

- Etter, M. C., MacDonald, J. C. & Bernstein, J. (1990). *Acta Cryst.* **B46**, 256–262.
- Ferguson, G., Gallagher, J. F., Glidewell, C. & Zakaria, C. M. (1993a). *J. Chem. Soc. Dalton Trans.*, pp. 3499–3506.
- Ferguson, G., Gallagher, J. F., Glidewell, C. & Zakaria, C. M. (1993b). *Acta Cryst.* **C49**, 967–971.
- Gabe, E. J., Le Page, Y., Charland, J.-P., Lee, F. L. & White, P. S. (1989). *J. Appl. Cryst.* **22**, 384–387.
- Glidewell, C., Ferguson, G., Lough, A. J. & Zakaria, C. M. (1994). *J. Chem. Soc. Dalton Trans.*, pp. 1971–1982.
- Glidewell, C., Zakaria, C. M. & Ferguson, G. (1996). *Acta Cryst.* **C52**, 1305–1309.
- Sheldrick, G. M. (1985). *SHELXS86. Program for the Solution of Crystal Structures.* University of Göttingen, Germany.
- Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.
- Spek, A. L. (1995a). *PLATON. Molecular Geometry Program*, July 1995 version. University of Utrecht, Utrecht, Holland.
- Spek, A. L. (1995b). *PLUTON. Molecular Graphics Program*, July 1995 version. University of Utrecht, Utrecht, Holland.

*Acta Cryst.* (1996). **C52**, 2014–2017

## 1-[3,5-Bis(trifluoromethyl)phenyl]-8-(4-methoxyphenyl)naphthalene: a Novel Three-Dimensional Non-Linear Optical Chromophore

ANDRÉ BAHL,<sup>a</sup> WALTER GRAHN<sup>a</sup> AND PETER G. JONES<sup>b\*</sup>

<sup>a</sup>Institut für Organische Chemie, Technische Universität Braunschweig, Hagenring 30, 38106 Braunschweig, Germany, and <sup>b</sup>Institut für Anorganische und Analytische Chemie, Technische Universität Braunschweig, Postfach 3329, 38023 Braunschweig, Germany. E-mail: jones@xray36.anchem.nat.tu-bs.de

(Received 21 May 1996; accepted 11 June 1996)

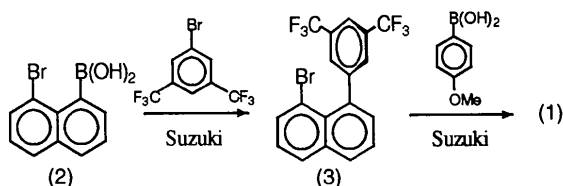
### Abstract

There are two molecules of C<sub>25</sub>H<sub>16</sub>F<sub>6</sub>O in the asymmetric unit. The interplanar angles between the naphthalene moiety and the phenyl substituents are 51.7, 52.5(1)° in the first molecule and 59.8, 58.1(1)° in the second for the trifluoromethyl- and methoxy-substituted rings, respectively. Calculations indicate that these are 'soft' parameters.

### Comment

As part of our continuing efforts to design materials for frequency doubling of diode laser sources, we are especially interested in donor(D)–acceptor(A)-substituted diarylnaphthalenes (Bahl *et al.*, 1995) such as the title compound (1). According to the classification introduced by Nalva, Watanabe & Miyata (1995) (one- and two-dimensional non-linear optical chromophores),

these molecules represent a novel three-dimensional type. The three-dimensional chromophoric system is constituted by two non-conjugated biphenylene subunits and a potential through-space charge–transfer (CT) subchromophore. To estimate the effectiveness of these interactions, which depend strongly on the inter-aryl angles and distances, and also to determine whether the substances crystallize in non-centrosymmetric space groups (a prerequisite for frequency doubling), we have embarked on a series of X-ray structure determinations (Jones, Grahn, Bahl & Reisner, 1995).



Compound (1) crystallizes in a centrosymmetric space group, which renders the crystals unsuitable for applications of quadratic non-linear optical effects. The two independent molecules, (1a) and (1b) [(1a) is shown in Fig. 1], display different conformations, the differences arising mostly from the relative orientation of the ring systems.

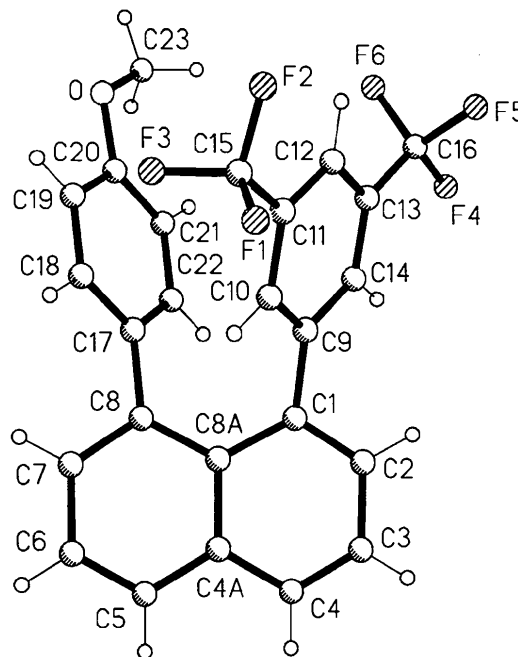


Fig. 1. One of the two independent molecules of the title compound in the crystal. Radii are arbitrary.

As is known from X-ray structures of other 1,8-diarylnaphthalenes (Clough, Kung, Marsh & Roberts 1976; Wahl, Krieger, Schweitzer & Staab, 1984; Jones *et al.*, 1995; Tsuji *et al.*, 1993), the steric strain

induced by the non-bonded interactions between the *peri*-phenyl groups strongly affects the geometry of the molecule. The two phenyl rings C9–C14 and C17–C22 display a face-to-face arrangement and subtend interplanar angles of 51.7 and 52.5 (1)°, respectively, in (1a) and 59.8 and 58.1 (1)°, respectively, in (1b) with the best naphthalene plane. The naphthalene moiety evades excessive steric stress in three main ways: (i) The bonds C1–C8A [1.443, 1.436 (4) Å for (1a) and (1b), respectively] and C8–C8A [1.438, 1.442 (4) Å] are slightly lengthened with respect to the 'standard' value of 1.420 Å for naphthalenes (Allen *et al.*, 1987); (ii) The atoms C1 and C8 undergo out-of-plane deformations [lying 0.133, –0.140 (2) Å out of the best plane in (1a) and –0.094, 0.092 (2) Å in (1b), which in turn renders the concept of the 'best' naphthalene plane less valid; the torsion angles C1···C4···C5···C8 are 7.8 (1) and –5.1 (1)° in (1a) and (1b), respectively]; (iii) The bond angles C8A–C1–C9 [123.4, 122.8 (2)°], C8–C8A–C1 [124.7, 125.2 (2)°] and C8A–C8–C17 [123.2, 124.4 (2)°] are widened. The overall effect is to 'splay' the *peri* substituents.

It is noteworthy that the distance C9···C17 [2.981, 2.962 (4) Å] is still significantly shorter than the van der Waals separation for parallel aromatic systems (*ca* 3.40 Å; Clough *et al.*, 1976) or the mean layer separation in  $\pi$ -donor/ $\pi$ -acceptor charge-transfer complexes (*ca* 3.3 Å; Foster, 1969). This close face-to-face arrangement is an important prerequisite for the through-space CT interaction of the donor-(OMe)- and the acceptor-(3,5-CF<sub>3</sub>) phenyl rings. The contact distances C12···C20 are 4.323, 4.074 (4) Å.

Considering the severe steric interactions, the interplanar angles as discussed above are surprisingly low compared to 1,8-diphenyl-naphthalene (67°; Tsuji *et al.*, 1993). As this parameter is decisive in estimating the electronic interaction between the naphthalene and the phenyl moieties, we have calculated the potential-energy surface as a function of the interplanar angles. The AM1 Hamiltonian (Dewar, Zoebisch, Healy & Stewart, 1985) has proved to be a good approximation for this purpose in related cases (Annunziata, Ponzini & Raimondi, 1995; Boyer *et al.*, 1993; Kranz, Clark & von Ragué Schleyer, 1993). Fig. 2 shows the results of the semi-empirical calculations (AM1, program VAMPC; Clark & Wiedel, 1992).

All main features of the X-ray structure are reproduced by the ground-state AM1 geometry. The only significant deviation occurs in the dihedral angles of the phenyl rings with respect to the naphthalene plane, which also represents the main difference between molecules (1a) and (1b). This could be explained by the shallow energy trough for dihedral angles between 50° and 140° (see Fig. 2). The AM1 energy difference of conformer (1a) and (1b) is only 12 kJ/mol [MM2 (Allinger & Yuh, 1977): 24 kJ/mol] so that crystal packing effects can exert a great influence on the con-

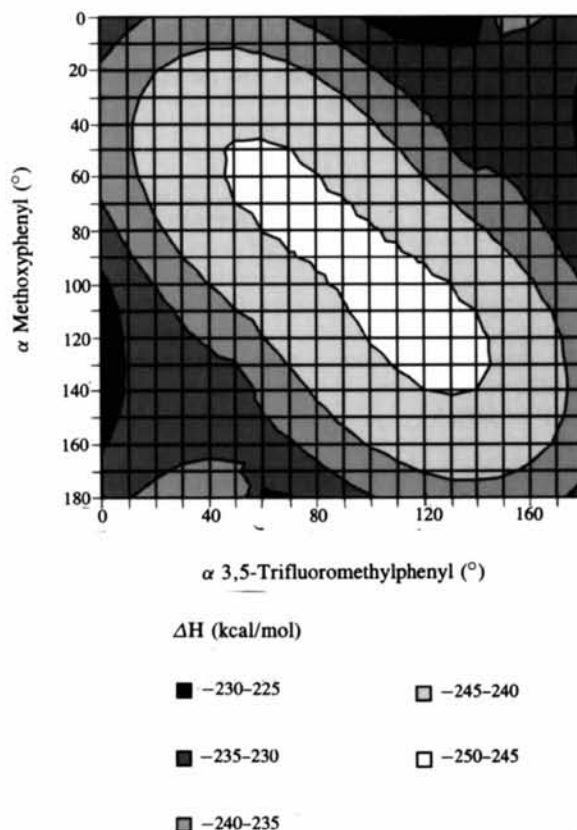


Fig. 2. Calculated potential-energy surface as a function of the interring dihedral angles C8A–C1–C9–C10 or C8A–C8–C17–C22 (see *Comment*). 1 kcal = 4.184 kJ.

formation these molecules. These findings agree well with calculations of the internal rotational pathways of *peri*-diarylnaphthalenes by other methods (Tsuzuki, Tanabe, Nagawa & Nakanishi, 1990) and investigations of solvated molecules by dynamic NMR experiments (Annunziata *et al.*, 1995). Even in these cases the comparatively low rotational barrier is explained by the way the naphthalene moiety reduces the severe steric strain (see above): the out-of-plane deformation of the naphthalene spacer [e.g. dihedral angles C4–C4A–C8A–C1 –8.0, 5.7 (4)°, C5–C4A–C8A–C8 –9.2, 5.5 (4)°] plays the dominating role. Hence *peri*-diarylnaphthalenes without *ortho* substituents are flexible molecules with respect to the interplanar angles in the region of the equilibrium geometry.

## Experimental

The title compound (1) was prepared similarly to our published reaction sequence (Bahl *et al.*, 1995) involving two consecutive Suzuki couplings (full details are given by Bahl, 1996). The cross-coupling between the boronic acid (2) and 1-bromo-3,5-bis(trifluoromethyl)-benzene [3% Pd(PPh<sub>3</sub>)<sub>4</sub>, 2 eq. Na<sub>2</sub>CO<sub>3</sub>, toluene/EtOH/H<sub>2</sub>O, 24 h reflux] gave the monoaryl-

ated compound (3) (52% yield). The second Suzuki reaction (conditions as above) with 4-(methoxyphenyl)boronic acid resulted in (1) (65 % yield), which was recrystallized by slow evaporation from chloroform.

### Crystal data

C<sub>25</sub>H<sub>16</sub>F<sub>6</sub>O  
*M<sub>r</sub>* = 446.38  
 Monoclinic  
*P*2<sub>1</sub>/*c*  
*a* = 14.817 (3) Å  
*b* = 17.322 (4) Å  
*c* = 16.788 (3) Å  
 $\beta$  = 107.24 (2)°  
*V* = 4115.4 (15) Å<sup>3</sup>  
*Z* = 8  
*D<sub>x</sub>* = 1.441 Mg m<sup>-3</sup>  
*D<sub>m</sub>* not measured

Mo K $\alpha$  radiation  
 $\lambda$  = 0.71073 Å  
 Cell parameters from 48 reflections  
 $\theta$  = 10–11.5°  
 $\mu$  = 0.124 mm<sup>-1</sup>  
*T* = 143 (2) K  
 Lath  
 0.80 × 0.35 × 0.15 mm  
 Colourless

### Data collection

Stoe Stadi-4 diffractometer  
 $\omega/\theta$ -scans  
 Absorption correction: none  
 11741 measured reflections  
 7260 independent reflections  
 4723 observed reflections [*I* > 2 $\sigma$ (*I*)]

*R*<sub>int</sub> = 0.0342  
 $\theta_{\max}$  = 25.04°  
*h* = -17 → 16  
*k* = -20 → 9  
*l* = 0 → 19  
 3 standard reflections  
 frequency: 60 min  
 intensity decay: 4%

### Refinement

Refinement on *F*<sup>2</sup>  
*R* [*F*<sup>2</sup> > 2 $\sigma$ (*F*<sup>2</sup>)] = 0.0535  
*wR*(*F*<sup>2</sup>) = 0.1365  
*S* = 1.078  
 7225 reflections  
 579 parameters  
 H atoms: rigid methyl groups, others riding  
 $w = 1/[\sigma^2(F_o^2) + (0.0387P)^2 + 2.2152P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$

( $\Delta/\sigma$ )<sub>max</sub> < 0.001  
 $\Delta\rho_{\max} = 0.245 \text{ e } \text{Å}^{-3}$   
 $\Delta\rho_{\min} = -0.270 \text{ e } \text{Å}^{-3}$   
 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 (Å<sup>2</sup>)

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

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>eq</sub>
C1	0.2262 (2)	0.3458 (2)	0.2975 (2)	0.0293 (6)
C2	0.1963 (2)	0.3262 (2)	0.3649 (2)	0.0339 (7)
C3	0.1083 (2)	0.3511 (2)	0.3722 (2)	0.0403 (8)
C4	0.0534 (2)	0.3988 (2)	0.3140 (2)	0.0393 (7)
C4A	0.0793 (2)	0.4194 (2)	0.2421 (2)	0.0358 (7)
C5	0.0220 (2)	0.4704 (2)	0.1826 (2)	0.0466 (8)
C6	0.0459 (2)	0.4899 (2)	0.1128 (2)	0.0505 (9)
C7	0.1231 (2)	0.4543 (2)	0.0961 (2)	0.0423 (8)
C8	0.1800 (2)	0.4022 (2)	0.1505 (2)	0.0327 (7)
C8A	0.1639 (2)	0.3888 (2)	0.2297 (2)	0.0303 (6)
C9	0.3263 (2)	0.3283 (2)	0.3034 (2)	0.0277 (6)
C10	0.3857 (2)	0.3862 (2)	0.2912 (2)	0.0283 (6)
C11	0.4805 (2)	0.3709 (2)	0.3006 (2)	0.0288 (6)
C12	0.5175 (2)	0.2984 (2)	0.3227 (2)	0.0321 (7)
C13	0.4589 (2)	0.2409 (2)	0.3362 (2)	0.0299 (6)

C14	0.3645 (2)	0.2552 (2)	0.3267 (2)	0.0295 (6)
C15	0.5414 (2)	0.4350 (2)	0.2861 (2)	0.0370 (7)
C16	0.4992 (2)	0.1626 (2)	0.3592 (2)	0.0408 (7)
C17	0.2493 (2)	0.3570 (2)	0.1206 (2)	0.0292 (6)
C18	0.3127 (2)	0.3928 (2)	0.0849 (2)	0.0350 (7)
C19	0.3743 (2)	0.3499 (2)	0.0555 (2)	0.0373 (7)
C20	0.3737 (2)	0.2696 (2)	0.0599 (2)	0.0334 (7)
C21	0.3109 (2)	0.2334 (2)	0.0943 (2)	0.0325 (7)
C22	0.2495 (2)	0.2771 (2)	0.1240 (2)	0.0324 (7)
C23	0.4382 (2)	0.1505 (2)	0.0324 (2)	0.0546 (9)
O	0.43716 (14)	0.23235 (13)	0.02874 (13)	0.0466 (6)
F1	0.53857 (13)	0.49746 (10)	0.33166 (12)	0.0545 (5)
F2	0.63208 (11)	0.41503 (11)	0.30392 (13)	0.0559 (5)
F3	0.51552 (14)	0.45836 (11)	0.20650 (11)	0.0606 (6)
F4	0.43925 (13)	0.11249 (10)	0.37591 (13)	0.0556 (5)
F5	0.57535 (13)	0.16330 (12)	0.42638 (14)	0.0699 (6)
F6	0.5296 (2)	0.13100 (11)	0.29912 (14)	0.0702 (6)
C1'	1.0110 (2)	0.3371 (2)	0.7423 (2)	0.0284 (6)
C2'	1.0355 (2)	0.3267 (2)	0.8273 (2)	0.0332 (7)
C3'	1.1223 (2)	0.3521 (2)	0.8808 (2)	0.0366 (7)
C4'	1.1833 (2)	0.3901 (2)	0.8485 (2)	0.0355 (7)
C4A'	1.1640 (2)	0.4009 (2)	0.7611 (2)	0.0303 (6)
C5'	1.2285 (2)	0.4410 (2)	0.7291 (2)	0.0363 (7)
C6'	1.2109 (2)	0.4516 (2)	0.6460 (2)	0.0386 (7)
C7'	1.1299 (2)	0.4185 (2)	0.5904 (2)	0.0342 (7)
C8'	1.0649 (2)	0.3769 (2)	0.6170 (2)	0.0273 (6)
C8A'	1.0777 (2)	0.3707 (2)	0.7053 (2)	0.0268 (6)
C9'	0.9110 (2)	0.3208 (2)	0.6939 (2)	0.0294 (6)
C10'	0.8541 (2)	0.3799 (2)	0.6505 (2)	0.0306 (6)
C11'	0.7603 (2)	0.3664 (2)	0.6065 (2)	0.0323 (7)
C12'	0.7219 (2)	0.2933 (2)	0.6052 (2)	0.0375 (7)
C13'	0.7779 (2)	0.2344 (2)	0.6491 (2)	0.0371 (7)
C14'	0.8716 (2)	0.2479 (2)	0.6940 (2)	0.0345 (7)
C15'	0.7001 (2)	0.4307 (2)	0.5613 (2)	0.0438 (8)
C16'	0.7385 (2)	0.1546 (2)	0.6439 (2)	0.0549 (9)
C17'	0.9890 (2)	0.3366 (2)	0.5514 (2)	0.0282 (6)
C18'	0.9297 (2)	0.3781 (2)	0.4853 (2)	0.0322 (7)
C19'	0.8612 (2)	0.3418 (2)	0.4225 (2)	0.0370 (7)
C20'	0.8506 (2)	0.2626 (2)	0.4241 (2)	0.0368 (7)
C21'	0.9100 (2)	0.2197 (2)	0.4881 (2)	0.0341 (7)
C22'	0.9785 (2)	0.2572 (2)	0.5509 (2)	0.0310 (6)
C23'	0.7712 (2)	0.1505 (2)	0.3537 (2)	0.0560 (10)
O'	0.77960 (14)	0.23210 (14)	0.35929 (13)	0.0499 (6)
F1'	0.74999 (13)	0.48978 (12)	0.5458 (2)	0.0787 (7)
F2'	0.64325 (13)	0.40880 (12)	0.48720 (12)	0.0649 (6)
F3'	0.64321 (15)	0.45879 (13)	0.60177 (14)	0.0756 (7)
F4'	0.7816 (2)	0.11186 (2)	0.71060 (13)	0.0735 (7)
F5'	0.7509 (2)	0.11567 (13)	0.5786 (2)	0.0967 (9)
F6'	0.6480 (2)	0.15211 (15)	0.6348 (2)	0.1018 (10)

Table 2. Selected geometric parameters (Å, °)

C1—C2	1.374 (4)	C1'—C2'	1.377 (4)
C1—C8A	1.443 (4)	C1'—C8A'	1.436 (4)
C2—C3	1.412 (4)	C2'—C3'	1.403 (4)
C3—C4	1.352 (4)	C3'—C4'	1.354 (4)
C4—C4A	1.417 (4)	C4'—C4A'	1.421 (4)
C4A—C5	1.413 (4)	C4A'—C5'	1.411 (4)
C4A—C8A	1.430 (4)	C4A'—C8A'	1.440 (4)
C5—C6	1.362 (5)	C5'—C6'	1.354 (4)
C6—C7	1.401 (4)	C6'—C7'	1.406 (4)
C7—C8	1.380 (4)	C7'—C8'	1.379 (4)
C8—C8A	1.438 (4)	C8'—C8A'	1.442 (4)
C2—C1—C8A	119.3 (2)	C2'—C1'—C8A'	119.8 (2)
C2—C1—C9	117.0 (2)	C2'—C1'—C9'	117.0 (2)
C8A—C1—C9	123.4 (2)	C8A'—C1'—C9'	122.8 (2)
C1—C2—C3	121.8 (3)	C1'—C2'—C3'	122.2 (3)
C4—C3—C2	119.8 (3)	C4'—C3'—C2'	119.3 (3)
C3—C4—C4A	120.8 (3)	C3'—C4'—C4A'	121.5 (3)
C5—C4A—C4	120.1 (3)	C5'—C4A'—C4'	120.4 (3)
C5—C4A—C8A	119.9 (3)	C5'—C4A'—C8A'	120.1 (3)
C4—C4A—C8A	120.0 (3)	C4'—C4A'—C8A'	119.5 (3)
C6—C5—C4A	120.5 (3)	C6'—C5'—C4A'	120.9 (3)
C5—C6—C7	120.0 (3)	C5'—C6'—C7'	119.6 (3)
C8—C7—C6	122.0 (3)	C8'—C7'—C6'	122.6 (3)
C7—C8—C8A	118.8 (3)	C7'—C8'—C8A'	118.7 (2)
C7—C8—C17	117.8 (3)	C7'—C8'—C17'	116.8 (2)

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.

## References

- Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–S19.
- Allinger, N. L. & Yuh, Y. (1977). *MM2*. QCPE No. 3951. Department of Chemistry, Indiana University, USA.
- Annunziata, R., Ponzini, F. & Raimondi, L. (1995). *Magn. Reson. Chem.* **33**, 297–307.
- Bahl, A. (1996). PhD thesis (in preparation), Technical University of Braunschweig, Germany.
- Bahl, A., Grahn, W., Stadler, S., Feiner, F., Bourhill, G., Bräuchle, C., Reisner, A. & Jones, P. G. (1995). *Angew. Chem.* **107**, 1587–1590; *Angew. Chem. Int. Ed. Engl.* **34**, 1485–1488.
- Boyer, G., Claramunt, R. M., Elguero, J., Fathalla, M., Foces-Foces, C., Jaime, C. & Llamas-Saiz, A. L. (1993). *J. Chem. Soc. Perkin Trans. 2*, pp. 757–766.
- Clark, T. & Wiedel, B. (1992). *VAMPC 4.41 Program Package*. University of Erlangen, Germany.
- Clough, R. L., Kung, W. J., Marsh, R. E. & Roberts, J. D. (1976). *J. Org. Chem.* **41**, 3603–3609.
- Dewar, M. J. S., Zoebisch, E. G., Healy, E. F. & Stewart J. J. P. (1985). *J. Am. Chem. Soc.* **107**, 3902–3909.
- Foster, R. (1969). In *Organic Charge-Transfer Complexes*. London: Academic Press.
- Jones, P. G., Grahn, W., Bahl, A. & Reisner, A. (1995). *Z. Kristallogr.* **210**, 229–230.
- Kranz, M., Clark, T. & von Ragué Schleyer, P. (1993). *J. Org. Chem.* **58**, 3317–3325.
- Nalva, H. S., Watanabe, T. & Miyata, S. (1995). *Adv. Mater.* **7**, 754–758.
- Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.
- Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
- Siemens (1994). *XP. Molecular Graphics Program*. Version 5.03. Siemens Analytical X-ray Instruments, Madison, Wisconsin, USA.
- Stoe & Cie (1991). *DIF4. Diffractometer Control Program*. Version 7.08. Stoe & Cie, Darmstadt, Germany.
- Stoe & Cie (1991). *REDU4. Data Reduction Program*. Version 7.08. Stoe & Cie, Darmstadt, Germany.
- Tsuji, R., Komatsu, K., Takeuchi, K., Shiro, M., Cohen, S. & Rabinovitz, M. (1993). *J. Phys. Org. Chem.* **6**, 435–444.
- Tsuzuki, S., Tanabe, K., Nagawa, Y. & Nakanishi, H. (1990). *J. Mol. Struct.* **216**, 279–295.
- Wahl, P., Krieger, C., Schweitzer, D. & Staab, H. A. (1984). *Chem. Ber.* **117**, 260–276.

*Acta Cryst.* (1996). **C52**, 2017–2020

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

ANDRÉ BAHL,<sup>a</sup> WALTER GRAHN<sup>a</sup> AND PETER G. JONES<sup>b\*</sup>

<sup>a</sup>Institut für Organische Chemie, Technische Universität Braunschweig, Hagenring 30, 38106 Braunschweig, Germany, and <sup>b</sup>Institut für Anorganische und Analytische Chemie, Technische Universität Braunschweig, Postfach 3329, 38023 Braunschweig, Germany. E-mail: jones@xray36.anchem.nat.tu-bs.de

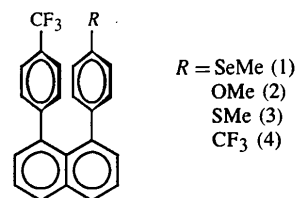
(Received 28 May 1996; accepted 11 June 1996)

## Abstract

The phenyl rings of the title compound, C<sub>24</sub>H<sub>17</sub>F<sub>3</sub>Se, make an angle of 21.1(2)° to each other and 59.1(1)° (CF<sub>3</sub>-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 ( $\beta$ ) than compounds of analogous transparency (Bahl *et al.*, 1995); *e.g.* for 1-(4-methoxyphenyl)-8-(4-trifluoromethylphenyl)naphthalene, (2),  $\beta$  is determined to be  $35 \times 10^{-30}$  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