C(23)	0.5387 (3)	−0.1857 (3)	0.8237 (6)	0.044 (3)
C(24)	0.5538 (4)	−0.1733 (3)	0.9520 (7)	0.069 (3)
C(25)	0.4744 (4)	−0.1944 (4)	0.8144 (8)	0.086 (4)
C(26)	0.5668 (4)	−0.2455 (3)	0.7870 (7)	0.075 (3)

Table 2. *Selected geometric parameters (Å, °)*

Si(1)—C(10)	1.909 (7)	O(1)—C(7)	1.437 (7)
Si(1)—C(11)	1.852 (7)	O(2)—C(9)	1.495 (7)
Si(1)—C(12)	1.859 (7)	O(2)—C(20)	1.381 (8)
Si(1)—C(13)	1.867 (7)	O(3)—C(20)	1.184 (8)
Si(2)—O(1)	1.643 (4)	C(8)—C(9)	1.505 (9)
Si(2)—C(21)	1.866 (7)	C(9)—C(10)	1.554 (8)
Si(2)—C(22)	1.850 (7)	C(10)—C(14)	1.549 (8)
Si(2)—C(23)	1.850 (7)	C(10)—C(20)	1.517 (9)
Si(2)—O(1)—C(7)	129.6 (4)	Si(1)—C(10)—C(20)	112.3 (5)
C(9)—O(2)—C(20)	91.4 (5)	C(9)—C(10)—C(14)	113.4 (5)
O(2)—C(9)—C(8)	110.4 (5)	C(9)—C(10)—C(20)	84.3 (5)
O(2)—C(9)—C(10)	89.1 (5)	C(14)—C(10)—C(20)	112.2 (6)
C(8)—C(9)—C(10)	122.1 (5)	O(2)—C(20)—O(3)	126.1 (7)
Si(1)—C(10)—C(9)	121.7 (4)	O(2)—C(20)—C(10)	95.1 (6)
Si(1)—C(10)—C(14)	110.4 (4)	O(3)—C(20)—C(10)	138.7 (8)

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1995). Program(s) used to solve structure: direct methods using *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *TEXSAN*. Molecular graphics: *ORTEP*II (Johnson, 1976).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: NA1256). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Johnson, C. K. (1976). *ORTEP*II. 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 (1995). *TEXSAN. Single Crystal Structure Analysis Software*. Version 1.7-1. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.

Pommier, A. & Pons, J.-M. (1993). *Synthesis*, pp. 441–459.

Pommier, A., Pons, J.-M. & Kocienski, P. J. (1995). *J. Org. Chem.* **60**, 7334–7339.

Pommier, A., Pons, J.-M., Kocienski, P. J. & Wong, L. (1994). *Synthesis*, pp. 1294–1300.

Shchukovskaya, L. L., Pal'chik, R. I. & Lazarev, A. N. (1965). *Dokl. Akad. Nauk SSSR*, **164**, 357–360; *Chem. Abstr.* **63**, 18138g.

Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.

Zaitseva, G. S., Vinokurova, N. G. & Baukov, Yu. I. (1975). *Zh. Obshch. Khim.* **45**, 1398; *Chem. Abstr.* **83**, 114548d.

Zemribo, R. & Romo, D. (1995). *Tetrahedron Lett.* **36**, 4159–4162.

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1,3-Diphenyl-4-imidazoline-2-thione

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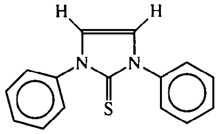
Abstract

In the title compound, 1,3-diphenyl-1,3-dihydro-2*H*-imidazole-2-thione, $C_{15}H_{12}N_2S$, the two phenyl rings are inclined at an angle of 71.9 (1)° with respect to one another.

Comment

The compounds methimazole (1-methyl-4-imidazoline-2-thione) and carbimazole (1-methyl-3-ethylcarboxylate-4-imidazoline-2-thione) are well known for their use in the treatment of hyperthyroidism (Reynolds, 1993). They block the production of thyroid hormones by inhibiting the enzyme thyroid peroxidase. In doing so, they become oxidized and these oxidized species are thought to be responsible for adverse effects observed in patients (Karkhanis & Field, 1985). 1,3-Diphenyl-4-imidazoline-2-thione, (I), is one of a series of compounds synthesized for the purpose of investigating the oxidation of thioimidazoles (Sohal, 1996).



(I)

In the molecule, the two phenyl rings are inclined at angles of 52.0 (1) and 61.6 (1)° with respect to the central ring, and at an angle of 71.9 (1)° with respect to one another. This conformation is also shown by the torsion angles about N1—C4 and N2—C10 (Table 2). The C2═C3 [1.332 (4) Å] and C1═S [1.671 (3) Å] double bonds are both normal. A search using *QUEST* (Allen & Kennard, 1993) on structures with *R* values less than 10% shows average S═C bond lengths of 1.67 (5) Å for over 5079 hits and 1.71 (3) Å for the 98 hits containing similar imidazole rings with exocyclic S═C bonds. In-plane bending is present at the C1 position, where the endocyclic valence angle is 103.8 (2)° and the two exocyclic angles are 127.5 (2) and 128.6 (2)°. Evidence for strain in the central ring is also found at the two N-atom positions, where the endocyclic angles are 110.6 (3) and 110.6 (2)°, and the exocyclic angles about the N atoms range from 123.1 (3) to 126.2 (3)°. Searches with *QUEST* again show that all these angular features are common for such five-membered rings. There are no short intermolecular contacts and parallel stacking of phenyl rings is only partially achieved.

Examples of related crystal structures are imidazoline-2-thione hemihydrate (Raper, Jackson & Gardiner, 1984), methimazole (Raper, Creighton, Oughtred & Nowell, 1983), carbimazole (Delage, Faure, Leger, Raby & Goursolle, 1990) and 1,3-dimethyl-4-imidazoline-2-thione (Ansell, 1972).

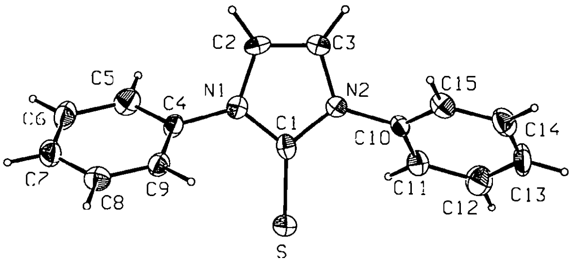


Fig. 1. The atomic arrangement in the title molecule. Displacement ellipsoids are shown at the 50% probability level and H atoms have been assigned arbitrary radii.

Experimental

1,3-Diphenyl-4-imidazoline-2-thione was synthesized according to the method of Schönerr & Wanzlick (1970) and recrystallized from ethanol.

Crystal data

$C_{15}H_{12}N_2S$
$M_r = 252.33$
Orthorhombic
Pbca
$a = 12.454$ (7) Å
$b = 11.382$ (8) Å
$c = 17.841$ (7) Å
$V = 2529$ (3) Å^3
$Z = 8$
$D_x = 1.325$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 250 reflections
$\theta = 2.28$–25.06°
$\mu = 0.238$ mm^{-1}
$T = 150$ (2) K
Plate
0.24 × 0.18 × 0.16 mm
Yellow

Data collection

Delft Instruments FAST diffractometer
Area detector scans
Absorption correction: none
9628 measured reflections
2008 independent reflections

1166 observed reflections [$I > 2\sigma(I)$]
$R_{\rm int} = 0.1078$
$\theta_{\rm max} = 25.06°$
$h = -14 \rightarrow 12$
$k = -13 \rightarrow 13$
$l = -19 \rightarrow 18$

Refinement

Refinement on F^2
$R(F) = 0.0492$
$wR(F^2) = 0.1075$
$S = 0.820$
2007 reflections
164 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0368P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.060$

$\Delta\rho_{\rm max} = 0.60$ e Å^{-3} e Å^{-3}
$\Delta\rho_{\rm min} = -0.22$ 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 (Å^2)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
S	0.26387 (6)	0.04660 (7)	0.12218 (4)	0.0289 (3)
N1	0.4765 (2)	0.0952 (2)	0.14460 (13)	0.0266 (7)
N2	0.4097 (2)	−0.0177 (2)	0.23041 (13)	0.0235 (7)
C1	0.3828 (2)	0.0405 (3)	0.1654 (2)	0.0229 (8)
C2	0.5573 (3)	0.0721 (3)	0.1961 (2)	0.0319 (9)
C3	0.5158 (3)	0.0036 (3)	0.2492 (2)	0.0290 (8)
C4	0.4907 (2)	0.1713 (3)	0.0812 (2)	0.0247 (8)
C5	0.5670 (3)	0.1426 (3)	0.0283 (2)	0.0321 (9)
C6	0.5876 (3)	0.2190 (3)	−0.0303 (2)	0.0344 (9)
C7	0.5318 (3)	0.3225 (3)	−0.0357 (2)	0.0314 (9)
C8	0.4535 (3)	0.3496 (3)	0.0172 (2)	0.0282 (8)
C9	0.4335 (3)	0.2743 (3)	0.0757 (2)	0.0258 (8)
C10	0.3357 (2)	−0.0804 (3)	0.2777 (2)	0.0220 (8)
C11	0.2738 (2)	−0.1700 (3)	0.2497 (2)	0.0263 (8)
C12	0.2043 (3)	−0.2275 (3)	0.2970 (2)	0.0396 (10)
C13	0.1985 (3)	−0.1975 (3)	0.3719 (2)	0.0402 (10)
C14	0.2616 (3)	−0.1096 (3)	0.3996 (2)	0.0360 (9)
C15	0.3302 (3)	−0.0496 (3)	0.3523 (2)	0.0299 (8)

Table 2. *Selected geometric parameters (Å, °)*

S—C1	1.671 (3)	N2—C1	1.377 (4)
N1—C1	1.374 (4)	N2—C3	1.385 (4)
N1—C2	1.387 (4)	N2—C10	1.439 (4)
N1—C4	1.436 (4)	C2—C3	1.332 (4)
C1—N1—C2	110.6 (3)	N1—C1—S	127.5 (2)
C1—N1—C4	126.2 (3)	N2—C1—S	128.6 (2)
C2—N1—C4	123.1 (3)	C3—C2—N1	107.5 (3)
C1—N2—C3	110.6 (2)	C2—C3—N2	107.5 (3)
C1—N2—C10	125.2 (2)	C9—C4—C5	120.7 (3)
C3—N2—C10	123.8 (3)	C9—C4—N1	120.5 (3)
N1—C1—N2	103.8 (2)	C5—C4—N1	118.7 (3)
C1—N1—C4—C9	61.2 (4)	C1—N2—C10—C11	56.9 (4)
C2—N1—C4—C9	−115.2 (3)	C3—N2—C10—C11	−131.0 (3)
C1—N1—C4—C5	−122.4 (3)	C1—N2—C10—C15	−124.3 (3)
C2—N1—C4—C5	61.2 (4)	C3—N2—C10—C15	47.7 (4)

The absence of crystal decay in the X-ray beam was confirmed by checking equivalent reflections at the beginning and end of data collection which lasted *ca* 8 h. The unit-cell and intensity data were collected on a Delft Instruments FAST diffractometer using the routines *ENDEX*, *REFINE* and *MADONL* in the *MADNES* software (Pflugrath & Messerschmidt, 1989) and processed using *ABSMAD* (Karaulov, 1992); detailed procedures are described by Darr, Drake, Hursthouse & Malik (1993). The H atoms were initially placed in calculated positions and thereafter allowed to ride on their attached C atoms with a common isotropic displacement parameter of 0.034 (3) Å^2.

Program(s) used to solve structure: *SIR*92 (Altomare, Cascarano, Giacovazzo, Guagliardi, Burla, Polidori & Camalli, 1994). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ZORTEP* (Zsolnai, 1996).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BM1103). 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. (1993). *Chem. Des. Autom. News*, **8**, 31–37.

Altomare, A., Cascarano, G., Giacovazzo, C., Guagliardi, A., Burla, M. C., Polidori, G. & Camalli, M. (1994). *J. Appl. Cryst.* **27**, 435–436.

Ansell, G. B. (1972). *J. Chem. Soc. Perkin Trans.* 2, pp. 841–843.

Darr, J. A., Drake, S. R., Hursthouse, M. B. & Malik, K. M. A. (1993). *Inorg. Chem.* **32**, 5704–5708.

Delage, C., Faure, F., Leger, J.-M., Raby, C. & Goursolle, M. (1990). *C. R. Acad. Sci. Ser.* 2, **311**, 781–784.

Karaulov, A. I. (1992). *ABSMAD. Program for FAST Data Processing*. University of Wales, Cardiff, Wales.

Karkhanis, D. W. & Field, L. (1985). *Phosphorus Sulfur*, **22**, 49–57.

Pflugrath, J. W. & Messerschmidt, A. (1989). *MADNES*. Version of 11 September, 1989. Distributed by Delft Instruments, Delft, The Netherlands.

Raper, E. S., Creighton, J. R., Oughtred, R. E. & Nowell, I. W. (1983). *Acta Cryst.* B**39**, 355–360.

Raper, E. S., Jackson, A. R. W. & Gardiner, D. J. (1984). *Inorg. Chim. Acta*, **84**, L1–L4.

Reynolds, J. E. F. (1993). *Martindale, The Extra Pharmacopoeia*, p. 531. London: The Pharmaceutical Press.

Schönerr, H.-J. & Wanzlick, H.-W. (1970). *Chem. Ber.* **103**, 1037–1046.

Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.

Sohal, B. (1996). Unpublished results.

Zsolnai, L. (1996). *ZORTEP. An Interactive ORTEP Program*. University of Heidelberg, Germany.

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2,2′:6′,2″-Terpyridinium Trifluoromethanesulfonate, [terpyH](CF_3SO_3)

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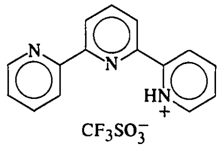
Abstract

In the title compound, $C_{15}H_{12}N_3^+.CF_3O_3S^-$, one terminal pyridine ring of the terpyridinium cation is protonated and forms an intramolecular N—H···N hydrogen bond of 2.646 (4) Å which stabilizes the *cis,trans* conformation in contrast to the *trans,trans* geometry of free terpyridine. An N—H···O hydrogen bond of 2.817 (5) Å connects the terpyridinium cations and the trifluoromethanesulfonate anions.

Comment

Terpyridine (terpy) is a well known tridentate ligand which forms numerous complexes with one, two or three terpyridines coordinated to the metal (Grdenić, Popović, Bruvo & Korpar-Čolig, 1991; Matković-Čalogović, Popović & Korpar-Čolig, 1995; Kepert, Patrick, Skelton & White, 1988). Only a few structures with terpy as a bidentate ligand have been published (for example, see Deacon, Patrick, Skelton, Thomas & White, 1984). The structure of free terpy was reported recently (Bessel, See, Jameson, Churchill & Takeuchi, 1992). A search of the Cambridge Structural Database (1996) (hereafter CSD) revealed no structure containing a free terpyridinium cation (terpyH). We report here the structure of terpyridinium trifluoromethanesulfonate, [terpyH](CF_3SO_3), (I).



(I)

The crystal structure consists of terpyridinium cations, since one terminal pyridine ring of terpy is protonated, and trifluoromethanesulfonate anions (Fig. 1). The numbering scheme of the terpyridinium cation is the same as that of free terpy. The H atom on the N11 atom is involved in a bifurcated hydrogen bond consisting of an intramolecular N11—H···N21 bond of 2.646 (4) Å [N—H 0.99, H···N 2.242 (3) Å and N—H···N 102.8 (2)°] and an intermolecular N11—H···O2 bond of 2.817 (5) Å [H···O 2.030 (3) Å and N—H···O 134.5 (2)°]. The pyridine rings in the terpy molecule are linked by C—C single bonds which enable rotation of the rings. Free terpy has a *trans,trans* configuration and upon coordination to a metal atom the rotation of the terminal pyridines results in the *cis,cis* geometry in the complexes. In terpyH, an intramolecular hydrogen bond stabilizes the *cis,trans* configuration. The deviation from coplanarity is small; the torsion angles N11—C12—C22—N21 and N21—C26—C32—N31 are 3.6 (5) and −172.9 (3)°, respectively (*cf.* 5.1 and 7.2° in the free terpy).

There are no significant differences in the bond lengths of the terpyH cation and free terpy. Some significant changes occur in the angles, the largest involving the protonated pyridinium ring, where an increase of the C12—N11—C16 angle and a decrease