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Azinyl sulfides. LXXXI.[1] 14-Phenyl-7-thiapyrano[2,3-*c*;6,5-*c*′]diquinoline-14-carbonitrile

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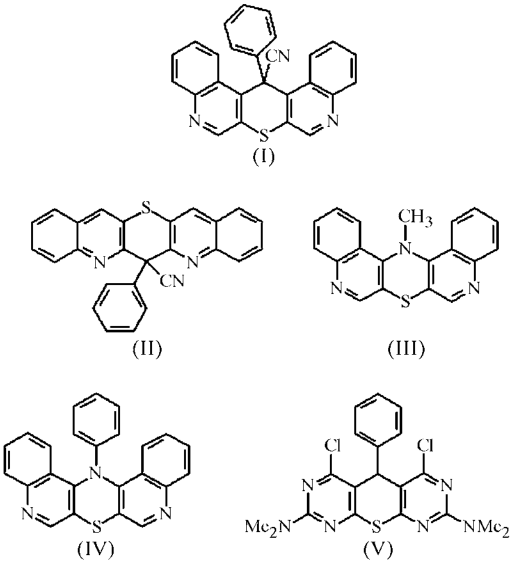
The molecules of the title compound, $C_{26}H_{15}N_3S$, have a pentacyclic ring system which is almost planar, with the central ring in a flattened boat conformation. The folding angle between the two quinoline rings is 6.75 (7)°. The 14-phenyl substituent is in a quasi-axial conformation, while the 14-cyano substituent is in a quasi-equatorial conformation with respect to the thiopyran ring. The $S\cdots C-C_{phenyl}$ and $S\cdots C-C_{CN}$ angles are 116.8 (2) and 129.3 (2)°, respectively. The plane of the phenyl group is nearly coplanar with the plane bisecting the dihedral angle of the pentacyclic ring system.

Comment

The incorporation of polarizable heteroatoms within the donor framework is regarded as an important way of designing new polyheterocyclic donor molecules in the search for organic materials with interesting electronic, optoelectronic and magnetic properties (Marti *et al.*, 1994). Very few papers have appeared in the literature to date on the synthesis and properties of fused pentacyclic heterocycles. Some pentacyclic heterocycles, such as azathiapentaphenes and diazadithiapentacenes, show photoelectric properties (Yoshida *et al.*, 1994), and diazapentacenes show photodynamic therapeutic activity against cancer cell lines, bacteria and viruses (Gloster *et al.*, 1999). Very recent studies demonstrated significant electronic conductivity enhancement of disubstituted homopentacenes (Anthony *et al.*, 2001). On the other hand, quinolines condensed with some heterocycles have become important compounds because of their affinity for benzodiazepine receptors (Moreau *et al.*, 1988; Anzini *et al.*, 1990) and their cytotoxic activity (Ma *et al.*, 1994, 1999; Tasdemir *et al.*, 2001).

The purpose of this study was to determine the structure of the title diazathiapentaphene, (I), and to compare it with the structures of related multicyclic heterocycles, (II)–(V) (see scheme).



The molecular conformation and atom labelling are shown in Fig. 1. In contrast with the isomeric thiopyranodiquinoline (II) (Nowak *et al.*, 2002), and the pentaphenes, (III) (Pluta & Suwińska, 2000) and (IV) (Besnard *et al.*, 2005), the overall pentacyclic ring system in (I) is close to being planar. It is only slightly folded along the S⋯C21 axis, as well as along the C3—C4 and C13—C14 axes between the thiopyran and quinoline rings. The butterfly angle between the two quinoline planes is very small in comparison with the pentacyclic heterocycles (II)–(IV): 6.75 (7)° *versus* 44.73 (3), 150.2 (1) and 20.5 (1)°, respectively.

The central thiopyran ring has a flattened boat conformation, with atoms S and C21 slightly displaced out of the basal C3/C4/C13/C14 plane by −0.092 (5) and −0.122 (5) Å, respectively, compared with displacements of 0.580 (3) and

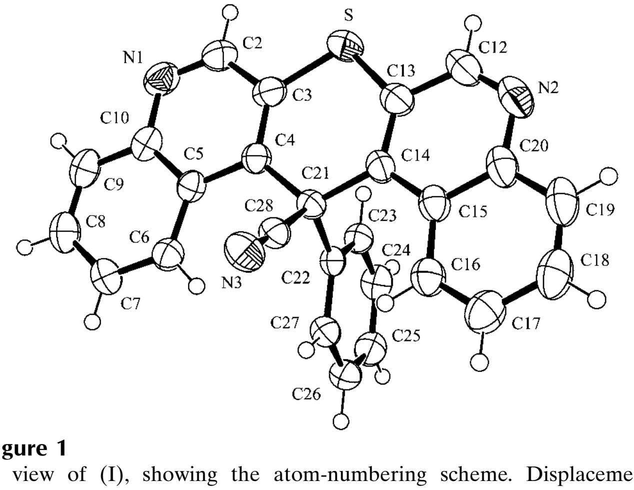


Figure 1
A view of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

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[1] Part LXXX: Michalik & Nazarski (2004).

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0.563 (3) Å, respectively, in thiopyranodiquinoline (II). The dihedral angle between the planes defined by the atoms of the two halves of the thiopyran ring (*i.e.* S/C3/C4/C21 and S/C13/C14/C21) is 9.32 (14)°. It is worth noting that the quinoline ring system is not quite planar, the dihedral angles between the pyridine and benzene rings being 0.91 (11) and 0.41 (11)°, respectively.

Bond lengths and angles are given in Table 1. Whereas the S—C, N—C and C—C bond lengths are similar to those found in the isomeric thiopyranodiquinoline, (II), the bond angles differ significantly. The C3—S—C13 and C4—C21—C14 angles are quite large compared with the corresponding angles in isomer (II), at 98.88 (10) and 110.53 (16)°, respectively. Bond angles C4—C3—S, C14—C13—S, C3—C4—C21 and C13—C14—C21 differ greatly from the unstrained sp^2 and sp^3 angles (Table 1). The increase of these bond angles is related to the requirements of the flattened boat conformation of the thiopyran ring.

The most intriguing molecular features of (I) are the location and orientation of the substituents. As was also observed for the phenylthiopyranodiarenes (II) and (V) (Quintela *et al.*, 2000), the phenyl substituent is in a quasi-axial conformation with respect to the thiopyran ring, with torsion angles C22—C21—C4—C3 = −111.66 (19)°, C22—C21—C4—C5 = 66.0 (2)°, C22—C21—C14—C13 = 108.9 (2)° and C22—C21—C14—C15 = −68.1 (2)°.

The S···C21—C22 angle is 116.8 (2)°, which is larger than in compounds (II) and (V). Whereas the plane of the phenyl group in isomer (II) is nearly perpendicular to the plane bisecting the dihedral angle of the thiopyranodiarene ring system, the phenyl group plane in (I) is nearly coplanar with the bisecting plane. The torsion angles C23—C22—C21—C4 and C27—C22—C21—C4 are 58.8 (2) and −120.2 (2)°, respectively, and the dihedral angle between the phenyl group plane and the C3/C4/C13/C14 plane is 88.91 (17)°.

The cyano group is in a quasi-equatorial position with respect to the central thiopyran ring, with torsion angles C28—C21—C4—C3 = 126.56 (19)°, C28—C21—C4—C5 = −55.8 (2)°, C28—C21—C14—C13 = −128.71 (19)° and C28—C21—C14—C15 = 54.3 (2)°, and an S···C21—C28 angle of 129.30 (2)°.

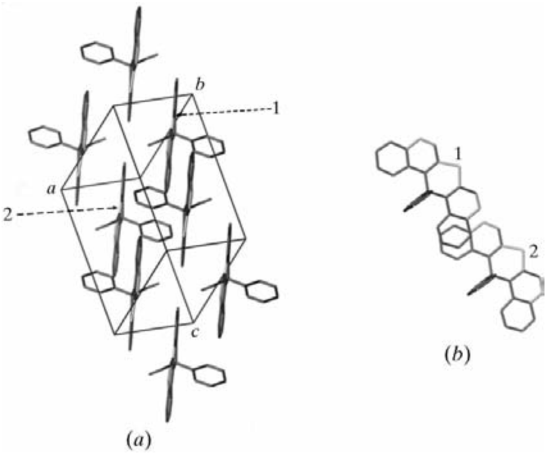

Figure 2
The packing of the molecules of (I) in the crystal. (*a*) A view showing the parallel arrangement of the main ring systems. (*b*) The overlap between molecules 1 and 2, indicated by arrows in (*a*).

There are very close contacts between quinoline atoms H6 and H16 and the substituent C atoms. The non-bonded distances H6···C27 = 2.66 Å, H16···C27 = 2.67 Å, H6···C28 = 2.44 Å and H16···C28 = 2.40 Å are each shorter than the sum of the van der Waals radii (2.90 Å; Bondi, 1964). These steric interactions cause deshielding of the H6/H16 and H23/H27 atoms in the ^{1}H NMR spectrum and were confirmed using the nuclear Overhauser enhancement effect (Pluta, 1994).

There are two molecules related by inversion symmetry in each unit cell. The main pentacyclic rings of the molecules are parallel to each other, as shown in Fig. 2(*a*). This parallel alignment does not, however, produce significant overlap between the pentacyclic ring systems, since they are shifted from each other in order to accomodate the bulky subtituents. The small overlap occurring between the C5–C10 ring of one molecule and the C15–C20 ring of another is shown in Fig. 2(*b*). The distance between the two planes that partly overlap is 3.36 (1) Å. Despite the π–π interactions, linear hydrogen bonding involving atoms C2, H2 and N1 can occur, as indicated by the distance between H2 and N1 of 2.53 Å and the H2···C2—N1 angle of 152°.

Experimental

The title compound was synthesized and purified as previously reported by Pluta (1994). Small needles were obtained on slow evaporation from a solution of the monomethyl ether of diethylene glycol. As a result of their limited size, the crystals diffracted too weakly to be studied with conventional X-ray diffraction techniques. Synchrotron radiation was therefore used.

Crystal data

$C_{26}H_{15}N_3S$
$M_r = 401.47$
Triclinic, $P\bar{1}$
$a = 7.9135$ (1) Å
$b = 9.3622$ (4) Å
$c = 13.328$ (5) Å
$\alpha = 75.724$ (2)°
$\beta = 84.369$ (1)°
$\gamma = 84.415$ (2)°
$V = 949.59$ (6) Å^3
$Z = 2$

$D_x = 1.404$ Mg m^{-3}
Synchrotron radiation
$\lambda = 0.996$ Å
Cell parameters from 300 reflections
$\theta = 5$–$45°$
$\mu = 0.42$ mm^{-1}
$T = 293$ (2) K
Needle, white
0.80 × 0.01 × 0.01 mm

Data collection

MARCCD 165 detector diffractometer
φ scans
4040 measured reflections
2099 independent reflections
1983 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.048$
$\theta_{\rm max} = 32.9°$
$h = -8 \rightarrow 8$
$k = -10 \rightarrow 10$
$l = -14 \rightarrow 14$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.051$
$wR(F^2) = 0.137$
$S = 1.06$
2099 reflections
271 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.092P)^2 + 0.2098P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.17$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.20$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

S—C13	1.740 (2)	C21—C4	1.553 (3)
N1—C10	1.369 (3)	C21—C14	1.549 (3)
N2—C12	1.298 (3)	C21—C22	1.549 (3)
C2—N1	1.296 (3)	C21—C28	1.492 (3)
C3—S	1.731 (2)	C22—C23	1.389 (3)
C4—C3	1.374 (3)	C22—C27	1.388 (3)
C13—C14	1.375 (3)	C28—N3	1.140 (3)
C20—N2	1.379 (3)		
C3—S—C13	102.44 (11)	C4—C21—C14	116.39 (16)
C3—C4—C21	122.8 (2)	C13—C14—C21	122.84 (19)
C4—C3—S	127.34 (19)	C14—C13—S	126.99 (19)

Due to the limited range of motion of the diffractometer available, the completness of the data was low. The H atoms could be located in difference Fourier maps but, due to the low number of reflections, they were fixed in their ideal positions, with C—H distances of 0.93 Å and with $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C).

Data collection: *MARCCD* (at beamline I711, MAXLAB, Lund, Sweden) (MAR, 2002); cell refinement: *TWINSOLVE* (Rigaku/MSC & Prekat, 2002); data reduction: *TWINSOLVE*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999) in *WinGX* (Farrugia, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997) in *WinGX* (Farrugia, 1999); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *enCIFer* (Allen *et al.*, 2004).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: TR1113). Services for accessing these data are described at the back of the journal.

References

Allen, F. H., Johnson, O., Shields, G. P., Smith, B. R. & Towler, M. J. (2004). *J. Appl. Cryst.* **37**, 335–338.

Altomare, A. Burla, M. C., Camalli, M., Cascarano, G. L., Giacovazzo, C., Guagliardi, A., Moliterni, A. G. G., Polidori, G. & Spagna, R. (1999). *J. Appl. Cryst.* **32**, 115–119.

Anthony, J. E., Brooks, J. S., Eaton, D. L. & Parkin, S. R. (2001). *J. Am. Chem. Soc.* **123**, 9482–9483.

Anzini, M., Capelli, A., Vomero, S., Botha, M., Voremo, S. & Cagnotto, A. (1990). *Il Farmaco*, **45**, 1169–1179.

Besnard, C., Kloc, C., Siegrist, T. & Pluta, K. (2005). *J. Chem. Crystallogr.* In the press.

Bondi, A. J. (1964). *J. Chem. Phys.* **68**, 441–451.

Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.

Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.

Gloster, D. F., Cincotta, L. & Foley, J. M. (1999). *J. Heterocycl. Chem.* **36**, 25–32.

Ma, Z.-Z., Hano, Y., Nomura, T. & Chen, Y.-J. (1994). *Heterocycles*, **46**, 541–546.

Ma, Z.-Z., Hano, Y., Nomura, T. & Chen, Y.-J. (1999). *Heterocycles*, **51**, 1593–1596.

MAR (2002). *MARCCD*. MAR X-ray Research GmbH, Norderstedt, Germany.

Marti, C., Irurre, J., Alvarez-Larena, A., Piniella, J. F., Brillas, E., Fajari, L., Alemàn, C. & Julià, L. (1994). *J. Org. Chem.* **59**, 6200–6207.

Michalik, E. & Nazarski, R. B. (2004). *Tetrahedron*, **60**, 9213–9222.

Moreau, G., Broto P., Fortin, M. & Turpin, C. (1988). *Eur. J. Med. Chem.* **93**, 964–968.

Nowak, M., Pluta, K. & Suwiǹska, K. (2002). *New J. Chem.* **26**, 1216–1220.

Pluta, K. (1994). *Phosphorus Sulfur Silicon*, **92**, 149–154.

Pluta, K. & Suwiǹska, K. (2000). *Acta Cryst.* C**56**, 374–375.

Quintela, J. M., Moreira, M. J. & Peinador, C. (2000). *Heterocycles*, **52**, 333–348.

Rigaku/MSC and Prekat (2002). *TWINSOLVE*. Rigaku/MSC, 9009 New Trails Drive, The Woodlands, TX 77381-5209, USA, and Prekat AB, Lund, Sweden.

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

Tasdemir, D., Marshall, K. M., Mangalindan, G. C., Barrows, L. R., Harper, M. K. & Ireland, C. M. (2001). *J. Org. Chem.* **66**, 3246–3248.

Yoshida, S., Nozawa, K., Sato, N. & Uchida, T. (1994). *Bull. Chem. Soc. Jpn*, **67**, 2017–2023.