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

Cl—C1	1.726 (1)	C2—C3	1.388 (2)
S—S^{i}	2.0432 (5)	C3—C4	1.398 (2)
S—C3	1.789 (1)	C4—C5	1.386 (2)
O1—N	1.221 (2)	C5—C6	1.370 (2)
O2—N	1.224 (2)	C2—H2	0.88 (2)
N—C4	1.462 (2)	C5—H5	0.93 (2)
C1—C2	1.381 (2)	C6—H6	0.96 (2)
C1—C6	1.384 (2)		
S—S^{i}—C3	104.11 (5)	S—C3—C2	121.8 (1)
O1—N—O2	123.5 (1)	S—C3—C4	121.2 (1)
O1—N—C4	118.3 (1)	C2—C3—C4	117.0 (1)
O2—N—C4	118.2 (1)	N—C4—C3	121.2 (1)
Cl—C1—C2	118.8 (1)	N—C4—C5	116.7 (1)
Cl—C1—C6	119.3 (1)	C3—C4—C5	122.1 (1)
C2—C1—C6	121.9 (1)	C4—C5—C6	120.1 (1)
C1—C2—C3	120.5 (1)	C1—C6—C5	118.4 (1)

Symmetry code: (i) $-x, y, \frac{1}{2} - z$.

Data collection: CAD-4 diffractometer software (Enraf–Nonius, 1977). Cell refinement: CAD-4 diffractometer software. Data reduction: *MolEN PROCESS* (Fair, 1990). Program(s) used to solve structure: *MULTAN*80 (Main *et al.*, 1980). Program(s) used to refine structure: *MolEN LSFM*. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *MolEN CIF IN*.

The purchase of the diffractometer was made possible by a National Science Foundation Chemical Instrumentation Grant, which we gratefully acknowledge.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BK1145). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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endo-5-Methyl-*exo*-6-phenylseleno-*endo*-tricyclo[5.2.1.0^{2,6}]dec-8-en-3-one

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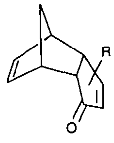
Abstract

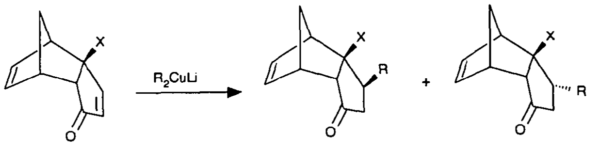
Structural analysis of the title compound, $C_{17}H_{18}OSe$, confirms the *endo* configuration of the C5-methyl group.

Comment

Tricyclo[5.2.1.0^{2,6}]decadienones, (1), have great potential as synthetic equivalents of cyclopentadienone and serve as building blocks in cyclopentanoid natural-product synthesis (Klunder, Bos & Zwanenburg, 1981; Klunder, Zwanenburg & Liu, 1991; Takano, Moriya & Ogasawara, 1992; Liu & Chu, 1993; Zhu, Klunder & Zwanenburg, 1994*a*). The *endo*-tricyclodecadienone system, which is racemic and optically active, is also readily accessible *via* the ester (2*b*).

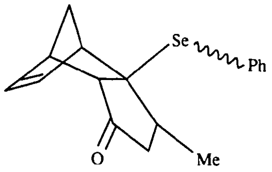


(1)



(2*a*) X = H (3*a*) (4*a*)
(2*b*) X = CO_2Et (3*b*) (4*b*)
(2*c*) X = SePh (3*c*) (4*c*)

Recently, we studied the nucleophilic addition of a variety of alkyllithiumcuprates to the enone double bond in the parent compound (2*a*), and the ester (2*b*). Whereas addition to (2*a*) proceeds with exclusively *exo* addition to give (3*a*), the presence of the *exo* ester function in (2*b*) apparently hinders attack from the *exo* side to some extent, as a considerable amount of the *endo*-addition product, (4*b*), is now also observed (Dols, Verstappen, Klunder & Zwanenburg, 1993). In order to establish the relationship between the nature of the functionality at the quarternary bridgehead position C6 and the stereochemistry observed for the conjugate addition of organolithiumcuprates to this tricyclic enone system, a series of differently substituted tricyclodecadienones, (2), are being studied. Most surprisingly, the conjugate addition of dimethyllithiumcuprate to the 6-phenylselenotricyclodecadienone (2*c*) gave a single addition product, the title compound (4*c*), in nearly quantitative yield.



(4*c*)

Although spectroscopic analysis suggested the formation of the *endo*-methyltricyclodecenone (4*c*) (*R* = Me), unambiguous confirmation of its structure was only possible by X-ray diffraction analysis. As no *exo* product, (3*c*) (*R* = Me), was observed at all in this addition reaction, this result reveals that the 6-phenylselenyl group completely controls the stereochemistry of the dimethyllithiumcuprate addition to the *endo*-tricyclodecadienone (2*c*).

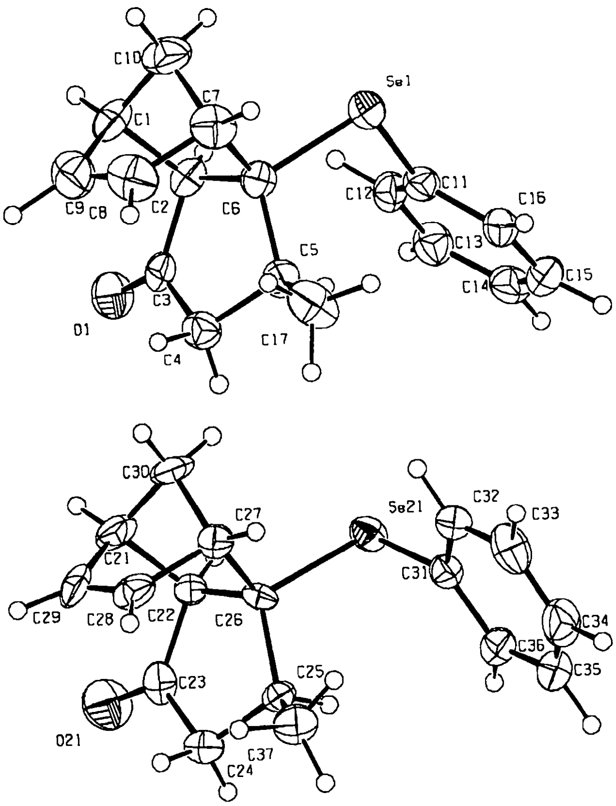


Fig. 1. Displacement ellipsoids (probability 50%) and atomic numbering for the two independent molecules in comparable orientations.

Although the bulk of the seleno function undoubtedly plays an important role in determining the observed *endo* addition, electronic factors may also be of considerable importance (Dols, 1993; Dols, Verstappen, Klunder & Zwanenburg, 1993). In order to evaluate such factors, studies involving tricyclodecadienones (2) substituted in the 6 position with O or S are currently in progress.

The Se—C bond lengths are 1.911 (5), 1.994 (5), 1.919 (5) and 2.000 (5) Å and the Se—C bond angles are close to 100° [C11—Se1—C6 101.1 (2) and C31—Se21—C26 98.8 (2)°].

Experimental

The preparation of the crystals (melting point 334–335 K; recrystallized from diisopropyl ether) will be described elsewhere (Zhu, Klunder & Zwanenburg, 1994*b*).

Crystal data

$C_{17}H_{18}OSe$
$M_r = 317.27$
Monoclinic
$P2_1/c$
$a = 16.4845\ (7)$ Å
$b = 8.0579\ (4)$ Å
$c = 21.8436\ (13)$ Å
$\beta = 98.812\ (5)°$
$V = 2867.2\ (3)$ Å^3
$Z = 8$
$D_x = 1.470$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 22.56–27.71°$
$\mu = 2.609$ mm^{-1}
$T = 293\ (2)$ K
Block
0.33 × 0.23 × 0.19 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
ω scans (Lehman & Larsen, 1974; Grant & Gabe, 1978)
Absorption correction: empirical (North, Phillips & Mathews, 1968; Walker & Stuart, 1983) (see below)
$T_{min} = 0.419$, $T_{max} = 0.692$

7132 measured reflections
6899 independent reflections
3021 observed reflections [$I > 2\sigma(I)$]
$R_{int} = 0.0460$
$\theta_{max} = 27.96°$
$h = 0 \rightarrow 21$
$k = 0 \rightarrow 10$
$l = -28 \rightarrow 28$
2 standard reflections
frequency: 60 min
intensity decay: 4.8%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0584$
$wR(F^2) = 0.0685$
$S = 1.293$

$(\Delta/\sigma)_{max} = -0.158$
$\Delta\rho_{max} = 0.417$ e Å^{-3}
$\Delta\rho_{min} = -0.472$ e Å^{-3}
Extinction correction: none

6896 reflections
487 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0007P)^2 + 4.5221P]$
where $P = (F_o^2 + 2F_c^2)/3$

Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

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

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

	x	y	z	$U_{\rm eq}$
Se1	0.12824 (4)	0.00609 (8)	0.19782 (3)	0.0512 (2)
C1	−0.0581 (4)	−0.2290 (8)	0.1078 (3)	0.055 (2)
C2	0.0254 (3)	−0.1593 (8)	0.0904 (2)	0.0435 (13)
C3	0.0543 (3)	−0.2559 (7)	0.0386 (3)	0.0476 (15)
C4	0.1238 (4)	−0.3680 (8)	0.0649 (3)	0.050 (2)
C5	0.1594 (4)	−0.2910 (8)	0.1278 (3)	0.049 (2)
C6	0.0878 (3)	−0.1957 (6)	0.1498 (2)	0.0436 (14)
C7	0.0325 (4)	−0.2859 (8)	0.1922 (3)	0.060 (2)
C8	0.0034 (5)	−0.4486 (9)	0.1617 (4)	0.071 (2)
C9	−0.0499 (4)	−0.4149 (9)	0.1114 (4)	0.069 (2)
C10	−0.0473 (4)	−0.1852 (9)	0.1762 (3)	0.065 (2)
C11	0.2011 (3)	0.0968 (7)	0.1464 (2)	0.0445 (14)
C12	0.1721 (4)	0.1735 (7)	0.0903 (3)	0.050 (2)
C13	0.2272 (4)	0.2415 (8)	0.0561 (3)	0.057 (2)
C14	0.3098 (5)	0.2411 (9)	0.0774 (3)	0.062 (2)
C15	0.3391 (4)	0.1721 (10)	0.1329 (3)	0.066 (2)
C16	0.2857 (4)	0.0952 (8)	0.1676 (3)	0.053 (2)
C17	0.2055 (7)	−0.4107 (12)	0.1742 (4)	0.085 (3)
O1	0.0252 (2)	−0.2436 (5)	−0.0152 (2)	0.0669 (13)
Se21	−0.40920 (4)	0.14441 (7)	−0.32519 (3)	0.0460 (2)
C21	−0.5353 (3)	−0.2588 (8)	−0.3546 (3)	0.055 (2)
C22	−0.4574 (3)	−0.1973 (7)	−0.3103 (3)	0.0420 (14)
C23	−0.4008 (3)	−0.3385 (7)	−0.2872 (2)	0.0486 (14)
C24	−0.3231 (4)	−0.3314 (8)	−0.3158 (3)	0.049 (2)
C25	−0.3215 (3)	−0.1613 (7)	−0.3464 (2)	0.0371 (13)
C26	−0.4106 (3)	−0.0913 (6)	−0.3540 (2)	0.0330 (12)
C27	−0.4677 (3)	−0.1095 (7)	−0.4170 (3)	0.0452 (15)
C28	−0.4660 (4)	−0.2894 (8)	−0.4366 (3)	0.052 (2)
C29	−0.5062 (4)	−0.3774 (8)	−0.4003 (3)	0.056 (2)
C30	−0.5516 (4)	−0.1058 (9)	−0.3954 (4)	0.063 (2)
C31	−0.3322 (3)	0.2327 (6)	−0.3742 (2)	0.0411 (13)
C32	−0.3594 (4)	0.2916 (7)	−0.4335 (3)	0.0475 (15)
C33	−0.3039 (5)	0.3578 (8)	−0.4684 (3)	0.062 (2)
C34	−0.2225 (5)	0.3649 (9)	−0.4447 (4)	0.070 (2)
C35	−0.1952 (4)	0.3072 (8)	−0.3864 (4)	0.063 (2)
C36	−0.2488 (4)	0.2408 (8)	−0.3501 (3)	0.052 (2)
C37	−0.2813 (5)	−0.1618 (10)	−0.4044 (3)	0.057 (2)
O21	−0.4166 (3)	−0.4454 (5)	−0.2520 (2)	0.0771 (14)

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

Se1—C11	1.911 (5)	Se21—C31	1.919 (5)
Se1—C6	1.994 (5)	Se21—C26	2.000 (5)
C1—C9	1.505 (9)	C21—C29	1.514 (8)
C1—C10	1.520 (8)	C21—C30	1.521 (9)
C1—C2	1.586 (7)	C21—C22	1.564 (7)
C2—C3	1.510 (7)	C22—C23	1.509 (7)
C2—C6	1.554 (7)	C22—C26	1.569 (6)
C3—O1	1.203 (6)	C23—O21	1.209 (6)
C3—C4	1.503 (8)	C23—C24	1.510 (7)
C4—C5	1.539 (8)	C24—C25	1.527 (8)
C5—C6	1.545 (7)	C25—C26	1.559 (6)
C6—C7	1.573 (7)	C26—C27	1.550 (7)
C7—C8	1.515 (9)	C27—C28	1.513 (8)
C7—C10	1.540 (9)	C27—C30	1.528 (8)
C8—C9	1.324 (9)	C28—C29	1.316 (8)
C11—Se1—C6	101.1 (2)	C31—Se21—C26	98.8 (2)
C9—C1—C10	100.6 (6)	C29—C21—C30	99.7 (5)
C9—C1—C2	106.9 (5)	C29—C21—C22	107.1 (5)
C10—C1—C2	100.2 (5)	C30—C21—C22	99.2 (5)
C3—C2—C6	106.6 (4)	C23—C22—C21	112.0 (5)
C3—C2—C1	112.4 (5)	C23—C22—C26	106.1 (4)
C6—C2—C1	102.8 (4)	C21—C22—C26	103.3 (4)
O1—C3—C4	126.1 (5)	O21—C23—C22	124.6 (5)
O1—C3—C2	124.5 (5)	O21—C23—C24	124.7 (6)
C4—C3—C2	109.4 (5)	C22—C23—C24	110.7 (5)
C3—C4—C5	105.2 (5)	C23—C24—C25	106.7 (5)
C4—C5—C6	105.9 (5)	C24—C25—C26	107.0 (4)
C5—C6—C2	105.8 (4)	C27—C26—C25	119.6 (4)
C5—C6—C7	119.5 (5)	C27—C26—C22	101.6 (4)
C2—C6—C7	102.1 (4)	C25—C26—C22	106.3 (4)
C5—C6—Se1	111.0 (4)	C27—C26—Se21	110.2 (3)
C2—C6—Se1	114.2 (4)	C25—C26—Se21	110.2 (3)
C7—C6—Se1	104.2 (4)	C22—C26—Se21	108.0 (3)
C8—C7—C10	98.9 (6)	C28—C27—C30	99.3 (5)
C8—C7—C6	108.3 (5)	C28—C27—C26	107.9 (4)
C10—C7—C6	100.1 (5)	C30—C27—C26	100.3 (5)
C9—C8—C7	108.2 (7)	C29—C28—C27	108.2 (6)
C8—C9—C1	106.9 (7)	C28—C29—C21	107.3 (6)
C1—C10—C7	93.9 (5)	C21—C30—C27	94.6 (5)

Application of *PATTY* in *DIRDIF* (Beurskens *et al.*, 1992) afforded the the non-H atom positions. The initial positions of the H atoms of the two methyl groups were obtained by rotation of an idealized methyl group to match maximum electron density in the difference Fourier synthesis. The initial positions of the H atoms of the phenyl groups and H(2) were calculated (C—H 1.00 Å). The remaining H atoms were found in a difference Fourier synthesis. All H atoms were refined with free isotropic displacement parameters.

After the isotropic refinement was completed using all atoms including H atoms, *DIFABS* (Walker & Stuart, 1983) was applied. Correction factors for all reflections were in the range 0.698–1.154, of which 113 reflections had correction factors > 1.10 (53 'observed' reflections and 60 'unobserved'). The conventional R factor reduced significantly from 0.088 to 0.072 [isotropic, $I > 3\sigma(I)$]. In retrospect, full-matrix anisotropic least-squares refinement on data without *DIFABS* correction resulted in an R value of 0.0715 as compared to 0.0584 [anisotropic, $I > 2\sigma(I)$] for the corrected data, and the standard deviations in the bond distances increased by about 40%. Recognizing that *DIFABS* can 'correct' more than just absorption effects, we think that this improvement in the results justifies its application. Uncorrected data are available from the authors on request.

The final difference Fourier results show that there is some residual electron density ranging from −0.47 to 0.42 e Å^{-3}. Most of this density is located near the Se atoms and may result from inadequate absorption correction.

Program used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics; *PLATON* (Spek, 1990). Software used to prepare material for publication: *SHELXL93*.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AB1222). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1995). C**51**, 2338–2340

2-Benzamido-3-(*p*-chlorophenyl)propenoic Acid (Antrex)

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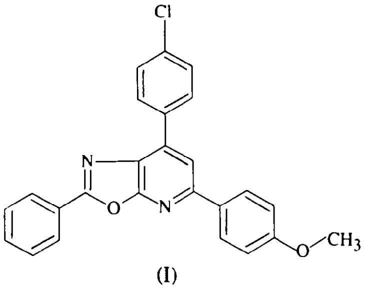
Abstract

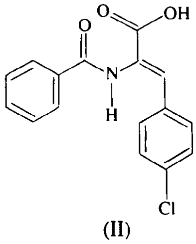
The phenyl and chlorophenyl rings are planar in the title compound, $C_{16}H_{12}ClNO_3$. The structure is stabilized by intermolecular hydrogen bonds involving the OH (donor) groups of the carboxylic acid moieties, the carbonyl O atoms (acceptor) of the carboxylic acid moieties and the Cl atoms (acceptor) of the chlorophenyl groups, together with hydrogen bonds between the amino N atoms (donor) and the carbonyl O atoms (acceptor) of the benzamide moieties.

Comment

In an attempt to prepare the compound 7-(4-chlorophenyl)-5-(4-methoxyphenyl)-2-phenyloxazolo[5,4-*b*]pyridine, (I), some colourless crystals were obtained (sample supplied by Dr V. Bansal, University of Rajasthan). The crystal structure determination was undertaken to obtain information for use in structure–function studies of 2-phenyloxazolo[5,4-*b*]pyridine compounds thought to possess analgesic properties (Clark *et al.*, 1978). The result of this analysis indicates that the compound is 2-benzamido-3-(*p*-chlorophenyl)propenoic acid, (II), which is a cleaved version of the originally proposed structure in which the two N-containing rings are broken. How this cleavage occurred remains open to conjecture.



(I)



(II)

The phenyl and chlorophenyl rings are planar. There are no significant deviations from the average bond lengths [1.380 (7) and 1.375 (7) Å]. The bond angles C13—C12—C17 [117.9 (4)°] and C3—C4—C5 [116.7 (4)°] in these rings show slight deviations from the average bond angles of 120.0 (4) and 120.0 (5)°, respectively. These distortions are in keeping with the findings of Domenicano, Murray-Rust & Vaciago (1983). The C—Cl bond length [1.741 (5) Å] is typical of C—Cl bond lengths in structures of the type C(ar)—Cl (Allen *et al.*, 1987). The Cl atom is displaced by 0.086 (7) Å from the least-squares plane calculated for the phenyl ring, the Cl atom and C7 (r.m.s. deviation of all eight atoms is 0.013 Å). The backbone chain of the molecule, C4–C12, is in an extended conformation between C7 and C12, while C4 is *cis* to N10, by rotation about C7—C8 (Table 2).

Hydrogen bonds involving the OH (donor) groups of the carboxylic acid moieties, the carbonyl O atoms (acceptor) of the carboxylic acid moieties and the Cl atoms (acceptor) of the chlorophenyl groups, together with hydrogen bonds between the amino N atoms (donor) and

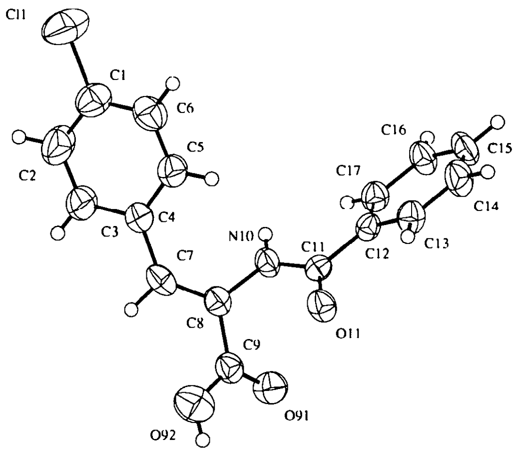


Fig. 1. Minimum overlap view of the molecule showing 50% probability displacement ellipsoids.

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