

C8A—C8—C17	123.2 (2)	C8A'—C8'—C17'	124.4 (2)
C4A—C8A—C8	117.9 (3)	C1'—C8A'—C4A'	117.2 (2)
C4A—C8A—C1	117.4 (3)	C1'—C8A'—C8'	125.2 (2)
C8—C8A—C1	124.7 (2)	C4A'—C8A'—C8'	117.6 (2)

Data collection: *DIF4* (Stoe & Cie, 1991). Cell refinement: *DIF4*. Data reduction: *REDU4* (Stoe & Cie, 1991). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *XP* (Siemens, 1994). Software used to prepare material for publication: *SHELXL93*.

This work forms part of the PhD thesis of A. Bahl. We gratefully acknowledge financial support by the Volkswagen-Stiftung and the Fonds der Chemischen Industrie. Mr A. Weinkauff provided technical assistance.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: FG1206). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Methyl {4-[8-(4-Trifluoromethylphenyl)-naphthalen-1-yl]phenyl} Selenide

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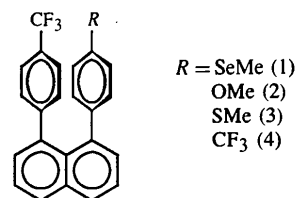
(Received 28 May 1996; accepted 11 June 1996)

Abstract

The phenyl rings of the title compound, C₂₄H₁₇F₃Se, make an angle of 21.1(2)° to each other and 59.1(1)° (CF₃-substituted) and 59.6(1)° (SeMe-substituted) with the naphthalene plane. The major distortion of the naphthalene ring system is seen in the angles C8a—C1—C9, C8—C8a—C1 and C8a—C8—C16, which are all *ca* 125°; there is little out-of-plane distortion.

Comment

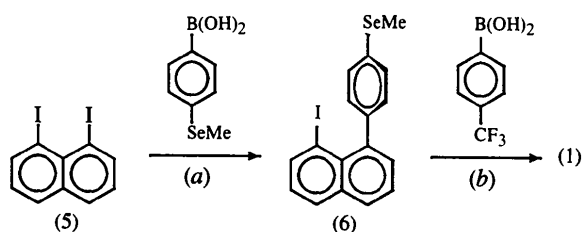
We have prepared selected 1,8-diarylnaphthalenes, including the title compound (1), to study the effects of through-space π–π interactions on linear and non-linear optical properties. We have shown that donor–acceptor (*D/A*)-substituted 1,8-diarylnaphthalenes possess similar or even higher first hyperpolarizabilities (β) than compounds of analogous transparency (Bahl *et al.*, 1995); *e.g.* for 1-(4-methoxyphenyl)-8-(4-trifluoromethylphenyl)naphthalene, (2), β is determined to be 35×10^{-30} e.s.u. (electrostatic units) by hyper-Rayleigh scattering (HRS) in chloroform solution (*cf.* parinitroaniline $\beta = 17 \times 10^{-30}$ e.s.u.). In an attempt to improve this value further, the sulfide, (3), and selenide, (1), derivatives have been prepared.



Aromatics with two (or more) potential leaving groups (*e.g.* I, Br) cause the formation of bis- or oligo-substitution products during C—C-crosscoupling reactions. Even with equimolar amounts, statistical product distributions are usually obtained. In the case of 1,8-diiodo- or dibromonaphthalene, a further complication is the facile dehalogenation, so that 1-arylnaphthalenes

without the required *peri*-halogen are often the main product in Kumada-type crosscouplings of Grignard reagents with diodonaphthalene (Kuroda *et al.*, 1993; Bahl, 1993). The idea of the sequence in the reaction scheme is the use of a less polar and thus less reactive and more selective organometallic species.

The Suzuki-type (Miyaura, Yanagi & Suzuki 1981) crosscoupling reaction, (a), results in the iodo derivative (6) (49%). The steric hindrance of the second arylation is sufficient to reduce the amount of the unwanted bis-product (4%) in the first step. Nevertheless the palladium-catalysed crosscoupling of aryl halides with aryl dihydroxyboranes is well suited to syntheses of sterically demanding and strained compounds such as 1,8-diarylnaphthalenes, as shown by the synthesis of (1) in 62% yield (full details are given by Bahl, 1996, and other examples by Bahl *et al.*, 1995).



It has recently been reported that the donor strength of the chalcogen substituents (with regard to β) decreases in the order SeMe \sim SMe \gg OMe (Blenkle *et al.* 1996). Although the selenide (1) and the sulfide (3) should therefore have comparable first hyperpolarizabilities, the selenide is expected to cause less trouble because of fluorescence in the HRS experiment. The internal heavy-atom effect should decrease the quantum yield of (1) compared to (2) or (3) (for a discussion of this effect, with comments on exceptions, see Dreeskamp, Koch & Zander, 1975).

Crystals of (1) belong to the monoclinic space group $P2_1/n$. As this is centrosymmetric, the compound (at least in this modification) is not suited for frequency doubling. Fig. 1 shows the conformation of the molecule in the crystalline state (143 K).

In the previous paper of this series (Bahl, Grahn & Jones, 1996), we drew attention to the flexibility of *peri*-diarylnaphthalenes, as revealed by a comparison of X-ray structures, AM1 calculations and solution properties. In this case, AM1 calculations on (1) also revealed a similar flat energy surface for a variation of the interring dihedral angles, as would be expected in view of the lack of *ortho*- or *meta*-substituents. The two phenyl rings of (1) face each other in an approximately parallel arrangement [interplanar angle $21.1(2)^\circ$], while subtending angles of $59.1(1)^\circ$ (C9–14) and $59.6(1)^\circ$ (C16–21) with the naphthalene plane. These angles are smaller than in the parent compound, 1,8-diphenylnaphthalene (67° ; Tsuji *et al.*, 1993) or in (4) ($66/69^\circ$

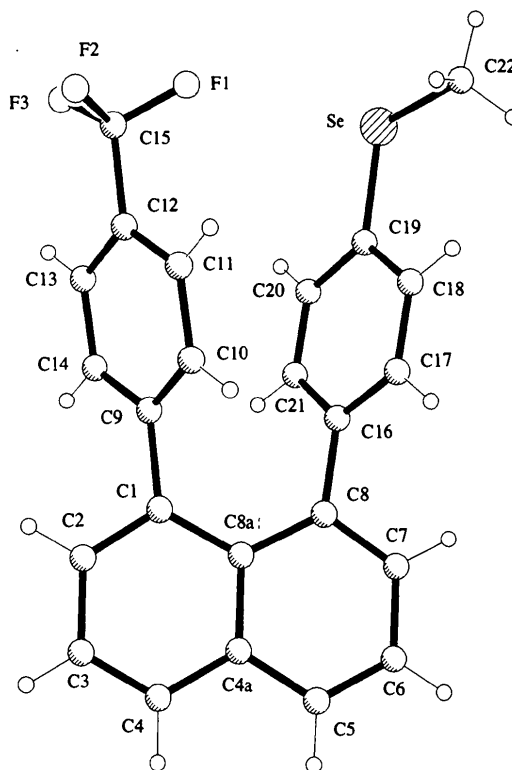


Fig. 1. The molecule of compound (1) in the crystal. Radii are arbitrary. Only one position of the disordered CF₃ group is shown.

and $62/64^\circ$ in two independent molecules; Jones, Grahn, Bahl & Reisner, 1995).

As known from X-ray structures of other 1,8-diarylnaphthalenes (Bahl *et al.*, 1996, and references therein), the steric strain induced by the non-bonded interactions between the *peri*-phenyl rings is reduced by in-plane (bond distances C8a—C1, C8a—C8; bond angles C8a—C1—C9, C8a—C8—C16) and out-of-plane deformations (dihedral angles C4—C4a—C8a—C1, C5—C4a—C8a—C8) of the naphthalene spacer. Interestingly, in (1) the out-of-plane deformation is quite small; the naphthalene moiety is planar within a mean deviation of 0.022 Å. [In contrast, compound (4) showed displacements of C1 and C8 up to 0.14 Å out of the best plane]. The main release of steric strain can therefore be attributed to in-plane deformations, namely the 125° angles C8a—C1—C9, C8—C8a—C1 and C8a—C8—C16 (Table 2). These are also responsible for the splaying of the phenyl rings, as illustrated by the contact distances C9...C16 3.003 (4), C12...C19 3.986 (4) Å.

Experimental

Compound (1) was synthesized in two steps: (a) equimolar amounts of compound (5) and the methylselenenyl phenylboronic acid were treated with 2 eq. K₂CO₃, 3% Pd[PPh₃]₄ in toluene, EtOH and water; (b) compound (6) was treated with

1.5 eq. of the trifluoromethyl phenylboronic acid as described in (a). Crystals of (1) were obtained by slow evaporation of a chloroform solution.

Crystal data

$C_{24}H_{17}F_3Se$
 $M_r = 441.34$
 Monoclinic
 $P2_1/n$
 $a = 9.3756$ (14) Å
 $b = 9.187$ (2) Å
 $c = 22.287$ (5) Å
 $\beta = 94.622$ (12)°
 $V = 1913.4$ (6) Å³
 $Z = 4$
 $D_x = 1.532$ Mg m⁻³
 D_m not measured

Data collection

Stoe Stadi-4 diffractometer
 ω/θ scans
 Absorption correction:
 ψ -scans (XEMP; Nicolet,
 1987)
 $T_{min} = 0.587$, $T_{max} =$
 1.000
 4663 measured reflections
 4402 independent reflections

Mo $K\alpha$ radiation
 $\lambda = 0.71073$ Å
 Cell parameters from 54
 reflections
 $\theta = 10$ – 11.5°
 $\mu = 1.997$ mm⁻¹
 $T = 143$ (2) K
 Tablet
 $0.50 \times 0.50 \times 0.20$ mm
 Colourless

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.0492$
 $wR(F^2) = 0.1327$
 $S = 1.038$
 4389 reflections
 267 parameters
 H atoms: rigid methyl group,
 others riding
 $w = 1/[\sigma^2(F_o^2) + (0.0502P)^2$
 $+ 4.0665P]$
 where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.926$
 $\Delta\rho_{max} = 0.959$ e Å⁻³
 $\Delta\rho_{min} = -0.803$ 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)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

$$U_{eq} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*a_i\cdot a_j.$$

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
Se	0.83281 (4)	0.17593 (5)	0.58593 (2)	0.03858 (14)
C1	0.2079 (3)	0.2087 (3)	0.74173 (13)	0.0198 (6)
C2	0.0623 (3)	0.1912 (4)	0.74448 (14)	0.0260 (6)
C3	-0.0031 (4)	0.1935 (4)	0.7992 (2)	0.0286 (7)
C4	0.0803 (4)	0.2135 (4)	0.85153 (15)	0.0278 (7)
C4a	0.2308 (4)	0.2264 (4)	0.85192 (14)	0.0251 (6)
C5	0.3125 (4)	0.2426 (4)	0.90779 (14)	0.0315 (7)
C6	0.4569 (4)	0.2589 (5)	0.9100 (2)	0.0374 (8)
C7	0.5262 (4)	0.2530 (4)	0.8563 (2)	0.0339 (8)
C8	0.4534 (3)	0.2312 (4)	0.80054 (14)	0.0242 (6)
C8a	0.2999 (3)	0.2222 (3)	0.79656 (13)	0.0217 (6)
C9	0.2554 (3)	0.2205 (3)	0.67948 (13)	0.0200 (6)
C10	0.3226 (3)	0.3458 (3)	0.66057 (13)	0.0217 (6)
C11	0.3630 (3)	0.3565 (4)	0.60229 (14)	0.0258 (7)
C12	0.3339 (3)	0.2432 (4)	0.56225 (14)	0.0260 (6)
C13	0.2631 (3)	0.1196 (4)	0.57985 (14)	0.0278 (7)
C14	0.2229 (3)	0.1093 (4)	0.63809 (14)	0.0245 (6)

C15	0.3811 (4)	0.2538 (4)	0.4992 (2)	0.0358 (8)
F1†	0.5147 (4)	0.2795 (13)	0.4989 (2)	0.148 (4)
F2†	0.3185 (7)	0.3654 (7)	0.4695 (2)	0.104 (3)
F3†	0.3424 (10)	0.1494 (6)	0.4647 (2)	0.125 (4)
F1'‡	0.4747 (10)	0.3515 (9)	0.4927 (5)	0.037 (3)
F2'‡	0.2912 (9)	0.2555 (14)	0.4604 (4)	0.053 (3)
F3'‡	0.4614 (11)	0.1326 (10)	0.4879 (5)	0.047 (3)
C16	0.5436 (3)	0.2190 (4)	0.74879 (14)	0.0237 (6)
C17	0.6355 (3)	0.3319 (4)	0.73632 (15)	0.0267 (6)
C18	0.7212 (3)	0.3242 (4)	0.68826 (15)	0.0288 (7)
C19	0.7172 (3)	0.2012 (4)	0.65187 (14)	0.0274 (7)
C20	0.6284 (3)	0.0852 (4)	0.66546 (15)	0.0280 (7)
C21	0.5437 (3)	0.0943 (4)	0.71281 (14)	0.0265 (7)
C22	0.9268 (5)	0.3634 (5)	0.5847 (2)	0.0501 (11)

† Site occupancy = 0.718 (8). ‡ Site occupancy = 0.282 (8).

Table 2. Selected geometric parameters (Å, °)

Se—C19	1.910 (3)	C4—C4a	1.416 (5)
Se—C22	1.936 (5)	C4a—C5	1.416 (5)
C1—C8a	1.443 (4)	C8—C8a	1.437 (4)
C1—C9	1.495 (4)	C8—C16	1.489 (4)
C8a—C1—C9	125.3 (3)	C8—C8a—C1	125.8 (3)
C8a—C8—C16	125.2 (3)		

The CF₃ fluorines are markedly anisotropic and are disordered over two positions with refined occupancies 0.718, 0.282 (8).

Data collection: *DIF4* (Stoe & Cie, 1991a). Cell refinement: *DIF4*. Data reduction: *REDU4* (Stoe & Cie, 1991b). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *XP* (Siemens, 1994). Software used to prepare material for publication: *SHELXL93*.

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Bis(2,4-diaminopyrimidinium) Sulfate Monohydrate, 2C₄H₇N₄⁺·SO₄²⁻·H₂O[†]

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Abstract

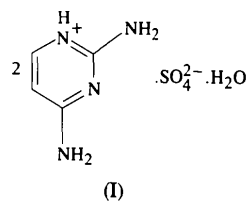
The asymmetric unit of the crystal consists of one sulfate ion, one water molecule and two 2,4-diaminopyrimidine (DAP) molecules stacked parallel to the *b* direction with average perpendicular separations of 3.310 (4) and 3.343 (4) Å, respectively. The tilt angle between the least-squares planes of the two DAP molecules in the asymmetric unit is 2.1 (1)°. The structure is stabilized by stacking forces, N—H···N hydrogen bonds and N—H···O hydrogen bonds.

Comment

2,4-Diaminopyrimidines and condensed pyrimidine systems are strong antagonists of folic acid (Hitchings, Elion, Vanderwerff & Falco, 1948; Hitchings, Falco, Vanderwerff, Russel & Elion, 1952) and some of these compounds possess growth-inhibitory properties affecting various living systems. It has also been found that 2,4-diaminopyrimidine has strong growth-inhibitory activity against *C. albicans*; the activities of 2,4,5,6-tetraamino- and 2,4,6-triaminopyrimidine are much weaker in that respect (Mukherjee, 1968). Therefore,

† The *Abstract* of this paper was presented at the National Seminar on Crystallography, Madras University, India, 15–17 December, 1993.

in continuation of our structural studies of nucleic acid components (Banerjee, Dattagupta, Saenger & Rabczenko, 1977; Banerjee, Saenger, Lesyng, Kazimierzczuk & Shugar, 1978; Biswas, Iitaka, Shugar & Banerjee, 1989), the structure of the title compound, (I), was determined.



The structure consists of columnar stacks of DAP molecules and linear arrays of alternating SO₄²⁻ ions and water molecules, both running in the *b* direction (Fig. 2). Both the DAP molecules (*A* and *A'*) are planar, the largest deviations from the least-squares planes of the appropriate ring atoms being 0.039 (4) Å for N2 and 0.032 (4) Å for N2' and N4'. The atoms N1 and N1' are protonated. The average perpendicular distance between successive molecules of a stack alternates between 3.310 (4) and 3.343 (4) Å. Significant base-stacking interaction is obvious from the degree of overlap between adjacent base molecules (Fig. 2) and the short stack contacts C2'···C4 (3.310 Å) and C6'···C2 (3.391 Å).

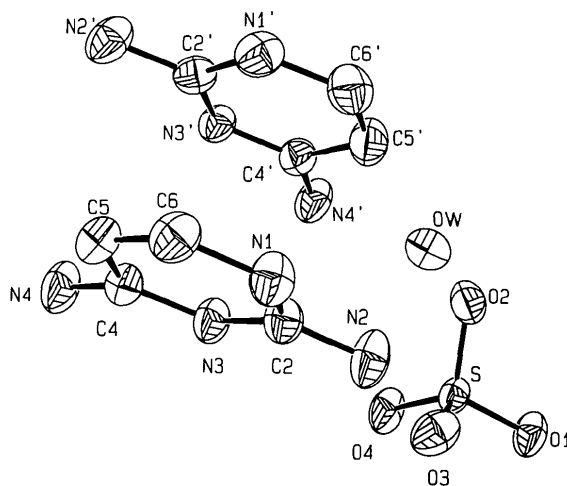


Fig. 1. ORTEP (Johnson, 1965) plot of the contents of the unit cell showing the atomic numbering scheme and displacement ellipsoids at the 50% probability level for non-H atoms. H atoms have been omitted for clarity.

Hydrogen-bonding parameters are given in Table 2. Fig. 2 shows that DAP molecules pair up (a characteristic feature of nucleobases) through two N—H···N type hydrogen bonds symmetrically disposed about a centre of inversion. Stacks of the base pairs form hydrophobic columns. Sulfate–water arrays, stabilized by OW—HW1···O2 and OW—HW2···O3 hydro-