Absorption correction:
by integration
$T_{min} = 0.965$, $T_{max} = 0.994$
2653 measured reflections
2205 independent reflections
1534 reflections with
$I > \sigma(I)$

$h = -23 \rightarrow 20$
$k = 0 \rightarrow 7$
$l = 0 \rightarrow 23$
2 standard reflections
every 50 reflections
intensity decay: 5%

Refinement

Refinement on F
$R = 0.065$
$wR = 0.069$
$S = 1.28$
1534 reflections
163 parameters
H atoms: see below
$w = 1/\{[\sigma_{cs}(F^2) + 1.03F^2]^{1/2} - |F|\}^2$
$(\Delta/\sigma)_{max} = 0.0010$

$\Delta\rho_{max} = 0.13\,(3)$ e Å^{-3}
$\Delta\rho_{min} = -0.12\,(3)$ e Å^{-3}
Extinction correction: Becker & Coppens (1974) type 1, Lorentzian isotropic
Extinction coefficient: $1.7\,(4) \times 10^4$
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. *Selected geometric parameters (Å, °)*

O1—C1	1.295 (3)	N3—C10	1.448 (5)
C6—C7	1.491 (4)	N3—C11	1.451 (4)
C7—N2	1.499 (4)	N1—O2	1.229 (3)
N2—C8	1.476 (4)	N1—O3	1.232 (4)
C8—C9	1.512 (5)	N1—C4	1.438 (4)
C9—N3	1.450 (4)		
O1—C1—C2	122.7 (3)	N2—C8—C9	109.3 (2)
O1—C1—C6	119.4 (3)	C8—C9—N3	112.8 (3)
C2—C1—C6	117.9 (3)	C9—N3—C10	111.7 (3)
C3—C4—N1	118.9 (3)	C9—N3—C11	110.6 (3)
N1—C4—C5	120.1 (3)	C10—N3—C11	110.0 (3)
C1—C6—C7	117.8 (2)	O2—N1—O3	122.2 (3)
C5—C6—C7	122.0 (3)	O2—N1—C4	119.1 (3)
C6—C7—N2	111.1 (3)	O3—N1—C4	118.6 (3)
C7—N2—C8	115.0 (2)		

Cell dimensions were determined from reflections measured at ±2θ. All H atoms were located from a difference map and could be refined satisfactorily, however, in the final refinements, the H atoms not involved in hydrogen bonding were kept fixed in calculated positions (with C—H 0.95 Å and displacement factors 20% larger than those of the atoms to which they were attached) so as to increase the ratio of observations to variables.

Data collection: *MAD* (Allibon, 1995). Cell refinement: *MAD*. Data reduction: *KRYSTAL* (Hazell, 1995). Program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994) and *KRYSTAL*. Program(s) used to refine structure: modified *ORFLS* (Busing, Martin & Levy, 1962) and *KRYSTAL*. Molecular graphics: *ORTEP*III (Burnett & Johnson, 1996) and *KRYSTAL*.

Financial support from Nanyang Technological University (grant No. RP9/92KLE) is gratefully acknowledged. AH is indebted to the Carlsberg Foundation and to the Danish Science Research Council for the diffractometer.

Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: AB1425). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Allibon, J. (1995). *MAD*. Aarhus version. Institut Laue-Langevin, Grenoble, France.

Altomare, A., Cascarano, G., Giacovazzo, C., Guagliardi, A., Burla, M. C., Polidori, G. & Camalli, M. (1994). *J. Appl. Cryst.* **27**, 435.

Becker, P. J. & Coppens, P. (1974). *Acta Cryst.* **A30**, 129–153.

Brzezinski, B., Maciejewska, H., Zundel, G. & Kramer, R. (1990). *J. Phys. Chem.* **94**, 528–531.

Burnett, M. N. & Johnson, C. K. (1996). *ORTEP*III. Report ORNL-6895. Oak Ridge National Laboratory, Tennessee, USA.

Burr, A. H. & Hobson, A. D. (1969). *Acta Cryst.* **B25**, 2662–2663.

Busing, W. R., Martin, K. O. & Levy, H. A. (1962). *ORFLS. Fortran Crystallographic Function and Error Program.* Report ORNL-TM-305. Oak Ridge National Laboratory, Tennessee, USA.

Hazell, A. (1995). *KRYSTAL. An Integrated System of Crystallographic Programs.* Aarhus University, Denmark.

Hazell, A., Hu, H. & Khoo, L. E. (1996). *Acta Cryst.* **C52**, 873–876.

Kamwaya, M. E. & Khoo, L. E. (1985). *J. Fiz. Malays.* **6**, 135–140; (1986). *Chem. Abstr.* **105**, 208211p.

Shukla, R., Bharadwaj, P. K., Hall, J. V. & Whitmire, K. H. (1994). *Polyhedron*, **13**, 2387–2394.

Vollano, J. F., Day, R. O., Rau, D. N., Chandrasekhar, V. & Holmes, R. R. (1984). *Inorg. Chem.* **23**, 3153–3160.

Yeap, G.-Y., Fun, H.-K., Teoh, S.-G, Teo, S.-B., Chinmnakali, K. & Yip, B.-C. (1992). *Acta Cryst.* **C48**, 2257–2258.

Acta Cryst. (1997). **C53**, 641–644

N-Butylthiophene-3-carboxamide and 2-Benzylseleno-*N*-butylthiophene-3-carboxamide at 130 K

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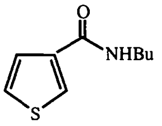
Abstract

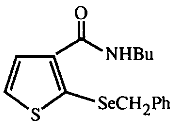
In *N*-butylthiophen-3-carboxamide, $C_9H_{13}NOS$, the *N*-butylcarboxamide group is almost planar with the aromatic thiophene ring, with the amide N atom *cis* to C2. In the 2-benzylseleno derivative, $C_{16}H_{19}NOSSe$, the *N*-butylcarboxamide group adopts an orientation with the amide O atom *cis* to C2 and forming a close contact with the Se atom. In both compounds, the amide N atom is involved in hydrogen bonding with the O atom of an adjacent molecule forming zigzag chains.

Comment

During the course of studies aimed at the preparation of thiophene-containing analogues of the anti-inflammatory compound ebselen, we had cause to prepare 2-benzylseleno-*N*-butylthiophene-3-carboxamide, (2), as a possible precursor to the target compounds. Two-dimensional NOESY NMR spectroscopy suggested that (2), in solution, exists in a conformation not conducive to further ring closure and that the carbonyl O atom lies in close proximity to the Se atom. In order to provide further insight into the factors affecting the conformational preference of the compound, the crystal structure of (2) and that of the parent *N*-butylthiophene-3-carboxamide, (1), were determined.



(1)



(2)

The five atoms of the thiophene ring in (1) are coplanar [maximum deviation of 0.003 (2) Å for C3], with bond lengths (Table 1) that are intermediate between double and single bonds, reflecting the aromatic nature of the ring. The amide group is almost coplanar with the thiophene ring and is oriented such that the N atom is *cis* to C2 [C2—C3—C6—N −9.9 (5)°], bringing H(N) close to H2 with a separation of 2.23 (5) Å.

The thiophene ring in (2) is less aromatic in character, with the C3—C4 bond length (Table 2) being much longer than the C2—C3 and C4—C5 bond lengths, and the two C—S bond lengths being significantly longer than the corresponding bonds in (1). The Se—C11 distance of 1.978 (2) Å is that expected for a single bond, however, the Se—C2 distance of 1.890 (2) Å lies between 1.97 and 1.78 Å, the values expected for single and double bonds, respectively (Brooks, Counter, Bishop & Tiekink, 1991), indicating partial double-bond character. This distance is similar to those observed in other compounds where an Se—C bond is adjacent to a C═C double bond. The atoms of the amide group are almost coplanar with those of the thiophene ring [maximum deviation of 0.004 (1) Å for C2]. However, the orientation is such that the O atom is now *cis* to C2 [C2—C3—C6—O 7.7 (3)°] and forms a close contact with the Se atom [Se···O 2.836 (1) Å]. This distance lies between the sum of the relevant covalent and van der Waals radii [1.87 and 3.5 Å, respectively; Bondi, 1964], indicating a weak interaction similar to that observed for 2-methylseleno-*N*-phenylbenzamide and 2-triphenylstannylseleno-*N*-phenylbenzamide (Fong, Gable & Schiesser, 1996). This orientation of the amide group now brings H(N) close to H4, the separation being 2.11 (4) Å.

For both structures, the amide N atom is involved in hydrogen bonding with the O atom of an adjacent molecule. For (1), the hydrogen bonds [$N\cdots O^{i}$ 2.868 (3), N—H(N) 0.86 (4), $H(N)\cdots O^{i}$ 2.03 (4) Å and $N—H(N)\cdots O^{i}$ 165 (4)°; symmetry code: (i) $\frac{1}{2}+x$, $\frac{1}{2}-y$, z] form zigzag chains which lie along the *a* axis. For (2), the hydrogen bonds [$N\cdots O^{ii}$ 2.928 (2), N—H(N) 0.83 (3), $H(N)\cdots O^{ii}$ 2.13 (3) Å and $N—H(N)\cdots O^{ii}$ 161 (2)°; symmetry code: (ii) $-\frac{1}{2}+x$, $\frac{1}{2}-y$, $-\frac{1}{2}+z$] form zigzag chains which lie along the $[\bar{1}01]$ direction.

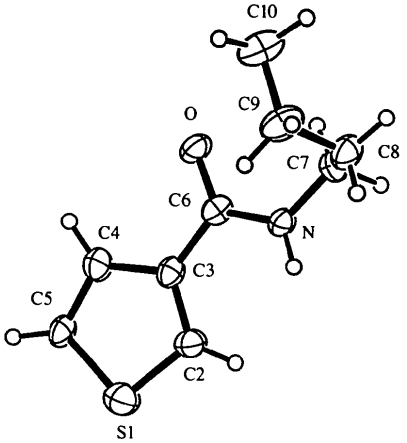


Fig. 1. *ORTEP*II (Johnson, 1976) drawing of (1). Displacement ellipsoids are drawn at the 70% probability level.

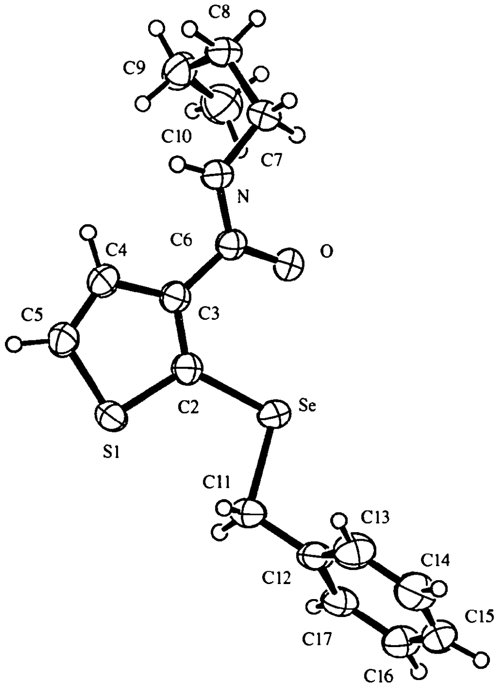


Fig. 2. *ORTEP*II (Johnson, 1976) drawing of (2). Displacement ellipsoids are drawn at the 70% probability level.

Experimental

Compound (1) was prepared by adding DMF (1 drop) and pyridine (0.286 ml, 3.5 mmol) to 3-thiophenecarboxylic acid (0.4545 g, 3.5 mmol) in dry dichloromethane (*ca* 27 ml). The reaction flask was flushed with N_2 and then oxalyl chloride (0.294 ml, 3.4 mmol) was added dropwise to the mixture which was left stirring overnight. Butylamine (0.701 ml, 7.1 mmol) was added slowly and the resulting solution stirred overnight. Dichloromethane (*ca* 10 ml) was added and the mixture was washed with 10% HCl (4 × 20 ml), saturated $NaHCO_3$ (3 × 20 ml) and brine (2 × 20 ml). The organic layer was collected, dried and the solvent removed *in vacuo*. The resulting product was collected to give *N*-butylthiophene-3-carboxamide (0.0981 g, 15%) as an orange solid. Recrystallization from ethanol/petrol gave the product as a single conformer (m.p. 326–328 K). ^1H NMR: δ 0.94 (*m*, 3H), 1.40 (*m*, 2H), 1.59 (*m*, 2H), 3.41 (*m*, 2H) 5.94 (*bs*, 1H), 7.35 (*m*, 2H), 7.84 (*m*, 1H). ^{13}C NMR: δ 13.70, 20.07, 31.69, 39.49, 126.04, 126.22, 127.83, 137.73, 163.14. MS (*m/z*): 183 (*M*, 18.35%), 141 (13), 111 (100), 83 (12), 56 (7). (Found: M^+ 183.0713; $C_9H_{13}NOS$ requires M^+ 183.0718). Compound (2) was prepared as described by Fong, Laws & Schiesser (1995) and crystallized from ethanol/petrol. Both crystals were cooled using an Oxford Cryosystems low-temperature device (Cosier & Glazer, 1986).

Compound (1)

Crystal data

$C_9H_{13}NOS$
$M_r = 183.27$
Orthorhombic
$Pna2_1$
$a = 9.7232\,(11)$ Å
$b = 9.2506\,(13)$ Å
$c = 10.6178\,(13)$ Å
$V = 955.0\,(2)$ Å^3
$Z = 4$
$D_x = 1.275$ Mg m^{-3}
D_m not measured

Cu $K\alpha$ (nickel-filtered) radiation
$\lambda = 1.5418$ Å
Cell parameters from 25 reflections
$\theta = 26.8$–$40.1°$
$\mu = 2.624$ mm^{-1}
$T = 130\,(1)$ K
Plate
0.59 × 0.22 × 0.07 mm
Light yellow

Data collection

Enraf–Nonius CAD-4-MachS diffractometer
$\omega/2\theta$ scans
Absorption correction: Gaussian integration (Sheldrick, 1976)
$T_{min} = 0.360$, $T_{max} = 0.844$
1459 measured reflections
1142 independent reflections

1128 reflections with $I > 2\sigma(I)$
$R_{int} = 0.0187$
$\theta_{max} = 74.44°$
$h = -1 \rightarrow 12$
$k = -1 \rightarrow 11$
$l = -13 \rightarrow 1$
3 standard reflections frequency: 160 min intensity decay: none

Refinement

Refinement on F^2
$R(F) = 0.0360$
$wR(F^2) = 0.1045$
$S = 1.072$
1142 reflections
147 parameters
All H-atom parameters refined, except those attached to C5, C9 and C10, which were geometrically constrained
$w = 1/[\sigma^2(F_o^2) + (0.0676P)^2 + 0.66P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = -0.001$
$\Delta\rho_{max} = 0.389$ e Å^{-3}
$\Delta\rho_{min} = -0.391$ e Å^{-3}
Extinction correction: *SHELXL*93
Extinction coefficient: 0.0029 (8)
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute configuration: Flack (1983)
Flack parameter = 0.05 (3)

Table 1. *Selected geometric parameters (Å, °) for (1)*

S1—C2	1.697 (3)	C4—C5	1.421 (4)
S1—C5	1.703 (3)	C6—O	1.247 (4)
C2—C3	1.382 (4)	C6—N	1.341 (4)
C3—C4	1.421 (4)	N—C7	1.462 (4)
C3—C6	1.480 (4)	C7—C8	1.518 (4)
C2—S1—C5	94.27 (15)	C4—C5—S1	109.0 (2)
C3—C2—S1	111.8 (2)	O—C6—N	122.2 (3)
C2—C3—C4	111.6 (3)	O—C6—C3	120.1 (3)
C2—C3—C6	126.2 (3)	N—C6—C3	117.6 (2)
C4—C3—C6	122.2 (2)	C6—N—C7	124.1 (3)
C5—C4—C3	113.4 (3)	N—C7—C8	112.3 (3)

Compound (2)

Crystal data

$C_{16}H_{19}NOSSe$
$M_r = 352.36$
Monoclinic
$P2_1/n$
$a = 8.4701\,(9)$ Å
$b = 21.624\,(2)$ Å
$c = 9.3400\,(9)$ Å
$\beta = 114.497\,(8)°$
$V = 1556.7\,(3)$ Å^3
$Z = 4$
$D_x = 1.503$ Mg m^{-3}
D_m not measured

Cu $K\alpha$ (nickel-filtered) radiation
$\lambda = 1.5418$ Å
Cell parameters from 25 reflections
$\theta = 25.4$–$49.7°$
$\mu = 4.470$ mm^{-1}
$T = 130\,(1)$ K
Thick plate
0.50 × 0.43 × 0.36 mm
Yellow

Data collection

Enraf–Nonius CAD-4-MachS diffractometer
$\omega/2\theta$ scans
Absorption correction: Gaussian integration (Sheldrick, 1976)
$T_{min} = 0.144$, $T_{max} = 0.342$
4031 measured reflections
3206 independent reflections

3125 reflections with $I > 2\sigma(I)$
$R_{int} = 0.0393$
$\theta_{max} = 75.04°$
$h = -1 \rightarrow 10$
$k = -1 \rightarrow 27$
$l = -11 \rightarrow 11$
3 standard reflections frequency: 160 min intensity decay: 2%

Refinement

Refinement on F^2
$R(F) = 0.0293$
$wR(F^2) = 0.0777$
$S = 1.169$
3206 reflections
258 parameters
All H atoms refined
$w = 1/[\sigma^2(F_o^2) + (0.0362P)^2 + 1.232P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.893$ e Å^{-3}
$\Delta\rho_{min} = -0.636$ e Å^{-3}
Extinction correction: *SHELXL*
Extinction coefficient: 0.0056 (3)
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

Se—C2	1.890 (2)	C3—C6	1.474 (3)
Se—C11	1.978 (2)	C4—C5	1.350 (3)
S1—C2	1.723 (2)	C6—O	1.241 (2)
S1—C5	1.726 (2)	C6—N	1.339 (3)
C2—C3	1.379 (3)	N—C7	1.457 (3)
C3—C4	1.434 (3)	C7—C8	1.525 (3)
C2—Se—C11	98.31 (9)	C5—C4—C3	112.9 (2)
C2—S1—C5	92.25 (10)	C4—C5—S1	111.6 (2)
C3—C2—S1	110.78 (15)	O—C6—N	122.7 (2)
C3—C2—Se	126.92 (15)	O—C6—C3	120.0 (2)
S1—C2—Se	122.25 (11)	N—C6—C3	117.2 (2)

C2—C3—C4	112.4 (2)	C6—N—C7	123.0 (2)
C2—C3—C6	121.5 (2)	N—C7—C8	111.3 (2)
C4—C3—C6	126.1 (2)		

For both compounds, data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *CAD*-4 *Software*; program(s) used to solve structures: *SHELXS*86 (Sheldrick, 1990); program(s) used to refine structures: *SHELXL*93 (Sheldrick, 1993); molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *SHELXL*93.

Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: SK1076). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Bondi, A. (1964). *J. Phys. Chem.* **68**, 441–451.
Brooks, P. R., Counter, J. A., Bishop, R. & Tiekink, E. R. T. (1991). *Acta Cryst.* C**47**, 1939–1941.
Cosier, J. & Glazer, A. M. (1986). *J. Appl. Cryst.* **19**, 105–107.
Enraf–Nonius (1989). *CAD-4 Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Fong, M. C., Gable, R. W. & Schiesser, C. H. (1996). *Acta Cryst.* C**52**, 1886–1889.
Fong, M. C., Laws, M. J. & Schiesser, C. H. (1995). *Aust. J. Chem.* **48**, 1221–1226.
Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Sheldrick, G. M. (1976). *SHELX76. Program for Crystal Structure Determination.* University of Cambridge, England.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.

Acta Cryst. (1997). C**53**, 644–646

2-(7,9-Diphenylcyclopenta[*a*]acenaphthadien-6b-yl)ethylbromide

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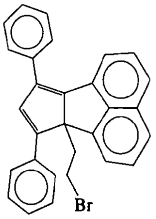
Abstract

The reaction between (7,9-diphenylcyclopenta[*a*]acenaphthadienyl)lithium and 1,2-dibromoethane resulted in the formation of the title compound, 6b-(2-bromoethyl)-7,9-diphenyl-6b*H*-cyclopenta[*a*]acenaphthylene, $C_{29}H_{21}Br$. Crystals suitable for X-ray structure determination were obtained from acetone.

Comment

The discovery of chiral group IV metallocene dichlorides as catalysts in stereospecific α-olefin polymerization has stimulated intensive research in academia as well as in industry for more than a decade now (Brintzinger, Fischer, Mülhaupt, Rieger & Waymouth, 1995). A well established way of synthesizing C_2-symmetric *ansa*-metallocenes is to prepare the ligand precursors by the reaction of cyclopentadienyl anions with 1,2-dibromoethane (Wild, Zsolnai, Huttner & Brintzinger, 1982; Alt, Milius & Palackal, 1994). Although we have used (7,9-diphenylcyclopenta[*a*]acenaphthadienyl)lithium, (2), for the preparation of unsymmetric *ansa*-zirconocenes bearing two different cyclopentadienyl fragments in the ethylene bridge (Rieger, Repo & Jany, 1994), it was not possible to prepare a C_2-symmetric ligand precursor by the reaction of (2) with 1,2-dibromoethane. Instead of the expected disubstitution, only monosubstitution of one Br atom occurred with 7,9-diphenylcyclopenta[*a*]acenaphthadienyl at the sterically and electronically unfavored 3-position of the five-membered ring, to give the title compound, (1) (Fig. 1).



(1)

If the structure of (1) in the solid state is compared with that of 2-(7,9-diphenylcyclopenta[*a*]acenaphthadien-6b-yl)-2-phenylethanol, (3) (Repo, Klinga, Leskelä, Polamo & Rieger, 1996), the same unequal C—C distances in the naphthalene unit [*e.g.* C12—C13 1.340 (13) and C13—C14 1.429 (11) Å] can be found. The bond lengths of the formally C—C single-bonded phenyl substituents [C4—C18 1.464 (10) and C6—C24 1.478 (10) Å] correspond to C_{sp^2}—C_{aryl} distances (Allen *et al.*, 1987; Norman, 1978). This is also indicated by the bright yellow luminescence of (1) in solution, which can be excited both by UV and visible light. Around the quaternary C3 atom, bond lengths [*e.g.* C2—C3 1.589 (9) and C3—C4 1.507 (9) Å], as well as bond angles [C4—C3—C15 125.0 (6), C7—C3—C15 101.2 (5) and C4—C3—C7 103.9 (6)°], are somewhat distorted from ideal tetrahedral values. There is no evidence of intermolecular interactions in the solid state other than van der Waals interactions.

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