Acta Crystallographica Section E
Structure Reports
Online
ISSN 1600-5368

Se-Phenyl 3-(1*H*-indol-3-yl)selenoacrylate

Rosa-Luisa Meza,[a] Leticia Quintero[a] and Sylvain Bernès[b]*

[a]Centro de Investigación de la Facultad de Ciencias Químicas, Universidad Autónoma de Puebla, AP 1607, 72001 Puebla, Pue., Mexico, and [b]Centro de Química, Instituto de Ciencias, Universidad Autónoma de Puebla, AP 1613, 72000 Puebla, Pue., Mexico

Correspondence e-mail:
sylvain_bernes@hotmail.com

Key indicators

Single-crystal X-ray study
T = 296 K
Mean σ(C–C) = 0.007 Å
Disorder in main residue
R factor = 0.045
wR factor = 0.108
Data-to-parameter ratio = 13.6

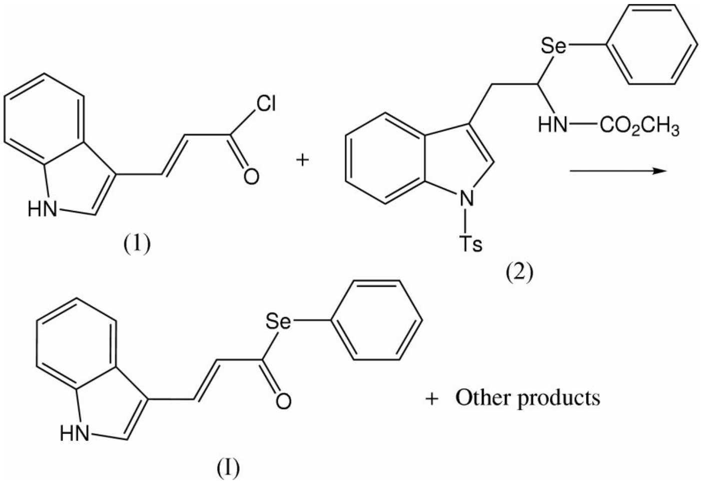
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The title compound, $C_{17}H_{13}NOSe$, has the expected planar indole core and is a rare case of a heavy-atom structure with positional disorder affecting only the heavy atom; the Se atom is disordered over two positions, with equal site-occupation factors (from refinement).

Received 28 September 2004
Accepted 1 October 2004
Online 9 October 2004

Comment

Enamides (*N*-acyl-1-aminoalkenes) are widely used synthons for the preparation of numerous heterocycles, including some attractive natural products, such as chondriamide A, terpeptine, aspergillamide A and coscinamide A, among others (Su *et al.*, 2003, and references therein). These indole enamides are currently studied mainly because of their cell-cycle inhibitor activity. During an attempt to synthesize a chondriamide A derivative, we unexpectedly obtained the title compound, (I), as the main product. Interestingly, although our initial goal was not achieved, (I) is of synthetic interest; selenoesters are a useful source of acyl radicals, when treated with trialkyltin hydrides in the presence of a free-radical initiator, generally a Lewis acid. The intramolecular free radical cyclization of free acyl radicals generated from phenyl selenoesters proceeds efficiently and, in most cases, with little or no competing reduction or decarbonylation (Studer & Bossart, 2001). Compound (I) is thus a potential entry to ergot alkaloids (Somei *et al.*, 2000), *via* an Uhle's ketone (Uhle, 1949; Teranishi *et al.*, 1995) or a Kornfeld's ketone (Kornfeld *et al.*, 1954, 1956). We report here the crystal structure of (I).



The indole core of (I) has the expected planar geometry. Atom C4 is bonded to an α,β-unsaturated moiety, lying almost in the indole plane; the dihedral angle between planes C4/C5/N6/C7/C8/C9/C10/C11/C12 and O1/C1/C2/C3 is 7.0 (3)°. A

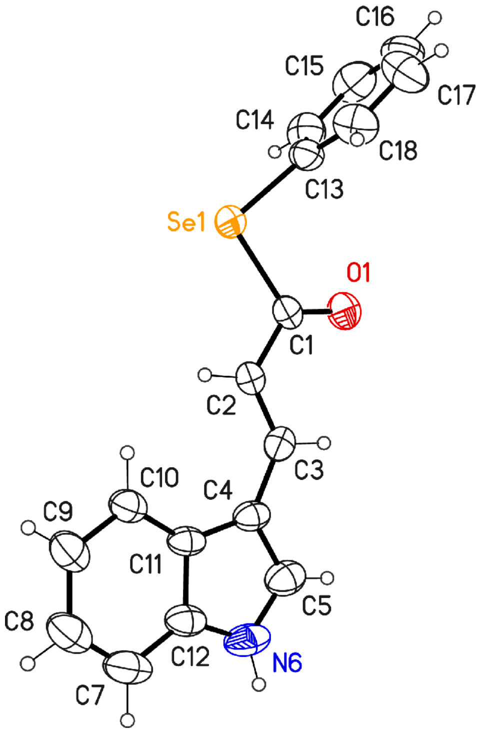


Figure 1
The structure of (I), with displacement ellipsoids drawn at the 30% probability level. Disordered atom Se2 has been omitted for clarity.

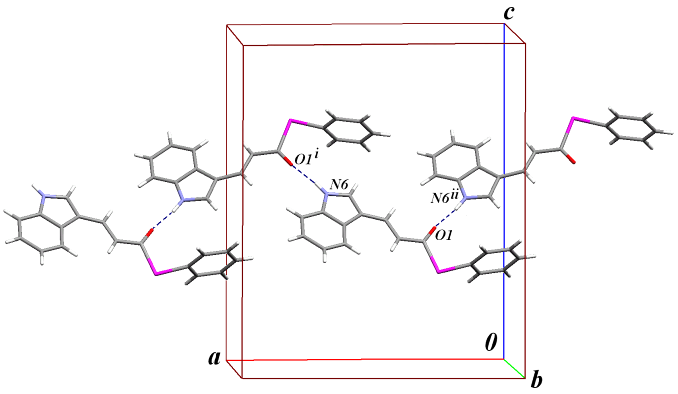


Figure 2
A view of the one-dimensional hydrogen-bond chain in the structure of (I). Four molecules are displayed and intermolecular hydrogen bonds are represented with dashed lines. Atoms Se2 of the asymmetric unit and symmetry-related molecules have been omitted for clarity. [Symmetry codes: (i) $\frac{1}{2} + x, \frac{1}{2} - y, 1 - z$; (ii) $x - -\frac{1}{2}, \frac{1}{2} - y, 1 - z$.]

similar conjugated system has been observed, for instance, in 3-(3-indolyl)acrylamide (Suescun *et al.*, 1999) and methyl (*E*)-3-(2-phenyl-1*H*-3-indolyl)prop-2-enoate (Perlick *et al.*, 2000). Formal double bonds C2═C3 and C1═O1 are clearly localized, as reflected by their respective bond lengths (Table 1). The C═C—(C═O) system adopts an s-*cis* conformation and atom C1 is bonded to the selenoester group.

An uncommon feature observed for (I) is positional disorder for the heavy atom, which is found on two equally occupied sites separated by 0.508 (8) Å, while the rest of the structure seems to be ordered, as evidenced by displacement parameters, which are close to isotropic behavior (Fig. 1). A scan of the Cambridge Structural Database (CSD, Version 5.25, updated July 2004; Allen, 2002) for organic molecules containing a C—Se—Ph fragment (329 hits) gives a single occurrence with such disorder (Zeng *et al.*, 2002), where an Se atom is disordered over two positions with occupation factors 0.90 and 0.10, respectively. In two cases, an approximate 1:1 disorder for an Se site was reported, but this induced two sets of positions for the phenyl group attached to the heavy atom (Chung *et al.*, 1998; Kocienski *et al.*, 2000). In spite of the disorder observed in (I), the geometry around the Se atom is unexceptional when compared to that found in numerous Se-containing compounds (Table 1).

Finally, functional groups in (I), namely a secondary amine and a carbonyl group, greatly favor the formation of a stabilizing hydrogen-bonding scheme in the solid state (Table 2). The observed network is a one-dimensional chain, with [100] as the base vector (Fig. 2).

Experimental

The acid chloride (1) (59 mg, 0.287 mmol) was dissolved in dry freshly distilled CH_2Cl_2 (15 ml) and stirred at 298 K under an argon atmosphere. Triethylamine (0.053 ml, 0.38 mmol) was added to this solution and after 15 min of stirring (2) (see scheme, 100 mg, 0.190 mmol) was added. This mixture was allowed to react until complete consumption of the starting materials (*ca* 1 h). The crude product was washed with HCl (10%, 10 ml) and then with water (10 ml). The organic phase was dried over Na_2SO_4, filtered and evaporated under reduced pressure. Chromatography on silica gel using hexanes–ethyl acetate as eluant (3:1) afforded the title compound (42 mg, 68%). Single crystals were obtained by slow evaporation of a hexane–dichloromethane solution (9:1) of (I).

Crystal data

$C_{17}H_{13}NOSe$
$M_r = 326.24$
Orthorhombic, *Pbca*
$a = 15.7845\ (16)$ Å
$b = 10.0900\ (13)$ Å
$c = 18.629\ (3)$ Å
$V = 2967.0\ (7)$ Å^3
$Z = 8$
$D_x = 1.461$ Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 69 reflections
$\theta = 4.6–12.5°$
$\mu = 2.53$ mm^{-1}
$T = 296\ (1)$ K
Block, yellow
0.60 × 0.28 × 0.16 mm

Data collection

Bruker *P*4 diffractometer
ω scans
Absorption correction: ψ scan (*XSCANS*; Siemens, 1996)
$T_{min} = 0.428$, $T_{max} = 0.667$
5420 measured reflections
2603 independent reflections
1314 reflections with $I > 2\sigma(I)$
$R_{int} = 0.052$
$\theta_{max} = 25.0°$
$h = -18 \rightarrow 1$
$k = -11 \rightarrow 9$
$l = -22 \rightarrow 1$
3 standard reflections every 97 reflections intensity decay: 1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.045$
$wR(F^2) = 0.108$
$S = 0.97$
2603 reflections
191 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0405P)^2 + 0.2818P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.21$ e Å^{-3}
$\Delta\rho_{min} = -0.30$ e Å^{-3}
Extinction correction: *SHELXTL-Plus*
Extinction coefficient: 0.0011 (2)

o1962 Rosa-Luisa Meza *et al.* • $C_{17}H_{13}NOSe$ *Acta Cryst.* (2004). E**60**, o1961–o1963

Table 1
Selected geometric parameters (Å, °).

Se1—C1	1.965 (7)	C2—C3	1.331 (5)
Se1—C13	1.892 (7)	C3—C4	1.433 (5)
Se2—C1	1.894 (8)	C4—C5	1.372 (5)
Se2—C13	1.940 (8)	C5—N6	1.353 (5)
C1—O1	1.196 (4)	N6—C12	1.366 (5)
C1—C2	1.454 (5)	C11—C12	1.408 (5)
C1—Se1—C13	98.2 (3)	C2—C1—Se1	114.6 (3)
C1—Se2—C13	99.0 (3)	C2—C1—Se2	111.7 (3)
O1—C1—C2	125.3 (4)	C1—C2—C3	120.8 (4)
O1—C1—Se1	119.6 (3)	C2—C3—C4	128.9 (4)
O1—C1—Se2	122.4 (4)	C5—N6—C12	109.2 (4)

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N6—H6*A*···O1$^{\mathrm{i}}$	0.86	1.91	2.762 (5)	169

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

Single crystals of (I) proved to be poorly diffracting samples, giving $\langle I/\sigma(I)\rangle = 7.54$ for raw collected data. A complete model, including H atoms, converged to somewhat disappointing *R* indices ($R = 0.068$ for 1314 'observed' data). This refinement was significantly improved by modeling disorder for the heavy atom, including two sites, Se1 and Se2. Refined occupation factors for Se1 and Se2 converged to almost equal values, and were then constrained to 0.5. No evidence was found for further disorder in (I). H atoms were placed at idealized positions and were treated as riding atoms, with C—H distances constrained to 0.93 Å and the N—H distance constrained to 0.86 Å. Isotropic displacement parameters for H atoms were fixed at $U_{\mathrm{iso}}(\mathrm{H}) = 1.2\, U_{\mathrm{eq}}$(parent atom).

Data collection: *XSCANS* (Siemens, 1996); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXTL-Plus* (Sheldrick, 1998); program(s) used to refine structure: *SHELXTL-Plus*; molecular graphics: *SHELXTL-Plus* and *MERCURY* (Bruno *et al.*, 2002); software used to prepare material for publication: *SHELXTL-Plus*.

The authors thank CONACyT for financial support (grant No. 35102) and studentship 91277 (RLM).

References

Allen, F. H. (2002). *Acta Cryst.* B**58**, 380–388.

Bruno, I. J., Cole, J. C., Edgington, P. R., Kessler, M., Macrae, C. F., McCabe, P., Pearson, J. & Taylor, R. (2002). *Acta Cryst.* B**58**, 389–397.

Chung, S.-K., Jeong, T.-H. & Kang, D.-H. (1998). *J. Chem. Soc. Perkin Trans.* 1, pp. 969–976.

Kocienski, P., Narquizian, R., Raubo, P., Smith, C., Farrugia, L. J., Muir, K. & Boyle, F. T. (2000). *J. Chem. Soc. Perkin Trans.* 1, pp. 2357–2384.

Kornfeld, E. C., Fornefeld, E. J., Kline, G. B., Mann, M. J., Jones, R. G. & Woodward, R. B. (1954). *J. Am. Chem. Soc.* **76**, 5256–5257.

Kornfeld, E. C., Fornefeld, E. J., Kline, G. B., Mann, M. J., Morrison, D. E., Jones, R. G. & Woodward, R. B. (1956). *J. Am. Chem. Soc.* **78**, 3087–3114.

Perlick, C., Pindur, U. & Schollmeyer, D. (2000). Private communication to the Cambridge Structural Database, refcode XASPEM. Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, England.

Sheldrick, G. M. (1998). *SHELXTL-Plus.* Release 5.10. Bruker AXS Inc., Madison, Wisconsin, USA.

Siemens (1996). *XSCANS.* Version 2.21. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Somei, M., Yokoyama, Y. & Murakami, Y. (2000). *The Alkaloids*, Vol. 54, pp. 191–257. San Diego: Academic Press.

Studer, A. & Bossart, M. (2001). *Radicals in Organic Synthesis*, Vol. 2, edited by P. Renaud & M. P. Sibi, pp. 62–80. Weinheim: Wiley-VCH.

Su, S., Kakeya, H., Osada, H. & Porco Jr., J. A. (2003). *Tetrahedron*, **59**, 8931–8946.

Suescun, L., Mariezcurrena, R. A., Mombrú, A. W., Davyt, D. & Manta, E. (1999). *Acta Cryst.* C**55**, 211–213.

Teranishi, K., Hayashi, S., Nakatsuka, S.-I. & Goto, T. (1995). *Synthesis*, pp. 506–508.

Uhle, F. C. (1949). *J. Am. Chem. Soc.* **71**, 761–766.

Zeng, X., Leng, X., Chen, L., Sun, H., Xu, F., Li, Q., He, X. & Zhang, Z.-Z. (2002). *J. Chem. Soc. Perkin Trans.* 2, pp. 796–801.

Acta Cryst. (2004). E**60**, o1961–o1963 Rosa-Luisa Meza *et al.* • $C_{17}H_{13}NOSe$ **o1963**