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THE CRYSTAL AND MOLECULAR STRUCTURE OF 2,3,5,6-TETRAPHENYL-1,4-DITHIIN

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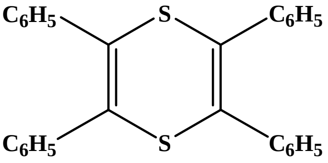
Abstract – The phenyl rings in 2,3,5,6-tetraphenyl-1,4-dithiin have neither of the two most obvious configurations: all perpendicular to the dithiin ring (paddlewheel), or parallel to the dithiin double bonds (butterfly). Instead, there are two phenyls in each orientation.

INTRODUCTION

In 1938 Mitra isolated a compound with the formula $C_{28}H_{20}S_2$ from the reaction of benzoin with H_2S in acidic ethanol.[1] This was correctly identified as 2,3,5,6-tetraphenyl-1,4-dithiin by Mayer and Nitzschke[2] and by Schrauzer and Finck.[3] Tetraphenyldithiin has also been made by the photolysis of 4,5-diphenyl-1,2,3-thiadiazole,[4] by the photolysis of 4,5-diphenyl-1,3-dithiol-2-one,[5] and by the bromine oxidation of bis(dithiobenzil)nickel.[6]



Tetraphenyldithiin is a particularly intriguing molecule because of the possibility of conjugation on each side of the dithiin ring. The two plausible structures would seem to be (a) a paddlewheel shape, in which all four phenyl rings are approximately perpendicular to the dithiin ring, minimizing steric interference but eliminating resonance effects between rings, or (b) a butterfly shape, in which the two phenyls on each side are coplanar, though the two sides would not be coplanar with each other, especially if the dithiin ring adopts a boat conformation. Mayer and Nitschke attributed shifts to lower frequency for C=C peaks in the IR spectrum, relative to those for *trans*-stilbene, to conjugation.[2]

To prepare crystals suitable for X-Ray diffractions studies, we prepared tetraphenyldithiin by a new photochemical procedure, starting with bis(dithiobenzil)nickel.

EXPERIMENTAL

Bis(dithiobenzil)nickel was prepared by the method of Schrauzer and Mayweg.[7] An approximately 0.05 M solution of $[Ni(dtb)_2]$ was prepared in 30 mL of $CHCl_3$ and placed in a 10-cm cylindrical fused silica cell. This was irradiated with a 350-W mercury arc lamp (Oriel) with fused silica optics for 48 h, or until the solution had turned from dark green to orange. The orange solution was decanted from the cell, and the chloroform was allowed to evaporate. Inside the cell, a film had formed, which was removed with water. The visible spectrum of this solution corresponded to that of aqueous Ni^{2+}. Evaporation of the orange solution was continued until it became quite viscous, with a white precipitate suspended in it. After diluting the viscous solution with acetone, the white product was collected by vacuum filtration, then redissolved in chloroform. It was recrystallized by vapor diffusion from acetone. The crystals that formed were long, pale yellow needles. Similar crystals were also produced in THF by vapor diffusion from ether. mp 177-184° (decomp). NMR ($CDCl_3$): ^{1}H: δ 7.24 (d), 7.23-7.195 (m), 7.19-7.145 (m); ^{13}C δ 164.4, 138, 135.5, 130, 128.33, 127.9. IR (neat) 1485(w), 1440(w), 763 (m), 735(s), and 693(vs). UV ($CHCl_3$): ~310 nm(sh). MS: *m/z* 420 (M, 100%). Anal. Calcd for $C_{28}H_{20}S_2$: C, 79.96; H, 5.09; S, 15.25. Found: C, 78.66; H, 4.57; S, 15.65.

NMR spectra were recorded on a Varian INOVA 400 spectrometer. ^{1}H and ^{13}C NMR chemical shifts are reported in parts per million (ppm) downfield from TMS and were calibrated to the residual signal of the

Table 1. Crystallographic Data for 2,3,5,6-Tetraphenyl-1,4-dithiin.

formula	$C_{28}H_{20}S_2$
fw	420.56
crystal system	Orthorhombic
space group	$P2_12_12_1$
a(Å)	5.879(3)
b(Å)	11.7274(18)
c(Å)	31.911(6)
V(Å^3)	2200.0(12)
Z	4
T(°C)	27
λ (Mo Kα) (Å)	0.71073 Å
ρ_{calcd} (g·cm^{-3})	1.270
μ (Mo Kα) (cm^{-1})	2.54
F(000)	880
θ range (deg)	3.09–25.00°
indepdt reflcns	2792
GOF on F^2	1.082
R1[a] $[I > 2\sigma(I)]$	0.0460
wR2[b]	0.1142
abs struct param	-0.23(15)
ext coeff	0.0063(17)
largest diff peak and hole (e· Å^3)	0.283 and -0.338

[a] $R1 = \sum ||F_0| - |F_c|| / \sum |F_0|$ [b] $wR2 = \{\sum w(F_0^2 - F_c^2)^2 / \sum wF_0^4\}^{1/2}$

solvent. IR spectra were recorded with a Nicolet Avatar 360 FTIR spectrometer, using pure solid pressed against a germanium window to obtain total attenuated reflection. Mass spectra were obtained with a Sciex API-1 electrospray quadropole mass spectrometer. Elemental analyses were performed by the Microanalytical Laboratory of the University of California at Berkeley.

A needle-shaped crystal of tetraphenyldithiin was mounted on a glass capillary in a Bruker/Siemens P4 X-Ray diffractometer. The unit cell was determined from 40 widely dispersed, centered reflections. An empirical absorption correction was applied.[8] The structure was solved by direct methods, and refined by full-matrix least squares procedures.[9] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were fixed on calculated positions and each was assigned an isotropic thermal parameter equal to $1.2U_{eq}$ of the atom to which it was attached. A summary of crystallographic data is given in Table 1.

RESULTS AND DISCUSSION

Tetraphenyldithiin crystallized in the space group $P2_12_12_1$. The structure, refined to a final R-value of 4.60%, is shown below. The dithiin ring adopts a boat configuration, while the rings are in neither the paddlewheel nor the butterfly arrangement. Instead, tetraphenyldithiin is a hybrid, with two rings in the paddlewheel position and two in the butterfly. This arrangement makes conjugation between phenyl rings impossible, but does allow conjugation of the two "butterfly" rings with the respective dithiin C=C double

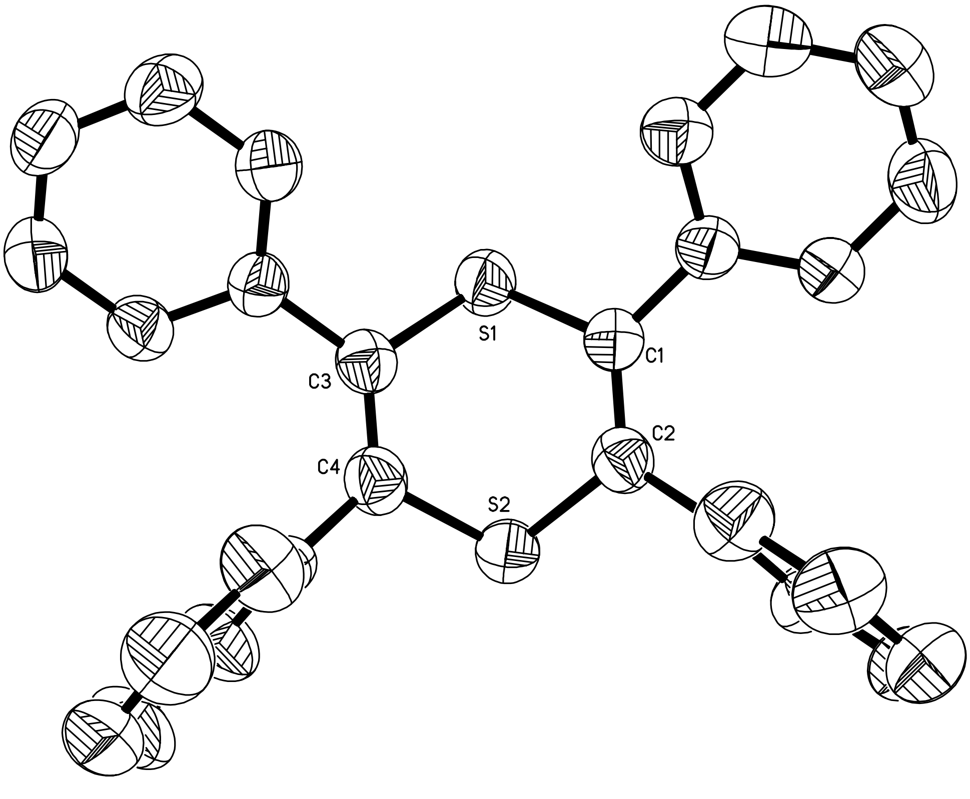


Figure 1. Molecular structure of 2,3,5,6-tetraphenyl-1,4-dithiin. Hydrogens are omitted for clarity.

bonds. This appears to offer the maximum degree of resonance without causing severe steric strain. The two "paddlewheel" phenyl rings are nearly perpendicular to the plane defined by the carbon atoms in the dithiin ring (89.6° and 91.4°). The "butterfly" rings are themselves coplanar (within 0.6°), and that plane is inclined by 31° from the plane of the dithiin carbons. Tables of atomic coordinates, bond lengths and angles, thermal parameters, and structure factors are available have been deposited with the Cambridge Crystallographic Data Centre.[10]

ACKNOWLEDGEMENT

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