Data collection and cell refinement: *CAD*-4 *Software* (Enraf–Nonius, 1993). Data reduction, structure solution, structure refinement, molecular graphics and preparation of material for publication: *NRCVAX* (Gabe, Le Page, Charland, Lee & White, 1989).

SF acknowledges the support of a SILO Undergraduate Research Fellowship.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and bond distances and angles involving non-H atoms have been deposited with the IUCr (Reference: BK1057). 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. (1994). C50, 1978–1980

(+)-*N*-Trichloroacetyl-7,8-dimethoxy-1-vinyl-2,3,4,5-tetrahydro-1*H*-3-benzazepine at 153 K

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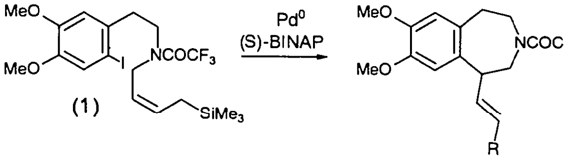
Abstract

The crystal structure analysis of the title compound, $C_{16}H_{18}Cl_3NO_3$, has been carried out at low temperature in order to determine the absolute configuration of the compound.

Comment

The Pd^0-catalyzed reaction of aryl or vinyl halides with alkenes, known as the Heck reaction, is an important method of C—C bond formation. A major drawback, however, is the low regioselectivity in constructing tertiary C_{sp^3} centres. The Si-terminated asymmetric Heck reaction now constitutes a new methodology for the regio- and enantioselective formation of such a centre (Tietze & Schimpf, 1994; Schimpf, 1994). With a catalyst system based on $Pd_2(dba)_3$ [tris(dibenzylideneacetone)dipalladium(0)] and (*S*)-BINAP [(*S*)-2,2′-bis(diphenylphosphino)-1,1′-binaphthyl] a mixture of compounds (2*a*) and (2*b*) (7 and 72%, respectively) was obtained, the latter in an enantiomeric excess of 64%. Recrystallization of (2*b*) gave an enantiomerically pure sample, which was converted to (2*c*) for elucidation of the absolute configuration by X-ray crystallography.



(2*a*) *R* = SiMe$_3$, *X* = F
(2*b*) *R* = H, *X* = F
(2*c*) *R* = H, *X* = Cl

Knowledge of the absolute configuration is required for the explanation of the mechanism of this enantioselective Heck reaction. Comparison of the optical rotation was not feasible because of the lack of reference compounds. All bond lengths and angles are within the expected range and comparable to values found for other 3-benzazepines (Eggleston, 1987; Berger, Chang, Clader, Hou, Chipkin & McPhail, 1989).

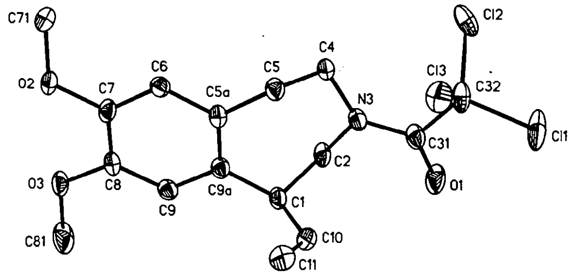


Fig. 1. Structure of the compound showing 50% probability displacement ellipsoids. The H atoms are omitted for clarity.

Experimental

Crystal data

$C_{16}H_{18}Cl_3NO_3$	Mo $K\alpha$ radiation
$M_r = 378.66$	$\lambda = 0.71073$ Å

Monoclinic
$P2_1$
$a = 7.717$ (6) Å
$b = 7.371$ (11) Å
$c = 14.901$ (18) Å
$\beta = 94.38$ (10)°
$V = 845.1$ (18) Å^3
$Z = 2$
$D_x = 1.488$ Mg m^{-3}

Cell parameters from 50 reflections
$\theta = 10$–12.5°
$\mu = 0.555$ mm^{-1}
$T = 153$ (2) K
Colourless
1.20 × 0.40 × 0.10 mm
Plates
Crystal source: *n*-hexane/ethanol by slow cooling from 337 K to room temperature

Data collection

Stoe Siemens four-circle diffractometer
Profile data from $2\theta/\omega$ scans
Absorption correction: none
2308 measured reflections
2125 independent reflections
2096 observed reflections [$I > 2\sigma(I)$]

$R_{\rm int} = 0.0243$
$\theta_{\rm max} = 22.54°$
$h = -8 \rightarrow 8$
$k = -7 \rightarrow 7$
$l = -16 \rightarrow 15$
3 standard reflections
frequency: 90 min
intensity variation: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0328$
$wR(F^2) = 0.0858$
$S = 1.078$
2123 reflections
210 parameters
$w = 1/[\sigma^2(F_o{}^2) + (0.0667P)^2 + 0.1913P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.001$

$\Delta\rho_{\rm max} = 0.256$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.359$ e Å^{-3}
Extinction correction: none
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), $\chi = 0.04$ (6)

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

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

	x	y	z	$U_{\rm eq}$
C1	−0.2831 (3)	−0.5202 (4)	−0.6769 (2)	0.0226 (6)
C2	−0.4592 (3)	−0.4181 (4)	−0.6834 (2)	0.0245 (6)
N3	−0.5086 (3)	−0.3399 (3)	−0.77162 (15)	0.0219 (5)
C4	−0.4135 (3)	−0.1775 (4)	−0.7939 (2)	0.0215 (6)
C5	−0.2217 (3)	−0.2148 (4)	−0.8079 (2)	0.0223 (6)
C5a	−0.1050 (3)	−0.2489 (4)	−0.7234 (2)	0.0201 (6)
C6	0.0350 (3)	−0.1324 (4)	−0.7048 (2)	0.0204 (6)
C7	0.1548 (3)	−0.1611 (4)	−0.6327 (2)	0.0217 (6)
C8	0.1383 (3)	−0.3108 (4)	−0.5781 (2)	0.0214 (6)
C9	−0.0049 (3)	−0.4229 (4)	−0.5941 (2)	0.0211 (6)
C9a	−0.1279 (3)	−0.3940 (3)	−0.6657 (2)	0.0202 (6)
C10	−0.2743 (4)	−0.6541 (4)	−0.7527 (2)	0.0285 (7)
C11	−0.1408 (4)	−0.6837 (4)	−0.8000 (2)	0.0330 (7)
C31	−0.6326 (4)	−0.4287 (4)	−0.8235 (2)	0.0264 (7)
C32	−0.6938 (3)	−0.3494 (4)	−0.9182 (2)	0.0289 (7)
Cl1	−0.85843 (11)	−0.48867 (13)	−0.96855 (5)	0.0484 (3)
Cl2	−0.78248 (9)	−0.12741 (11)	−0.91059 (5)	0.0355 (2)
Cl3	−0.52019 (9)	−0.34558 (10)	−0.98992 (4)	0.0314 (2)
O1	−0.6998 (3)	−0.5676 (3)	−0.8012 (2)	0.0401 (6)
O2	0.2929 (2)	−0.0477 (3)	−0.61015 (14)	0.0292 (5)
C81	0.2640 (4)	−0.4970 (5)	−0.4609 (2)	0.0442 (9)
C71	0.2933 (4)	0.1223 (4)	−0.6557 (2)	0.0364 (8)
O3	0.2667 (2)	−0.3339 (3)	−0.51025 (12)	0.0270 (5)

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

C1—C10	1.505 (4)	C7—C8	1.382 (4)
C1—C9a	1.516 (4)	C8—O3	1.371 (4)
C1—C2	1.550 (4)	C8—C9	1.385 (4)
C2—N3	1.459 (4)	C9—C9a	1.390 (4)
N3—C31	1.352 (4)	C10—C11	1.310 (5)
N3—C4	1.455 (4)	C31—O1	1.206 (4)
C4—C5	1.535 (4)	C31—C32	1.566 (5)
C5—C5a	1.512 (4)	C32—Cl1	1.756 (3)
C5a—C6	1.391 (4)	C32—Cl3	1.776 (3)
C5a—C9a	1.391 (4)	C32—Cl2	1.781 (4)
C6—C7	1.380 (4)	O2—C71	1.425 (4)
C7—O2	1.376 (4)	C81—O3	1.410 (4)
C10—C1—C9a	113.8 (2)	C7—C8—C9	118.9 (3)
C10—C1—C2	111.2 (2)	C8—C9—C9a	122.0 (3)
C9a—C1—C2	113.0 (2)	C9—C9a—C5a	118.7 (2)
N3—C2—C1	114.5 (2)	C9—C9a—C1	118.5 (2)
C31—N3—C4	127.9 (2)	C5a—C9a—C1	122.7 (2)
C31—N3—C2	116.6 (2)	C11—C10—C1	126.6 (3)
C4—N3—C2	115.4 (2)	O1—C31—N3	123.6 (3)
N3—C4—C5	113.1 (2)	O1—C31—C32	117.3 (3)
C5a—C5—C4	115.9 (2)	N3—C31—C32	119.1 (3)
C6—C5a—C9a	119.0 (2)	C31—C32—Cl1	109.0 (2)
C6—C5a—C5	117.8 (2)	C31—C32—Cl3	111.0 (2)
C9a—C5a—C5	123.1 (2)	Cl1—C32—Cl3	107.9 (2)
C7—C6—C5a	121.6 (3)	C31—C32—Cl2	112.1 (2)
O2—C7—C6	123.9 (3)	Cl1—C32—Cl2	107.2 (2)
O2—C7—C8	116.5 (3)	Cl3—C32—Cl2	109.6 (2)
C6—C7—C8	119.6 (2)	C7—O2—C71	116.6 (2)
O3—C8—C7	116.0 (2)	C8—O3—C81	116.8 (2)
O3—C8—C9	125.1 (2)		

Data were collected with a learnt-profile method (Clegg, 1981). All non-H atoms were refined anisotropically. H atoms were included in calculated positions and refined using a riding model [U(H) = 1.2$U_{\rm eq}$ for CH and CH$_2$ groups, U(H) = 1.5$U_{\rm eq}$ for CH$_3$ groups]. The torsion angles of the two CH$_3$ groups were refined and counted in the number of parameters. The origin along the polar axis was fixed with a restraint (Flack & Schwarzenbach, 1988).

Data collection and cell refinement: *DIF*4 (Stoe & Cie, 1988*a*). Data reduction: *REDU*4 (Stoe & Cie, 1988*b*). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL-Plus* (Sheldrick 1991). Software used to prepare material for publication: *SHELXL*93.

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Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: SH1101). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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(*Z*)-(–)-(*R*)-β-Styryl *p*-Tolyl Sulfoxide

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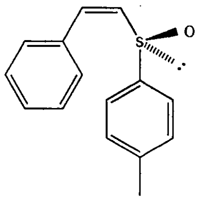
Abstract

The crystal structure determination of (*Z*)-(−)-(*R*)-β-styryl *p*-tolyl sulfoxide, $C_{15}H_{14}OS$, confirms its absolute configuration and establishes that the slightly twisted olefinic bond is not antiperiplanar to the S—O bond. It also provides a molecular basis for the theoretical study of cycloadditions between nitrones and vinylic sulfoxides.

Comment

The 1,3-dipolar cycloaddition of nitrones with alkenes constitutes a powerful method for the synthesis of alkaloids and related bases (Tufariello, 1984). In order to perform a theoretical study concerning the regiochemistry of cycloadditions between nitrones and vinylic sulfoxides, the molecular parameters of this latter type of compound were required. A search through the Cambridge Structural Database, version 5.06 (Allen *et al.*, 1991), revealed several X-ray crystallographic studies on sulfoxides (Hua, Badejo, McCann & Takusagawa, 1987; Swindell, Blase, Eggleston & Krause, 1990), but with the exception of one paper (Koizumi, Arai, Takayama, Kuriyama & Shiro, 1987), no information was found on (*Z*)-sulfinylethene derivatives. The title compound, (I), was synthesized by Andersen's method (House *et al.*, 1987); m.p. 330–331 K, $[\alpha]_{D22} = -738°$ ($CHCl_3$; $c = 1.0$) {literature: $[\alpha]_{D22} = -736°$ ($CHCl_3$; $c = 1.0$)}, NMR and MS spectra are all in agreement with the published data (Mikolajczyk, Midura, Grzejszczak, Zatorski & Chefczynska, 1978).



(I)

The complete structure was determined by a single-crystal X-ray diffraction study. The absolute configuration established by the X-ray analysis [Flack (1983) parameter = −0.02 (2)] confirms the previously determined stereochemistry (Mikolajczyk, Midura, Grzejszczak, Zatorski & Chefczynska, 1978); the S atom has an *R* configuration. The C1═C2 bond is slightly twisted owing to steric hindrance; the dihedral angle defined by C12—C1═C2—S3 is 11.9 (4)°. Noteworthy is the conformation of the vinyl sulfoxide moiety, where the S3—O4 and C1═C2 bonds are not *anti* coplanar (*s-trans*), as observed in benzyl (*Z*)-3-*p*-tolylsulfinylacrylate (Koizumi, Arai, Takayama, Kuriyama & Shiro, 1987), but have a dihedral angle of 121.9 (3)°, compared to 157° in the acrylate compound. The S-atom lone pair, therefore, lies more or less in the plane of the alkene; this observation corroborates the conformation assumed by Kimmelma (1993) for (*Z*)-vinylic sulfoxides on the basis of *ab initio* calculations. Indeed, in (*Z*)-vinylic sulfoxides steric strain between the sulfoxide group and the β-substituent precludes the *s-cis* conformation which would allow conjugation between the S—O and the olefinic bonds.

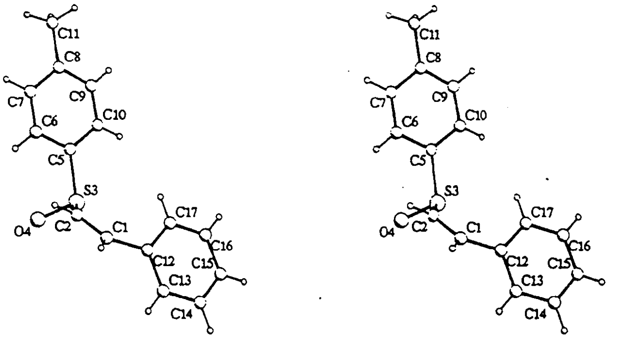


Fig. 1. View of the molecule with the atom-numbering scheme.

Experimental

Crystal data

$C_{15}H_{14}OS$	Cu $K\alpha$ radiation
$M_r = 242.32$	$\lambda = 1.54178$ Å

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