

References

- DÍAZ, E., BARRIOS, H., VILLENA, R. & TOSCANO, R. A. (1991). *Acta Cryst. C* **47**, 2720–2723.
 DÍAZ, E., DOMÍNGUEZ, G. G., MANNINO, A., NEGRÓN, G. & JANKOWSKI, K. (1985). *Magn. Reson. Chem.* **23**, 494–502.

- DÍAZ, E., ONTIVEROS, G., SALAZAR, I., NEGRÓN, G. & JOSEPH-NATHAN, P. (1981). *Spectrochimica Acta Part A*, **37**, 569–573.
 SALAZAR, I. & DÍAZ, E. (1978). *Tetrahedron*, **35**, 815–818.
 SHELDRIK, G. M. (1983). *SHELXTL Users Manual*. Revision 4. Nicolet XRD Corporation, Madison, Wisconsin, USA.

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Structure of the Mosher's Ester Derivative of 5-Phenyldeltacyclene

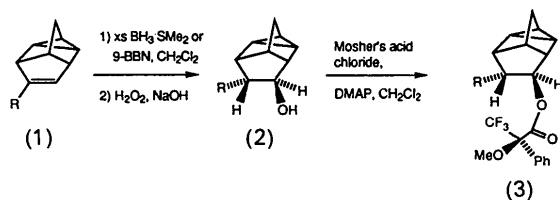
BY JULIA C. LAUTENS, MARK LAUTENS AND ALAN J. LOUGH*

Department of Chemistry, University of Toronto, Toronto, Ontario, Canada M5S 1A1

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Abstract. Octahydro-5-phenyl-1,2,4-methenopentalen-6-yl 3,3,3-trifluoro-2-methoxy-2-phenylpropanoate, $C_{25}H_{23}F_3O_3$, $M_r = 428.5$, monoclinic, $P2_1$, $a = 10.747$ (3), $b = 7.975$ (3), $c = 12.435$ (5) Å, $\beta = 92.81$ (3)°, $V = 1064.5$ (12) Å³, $Z = 2$, $D_x = 1.34$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 0.98$ cm⁻¹, $F(000) = 448$, room temperature, $R = 0.035$ for 1523 observed reflections. The X-ray structure determination establishes the relative stereochemistry. The $C(sp^3)$ — $C(sp^3)$ bond distances range from 1.492 (6) to 1.554 (5) Å.

Experimental. Hydroboration and oxidation of 5-phenyldeltacyclene followed by the reaction of the product alcohol with Mosher's acid chloride gave the desired compound (3).



DMAP = 4-dimethylaminopyridine;
 9-BBN = 9-borabicyclo[3.3.1]nonane; $R = C_6H_5$

Crystals from pentane. Accurate cell dimensions and crystal orientation matrix were determined on a CAD-4 diffractometer by a least-squares treatment of the setting angles of 25 reflections in the range $8 < \theta < 17^\circ$. Crystal dimensions $0.2 \times 0.2 \times 0.3$ mm; intensities of reflections with indices $h - 1$ to 12, $k 0$ to 9, $l - 14$ to 14, with $2 < 2\theta < 50^\circ$ measured, $\omega - 2\theta$ scans, ω scan width $(0.6 + 0.35 \tan \theta)^\circ$; graphite-monochromated Mo $K\alpha$ radiation; intensities of

three reflections measured every 2 h showed no evidence of crystal decay. 2316 reflections measured, 1886 unique ($R_{\text{int}} = 0.022$) and 1523 reflections with $I > 2\sigma(I)$ observed and used in the structure solution and refinement. Data corrected for Lorentz and polarization effects. The space group was assigned as $P2_1$ from the systematic absences ($0k0$ absent if $k = 2n + 1$) and confirmed by the successful structure solution and refinement. The y coordinate of one of the F atoms was fixed to define the origin along the 2_1 screw axis. The structure was solved by direct methods using *SHELXS86* (Sheldrick, 1986). The hand of the molecule was chosen according to the known configuration of the Mosher's ester group. Refinement was by full-matrix least-squares calculations, initially with isotropic and then with anisotropic thermal parameters for C, O and F atoms. A difference map showed maxima in positions consistent with the expected locations of H atoms. In the final rounds of calculations H atoms were positioned on geometric grounds ($C-H$ 0.95 Å) and included (as riding atoms) in the structure-factor calculation. The thermal parameters of these atoms were refined as a single free variable, final value $U_{\text{iso}} = 0.078$ (3) Å². Final cycles of least squares included 281 parameters, $R = 0.035$, $wR = 0.036$, goodness of fit 1.721 and $w = 1/[\sigma^2(F_o) + 0.00025(F_o)^2]$. Final value for the isotropic extinction parameter was $g = 2.8$ (6) $\times 10^{-7}$ where $F_c' = F_c(1 - gF_c^2/\sin \theta)$ (Sheldrick, 1976). Max. shift/e.s.d. in final refinement cycle 0.005; density in final difference map in range -0.14 to 0.14 e Å⁻³; there were no chemically significant features. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). All calculations carried out on a PDP 11/23 computer using *SDP* (Frenz, 1982) and an Apollo computer using *SHELX76* and *SHELXS86* (Sheldrick, 1976, 1986). Atomic

* To whom correspondence should be addressed. E-mail address: ALOUGH@ALCHEMY.CHEM.UTORONTO.CA

Table 1. Atomic coordinates and equivalent isotropic thermal parameters (Å²) with e.s.d.'s in parentheses
$$U_{eq} = (U_{11} + U_{22} + U_{33})/3.$$

	x	y	z	U_{eq}
F1	-0.15581 (24)	0.25281*	0.15658 (21)	0.0760 (16)
F2	-0.26734 (25)	0.3247 (4)	0.01729 (19)	0.0717 (16)
F3	-0.33154 (22)	0.3769 (5)	0.17320 (20)	0.0732 (17)
O1	-0.00587 (21)	0.6867 (4)	0.21306 (16)	0.0415 (13)
O2	-0.14063 (24)	0.5347 (5)	0.30447 (18)	0.0639 (17)
O3	-0.08162 (20)	0.5449 (4)	0.02803 (15)	0.0424 (13)
C1	0.05590 (29)	0.7485 (6)	0.31346 (25)	0.0385 (19)
C2	0.1979 (3)	0.7567 (6)	0.29603 (26)	0.0424 (20)
C3	0.2265 (3)	0.9447 (6)	0.31263 (26)	0.0427 (21)
C4	0.1088 (3)	1.0326 (6)	0.26611 (25)	0.0466 (22)
C5	0.0195 (3)	0.9300 (6)	0.33205 (26)	0.0421 (20)
C6	0.0725 (3)	0.9819 (6)	0.44275 (26)	0.0456 (22)
C7	0.2114 (3)	0.9939 (6)	0.42986 (26)	0.0465 (22)
C8	0.1342 (4)	1.1492 (6)	0.4321 (3)	0.0512 (23)
C9	0.1097 (4)	1.2063 (6)	0.3166 (3)	0.0586 (26)
C10	-0.10218 (29)	0.5853 (5)	0.22253 (26)	0.0361 (19)
C11	-0.16518 (29)	0.5444 (5)	0.11133 (23)	0.0355 (18)
C12	0.0276 (4)	0.4397 (6)	0.0362 (3)	0.0611 (26)
C13	-0.2300 (4)	0.3737 (6)	0.1159 (3)	0.0526 (25)
C21	-0.2614 (3)	0.6809 (5)	0.08251 (27)	0.0399 (19)
C22	-0.2888 (3)	0.7172 (6)	-0.0237 (3)	0.0548 (25)
C23	-0.3733 (4)	0.8403 (8)	-0.0519 (4)	0.077 (3)
C24	-0.4289 (4)	0.9297 (8)	0.0244 (7)	0.101 (4)
C25	-0.4040 (5)	0.8946 (9)	0.1294 (6)	0.101 (4)
C26	-0.3205 (4)	0.7688 (7)	0.1597 (4)	0.071 (3)
C31	0.2795 (3)	0.6416 (6)	0.3645 (3)	0.0464 (21)
C32	0.3871 (4)	0.5749 (7)	0.3232 (4)	0.0683 (28)
C33	0.4651 (5)	0.4704 (9)	0.3841 (5)	0.094 (4)
C34	0.4387 (5)	0.4303 (8)	0.4867 (6)	0.094 (4)
C35	0.3360 (5)	0.4987 (8)	0.5304 (4)	0.079 (3)
C36	0.2556 (4)	0.6032 (6)	0.4704 (3)	0.0592 (26)

* y coordinate of F1 was fixed to define the origin.

coordinates* are given in Table 1. Details of the molecular geometry are given in Table 2. Fig. 1 is a view of the molecule prepared using ORTEP (Johnson, 1976).

Related literature. The reaction between norbornadiene and a substituted acetylene (or acetylene itself) yields a substituted deltacyclene (1). Recently we have reported (Lautens, Lautens & Smith, 1990; Lautens & Crudden, 1989) that a chiral cobalt-phosphine catalyst promotes this reaction with high levels of enantioselectivity (up to 91% enantiomeric excess). Our long-term goal is to make use of the cycloadducts in the formation of natural products *via* a cycloaddition/ring-cleavage sequence. Deltacyclene itself forms novel and interesting polymers *via* ring-opening metathesis polymerization (ROMP) (Lautens, Abd-El-Aziz & Reibel, 1989; Lautens, Abd-El-Aziz & Schmidt, 1990). The assignment of the absolute stereochemistry of phenyldeltacyclene (1) was made on the basis of a well known empirical method, the preparation and NMR analysis of Mosher's esters for racemic and enantiomerically enriched materials (Dale, Dull & Mosher, 1969; Dale

* Lists of structure factors, thermal parameters, calculated H-atom coordinates and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54151 (12 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Bond distances (Å) and angles (°) with e.s.d.'s in parentheses

F1—C13	1.335 (5)	C6—C8	1.499 (7)
F2—C13	1.330 (5)	C7—C8	1.492 (6)
F3—C13	1.332 (5)	C8—C9	1.517 (5)
O1—C1	1.470 (4)	C10—C11	1.544 (4)
O1—C10	1.323 (5)	C11—C13	1.531 (6)
O2—C10	1.189 (4)	C11—C21	1.532 (5)
O3—C11	1.404 (4)	C21—C22	1.369 (5)
O3—C12	1.442 (5)	C21—C26	1.369 (6)
C1—C2	1.554 (5)	C22—C23	1.372 (7)
C1—C5	1.520 (6)	C23—C24	1.349 (9)
C2—C3	1.542 (6)	C24—C25	1.349 (11)
C2—C31	1.505 (6)	C25—C26	1.387 (8)
C3—C4	1.534 (5)	C31—C32	1.394 (6)
C3—C7	1.526 (5)	C31—C36	1.387 (6)
C4—C5	1.530 (5)	C32—C33	1.380 (8)
C4—C9	1.521 (6)	C33—C34	1.359 (9)
C5—C6	1.521 (5)	C34—C35	1.367 (8)
C6—C7	1.512 (5)	C35—C36	1.391 (7)
F2—C13—F1	106.5 (4)	C9—C4—C3	105.8 (3)
F3—C13—F1	107.5 (3)	C6—C7—C3	103.69 (27)
C11—C13—F1	113.1 (3)	C8—C7—C3	108.5 (3)
F3—C13—F2	106.3 (3)	C9—C4—C5	104.89 (30)
C11—C13—F2	110.1 (3)	C6—C5—C4	97.06 (29)
C11—C13—F3	112.9 (4)	C8—C9—C4	96.6 (3)
C10—O1—C1	116.87 (25)	C7—C6—C5	104.41 (27)
C2—C1—O1	107.54 (25)	C8—C6—C5	108.0 (3)
C5—C1—O1	109.86 (29)	C8—C6—C7	59.39 (28)
O2—C10—O1	126.1 (3)	C8—C7—C6	59.85 (28)
C11—C10—O1	111.09 (27)	C7—C8—C6	60.76 (28)
C11—C10—O2	122.7 (3)	C9—C8—C6	107.1 (3)
C12—O3—C11	119.63 (28)	C9—C8—C7	107.6 (3)
C10—C11—O3	113.07 (25)	C13—C11—C10	109.54 (29)
C13—C11—O3	109.8 (3)	C21—C11—C10	108.7 (3)
C21—C11—O3	105.93 (28)	C21—C11—C13	109.71 (29)
C5—C1—C2	104.1 (3)	C22—C21—C11	119.1 (3)
C3—C2—C1	102.3 (3)	C26—C21—C11	122.0 (3)
C31—C2—C1	116.4 (3)	C26—C21—C22	118.9 (4)
C4—C5—C1	104.76 (29)	C23—C22—C21	120.4 (4)
C6—C5—C1	108.0 (3)	C25—C26—C21	119.7 (5)
C31—C2—C3	114.27 (30)	C24—C23—C22	120.5 (5)
C4—C3—C2	103.82 (29)	C25—C24—C23	119.9 (6)
C7—C3—C2	110.4 (3)	C26—C25—C24	120.5 (6)
C32—C31—C2	119.7 (3)	C36—C31—C32	117.4 (4)
C36—C31—C2	122.8 (3)	C33—C32—C31	121.4 (4)
C7—C3—C4	96.80 (28)	C35—C36—C31	120.2 (4)
C5—C4—C3	94.63 (29)	C34—C33—C32	120.5 (5)
C35—C34—C33	119.3 (6)	C36—C35—C34	121.1 (5)

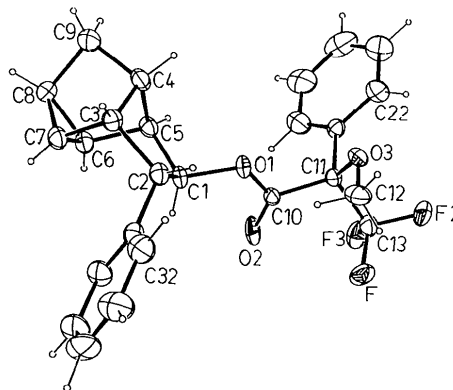


Fig. 1. View of the molecule indicating the atomic labelling scheme. The thermal ellipsoids of the C, O and F atoms are drawn at the 25% probability level. H atoms are represented by spheres of arbitrary radii.

& Mosher, 1973). Details of the NMR analysis are given in our previous work (Lautens, Lautens & Smith, 1990; Lautens & Crudden, 1989).

The X-ray structure establishes the relative stereochemistry of (3) shown in Fig. 1. Since the absolute stereochemistry of the Mosher's acid was known, determination of the absolute stereochemistry of (3) and hence (1) was achieved (see scheme 1). The geometry of the tetracyclononane cage in the title structure is similar to that in two other norbornadiene adducts (De Lucchi & Valle, 1984; Caughlan, Smith, Jennings & Voeks, 1976).

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References

CAUGHLAN, C. N., SMITH, G. D., JENNINGS, P. W. & VOECKS, G. E. (1976). *Acta Cryst.* **B32**, 1390–1393.

DALE, J. A., DULL, D. L. & MOSHER, H. S. (1969). *J. Org. Chem.* **34**, 2543–2549.
 DALE, J. E. & MOSHER, H. S. (1973). *J. Am. Chem. Soc.* **95**, 512–519.
 DE LUCHI, O. & VALLE, G. (1984). *Z. Kristallogr.* **167**, 293–297.
 FRENZ, B. A. (1982). *SDP Structure Determination Package*. College Station, Texas, USA, and Enraf–Nonius, Delft, The Netherlands.
 JOHNSON, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
 LAUTENS, M., ABD-EL-AZIZ, A. S. & REIBEL, J. (1989). *Macromolecules*, **22**, 4132–4134.
 LAUTENS, M., ABD-EL-AZIZ, A. S. & SCHMIDT, G. (1990). *Macromolecules*, **23**, 2819–2821.
 LAUTENS, M. & CRUDDEN, C. (1989). *Organometallics*, **8**, 2733–2735.
 LAUTENS, M., LAUTENS, J. C. & SMITH, A. C. (1990). *J. Am. Chem. Soc.* **112**, 5627–5628.
 SHELDRIK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.
 SHELDRIK, G. M. (1986). *SHELX86*. Program for the solution of crystal structures. Univ. of Göttingen, Germany.

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Methyl 2-[(2,6-Dimethoxyphenyl)ethynyl]benzoate

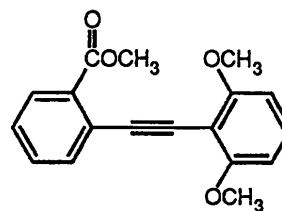
BY ENOCH T. HUANG, KEVIN L. EVANS, FRANK R. FRONCZEK AND RICHARD D. GANDOUR*

Department of Chemistry, Louisiana State University, Baton Rouge, LA 70803-1804, USA

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Abstract. $C_{18}H_{16}O_4$, $M_r = 296.3$, orthorhombic, $P2_12_12_1$, $a = 7.6025$ (10), $b = 13.948$ (2), $c = 14.428$ (3) Å, $V = 1530.0$ (4) Å³, $Z = 4$, $D_x = 1.286$ g cm⁻³ at 298 K, $\lambda(\text{Cu } K\alpha) = 1.54184$ Å, $\mu = 7.05$ cm⁻¹, $F(000) = 624$, 2918 unique data, final $R = 0.034$ for 2818 reflections with $I > 3.0\sigma(I)$. Maximum deviations from planarity of the two aromatic rings are 0.004 (1) Å for the ring containing the methoxy substituents and 0.012 (1) Å for the ring containing the ester substituent. The dihedral angle formed by the two rings is 4.7 (3)°. The triple-bond distance is 1.195 (2) Å. The triple bond deviates markedly from linearity, as the bond angle about the ethynyl carbon bonded to the benzoate group is 170.5 (1)°.

Experimental. The title compound was prepared by the copper iodide and palladium-catalyzed coupling of 2-ethynyl-1,3-dimethoxybenzene with methyl 2-iodobenzoate. A colorless crystal of (1) was isolated by slow evaporation from diethyl ether. Crystal size 0.30 × 0.37 × 0.50 mm, space group from systematic



(1)

absences $h00$ with h odd, $0k0$ with k odd and $00l$ with l odd, cell dimensions from setting angles of 25 reflections having $25 < \theta < 30^\circ$. Data collection on an Enraf–Nonius CAD-4 diffractometer, Cu $K\alpha$ radiation, graphite monochromator, ω - 2θ scans designed for $I = 25\sigma(I)$, subject to max. scan time = 90 s, scan rates varied 0.75–3.30° min⁻¹. Two octants of data having $2 < \theta < 75^\circ$, $0 \leq h \leq 9$, $0 \leq k \leq 17$, $-18 \leq l \leq 18$ measured. Data corrected for background, Lorentz and polarization effects. The standard reflections 400, 020, 008 varied randomly, and no decay correction was applied. Absorption corrections were based on ψ scans, with relative transmission coefficients ranging from 0.9279 to 0.9910. 3468 total

* To whom correspondence should be addressed.