

Table 3. *Selected geometric parameters* ($\text{\AA}$, $^\circ$) *for (II)*

S1—O1	1.402 (2)	S2—O5	1.446 (2)
S1—O2	1.424 (3)	S2—O6	1.431 (3)
S1—O3	1.439 (3)	S2—C10	1.773 (3)
S1—C3	1.783 (3)	N1—C4	1.465 (4)
S2—O4	1.438 (2)	N2—C11	1.461 (4)
O1—S1—O2	115.4 (2)	O5—S2—C10	107.0 (1)
O1—S1—O3	112.8 (2)	O6—S2—C10	106.0 (2)
O1—S1—C3	108.1 (1)	S1—C3—C2	120.1 (2)
O2—S1—O3	110.9 (2)	S1—C3—C4	121.4 (2)
O2—S1—C3	105.1 (2)	N1—C4—C3	120.8 (3)
O3—S1—C3	103.4 (2)	N1—C4—C5	118.3 (3)
O4—S2—O5	112.6 (2)	S2—C10—C9	118.5 (2)
O4—S2—O6	112.9 (2)	S2—C10—C11	123.1 (2)
O4—S2—C10	106.4 (1)	N2—C11—C10	120.3 (3)
O5—S2—O6	111.5 (2)	N2—C11—C12	118.8 (3)

Table 4. *Hydrogen-bonding geometry* ($\text{\AA}$, $^\circ$) *for (II)*

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H7 $\cdots$ O6 ⁱ	0.86 (3)	2.09 (3)	2.821 (5)	143 (3)
N1—H8 $\cdots$ O2	0.77 (3)	2.34 (3)	2.947 (4)	137 (3)
N1—H8 $\cdots$ O4 ⁱⁱ	0.77 (3)	2.44 (3)	2.847 (4)	114 (3)
N1—H9 $\cdots$ O4	0.92 (3)	2.08 (3)	2.907 (5)	149 (3)
N2—H16 $\cdots$ O3 ⁱⁱⁱ	0.95 (3)	1.75 (3)	2.696 (4)	175 (3)
N2—H17 $\cdots$ O7 ^{iv}	0.87 (3)	1.92 (4)	2.779 (5)	169 (3)
N2—H18 $\cdots$ O6 ^v	0.92 (3)	2.41 (3)	2.900 (4)	114 (2)
O7—H19 $\cdots$ O2 ^{vi}	0.83 (4)	2.00 (4)	2.762 (4)	151 (4)
O7—H20 $\cdots$ O5	0.89 (4)	2.15 (4)	2.996 (4)	160 (4)

Symmetry codes: (i) $x, 1+y, z$; (ii) $2-x, \frac{1}{2}+y, \frac{1}{2}-z$; (iii) $x, -\frac{1}{2}-y, z-\frac{1}{2}$; (iv) $2-x, -y, -z$; (v) $2-x, -1-y, -z$; (vi) $2-x, y-\frac{1}{2}, \frac{1}{2}-z$.

Phenyl C—C bond distances: (I), 1.379 (4)–1.393 (4), mean 1.386 (4) $\text{\AA}$; (II), 1.363 (4)–1.396 (4), mean 1.385 (4) $\text{\AA}$. All H atoms were located on difference electron-density maps and refined with fixed isotropic B values equal to 1.2 times those of the attached atoms at the time of their inclusion. Bond distance ranges: (I), C—H 0.91 (3)–1.02 (3) and N—H 0.92 (3)–0.98 (3) $\text{\AA}$; (II), C—H 0.80 (3)–1.04 (3), N—H 0.77 (3)–0.95 (3) and O—H 0.83 (4)–0.89 (4) $\text{\AA}$.

For both compounds, data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1992); program(s) used to solve structures: *MITHRIL* (Gilmore, 1983); program(s) used to refine structures: *TEXSAN*; molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *TEXSAN*.

Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: FR1011). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

- Gilmore, C. J. (1983). *M'THRIL. Computer Program for the Automatic Solution of Crystal Structures from X-ray Data*. Department of Chemistry, University of Glasgow, Scotland.
- Gunderman, B. J. & Squattrito, P. J. (1996). *Acta Cryst.* **C52**, 940–942.
- Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- Molecular Structure Corporation (1988). *MSC/AFC Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Molecular Structure Corporation (1992). *TEXSAN. TEXRAY Structure Analysis Package*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Pirard, B., Baudoux, G. & Durant, F. (1995). *Acta Cryst.* **B51**, 103–107.

Shubnell, A. J. & Squattrito, P. J. (1994). *Acta Cryst.* **C50**, 1296–1299.

Acta Cryst. (1997). **C53**, 651–654

3-Acetamido-4-(cyclooctylamino)nitrobenzene

J. GONZÁLEZ-PLATAS,^a C. RUIZ-PÉREZ,^a M. TORRES^b
AND C. YANES^b

^a*Departamento de Física Fundamental y Experimental: Grupo de Rayos X, Universidad de La Laguna, Avda. Astrofísico Francisco Sánchez s/n, 38204 La Laguna – Tenerife, Canary Islands, Spain, and* ^b*Departamento de Física Fundamental y Experimental: Grupo de Crecimiento Cristalino, Universidad de La Laguna, Avda. Astrofísico Francisco Sánchez s/n, 38204 La Laguna – Tenerife, Canary Islands, Spain. E-mail: caruiz@ull.es*

(Received 15 March 1996; accepted 8 October 1996)

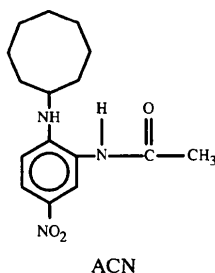
Abstract

The crystal and molecular structure of the title compound, *N*-(2-cyclooctylamino-4-nitrophenyl)acetamide, $C_{16}H_{23}N_3O_3$, has been determined as part of an investigation into substituted benzene derivatives having non-linear optical properties. There are two similar independent molecules in the asymmetric unit. The eight-membered rings have very distorted conformations. The molecules are linked by N—H $\cdots$ O hydrogen bonds, with N $\cdots$ O distances in the range 2.889 (5)–3.071 (6) $\text{\AA}$.

Comment

There is currently extensive interest in substituted benzene derivatives because of their exceptional non-linear optical properties (Williams, 1983, 1984). Many of these compounds, such as *p*-nitroaniline, exhibit extremely large microscopic second-order non-linear susceptibilities, which are the result of a highly asymmetric charge correlated with the excited states of the π -electronic structure of the molecule, as shown by theoretical calculations (Lalama & Garito, 1979). However, most substituted benzene molecular crystals, for example *p*-nitroaniline, have a centrosymmetric crystal structure which forbids any macroscopic second-order non-linear optical effects (Lalama & Garito, 1979; Oudar & Chemla, 1971; Southgate & Hall, 1971; Carencio, Jerphagnon & Periquard, 1977).

The title compound (ACN) is a donor–acceptor (*D–A*) substituted benzene derivative, with a charge-transfer (CT) interaction between the *para*-substituted groups, *i.e.* cyclooctylamino as donor and the nitro group as acceptor, which are known to produce high molecular non-linearity (Chemla & Zyss, 1986). The acetamido (NHCOCH₃) substituent provides only a minor contribution to the non-linearity, but serves the important function of promoting non-centrosymmetric crystal growth involving hydrogen bonding.



The title compound crystallizes with two independent molecules (labelled *A* and *B*) in the asymmetric unit. Molecules *A* and *B* have identical relative stereochemistries and very similar dimensions. An analysis of seminormal probability (Abrahams & Keve, 1971), indicates that differences between the two molecules with respect to bond lengths and angles are statistically insignificant, therefore, the average values will be used in the following discussion. An *ORTEP*II (Johnson, 1976) plot of molecule *B* with the crystallographic numbering scheme is shown in Fig. 1, while a similar plot of molecule *A* has been deposited with the supplementary material. Because of the structural similarity to both MNA (2-methyl-4-nitroaniline; Lipscomb, Garito & Narang, 1981) and DAN [4-(*N,N*-dimethylamino)-3-(acetamido)nitrobenzene; Baumert, Twieg, Bjorklund, Logan & Dirk, 1987], this discussion of ACN will include some points of comparison with them.

The N atoms of ACN are *sp*² hybridized (bond angles sum to 360°). As expected, the nitro group is only slightly rotated out of the aromatic plane [7.7(3)° in molecule *A* and 4.2(3)° in molecule *B*]. The average N—O bond length is 1.223(8) Å. The acetamido group is significantly twisted [45.9(2)° in molecule *A* and 47.5(2)° in molecule *B*] with respect to the plane of the benzene ring (41.6° in DAN).

The eight-membered ring in each molecule has a highly distorted conformation [molecule *A*: C7A, C8A, C9A1, C10A, C11A, C12A, C131, C14A has *Q*(2) 0.869, *Q*(3) 0.575 and *Q*(4) −0.298 Å, and φ (2) 170.7 and φ (3) 255.4°; C7A, C8A, C9A2, C10A, C11A, C12A, C132, C14A has *Q*(2) 0.936, *Q*(3) 0.283 and *Q*(4) −0.247 Å, and φ (2) 170.8 and φ (3) 120.6°; molecule *B*: C7B, C8B, C9B, C10B, C11B, C12B, C13B, C14B has *Q*(2) 0.926, *Q*(3) 0.592 and *Q*(4) 0.333 Å, and φ (2) 275.4 and φ (3)

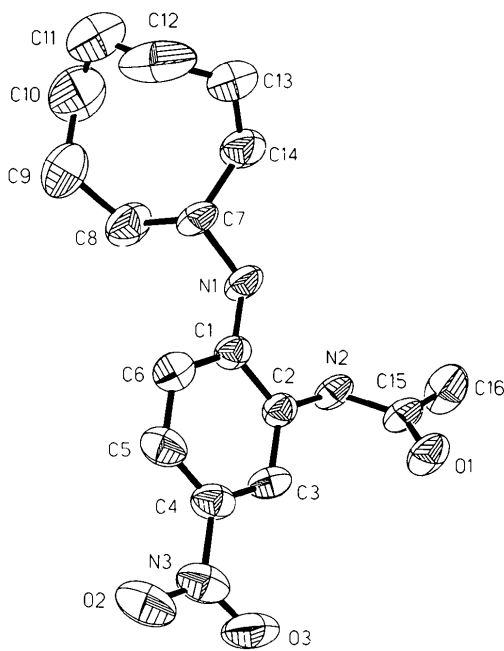


Fig. 1. A view of molecule *B* with the crystallographic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

47.5° (Spek, 1990)]. The average C_{sp}³—C_{sp}³ distance is 1.482(4) Å. The molecules are linked by N—H···O hydrogen bonds to form infinite chains along the *a* axis, with molecules in the sequence *A*···*B*···*A*···*B*. These chains are the result of the N—H group of the *A* molecules forming bifurcated N—H···O hydrogen bonds to adjacent carbonyl O atoms of the *B* molecules and so on.

Experimental

ACN was synthesized from commercially available 2-fluoro-5-nitroaniline in two steps. In the first step, a mixture of 2-fluoro-5-nitroaniline, acetic anhydride and pyridine (4 ml) was stirred for 24 h at room temperature. The mixture was poured into ice water and the pH adjusted by the addition of 5 *M* hydrochloric acid and extracted with ethyl acetate. The organic phase was washed with saturated sodium hydrogen carbonate, water and saturated brine, and dried (MgSO₄). After removal of the ethyl acetate, the crude reaction product obtained was used in the next step without purification. In the second step, a mixture of cyclooctylamine, triethylamine and DMF was added dropwise over 1 h to a stirred mixture of the intermediate 3-acetamido-4-fluoronitrobenzene and dry DMF under a nitrogen atmosphere. The reaction was stirred at reflux temperature for 1 h and then overnight at room temperature. TLC analysis then showed the 3-acetamido-4-fluoronitrobenzene to be completely consumed. The reaction mixture was slightly acidified with cold 5% aqueous HCl and extracted with ethyl acetate. The organic layer was washed with saturated aqueous sodium hydrogen carbonate, water and brine and dried (MgSO₄). After removal

of ethyl acetate, the residue was twice purified by fractional recrystallization from 96% ethanol to give yellow needles of the title compound (m.p. 448.5–449.5 K).

Crystal data

$C_{16}H_{23}N_3O_3$
 $M_r = 305.37$
 Orthorhombic
 $Pc2_1b$
 $a = 9.556(3) \text{ \AA}$
 $b = 18.257(3) \text{ \AA}$
 $c = 18.629(3) \text{ \AA}$
 $V = 3250.1(13) \text{ \AA}^3$
 $Z = 8$
 $D_x = 1.248 \text{ Mg m}^{-3}$
 D_m not measured

Data collection

Enraf–Nonius CAD-4
 diffractometer
 $\omega/2\theta$ scans
 Absorption correction: none
 4491 measured reflections
 4433 independent reflections
 2256 reflections with
 $I > 2\sigma(I)$

Refinement

Refinement on F^2
 $R(F) = 0.0639$
 $wR(F^2) = 0.2117$
 $S = 1.034$
 4409 reflections
 416 parameters
 All H atoms refined
 $w = 1/[\sigma^2(F_o^2) + (0.0971P)^2 + 0.6735P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = -0.004$
 $\Delta\rho_{\max} = 0.313 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.227 \text{ e \AA}^{-3}$

Mo $K\alpha$ radiation
 $\lambda = 0.71069 \text{ \AA}$
 Cell parameters from 25
 reflections
 $\theta = 6\text{--}18^\circ$
 $\mu = 0.087 \text{ mm}^{-1}$
 $T = 293(2) \text{ K}$
 Prism
 $0.45 \times 0.40 \times 0.30 \text{ mm}$
 Yellow

$R_{\text{int}} = 0.0100$
 $\theta_{\max} = 29.95^\circ$
 $h = -2 \rightarrow 13$
 $k = 0 \rightarrow 25$
 $l = 0 \rightarrow 20$
 1 standard reflection
 frequency: 120 min
 intensity decay: none

Extinction correction:
 $SHELXL93$ (Sheldrick,
 1993)
 Extinction coefficient:
 0.0096 (16)
 Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)
 Absolute configuration:
 Flack (1983)
 Flack parameter = 0 (2)

Table 1. Selected geometric parameters ($\text{\AA}$, $^\circ$)

O1A—C15A	1.232 (6)	O1B—C15B	1.225 (5)
O2A—N3A	1.239 (8)	O2B—N3B	1.215 (6)
O3A—N3A	1.205 (8)	O3B—N3B	1.231 (7)
N1A—C1A	1.340 (6)	N1B—C1B	1.344 (6)
N1A—C7A	1.466 (6)	N1B—C7B	1.463 (6)
N2A—C15A	1.339 (7)	N2B—C15B	1.358 (6)
N2A—C2A	1.406 (7)	N2B—C2B	1.403 (6)
N3A—C4A	1.461 (7)	N3B—C4B	1.450 (7)
C1A—C6A	1.400 (8)	C1B—C6B	1.401 (7)
C1A—C2A	1.424 (7)	C1B—C2B	1.416 (6)
C2A—C3A	1.374 (7)	C2B—C3B	1.382 (7)
C3A—C4A	1.383 (8)	C3B—C4B	1.367 (7)
C4A—C5A	1.381 (9)	C4B—C5B	1.365 (8)
C5A—C6A	1.360 (8)	C5B—C6B	1.365 (7)
C15A—C16A	1.475 (9)	C15B—C16B	1.489 (8)
C1A—N1A—C7A	125.0 (4)	C1B—N1B—C7B	125.8 (4)
C15A—N2A—C2A	126.5 (4)	C15B—N2B—C2B	124.5 (4)
O3A—N3A—O2A	124.4 (6)	O2B—N3B—O3B	123.1 (5)
O3A—N3A—C4A	118.7 (6)	O2B—N3B—C4B	118.3 (5)
O2A—N3A—C4A	116.8 (7)	O3B—N3B—C4B	118.6 (5)
N1A—C1A—C6A	121.8 (5)	N1B—C1B—C6B	121.9 (4)
N1A—C1A—C2A	119.9 (5)	N1B—C1B—C2B	120.1 (4)

C6A—C1A—C2A	118.2 (4)	C6B—C1B—C2B	117.9 (4)
C3A—C2A—N2A	121.2 (5)	C3B—C2B—N2B	121.0 (4)
C3A—C2A—C1A	119.7 (5)	C3B—C2B—C1B	119.8 (4)
N2A—C2A—C1A	119.1 (4)	N2B—C2B—C1B	119.2 (4)
C2A—C3A—C4A	119.8 (5)	C4B—C3B—C2B	120.0 (4)
C5A—C4A—C3A	121.4 (5)	C5B—C4B—C3B	121.3 (5)
C5A—C4A—N3A	120.6 (6)	C5B—C4B—N3B	119.8 (5)
C3A—C4A—N3A	117.9 (6)	C3B—C4B—N3B	118.8 (5)
C6A—C5A—C4A	119.4 (6)	C4B—C5B—C6B	120.0 (5)
C5A—C6A—C1A	121.5 (5)	C5B—C6B—C1B	121.0 (5)
N1A—C7A—C14A	107.8 (4)	N1B—C7B—C8B	109.5 (5)
N1A—C7A—C8A	109.7 (5)	N1B—C7B—C14B	108.9 (4)
O1A—C15A—N2A	120.7 (5)	O1B—C15B—N2B	122.2 (5)
O1A—C15A—C16A	122.6 (5)	O1B—C15B—C16B	122.6 (5)
N2A—C15A—C16A	116.7 (4)	N2B—C15B—C16B	115.2 (4)

Table 2. Hydrogen-bonding geometry ($\text{\AA}$, $^\circ$)

D—H...A	D—H	H...A	D...A	D—H...A
N1A—H1A...O1B	0.860 (6)	2.331 (6)	3.071 (6)	144.3 (5)
N2A—H2A...O1B	0.860 (5)	2.151 (5)	2.934 (5)	151.2 (4)
N1B—H1B...O1A ⁱ	0.860 (6)	2.308 (6)	3.069 (6)	147.6 (5)
N2B—H2B...O1A ⁱ	0.860 (5)	2.105 (5)	2.889 (5)	151.1 (4)

Symmetry code: (i) $1 + x, y, z$.

The title structure was solved by direct methods and refined by anisotropic full-matrix least squares for all the non-H atoms. All H atoms were placed in calculated positions, riding on the coordinates of the atoms to which they are attached. Molecule A showed high thermal motion or disorder, particularly for atoms C9A and C13A. Moreover, the shortness of the C8A—C9A, C9A—C10A, C12A—C13A and C13A—C14A bonds could indicate multiple character. A model with the cyclooctane ring disordered over two positions, C7A, C8A, C9A1, C10A, C11A, C12A, C131, C14A and C7A, C8A, C9A2, C10A, C11A, C12A, C132, C14A, was refined and gave values of 0.50 (2) for the occupancy factors of the two disordered groups. We assigned the first disordered position to PART1, the second to PART2 and the remaining ring atoms (C7A and C11A) to PART0 in order to generate the correct connectivity and also to generate H atoms for both disordered components.

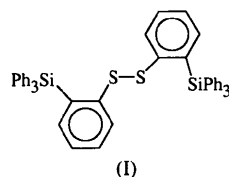
Data collection: *CAD-4 Operations Manual* (Enraf–Nonius, 1977). Cell refinement: *CAD-4 Operations Manual*. Data reduction: *CFEO* (Solans, 1978). Program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ORTEPII* (Johnson, 1976; Brueggemann & Schmid, 1990). Software used to prepare material for publication: *PARST95* (Nardelli, 1995), *PLATON* (Spek, 1993) and *SHELXL93*.

Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: KA1198). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

- Abrahams, S. & Keve, E. T. (1971). *Acta Cryst.* **A27**, 157–165.
- Altomare, A., Cascarano, G., Giacovazzo, C., Guagliardi, A., Burla, M. C., Polidori, G. & Camalli, M. (1994). *J. Appl. Cryst.* **27**, 435–436.
- Baumert, J. C., Twieg, R. J., Bjorklund, G. C., Logan, J. A. & Dirk, C. W. (1987). *Appl. Phys. Lett.* **51**, 1484–1486.
- Brueggemann, R. & Schmid, G. (1990). PC adaptation of *ORTEP*. University of Ulm, Germany.
- Carenco, A., Jerphagnon, J. & Periquard, A. (1977). *J. Chem. Phys.* **66**, 3806–3813.

- Chemla, D. S. & Zyss, J. (1986). In *Nonlinear Optical Properties of Organic Molecules and Crystals*, Vols. 1 and 2. Orlando: Academic Press.
- Enraf-Nonius (1977). *CAD-4 Operations Manual*. Enraf-Nonius, Delft, The Netherlands.
- Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.
- Johnson, C. K. (1976). *ORTEP*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- Lalama, S. J. & Garito, A. F. (1979). *Phys. Rev. A*, **20**, 1179–1194.
- Lipscomb, G. F., Garito, A. F. & Narang, R. S. (1981). *J. Chem. Phys.* **75**, 1509–1516.
- Nardelli, M. (1995). *J. Appl. Cryst.* **28**, 659.
- Oudar, J. L. & Chemla, D. S. (1971). *J. Chem. Phys.* **66**, 2664–2668.
- Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
- Solans, X. (1978). *CFEO*. University of Barcelona, Spain.
- Southgate, P. D. & Hall, D. S. (1971). *Appl. Phys. Lett.* **18**, 456–461.
- Spek, A. L. (1990). *Acta Cryst.* **A46**, C-34.
- Spek, A. L. (1993). *PLATON. Molecular Geometry Program*. University of Utrecht, The Netherlands.
- Williams, D. J. (1983). *Nonlinear Optical Properties of Organic and Polymeric Materials*. Am. Chem. Soc. Symp. Ser. p. 233. Washington, DC: American Chemical Society.
- Williams, D. J. (1984). *Angew. Chem. Int. Ed. Engl.* **23**, 690–703.



A database survey of C—S—S—C fragments (Allen *et al.*, 1987) found that S—S bond distances are bimodally distributed; for torsion angles in the ranges 75–105 and 0–20°, S—S bond-distance means were found to be 2.031 (15) and 2.070 (22) Å, respectively. The corresponding values in (I) are 84.1 (1)° and 2.037 (1) Å, placing (I) in the upper quartile of Allen's first set. The C—S and C—Si distances are in the upper ranges of Allen's survey. The title compound contains no intramolecular non-bonded distances (hydrogen excluded) between individual TPST half molecules shorter than 3.5 Å, except for C52—S1, C53—S1 and C12—S2; it therefore seems unlikely that steric factors constrain this molecule. The dispositions of the triphenylsilyl fragments in this molecule and in metal complexes have been discussed elsewhere (Ahmet *et al.*, 1995).

Acta Cryst. (1997). **C53**, 654–655

Bis[2-(triphenylsilyl)phenyl] Disulfide

JOHN R. MILLER, CANZHONG LU AND YIFAN ZHENG

Department of Biological and Chemical Sciences, Central Campus, University of Essex, Colchester CO4 3SQ, England.
E-mail: john@essex.ac.uk

(Received 16 October 1996; accepted 29 January 1997)

Abstract

The title compound, C₄₈H₃₈S₂Si₂, was obtained by the oxidation of the corresponding thiol in the presence of copper(I) chloride; the molecular structure is reported.

Comment

Bis[2-(triphenylsilyl)phenyl] disulfide, (I), was obtained fortuitously from the reaction under basic conditions of the corresponding thiol (TPSTH) with copper(I) chloride. The TPST unit has been studied (Ahmet *et al.*, 1995) as an example of a sterically hindered thiolate ligand to transition metals. The molecular geometry of the title compound suggests that steric interactions between the two halves of the molecule do not play an important role in governing bond distances, bond angles or even the torsion angle across the S1—S2 bond.

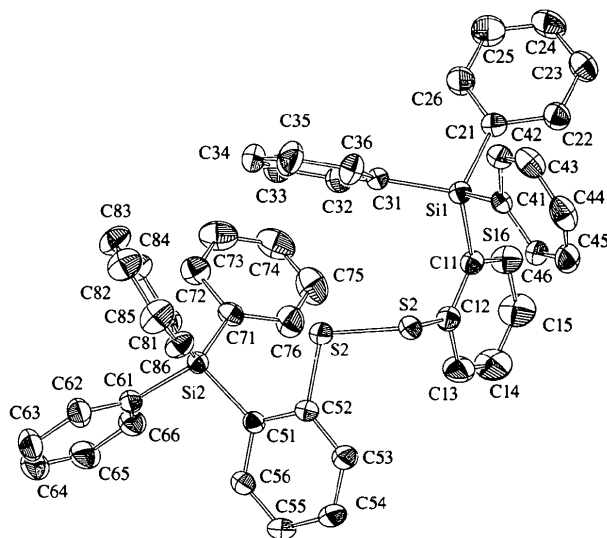


Fig. 1. The structure of the title compound; displacement ellipsoids are drawn at the 30% probability level and H atoms have been omitted for clarity (Zsolnai, 1994).

Experimental

2-(Triphenylsilyl)benzenethiol (TPSTH) was synthesized according to the method of Zheng (1993). A mixture of 0.01 g (0.1 mmol) CuCl, 0.15 g (0.14 mmol) TPSTH and 0.04 g (0.6 mmol) EtONa in 15 ml of dimethoxyethane and 10 ml of ethanol was heated under reflux for 3 h. Triphenylphosphine (0.05 g, 0.2 mmol) was added to the yellow solution which was then refluxed for a further 2 h. The solution was concentrated *in vacuo*, 10 ml acetone was added and a white solid formed which was filtered off, washed twice with 10 ml ether and air-