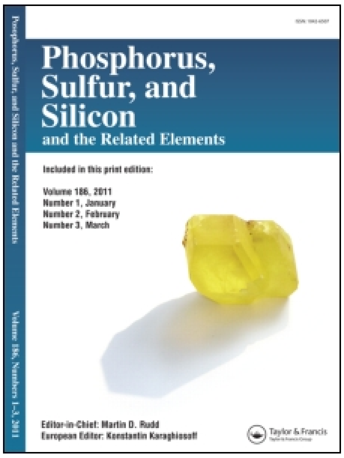

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THE CRYSTAL STRUCTURE OF THE HYDROGEN BONDED MOLECULAR ADDUCT THIOBISPHTHALIMIDE · DIPHENYLAMINE

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THE CRYSTAL STRUCTURE OF THE HYDROGEN BONDED MOLECULAR ADDUCT THIOBISPHTHALIMIDE · DIPHENYLAMINE

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The structure of the complex $(PHL)_2S \cdot HN(C_6H_5)_2$ has been determined by single-crystal X-ray diffraction methods. The compound crystallizes in the triclinic system, space group $P\bar{1}$, with unit cell dimensions $a = 896.1$, $b = 1730.8$, $c = 846.7$ pm; $\alpha = 88.66°$, $\beta = 115.66°$, $\gamma = 93.98°$ and $Z = 2$. In the adduct the thiobisphthalimide molecule is bonded to the diphenylamine through a $C{=}O \cdots HN$ hydrogen bonding. UV-visible data reveal some charge transfer between the donor $HN(C_6H_5)_2$ and the acceptor $(PHL)_2S$.

Key words: Thiobisphthalimide; diphenylamine; adduct; hydrogen bonding; charge transfer; X-ray structure.

INTRODUCTION

In the sulphur(II) chemistry the compounds more widely studied are those with S—N bonds, especially the thiobisamines. The thiobisdialkylamines are in general rather inert compounds. However, in the presence of Brønsted or Lewis acids, they undergo hydrolysis[1] and alcoholysis reactions[2] leading to oxidation products arising from the sulfoxylic acid $S(OH)_2$ and to alkoxy derivatives, respectively. A similar effect can also be achieved by electrochemical oxidation.[3] Molecular orbitals calculations show that the relative reactivities of thiobisamines toward nucleophilic reagents correlate with both, the net charge on the sulfur atom and the HOMO-LUMO gap arising from the nucleophile-sulfur compound interaction.[4]

Although the thiobisphthalimide ($S(PHL)_2$) has a N—S—N moiety, similar to those in thiobisdialkylamines, its chemical behavior is quite different. Thus, $S(PHL)_2$ does not react with Brønsted or Lewis acids but it reacts with nucleophiles like amines, thiols, and alkoxides to give substitution products.[5]

Sulfur(II)-nitrogen compounds are in general poor ligands. Nevertheless, thiobisamines form carbonyl complexes of type $M(CO)_5S(NR_2)_2$. This property is not observed for $S(PHL)_2$ which in turn is peculiarly able to give donor-acceptor molecular complexes with potassium thiocyanate or diphenylamine, still not totally characterized.

In order to contribute to the apparently anomalous chemistry of the phthalimide-sulfur(II) compound, the structural study of the title compound has been performed.

RESULTS AND DISCUSSION

The reaction of thiobisphthalimide $(PHL)_2S$ and diphenylamine results in the formation of the stable adduct $(PHL)_2S \cdot HN(Ph)_2$.

Although the $(PHL)_2S$ has the same N—S—N moiety as the thiobisamines $(R_2N)_2S$, their chemical behavior presents some differences. Thus, the typical reactions of thiobisamines with Cu(II) ions or with pentacarbonyls of the group VI metals[1,6] could not be observed for the phthalimide derivatives. In contrast, the thiobisamines do not react with diphenylamine.

The IR spectrum of the molecular adduct $(PHL)_2S \cdot HN(Ph)_2$ virtually corresponds to the superposition of the spectra of their components.[5] Only the N—H bond of diphenylamine shows a shift to lower frequencies, indicating a hydrogen bonding association. Thus, according to the IR spectra, the nature and strength of the S—N bond in the N—S—N fragment remains unaltered after the formation of the adduct. These features are corroborated by analysis of the X-ray photoelectron spectra. The binding energies of the electrons S(2p) and N(1s) for the free thiobisphthalimide and for the molecular adduct are very similar, indicating that no significant charge changes occur during the adduct formation.[5]

The diffuse reflecting spectrum of the adduct indicates a considerable charge transfer in the solid state. $(PHL)_2$ and diphenylamine are uncolored while the adduct is yellow.

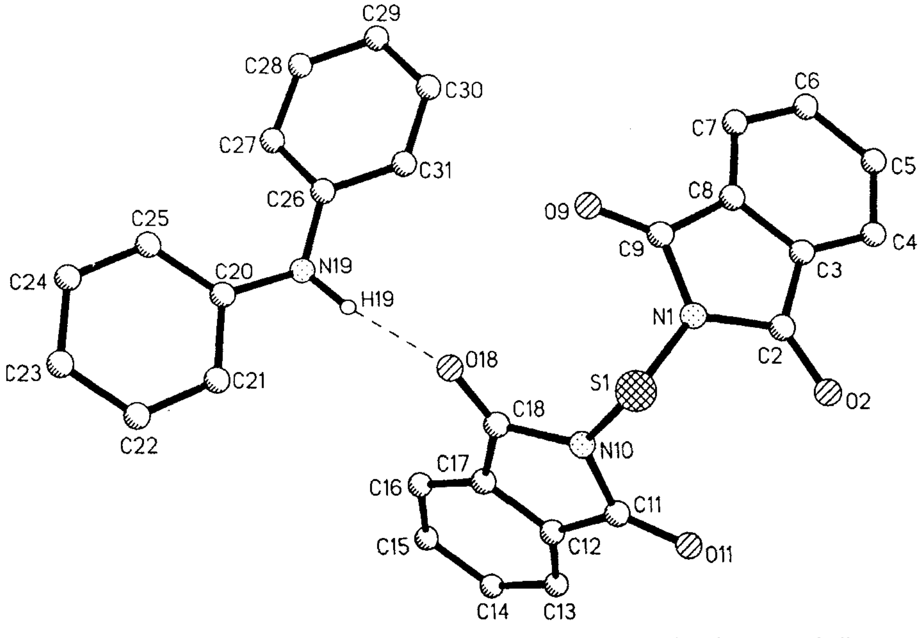

FIGURE 1 A perspective drawing of the molecular adduct showing the atom labeling.

TABLE I

Data collection and structure refinement parameters

Crystallographic Section	
compound	$(C_8H_4NO_2)_2S \cdot C_{12}H_{10}NH$
molecular mass	493.54
a [pm]	896.1(1)
b [pm]	1730.8(4)
c [pm]	846.7(2)
α [deg]	88.66(2)
ß [deg]	115.66(1)
γ [deg]	93.98(1)
V [pm^3]	$1180.8(4) \cdot 10^6$
Z	2
d(calcd) [$g \cdot cm^{-3}$]	1.388
crystal system	triclinic
space group	$P\bar{1}$
Data Collection	
diffractometer	Nicolet R3m/V
radiation	MoKα
monochromator	graphite
crystal size [mm]	0.4 x 0.4 x 0.15
data collection mode	Wyckoff-scan
theta range [deg]	1.75 - 27.5
recip. latt. segment	h = -10 - 10
	k = -22-22
	l = 0-11
no. refl. measd.	5440
no. unique refl.	5440
no. refl. F > 3σ(F)	3095
lin. abs. coeff. [mm^{-1}]	0.17
abs. correction	ψ-scan
Structural Analysis and Refinement	
solution by	direct phase determination
method of refinement	Full-Matrix LSQ. Hydrogen positions of riding model with fixed isotropic U
data-to-parameter ratio	9.41
R, R_w	0.085, 0.059
weighting scheme	$w = 1/\sigma^2(F)$
largest difference peak	0.35 $e\text{Å}^{-3}$
largest difference hole	0.30 $e\text{Å}^{-3}$
program used	Siemens SHELXTL PLUS (MicroVAX II)

TABLE II

Refined atomic coordinates (x10^4) and isotropic thermal parameters ($pm^2 \cdot 10^{-1}$) with e.s.d.'s in parentheses.

Atom	x	y	z	U(eq)
S(1)	963(1)	6809(1)	2232(1)	60(1)
N(1)	2761(4)	7358(2)	2861(4)	53(2)
C(2)	4043(5)	7205(3)	2350(6)	61(2)
O(2)	3969(4)	6666(2)	1444(4)	84(2)
C(3)	5339(5)	7826(2)	3133(5)	58(2)
C(4)	6867(6)	7941(3)	3099(6)	75(2)
C(5)	7868(6)	8584(3)	3960(7)	88(3)
C(6)	7352(7)	9092(3)	4828(6)	90(3)
C(7)	5835(6)	8977(3)	4882(5)	76(3)
C(8)	4830(5)	8334(2)	4023(5)	58(2)
C(9)	3186(5)	8057(2)	3867(5)	58(2)
O(9)	2303(4)	8337(2)	4418(4)	74(2)
N(10)	1386(3)	6210(2)	3953(4)	51(2)
C(11)	2192(5)	5500(2)	4202(5)	55(2)
O(11)	2647(4)	5248(2)	3181(4)	76(2)
C(12)	2326(5)	5190(2)	5901(5)	50(2)
C(13)	3052(5)	4542(2)	6776(6)	62(2)
C(14)	3039(5)	4395(2)	8390(6)	70(2)
C(15)	2321(5)	4892(3)	9086(6)	69(2)
C(16)	1592(5)	5546(2)	8193(5)	60(2)
C(17)	1598(4)	5689(2)	6583(5)	48(2)
C(18)	972(5)	6337(2)	5378(5)	54(2)
O(18)	271(3)	6892(2)	5492(3)	67(1)
N(19)	152(4)	2263(2)	1624(5)	64(2)
C(20)	1746(5)	2441(2)	1744(5)	51(2)
C(21)	2496(5)	3167(2)	2430(5)	61(2)
C(22)	4052(6)	3392(3)	2580(6)	72(2)
C(23)	4915(5)	2905(3)	2059(5)	71(2)
C(24)	4191(5)	2184(3)	1401(5)	67(2)
C(25)	2618(5)	1945(2)	1243(5)	57(2)
C(26)	-799(5)	1559(2)	1143(5)	52(2)
C(27)	-948(5)	1109(2)	-262(5)	57(2)
C(28)	-1947(5)	428(3)	-675(6)	71(2)
C(29)	-2808(5)	188(3)	274(7)	88(3)
C(30)	-2691(5)	645(3)	1621(7)	79(3)
C(31)	-1710(5)	1319(2)	2072(6)	64(2)

Equivalent isotropic U defined as one third of the trace of the orthogonalized Uij tensor

The structure of $(PHL)_2S \cdot HN(Ph)_2$ was determined by X-ray structure analysis. The crystal can be described as consisting of discrete molecules of $(PHL)_2S$ linked by hydrogen bonding to $(Ph)_2NH$. The presence of the hydrogen bond agrees with the IR spectrum of the compound. A drawing of the molecule is shown in Figure 1, where the numbering of the atoms is also indicated. The final positional param-

TABLE III

Selected interatomic distances (pm), angles (°) and torsion angles (°) with e.s.d.'s in parentheses.

S(1)-N(1)	168.8 (3)	N(1)-S(1)-N(10)	102.0(1)
S(1)-N(10)	168.8 (3)	S(1)-N(1)-C(2)	123.8(3)
N(1)-C(2)	143.4 (7)	S(1)-N(1)-C(9)	125.7(3)
N(1)-C(9)	142.7 (5)	C(2)-N(1)-C(9)	110.3(3)
C(2)-O(2)	120.1 (6)	N(1)-C(2)-O(2)	123.8(4)
C(9)-O(9)	120.9 (6)	N(1)-C(9)-O(9)	124.4(4)
N(10)-C(11)	143.4 (5)	S(1)-N(10)-C(11)	125.4(3)
N(10)-C(18)	143.3 (6)	S(1)-N(10)-C(18)	124.6(3)
C(11)-O(11)	120.5 (6)	C(11)-N(10)-C(18)	110.0(3)
C(18)-O(18)	121.1 (5)	N(10)-C(11)-O(11)	123.8(4)
N(19)-H(19)	84.6 (46)	N(10)-C(18)-O(18)	123.8(4)
N(19)-C(20)	140.0 (6)	H(19)-N(19)-C(20)	110.4(26)
N(19)-C(26)	139.8 (5)	H(19)-N(19)-C(26)	116.0(29)
O(18)-H(19)	221.5	C(20)-N(19)-C(26)	128.2(4)
		N(19)-H(19)-O(18)	168.8
N(1)-S(1)-N(10)-C(11)	-85.09		
N(1)-S(1)-N(10)-C(18)	95.53		
N(10)-S(1)-N(1)-C(9)	-88.21		
N(10)-S(1)-N(1)-C(2)	95.94		

eters of all non-hydrogen atoms are reproduced in Table II. Selected interatomic distances, bond angles and torsion angles are given in Table III. Table IV compares relevant structural parameters with those of similar compounds.

The N—S—N bond angle of 102.0°(1) is comparable with the C—S—C bond angle in R_2S for which angles close to 100° are generally observed[7]; however, the same angle is significantly shorter than tetrahedral angles in similar compounds, cf. Table IV.

The N—S—N fragment has a geometry characteristic for bis(dialkylamine) sulfides. In compounds of the general type $(R_2N)_2S$, only the cisoidal conformation of the nitrogen and sulfur lone pairs has been observed in the solid state.[8] Apparently, the repulsive interaction between nitrogen and sulfur lone pairs is the determining factor in the discussed structure. In $(PHL)_2S$ the two phthalimide groups are twisted in opposite directions; the torsion angles NSNC are $-86.65°$ and 95.74°, respectively, so that the $d\pi$-$p\pi$ overlap is not maximized. As a result,

TABLE IV
Structural parameters of related compounds

	S - N	Σ < N	N - S - N	Reference
$[(C_6H_{12})_2N]_2S$	1.657(4)	358-359	110.7(2)	10
$[(CH_3)_2N]_2S$	1.688(6)	351	114.5(16)	11
$[OC_4H_8N]_2S$	1.678(4)	349.5	113.2(2)	δ
$[C_8H_4NO_2]_2S \cdot C_{12}H_{10}NH$	1.688(3)	360	102.0(1)	this work

the delocalization of the nitrogen lone pair on the sulfur orbitals is limited. The S—N bond length of 168.8 pm is only slightly shorter than the S—N single-bond length of 173.5 pm.[9] A similar structure for (PHL) was deduced from CNDO/2 calculations.[4]

The sum of the bond angles around the nitrogen atoms is 360°, and the hybridization of the nitrogen atoms appear to have sp^2 character. There are no unusual bond lengths or bond angles in the diphenylamine. The two phenyl groups are slightly twisted in opposite directions. The diphenylamine molecule is hydrogen bonded to $(PHL)_2S$. The distance N—H(19) is 221.5 pm and the angle N—H(19)—O(18) is 168.8°. This contact seems to be responsible for the twist of both phenyl and phthalimide groups. The hydrogen bond length is slightly larger than that found in other N—H—O compounds.[12,13] It is interesting to note that only one oxygen atom of the phthalimide moiety, the O(18), is involved in hydrogen bonding. This structural behavior appears to be characteristic for imides[14] and other compounds containing the —C(O)—R—(O)C-framework.[12]

Considering the results of the X-ray analysis, the compound $(PHL)_2S \cdot HN(Ph)_2$ can be defined as a charge transfer complex, assisted by a hydrogen bond and can be classified as $n + k\sigma a$ in the Mulliken notation.[15] These complexes are loose compounds in which the nature of the donor-acceptor interaction has an electrostatic rather than a charge transfer character. In general, this kind of interaction is assisted by cooperative effects, involving non-neighboring molecules. The enhancement of permitivity shown by the adduct $(PHL)_2S \cdot HN(Ph)_2$ of going from the solution to the solid state, indicates that the effect of N—H—O hydrogen bonding in the solid is assisted by other reticular cooperative effects.

EXPERIMENTAL

0.28 g (0.88 mmol) of thiobisphthalimide and 0.27 g (1.6 mmol) of diphenylamide were stirred at 40°C for 5 min in 25 ml of CH_2Cl_2. The solution was slowly evaporated at room temperature to give 0.38 g (90% yield) of yellow crystals which were dried under a stream of N_2. m.p. 216–217°C (dec). Anal. Calc. for $C_{28}H_{19}N_3O_4S$: C, 68.15; H, 3.85; N, 8.51. Found: C, 67.78; H, 3.81; N, 8.33. IR (KBr, Pellet): 3360(s) [(NH)], 3050(w), 1790(m), 1750(m), 1710(w), 1600(s), 1582(vs), 1525(s), 1490(vs), 1460(s), 1418(w), 1345(m), 1315(m), 1300(s), 1280(s), 1230(vs), 1215(s), 1155(m), 1128(m), 1030(s), 1020(s), 1000(w), 988(w), 900(w), 860(s), 830(w), 785(w), 780(w), 740(vs), 708(vs), 700(vs,sh), 695(s), 680(vs), 565(m), 520(m), 495(w), 460(w). ^1H NMR (CD_2Cl_2, δ ppm from TMS): 7.8 (8H, mult.); 7.1 (10H, mult.).

Diffraction intensities were collected on a Nicolet R3m/V diffractometer using graphite monochromated MoKα radiation. Cell parameters were obtained from 22 strong reflections in the range $12° \leq 2\theta \leq 25°$. Wyckoff-scan was used for data collection. The crystal data and important details are summarized in Table I.

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SUPPLEMENTARY MATERIAL AVAILABLE

Further details of the crystal structure investigation are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-7514 Eggenstein-Leopoldshafen 2, on quoting the despository number CSD-55381, the names of the authors, and the journal citation.

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