)	C(12)—C(13)—C(14)	120.89 (24)
C(15)—C(1)—C(18)	112.58 (24)	C(4)—C(14)—C(13)	110.25 (22)
C(16)—C(1)—C(18)	109.24 (23)	C(4)—C(14)—C(15)	114.79 (22)
C(1)—C(2)—C(3)	112.41 (22)	C(13)—C(14)—C(15)	111.78 (22)
C(2)—C(3)—C(4)	113.78 (22)	C(1)—C(15)—C(14)	113.06 (22)
C(3)—C(4)—C(5)	111.38 (21)	C(1)—C(16)—O(1)	124.1 (3)
C(3)—C(4)—C(14)	106.54 (21)	C(1)—C(16)—O(2)	111.9 (3)
C(3)—C(4)—C(24)	110.84 (22)	O(1)—C(16)—O(2)	124.0 (3)
C(5)—C(4)—C(14)	106.28 (21)	C(1)—C(18)—O(3)	125.5 (3)
C(5)—C(4)—C(24)	112.28 (21)	C(1)—C(18)—O(4)	111.4 (3)
C(14)—C(4)—C(24)	109.23 (21)	O(3)—C(18)—O(4)	123.1 (3)
C(4)—C(5)—C(6)	115.14 (22)	C(8)—C(20)—O(5)	122.3 (3)
C(4)—C(5)—C(11)	113.46 (21)	C(8)—C(20)—O(6)	114.1 (3)
C(6)—C(5)—C(11)	111.98 (21)	O(5)—C(20)—O(6)	123.6 (3)
C(5)—C(6)—C(7)	113.65 (22)	C(8)—C(22)—O(7)	124.8 (3)
C(6)—C(7)—C(8)	116.37 (22)	C(8)—C(22)—O(8)	112.0 (3)
C(7)—C(8)—C(9)	113.81 (22)	O(7)—C(22)—O(8)	123.1 (3)
C(7)—C(8)—C(20)	108.31 (23)	C(4)—C(24)—O(9)	109.61 (21)
C(7)—C(8)—C(22)	108.33 (23)	O(9)—C(25)—O(10)	112.67 (24)
C(9)—C(8)—C(20)	114.24 (24)	C(16)—O(2)—C(17)	116.04 (23)
C(9)—C(8)—C(22)	105.95 (23)	C(18)—O(4)—C(19)	115.64 (24)
C(20)—C(8)—C(22)	105.72 (22)	C(20)—O(6)—C(21)	115.81 (24)
C(8)—C(9)—C(10)	117.69 (23)	C(22)—O(8)—C(23)	116.15 (24)
C(9)—C(10)—C(11)	114.21 (23)	C(24)—O(9)—C(25)	112.87 (21)
C(5)—C(11)—C(10)	115.84 (22)	C(25)—O(10)—C(26)	112.46 (23)

The structure was solved by the application of direct methods and refined using full-matrix least squares on F. All H-atom positional parameters were calculated and refined. Atomic scattering factors as stored in the *NRCVAX* program are those of Cromer & Waber (1974).

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71256 (14 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: CD1042]

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Ethynylenebis(2-methoxybenzene)

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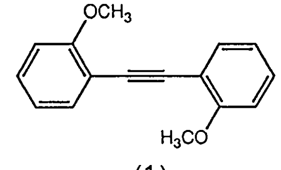
Abstract

The title compound is centrosymmetric, requiring *anti* methoxy groups about the ethynediyl link. The ethynyl bond length is 1.194 (2) Å; the ethynyl bond angle is 177.8 (1)°. The tolane ring is planar to within 0.0073 (13) Å, and the methoxy groups are almost coplanar with the ring, forming C—C—O—C torsion angles of magnitude −7.6 (2)°.

Comment

The title compound is an intermediate in the synthesis of diarylethynes that we designed to probe intramolecular recognition (Evans, Prince, Huang, Boss & Gandour, 1990). The determination of this structure contributes to our knowledge of the geometrical effects of various substituents in the *ortho* positions of diarylethynes and serves as a reference for molecular modeling studies. Our designs follow from Letsinger & Nazy (1959) who proposed that *o,o′*-disubstituted diarylethynes can be used as a framework to hold groups in ‘a prescribed geometry’.

Compound (1) was prepared by a modification of the procedure of Arcadi, Cacchi & Marinelli (1989). The reaction of 2-iodoanisole, 2-methoxyphenylethyne, tetrakis(triphenylphosphine)palladium(0), copper(I) iodide and diethylamine produced the title compound in good yield. Coleman, Holst & Maxwell (1936) first made the compound in a study of a new method for synthesizing tolanes.



(1)

A search of the January 1992 version of the Cambridge Structural Database (version 4.6; Allen, Kennard & Taylor, 1983) revealed one structure composed of a tolane backbone with oxygens in the *o,o′* positions (Evans, Horn, Fronczek & Gandour, 1990). That compound has all *ortho* positions substituted with three methoxy groups and a methoxycarbonyl. A comparison of the two molecules reveals that the three bond lengths of the ethynediyl link are identical. In the tetrasubstituted compound, the bond angles that are analogous to the C6—C7—C7′ bond angle in (1) differ – 175.0 (1) and 177.7 (1)°. The latter angle, which is on the side with two *ortho* methoxy groups, is identical to the C6—C7—C7′ bond angle in (1). The methoxy substituents display a slight deviation from planarity in relation to the phenyl ring with a C8—O1—C1—C2 torsion angle of −7.6 (2)°. The maximum deviation from planarity in the phenyl ring is 0.0073 (13) Å.

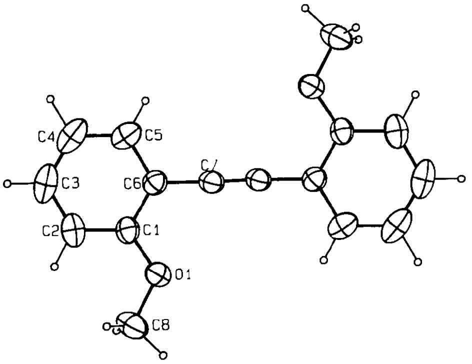


Fig. 1. *ORTEP* (Johnson, 1965) drawing of the title compound, with thermal ellipsoids drawn at the 40% probability level.

Experimental

Crystal data

$C_{16}H_{14}O_2$
M_r = 238.3
Orthorhombic

Cell parameters from 25 reflections
θ = 25-30°

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