P2—O*E*21	1.473 (2)	N2—C2	1.494 (3)
P2—O*E*22	1.484 (2)	C1—C1^{ii}	1.508 (6)
P2—O*L*21^{i}	1.602 (2)	C2—C2^{iii}	1.519 (5)
P2—O*L*12	1.602 (2)	P1···P2	2.955 (1)
N1—C3	1.469 (4)	P1···P2^{i}	2.959 (1)
O*E*11—P1—O*E*12	120.90 (12)	P2—O*L*12—P1	133.37 (12)
O*E*11—P1—O*L*21	110.42 (11)	P2^{i}—O*L*21—P1	134.11 (12)
O*E*12—P1—O*L*21	106.81 (11)	P2—P1—P2^{i}	96.82 (3)
O*E*11—P1—O*L*12	110.62 (11)	P1—P2—P1^{i}	83.18 (3)
O*E*12—P1—O*L*12	106.54 (11)	C3—N1—C1^{ii}	115.3 (3)
O*L*21—P1—O*L*12	99.32 (10)	C3—N1—C4	110.2 (3)
O*E*21—P2—O*E*22	118.64 (12)	C1^{ii}—N1—C4	108.9 (2)
O*E*21—P2—O*L*21^{i}	110.82 (11)	C5—N2—C6	109.5 (3)
O*E*22—P2—O*L*21^{i}	105.71 (11)	C5—N2—C2	110.0 (2)
O*E*21—P2—O*L*12	106.89 (12)	C6—N2—C2	113.5 (2)
O*E*22—P2—O*L*12	109.73 (10)	N1^{ii}—C1—C1^{ii}	110.4 (3)
O*L*21^{i}—P2—O*L*12	104.14 (10)	N2—C2—C2^{iii}	111.1 (3)

Symmetry codes: (i) $-x, 1-y, 1-z$; (ii) $-1-x, 1-y, 1-z$; (iii) $-x, 1-y, -z$.

Table 3. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O*W*1—H1*W*1···O*E*21^{i}	0.85 (5)	2.11 (5)	2.921 (4)	159 (4)
O*W*1—H2*W*1···O*W*2	0.77 (6)	2.09 (6)	2.816 (4)	158 (5)
O*W*2—H1*W*2···O*E*21	0.83 (4)	1.93 (4)	2.757 (3)	173 (4)
O*W*2—H2*W*2···O*E*12^{ii}	0.85 (5)	1.97 (5)	2.791 (3)	166 (4)
N1—HN1···O*E*11	0.85 (3)	1.81 (4)	2.647 (3)	173 (3)
N2—HN2···O*E*22	0.86 (4)	1.85 (4)	2.700 (3)	169 (4)
H1*W*1—O*W*1···H2*W*1	–	–	–	99 (5)
H1*W*2—O*W*2···H2*W*2	–	–	–	109 (4)

Symmetry codes: (i) $1-x, 1-y, -z$; (ii) $1-x, -y, 1-z$.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Software used to prepare material for publication: *SHELXL*93.

The authors express their most grateful thanks to Dr T. Jouini (Département de Chimie, Faculté des Sciences, Tunisia) for the X-ray data collection.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: DU1166). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Averbuch-Pouchot, M. T. & Durif, A. (1987). *Acta Cryst.* C**43**, 1894–1896.

Averbuch-Pouchot, M. T. & Durif, A. (1993). *C. R. Acad. Sci. Paris Ser.* II, pp. 187–192.

Averbuch-Pouchot, M. T., Durif, A. & Guitel, J. C. (1989). *Acta Cryst.* C**45**, 1320–1322.

Bdiri, M. & Jouini, A. (1989). *Eur. J. Solid State Inorg. Chem.* **26**, 585–592.

Durif, A. & Averbuch-Pouchot, M. T. (1989). *Acta Cryst.* C**45**, 1884–1987.

Enraf–Nonius (1989). *CAD*-4 *Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.

Fair, C. K. (1990). *MolEN. An Interactive Intelligent System for Crystal Structure Analysis*. Enraf–Nonius, Delft, The Netherlands.

Gharbi, A., Charfi, M. & Jouini, A. (1996). *Acta Cryst.* C**52**, 2246–2248.

Gharbi, A., Jouini, A., Averbuch-Pouchot, M. T. & Durif, A. (1994). *J. Solid State Chem.* **111**, 330–337.

Gharbi, A., Jouini, A. & Durif, A. (1995). *J. Solid State Chem.* **114**, 42–51.

Jouini, A. (1989). *Acta Cryst.* C**45**, 1877–1879.

Kamoun, S., Jouini, A. & Daoud, A. (1990). *Acta Cryst.* C**46**, 1481–1483.

Kamoun, S., Jouini, A. & Daoud, A. (1992). *J. Solid State Chem.* **99**, 18–29.

Kamoun, S., Jouini, A., Kamoun, M. & Daoud, A. (1989). *Acta Cryst.* C**45**, 481–482.

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**, 320–322

3-Anilino-*N*-phenyl-1*H*-indole-2-carbothioamide

LI JING,[a] FU HE-LIANG,[b] SUN JIE[c] AND CHEN WEI-XING[a]

[a]*Department of Chemistry, Nanjing University, Nanjing 210093, People's Republic of China,* [b]*Techpool Biochem. Pharma. Co., Guangzhou 510630, People's Republic of China, and* [c]*Shang Hai Institute of Organic Chemistry, Chinese Academy of Science, Shang Hai 200032, People's Republic of China. E-mail: postche1@netra.nju.edu.cn*

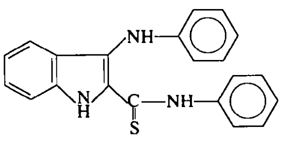
(*Received 14 March 1996; accepted 22 October 1996*)

Abstract

The title compound, $C_{21}H_{17}N_3S$, prepared by the reaction of phenyl isothiocyanate with a low-valent titanium reagent, has an intramolecular N—H···N hydrogen bond between the two exocyclic NH groups and a C=S bond length of 1.660 (3) Å.

Comment

The reductive coupling of carbonyl compounds with low-valent titanium reagents is an attractive method for the formation of C—C bonds which has found considerable application in synthesis (Wei-Xing, 1993). Under the action of the low-valent titanium $TiCl_4$–Zn reagent, phenyl isothiocyanate was converted into the title compound, (I), *via* a trimolecular cyclodesulfuration reaction in *ca* 44% yield.



(I)

The molecular structure of (I) is illustrated in Fig. 1. Bond lengths and angles in the compound are generally normal. The C═S bond length of 1.660 (3) Å is in the range found for similar compounds; in *N*,*N'*-diphenylthiourea, the bond length is 1.681 (5) Å (Ramnathan, Sivakumar & Subramanian, 1995). The S1, N1, C1, C2 and C3 atoms lie in one plane, the largest deviation being 0.047 (3) Å for the C2 atom. The N3 atom lies 0.221 Å from this plane. There is an intramolecular N1—H1···N3 hydrogen bond, with a H1···N3 distance of 2.11 (3) Å and an N1—H1···N3 angle of 145 (3)°.

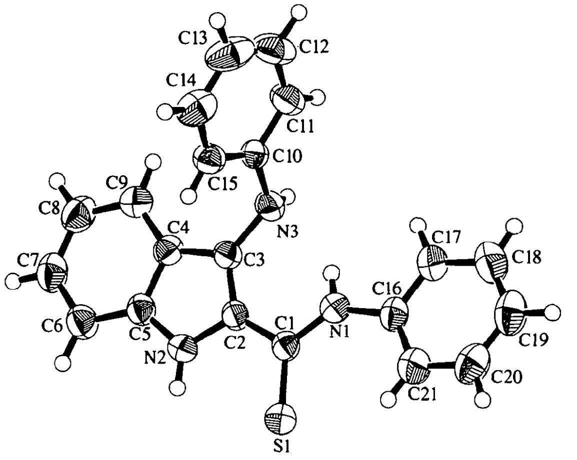


Fig. 1. View of the title compound with displacement ellipsoids at the 50% probability level.

Experimental

A dry flask (100 ml) was charged with zinc dust (3.90 g, 60 mmol), THF (50 ml) and $TiCl_4$ (3.30 ml, 30 mmol). The mixture was refluxed for 2 h under argon after which a solution of phenyl isothiocyanate (2.28 g, 10 mmol) in THF (10 ml) was added and refluxing continued for 20 h. After removal of THF, the mixture was quenched with 20% K_2CO_3 solution (200 ml) and extracted with $CHCl_3$ (3 × 100 ml). The crude product was purified by chromatography on silica gel [1:4 ethyl acetate–petroleum ether (333–363 K)]. Yellow single crystals suitable for X-ray diffraction analysis were obtained from the eluted solution.

Crystal data

$C_{21}H_{17}N_3S$
$M_r = 343.45$
Monoclinic
$P2_1/c$
$a = 13.991$ (1) Å
$b = 5.748$ (1) Å
$c = 21.569$ (2) Å
$\beta = 90.619$ (8)°
$V = 1734.5$ (4) $Å^3$
$Z = 4$
$D_x = 1.315$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 22 reflections
$\theta = 18.43$–$21.43°$
$\mu = 0.194$ mm^{-1}
$T = 293$ K
Plate
0.30 × 0.20 × 0.10 mm
Yellow

Data collection

Rigaku AFC-7*R* diffractometer
$\omega/2\theta$ scans
Absorption correction: none
2737 measured reflections
2593 independent reflections
1619 reflections with $I > 2\sigma(I)$

$R_{int} = 0.040$
$\theta_{max} = 25°$
$h = 0 \rightarrow 15$
$k = 0 \rightarrow 6$
$l = -25 \rightarrow 24$
3 standard reflections every 200 reflections intensity decay: 0.4%

Refinement

Refinement on *F*
$R = 0.034$
$wR = 0.040$
$S = 1.38$
1619 reflections
294 parameters
Isotropic H atoms freely refined
$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{max} = 0.01$

$\Delta\rho_{max} = 0.12$ e $Å^{-3}$
$\Delta\rho_{min} = -0.17$ e $Å^{-3}$
Extinction correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV) and *International Tables for Crystallography* (Vol. C)

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

S1—C1	1.660 (3)	N1—C1	1.341 (3)
N1—C16	1.422 (3)	N2—C2	1.381 (3)
N2—C5	1.370 (3)	N3—C3	1.423 (3)
N3—C10	1.410 (3)	C1—C2	1.466 (4)
C2—C3	1.372 (4)	C3—C4	1.422 (4)
C1—N1—C16	134.2 (3)	C2—N2—C5	109.7 (2)
C3—N3—C10	120.1 (2)	S1—C1—N1	126.2 (2)
S1—C1—C2	121.2 (2)	N1—C1—C2	112.6 (2)
N2—C2—C1	120.7 (2)	N2—C2—C3	107.9 (2)
C1—C2—C3	131.4 (2)	N3—C3—C2	125.4 (2)
N3—C3—C4	126.5 (3)	C2—C3—C4	108.1 (2)

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1992*a*). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN PROCESS* (Molecular Structure Corporation, 1992*b*). Program(s) used to solve structure: *SAPI91* (Fan, 1991) and *PATTY* in *DIRDIF92* (Beurskens *et al.*, 1992). Program(s) used to refine structure: *TEXSAN*. Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *TEXSAN*.

This research was supported by the National Natural Science Foundation of China and the Chinese University Doctoral Research Fund.

Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: CF1106). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Beurskens, P. T., Admiraal, G., Beurskens, G., Bosman, W. P., Garcia-Granda, S., Gould, R. O., Smits, J. M. M. & Smykalla, C. (1992). *The DIRDIF Program System*. Technical Report. Crystallography Laboratory, University of Nijmegen, The Netherlands.

Fan, H.-F. (1991). *SAPI91. Structure Analysis Programs with Intelligent Control*. Rigaku Corporation, Tokyo, Japan.

Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Molecular Structure Corporation (1992*a*). *MSC/AFC Diffractometer Control Software*. Revised edition. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
Molecular Structure Corporation (1992*b*). *TEXSAN. Single Crystal Structure Analysis Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
Ramnathan, A., Sivakumar, K. & Subramanian, K. (1995). *Acta Cryst.* C**51**, 2446–2450.
Wei-Xing, C. (1993). *Advances in Organic Synthesis*, edited by D. Li-Xin & Q. Yan-Long, pp. 469–491. Beijing: Chemical Industry Press.

Acta Cryst. (1997). C**53**, 322–325

meso-1,11-Dimethylcyclotrideca-2,9-diyne-1,11-diol

CHRISTOPH BOSS,[a] HELEN STOECKLI-EVANS[b] AND REINHART KEESE[a]

[a]*Institut für Organische Chemie, Universität Bern, Freiestr. 3, CH-3012 Bern, Switzerland, and* [b]*Institut de Chimie, Université de Neuchâtel, Avenue de Bellevaux 51, CH-2000 Neuchatel, Switzerland. E-mail: keese@ioc.unibe.ch*

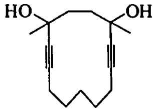
(*Received 21 August 1996; accepted 5 November 1996*)

Abstract

The title compound, $C_{15}H_{22}O_2$, (5), has been prepared and its structure determined. At room temperature, two conformations are observed, but at 193 K, the compound shows only the conformation which has 67% occupancy at room temperature. The appearance of two conformations and the low symmetry of compound (5) are in accordance with the general structural behaviour of 13-membered-ring systems. *meso*-(5) crystallizes in the monoclinic space group *I*2/*a*. The lengths of the triple bonds are close to 1.175 Å at room temperature and 1.188 Å at 193 K. The bond angles at the triple bonds deviate by less than 7° from being linear and are almost temperature independent.

Comment

Medium-sized ring compounds are of considerable interest because of their unique structure and transannular reactivity (Dunitz & Meyer, 1965; Johnson, 1986; Gleiter, Merger, Irngartinger & Nuber, 1993; Meier, 1991). The cyclotridecadiynediol (5), as well as the recently published substituted cyclododecadiynes (Boss, Keese & Förtsch, 1996; Boss, Stoeckli-Evans & Keese, 1996), have been prepared both for investigation of the reactions of the juxtaposed triple bonds with doubly functionalized reagents and for comparison of different ring sizes and substitution patterns at the propargylic centres of homologous ring compounds.



(5)

In the crystalline state at 193 K, the unit cell contains two enantiomorphic forms of *meso*-(5) in a ratio of 1:1. The population of the two conformations at room temperature corresponds to the general conformational behaviour of unsubstituted cyclotridecane (Dale, 1978). Quite different from the 12-membered-ring compounds where the racemic form crystallizes (Boss, Stoeckli-Evans & Keese, 1996), it is the *meso*-(5) compound that affords crystals which are composed of layers with the hydrophilic and hydrophobic areas separated.

In *meso*-(5), the lengths of the two triple bonds at room temperature are 1.174 (5) (C2≡C3) and 1.177 (5) Å (C9≡C10). At 193 K, the triple bonds show lengths of 1.187 (5) (C2≡C3) and 1.189 (5) Å (C9≡C10), and are exactly within the range of triple-bond lengths found for the cyclododecadiyne diols (Boss, Stoeckli-Evans & Keese, 1996). The angles at the triple bonds [173.9 (4) (C1—C2≡C3), 175.0 (5) (C2≡C3—C4), 176.1 (5) (C8—C9≡C10) and 176.2 (4)° (C9≡C10—C11) at room temperature; 173.3 (4) (C1—C2≡C3), 175.3 (4) (C2≡C3—C4), 175.2 (4) (C8—C9≡C10) and 175.9 (4)° (C9≡C10—C11) at 193 K] show practically no temperature dependence and lie within the same range as those determined for 12-membered-ring systems. The transannular distances of the two alkyne moieties in *meso*-(5) are 4.126 (5) (C2···C10) and 4.333 (6) Å (C3···C9) at 193 K, and 4.155 (5) and 4.384 (6) Å, respectively, at room temperature.

These structural features are well within the range found for other cycloalkadiynes in the Cambridge Structural Database (Allen *et al.*, 1979). Other salient features of diol (5) are the bond angles at the other centres. The C2—C1—C13 bond angle at the quaternary C atom is 110.1 (3)° and the value at the corresponding centre (C10—C11—C12) is 109.2 (3)°, whereas the adjacent bond angles C1—C13—C12 and C11—C12—C13 are 117.7 (3) and 112.4 (3)°, respectively. This is reminiscent of the bond angles at the quaternary C atoms of type $(H_3C)_2C(C)_2$ (Keese & Meyer, 1993). The values determined at 193 K are very similar to those obtained at room temperature.

The disordered part of the molecule shows very different values for bond angles at the CH_2 groups [C4—C5—C6 124.8 (3) and C4—C5—C6*A* 91.1 (7)°]. At 193 K, the corresponding angle is 118.0 (4)°. In the cell packing diagram of *meso*-(5) (Fig. 2), hydro-

Acta Crystallographica Section C
ISSN 0108-2701 © 1997