Crystal structure of 2,2′-diphenyl-4,4′-bithiazole, $C_{18}H_{12}N_2S_2$

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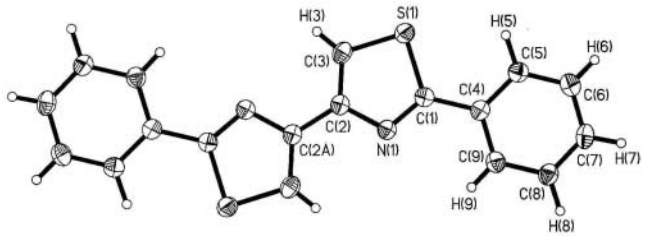

Abstract

$C_{18}H_{12}N_2S_2$, monoclinic, $P12_1/c1$ (No. 14), a = 8.850(1) Å, b = 4.9724(6) Å, c = 16.247(2) Å, β = 90.188(2)°, V = 715.0 Å^3, Z = 2, $R_{gt}(F)$ = 0.060, $wR_{ref}(F^2)$ = 0.142, T = 110 K.

Source of material

The 2,2′-diphenyl-4,4′-bithizole ligand was prepared from thiobenzamide and 1,4-dibromo-2,3-butadiene and recrystallized from $CHCl_3$. The single crystals suitable for X-ray analysis were then obtained by slow evaporation at room temperature from benzine-acetonitrile solvent. The white crystals were filtered off, washed with cold methanol and ether and dried in vacuum over P_4O_{10} (mp 458 K; yield 80%). Elemental analyses were consistent with the stiochiometry $C_{18}H_{12}N_2S_2$: (found) C, 67.10%; H, 3.24%; N, 8.55%; (calc.) C, 67.50%; H, 3.75%; N, 8.75%.

Experimental details

Melting points were measured on an Electrothermal 9100 apparatus and are uncorrected. Elemental analyses were performed using a Heraeus CHN-O-Rapid analyzer.

Discussion

Bithiazole derivation are of interest in the area of organic metals and as materials for nonlinear optics [1]. In the solid, bithiazoles take a planar or near planar configuration. In solution as well as in the gas state significant deviation from planarity can occur owing to a balance between conjugative and steric intramolecular interaction. Evidence of chain flexibility in solution comes from thermochromic and solvatochromic studies. In our aim to correlate stereoactive of valence shell lone electron pairs ($6s^2$) and overcrowding [2] in the coordination environment of lead(II) [3-4], bismuth(III) [5] and thallium(I) [6] complexes, we prepared the 2,2′-diphenyl-4,4′-bithiazole ligand.

Molecules of the title compound lie at an inversion centre and have approximately D_{2h} symmetry so that only half of the atoms are symmetrically independent. The C1—C1A bond length of 1.469 Å is close to the standard value for a single-bond length between trigonally linked C atoms. The bond lengths of C—N in the bithiazole ring are in the range 1.298 Å – 1.378 Å, which are shorter than the single-bond length of 1.48 Å and longer than the typical C=N distances of 1.28 Å, indicating partial double-bond character. This can be interpreted in term of conjugation in the heterocycle [7]. The molecule forms a two-dimensional network bonded through intermolecular C–H···N hydrogen bonds. The attempt to isolation of Pb^{+2}, Bi^{+3}, and Tl^{+1} complexes was not successful, this point can be regarded as the initial electron withdrawing of phenyl rings and also their spatial strict effects.

Table 1. Data collection and handling.

Crystal:	white prism, size 0.07 × 0.10 × 0.20 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	3.69 cm^{-1}
Diffractometer, scan mode:	Bruker SMART 1000 CCD, φ/ω
$2\theta_{max}$:	52.74°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	3690, 1454
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 1048
$N(param)_{refined}$:	124
Programs:	SHELXTL-plus [8], SHELXTL-97 [9], SADABS [10]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(3)	4*e*	0.344(5)	0.419(9)	0.890(3)	0.05(1)
H(5)	4*e*	0.099(4)	–0.302(8)	1.045(2)	0.03(1)
H(6)	4*e*	0.015(4)	–0.607(7)	1.149(2)	0.016(8)
H(7)	4*e*	0.138(4)	–0.648(8)	1.271(2)	0.03(1)
H(8)	4*e*	0.332(4)	–0.348(7)	1.309(2)	0.026(9)
H(9)	4*e*	0.407(4)	–0.030(8)	1.210(2)	0.03(1)

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Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S(1)	4*e*	0.2218(1)	0.0939(2)	0.96399(5)	0.0321(5)	0.0286(5)	0.0274(5)	0.0000(4)	–0.0023(3)	0.0018(4)
N(1)	4*e*	0.4249(3)	0.2335(6)	1.0686(2)	0.025(2)	0.020(2)	0.026(1)	0.003(1)	0.001(1)	–0.000(1)
C(1)	4*e*	0.3143(4)	0.0651(7)	1.0585(2)	0.020(2)	0.023(2)	0.026(2)	0.005(1)	0.002(1)	–0.001(1)
C(2)	4*e*	0.4409(4)	0.3963(7)	1.0006(2)	0.027(2)	0.019(2)	0.025(2)	0.004(1)	0.004(1)	–0.002(1)
C(3)	4*e*	0.3410(4)	0.3505(8)	0.9382(2)	0.032(2)	0.028(2)	0.026(2)	0.005(2)	0.005(2)	0.002(2)
C(4)	4*e*	0.2632(4)	–0.1349(7)	1.1192(2)	0.024(2)	0.021(2)	0.025(2)	0.006(1)	0.003(1)	–0.001(1)
C(5)	4*e*	0.1457(4)	–0.3133(7)	1.1014(2)	0.027(2)	0.027(2)	0.030(2)	0.003(2)	–0.001(2)	–0.000(2)
C(6)	4*e*	0.0965(4)	–0.4975(8)	1.1595(2)	0.025(2)	0.027(2)	0.038(2)	0.001(2)	0.004(2)	–0.001(2)
C(7)	4*e*	0.1668(4)	–0.5077(8)	1.2363(2)	0.037(2)	0.023(2)	0.034(2)	0.003(2)	0.008(2)	0.004(2)
C(8)	4*e*	0.2841(4)	–0.3364(8)	1.2545(2)	0.033(2)	0.028(2)	0.026(2)	0.001(2)	0.003(2)	0.001(2)
C(9)	4*e*	0.3325(4)	–0.1469(8)	1.1971(2)	0.028(2)	0.027(2)	0.028(2)	–0.001(2)	0.004(2)	–0.001(2)

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References

1. Zyss, J.: Molecular Nonlinear Optics: Materials,Physics and devices, Academic Press, London 1994.
2. Shimoni-Livny, L.; Glusker, J. P.; Bock, C. W.: Lone pair Functionality in Divalent lead compounds. Inorg. Chem. **37** (1998) 1853-1867.
3. Holl, A. K.; Harrowfield, J. M.; Morsali, A.; Soudi, A. A.; Yanovsky A.: Bonds and lone pairs in the flexible coordination sphere of lead(II). CrystEngComm (2000) 13.
4. Morsali, A.; Payheghader, M.; Salehi, M. S.: A New Polymer Of Mixed-Anions Complex Containing (μ-acetate)(Nitrate)(phen)Lead(II) molecule $[Pb(phen)(O_2CCH_3)(O_2NO)]_n$ (phen = 1,l0-phenantroline). Z. Anorg. Allg. Chem **628** (2002) 12-14.
5. Morsali, A.; Tadjarodi, A.; Mohammadi, R.; Mahjoub, A. R.: Crystal structure of bis(4,4′-bitiazole)bismuth(III) trinitrate hemihydrate, $Bi(C_6H_4N_2S_2)_2(NO_3)_2 \cdot 0.5H_2O$. Z. Kristallogr. NCS **216** (2001) 379-380.
6. Mahjoub, A. R.; Morsali, A.; Bagherzadeh, H.: Syntheses and Characterization of Thalium(I) complexes with Phenoxide derivations Ligand. Polyhedron, accepted.
7. Fengli, B.; Fangfang, J.; Yujie, Y.; Lude, L.; Xin, W.; Shanmuga, S. R.; Hoong-Kun, F.: 1,4-Bis(2-benzimidazole)benzene. Acta Crystallogr. C**56** (2000) 718-719.
8. Sheldrick G. M.: SHELXTL-plus, Version 5.o. Software Reference Map Siemens Industrial Automation, Inc., Madison, USA 1995.
9. Sheldrick G. M.: SHELXTL-97. A Program for Refining Crystal Structures. Version 5.1o, Bruker AXS Inc., Madison, WI-53719, USA 1997.
10. Sheldrick G. M.: SADABS, Bruker AXS Inc., Madison, WI-53719, USA 1997.