Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

1,2-Dimethyl-3-(thiazol-2-yldiazenyl)-1*H*-indole

Zeynel Seferoğlu,[a] Tuncer Hökelek,[b]* Ertan Şahin[c] and Nermin Ertan[a]

[a]Gazi University, Department of Chemistry, 06500 Beşevler, Ankara, Turkey, [b]Hacettepe University, Department of Physics, 06800 Beytepe, Ankara, Turkey, and [c]Atatürk University, Department of Chemistry, 22240 Erzurum, Turkey

Correspondence e-mail:
merzifon@hacettepe.edu.tr

Key indicators

Single-crystal X-ray study
T = 294 K
Mean σ(C–C) = 0.004 Å
R factor = 0.066
wR factor = 0.202
Data-to-parameter ratio = 22.8

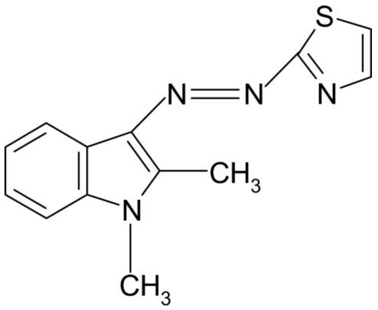
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The asymmetric unit of the title compound, $C_{13}H_{12}N_4S$, contains two independent molecules. The dihedral angles between the thiazole ring and the indole mean plane are 4.46 (6) and 4.92 (7)° in the two independent molecules.

Received 8 December 2006
Accepted 12 December 2006

Comment

Indole and its derivatives form a class of toxic recalcitrant *N*-heterocyclic compounds that are considered to be pollutants (Florin *et al.*, 1980). Heterocycles containing the 1,3-thiazole ring system exhibit a wide spectrum of biological activities, including acting as antiviral and antifungal agents, and that ring has been identified as a central structural element of a number of biologically active natural products (Zabriskie *et al.*, 1988) and of pharmacologically active compounds (Metzger, 1984). Azo derivatives are used extensively in analytical chemistry and in the dyestuff industry as metallochromic and acid-base indicators (Rau, 1990). They are also used in the fields of non-linear optics and optical data storage (Bach *et al.*, 1996). Azo dyes have wide applicability as optical materials and their structures have also attracted considerable attention (Biswas & Umapathy, 2000). Many azo-dye breakdown products are carcinogenic, toxic or mutagenic to life (Ochiai *et al.*, 1986). Although there are many publications on the industrial applications of azo dyes (Tsuda *et al.*, 2000), to the best of our knowledge, few structures of azoindole derivatives have been reported to date (Bruni *et al.*, 1995; Seferoğlu *et al.*, 2006*a*,*b*,*c*,*d*; Seferoğlu *et al.*, 2007). This study was undertaken in order to ascertain the crystal structure of the title compound, (I).



(I)

The asymmetric unit of (I) contains two crystallographically independent molecules, denoted by primed and unprimed labels in Fig. 1. The bond lengths and angles are in normal ranges (Allen *et al.*, 1987).

An examination of the deviations from the least-squares planes through the individual rings shows that all of the rings

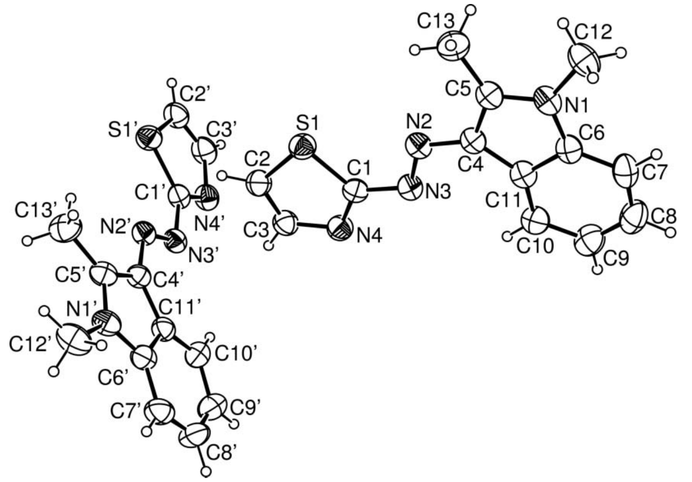


Figure 1
The asymmetric unit of (I) with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

are planar. The indole ring systems are nearly planar, with dihedral angles of 2.07 (9)° and 2.04 (9)° between rings *A* (C6—C11) and *B* (N1/C4/C5/C6/C11) and between rings *A*′ (C6′–C11′) and *B*′ (N1′/C4′–C6′/C11′). In the closely related compounds 3-(4-chlorophenyldiazenyl)-1-methyl-2-phenyl-1*H*-indole, (II) (Seferoğlu *et al.*, 2006*a*), *N*-{4-[(2-phenyl-1*H*-indol-3-yl)diazenyl]phenyl}acetamide, (III) (Seferoğlu *et al.*, 2006*b*), ethyl[2-(2-phenyl-1*H*-indol-3-yldiazenyl)-1,3-thiazol-4-yl]acetate, (IV) (Seferoğlu *et al.*, 2006*c*), ethyl 2-{2-[(1-methyl-2-phenyl-1*H*-indol-3-yl)diazenyl]thiazol-4-yl}acetate, (V) (Seferoğlu *et al.*, 2006*d*) and 1-methyl-2-phenyl-3-(1,3,4-thiadiazol-2-yldiazenyl)-1*H*-indole, (VI) (Seferoğlu *et al.*, 2007), the observed *A*/*B* and/or *A*′/*B*′ dihedral angles are 1.56 (11) and 0.77 (12)° in (II), 1.63 (14)° in (III), 0.99 (10)° in (IV), 0.59 (7)° in (V) and 4.26 (7)° in (VI). The orientations of the thiazole rings *C* (S1/N4/C1–C3) and *C*′ (S1′/N4′/C1′-C3′) with respect to the indole ring systems may be described by the dihedral angles of 4.46 (6)° (for the unprimed molecule) and 4.92 (7)° (for the primed molecule), respectively.

Dipole–dipole and van der Waals interactions are effective in the molecular packing.

Experimental

For the preparation of (I), 2-aminothiazole (200 mg, 2 mmol) was dissolved in a hot glacial acetic acid–propionic acid mixture (2:1, 6 ml). The solution was rapidly cooled in an ice–salt bath and then added dropwise with stirring to a cold solution of nitrosylsulfuric acid (95%, 4 ml) over a period of 30 min. The mixture was stirred for an additional 2 h at 273 K. The resulting diazonium salt was cooled in an ice–salt bath and then added dropwise with stirring to 1,2-dimethylindole (290 mg, 2 mmol) in an acetic acid–propionic acid mixture (3:1, 8 ml). The solution was stirred at 273–278 K for 2 h and the pH of the reaction mixture was maintained at 4–6 by the addition of a saturated sodium carbonate solution (40 ml). The mixture was stirred for a further 1 d. The resulting solid was filtered, washed with cold water and crystallized from ethanol (yield 440 mg, 86%).

Crystal data

$C_{13}H_{12}N_4S$
$M_r = 256.33$
Triclinic, $P\bar{1}$
$a = 8.7257$ (2) Å
$b = 10.3070$ (2) Å
$c = 14.4948$ (6) Å
$\alpha = 83.828$ (6)°
$\beta = 88.489$ (6)°
$\gamma = 79.757$ (5)°

$V = 1275.35$ (7) Å^3
$Z = 4$
$D_x = 1.335$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 0.24$ mm^{-1}
$T = 294$ (2) K
Block, purple
0.35 × 0.20 × 0.15 mm

Data collection

Rigaku R-AXIS RAPID-S diffractometer
ω scans
Absorption correction: multi-scan (Blessing, 1995)
$T_{\min} = 0.920$, $T_{\max} = 0.965$

38418 measured reflections
7756 independent reflections
4027 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.076$
$\theta_{\max} = 30.6°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.066$
$wR(F^2) = 0.202$
$S = 1.02$
7756 reflections
340 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0774P)^2 + 0.1466P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.21$ e Å^{-3}
$\Delta\rho_{\min} = -0.33$ e Å^{-3}

H atoms of the C12′-methyl group were located in a difference map and refined isotropically [C—H = 0.89 (4)–0.98 (5) Å and $U_{\rm iso}$(H) = 0.115 (13)–0.20 (2) Å^2]. The remaining H atoms were positioned geometrically, with C—H = 0.93 and 0.96 Å, respectively, for aromatic and methyl H atoms, and constrained to ride on their parent atoms, with $U_{\rm iso}(H) = xU_{\rm eq}(C)$, where $x = 1.2$ for aromatic and $x = 1.5$ for methyl H atoms.

Data collection: *CrystalClear* (Rigaku/MSC, 2005); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

The authors are indebted to the Department of Chemistry, Atatürk University, Erzurum, Turkey, for the use of the X-ray diffractometer purchased under grant No. 2003/219 of the University Research Fund.

References

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–19.
Bach, H., Anderle, K., Fuhrmann, Th. & Wendorff, J. H. (1996). *J. Phys. Chem.* **100**, 4135–4140.
Biswas, N. & Umapathy, S. (2000). *J. Phys. Chem. A*, **104**, 2734–2745.
Blessing, R. H. (1995). *Acta Cryst.* A**51**, 33–38.
Bruni, P., Bocelli, G., Cantoni, A., Giorgini, E., Iacussi, M., Maurelli, E. & Tosi, G. (1995). *J. Chem. Crystallogr.* **25**, 683–691.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
Florin, I., Rutburge, L., Curvall, M. & Enzell, C. R. (1980). *Toxicology*, **18**, 219–232.
Metzger, J. V. (1984). In *Thiazoles and their Benzo Derivatives*, edited by K. T. Potts, Vol. 6. New York: Pergamon Press.
Ochiai, M., Wakabayashi, K., Sugimura, T. & Nagao, M. (1986). *Mutat. Res. Genet. Toxicol. Environ. Mutagen.*, **172**, 189–197.
Rau, H. (1990). *Photochromism. Molecules and Systems*, edited by H. Dürr and H. Bouas-Laurent, ch 4, p. 165. Amsterdam: Elsevier.

o352 Seferoğlu *et al.* • $C_{13}H_{12}N_4S$ *Acta Cryst.* (2007). E**63**, o351–o353

Rigaku/MSC (2005). *CrystalClear*. Rigaku/MSC, The Woodlands, Texas, USA.

Seferoğlu, Z., Hökelek, T., Şahin, E. & Ertan, N. (2006*a*). *Acta Cryst.* E**62**, o2108–o2110.

Seferoğlu, Z., Hökelek, T., Şahin, E. & Ertan, N. (2006*b*). *Acta Cryst.* E**62**, o3492–o3494.

Seferoğlu, Z., Hökelek, T., Şahin, E. & Ertan, N. (2006*c*). *Acta Cryst.* E**62**, o3835–o3837.

Seferoğlu, Z., Hökelek, T., Şahin, E. & Ertan, N. (2007). *Acta Cryst.* E**63**, o148–o150.

Seferoğlu, Z., Hökelek, T., Şahin, E., Saylam, A. & Ertan, N. (2006*d*). *Acta Cryst.* E**62**, o5488–o5489.

Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.

Tsuda, S., Matsusaka, N., Madarame, H., Ueno, S., Susa, N., Ishida, K., Kawamura, N., Sekihashi, K. & Sasaki, Y. F. (2000). *Mutat. Res. Genet. Toxicol. Environ. Mutagen.*, **465**, 11–26.

Zabriskie, T. M., Mayne, C. L. & Ireland, C. M. (1988). *J. Am. Chem. Soc.* **110**, 7919–7920.

Acta Cryst. (2007). E**63**, o351–o353 Seferoğlu *et al.* • $C_{13}H_{12}N_4S$ **o353**