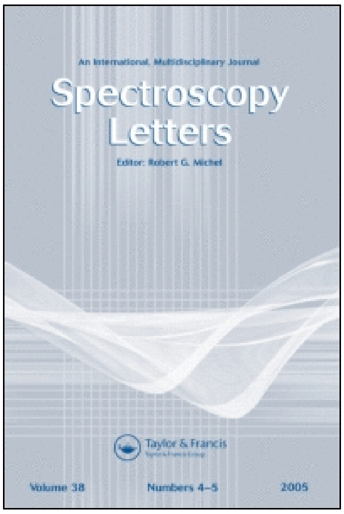

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# Synthesis, Redetermination and Molecular Conformation Analysis of the Structure of 2,2'-Diaminodiphenyl Disulfide

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# *SYNTHESIS, REDETERMINATION AND MOLECULAR CONFORMATION ANALYSIS OF THE STRUCTURE OF 2,2'-DIAMINODIPHENYL DISULFIDE*

**Keywords :** Structure, crystal, conformation, disulfide, diaminodiphenyl, MNDO,AM1, PM3.

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## ABSTRACT

A new synthesis and the crystal structure of $C_{12}H_{12}N_2S_2$ have been described and redetermined. In order to optimize the geometry of the molecule, the semi empirical methods MNDO, AM1 and PM3 were used. The conformation of the energy profile showed that the minimum energy conformation has the torsion angle $\theta$ [ C1-S1-S1'-C1' ] near 90°. The energy barrier at 0° attributed to the lone pair repulsion of sulphur atoms and interactions between NH... S and H(C6) ... S non-bonded atoms.

## INTRODUCTION

Disulfide compounds have been the subject of both extensive theoretical and experimental studies, because it plays an important role in chemical and biological systems.

The crystal structure of the title compound was determined by Lee and Bryant [1] using photographic recording techniques. The unambigous determination of the H-atom positions, the packing of the molecules, molecular orbital calculations and conformational analysis of the molecule have been established in the present work. On the other hand, a new synthesis method was used to obtain crystals which crystallizes easily. Oxidation of thiols to disulphides is important from both synthetic and biochemical points of view and accordingly numerous studies have appeared. Various methods are available for oxidizing thiols to disulfides [2,3,4,5,6,7]

TABLE 1.
Crystal and relevant x-ray data

| | |
|---|---|
| Formula | $C_{12}H_{12}N_2S_2$ |
| Crystal system | orthorhombic |
| Space group | Pbca |
| Mol. Wt. | 271.34 |
| Crystal size | 0.60x0.40x0.20 |
| a(Å) | 8.225(1) |
| b(Å) | 13.160(1) |
| c(Å) | 22.754(1) |
| V(Å$^3$) | 2462.9(3) |
| Dc(g cm$^{-3}$) | 1.463 |
| Z | 8 |
| Nuniq | 2500 |
| Nobs | 1466 |
| R | 0.053 |
| Rw | 0.054 |
| Rtot | 0.035 |
| $\lambda MoK_\alpha$ (Å) | 0.7103 |

## EXPERIMENTAL

2,2'-Diaminodiphenyl disulfide was prepared with 2-aminothiophenol and iodic acid. Ethanolic solution of iodic acid ($HIO_3$) (2.14 mmol) was added to 2-aminothiophenol (12.8 mmol) in 20 ml of ethanol. The resulting yellow solution yielded a yellow crystals. The product was filtered and recrystallized from ethanol. The yielded was 1.51069 g (95 %). m.p. 91-92 °C. The IR and NMR spectra were consistent with the proposed structure.

Intensity measurement for crystal structure analysis were carried out at room temperature on an Enraf-Nonius CAD4 diffractometer operating in the w/2θ scanning mode using suitable crystals for data collection. Unit cell constants were obtained by least-squares analysis of 25 well-centered reflections in the ranges $9.98<\theta < 18.17°$. The measurements were carried out up to $2\theta max= 50°$. During data collection three standart reflections periodically observed ( frequency: 120 min. ) and showed no significant intensity variations (-0.61%). The ranges h,k,*l* are $-10< h <0$, $0 < k < 16$ and $0 < l < 28$. 2500 unique reflections were measured of which 1466 had $I>\sigma(I)$ . Corrections for Lorentz and polarization factors were applied to the intensity values. These observed reflections were used for structure determination and refinement . The structure was determined by direct

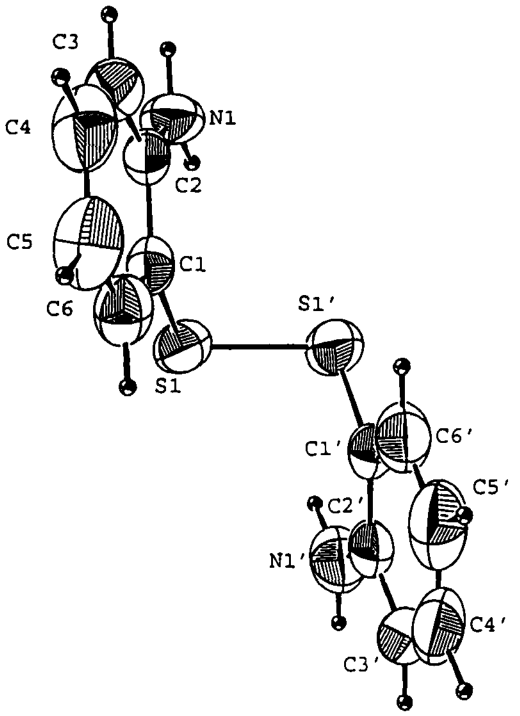

FIG. 1. An ORTEP drawing of the title compound with the atomic labelling. The displacement ellipsoids are drawn at the 50 % probability level.

methods (Simpel-MolEN ) and refined full-matrix least squares methods (LSFM-MolEN)[8]. The function minimised was ( w(|Fo|-|Fc|)2 with modified Killean-Lawrence method[8].

H atom positions were located from a difference synthesis and refined isotropically. Three H atom positions (H11, H12 and H4') were calculated positions at a distance of 0.95 Å from the corresponding atoms. A riding model was used in the refinement of the calculated H positions. The refinement process converged at R=0.053, Rw=0.054; s= 0.70; $\Delta/\sigma$max=0.0001 for 182 parameters.The final difference map showed no unusual features, with residual extrema ranging from -0.539 to 0.294 e Å$^{-3}$. Atomic scattering factors were taken from standart tables incorporeted in the Enraf-Nonius MolEN program package[8].

Table 1. shows the crystal and relevant x-ray data.

## TABLE 2.

**Fractional atomic coordinates and Beq values ($\AA^2$) for non-hydrogen atoms and H-atoms participating in hydrogen bonds with e.s.d.s in parentheses**

| | x | y | z | Beq |
|---|---|---|---|---|
| S1 | 0.4747(2) | 0.0606(1) | 0.70713(5) | 5.29(3) |
| S1' | 0.6802(1) | 0.01097(8) | 0.66422(6) | 4.64(2) |
| N1 | 0.3548(5) | -0.1523(3) | 0.7264(2) | 6.7(1) |
| N1' | 0.8468(5) | 0.2139(3) | 0.6765(2) | 5.39(9) |
| C1 | 0.3139(5) | 0.0010(3) | 0.6693(2) | 4.10(8) |
| C1' | 0.7083(5) | 0.1020(3) | 0.6082(2) | 3.84(9) |
| C2 | 0.2686(5) | -0.0979(3) | 0.6847(2) | 4.9(1) |
| C2' | 0.7928(5) | 0.1918(3) | 0.6203(2) | 3.93(9) |
| C3 | 0.1368(6) | -0.1396(4) | 0.6544(3) | 6.9(1) |
| C3' | 0.8202(6) | 0.2573(4) | 0.5743(2) | 5.9(1) |
| C4 | 0.0573(6) | -0.0850(5) | 0.6119(3) | 7.7(1) |
| C4' | 0.7652(7) | 0.2359(4) | 0.5186(2) | 7.0(1) |
| C5 | 0.1036(6) | 0.0114(5) | 0.5974(3) | 7.0(1) |
| C5' | 0.6831(7) | 0.1471(5) | 0.5070(2) | 6.6(1) |
| C6 | 0.2318(6) | 0.0536(4) | 0.6263(2) | 5.4(1) |
| C6' | 0.6530(5) | 0.0807(4) | 0.5519(2) | 5.1(1) |
| H3 | 0.111(5) | -0.201(3) | 0.666(2) | 7(1) |
| H3' | 0.877(5) | 0.313(3) | 0.582(2) | 5(1) |
| H4 | -0.027(7) | -0.116(4) | 0.596(2) | 10(2) |
| H4' | 0.784 | 0.283 | 0.488 | 8.5 |
| H5 | 0.054(6) | 0.043(3) | 0.566(2) | 8(1) |
| H5' | 0.640(6) | 0.128(4) | 0.470(2) | 9(1) |
| H6' | 0.590(5) | 0.018(3) | 0.545(2) | 7(1) |
| H6 | 0.271(5) | 0.124(3) | 0.616(2) | 6(1) |
| H11 | 0.300 | -0.204 | 0.748 | 9.3 |
| H11' | 0.868(6) | 0.163(3) | 0.695(2) | 8(1) |
| H12 | 0.300 | -0.204 | 0.748 | 9.3 |
| H12' | 0.910(6) | 0.258(4) | 0.677(2) | 8(1) |

$Beq=(8\pi^2/3)\Sigma\ i\Sigma jUij\ ai^*aj^*aiaj$

## RESULTS AND DISCUSSION

The structure of the molecule is shown in Fig. 1. (ORTEP-MolEN [8]).The fractional coordinates and mean temperature factors with estimated standard deviations for non hydrogen and hydrogen atoms participating in hydrogen bonds are listed in Table 2, and the bond lengths and bond angles are given in Table 3.

According to x-ray analysis results, the observed bond lengths are in agreement with the values reported in the literature [9,10,11]. The bond lengths and angles are nearly identical between the two halves of the molecule.

**TABLE 3.**

**Bond lengths (Å) and angles (°) with e.s.d.s in parentheses**

| | | | | | |
|---|---|---|---|---|---|
| S1 | S1' | 2.058(2) | | | |
| S1 | C1 | 1.762(4) | S1' | C1' | 1.764(4) |
| N1 | C2 | 1.385(6) | N1' | C2' | 1.385(6) |
| C1 | C2 | 1.398(6) | C1' | C2' | 1.398(6) |
| C2 | C3 | 1.397(7) | C2' | C3' | 1.374(6) |
| C3 | C4 | 1.371(8) | C3' | C4 | 1.374(7) |
| C4 | C5 | 1.365(9) | C4' | C5' | 1.375(8) |
| C6 | C1 | 1.376(6) | C6' | C1' | 1.388(6) |
| C6 | C5 | 1.361(7) | C6' | C5' | 1.368(7) |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| S1' | S1 | C1 | 104.1(1) | S1 | S1' | C1' | 103.5(1) |
| S1' | C1' | C6' | 119.1(3) | S1 | C1 | C6 | 119.5(3) |
| S1' | C1' | C2' | 119.9(3) | S1 | C1 | C2 | 119.5(3) |
| C6' | C1' | C2' | 121.0(4) | C6 | C1 | C2 | 121.0(4) |
| C1' | C6' | C5' | 120.1(4) | C1 | C6 | C5 | 121.2(5) |
| C2 | C3 | C4 | 120.8(5) | C2' | C3' | C4' | 121.3(5) |
| C1' | C2' | C3' | 117.6(4) | C1 | C2 | C3 | 116.7(4) |
| C1' | C2' | N1' | 121.2(4) | C1 | C2 | N1 | 121.1(4) |
| C3' | C2' | N1' | 121.3(4) | C3 | C2 | N1 | 122.1(4) |
| C6' | C5' | C4' | 119.2(5) | C6 | C5 | C4 | 118.6(5) |
| C3 | C4 | C5 | 121.6(5) | C3' | C4' | C5' | 120.9(5) |

The structure can be described as two planar amino - phenyl - moieties connected by an S - S single bond with a dihedral angle of 89,4 (2)°. This angle is similar for N,N'- bis ( 4 - chlorobenzylidene ) - 2,2' - diamino - diphenyl disulfide [-89,8 (2)°] [12], tetramethylthiuram disulfide [92.98 (1)°] and tetraethylthiuram disulfide [94,05 (3)°] [13].

In order to optimize the geometry of the molecule, the semi empirical methods MNDO[14], AM1[15] and PM3 [16] were used. The results were compared with the x-ray results in order to evaluate the realiability of these methods for disulfide compounds. All the geometric parameters were fully optimized at the SCF level using the program MOPAC 6.0[17] and starting from the crystallographic coordinates of the atoms. Selected torsion angles calculated by the above mentioned methods are given in Table 4 together with the experimental values. Calculated average bond lengths and angles together with average experimental values for the title compound are compared in Table 5. In all cases the calculated C-C bond lengths are slightly too long and N-C

### TABLE 4.

### Selected torsion angles experimental and calc ulated by MNDO, AM1, PM3

| | X-ray | MNDO | AM1 | PM3 |
|---|---|---|---|---|
| C3-C4-C5-C6 | -0.1 (9) | 0.85 | 0.27 | 1.38 |
| S1-C1-C2-N1 | -4.4 (6) | -177.63 | -174.94 | -176.77 |
| S1'-S1-C1-C2 | 84.7 (4) | -96.94 | -96.46 | -93.08 |
| C1-S1-S1'-C1' | 89.4 (2) | 91.47 | 86.55 | 86.10 |
| S1-S1'-C1'-C2' | 85.3 (3) | 87.53 | 91.15 | 94.38 |
| C3'-C4'-C5'-C6' | 1.6 (8) | -7.66 | 2.47 | -11.32 |
| S1'-C1'-C2'-N1' | -4.1 (5) | -7.66 | 2.47 | -11.32 |

### TABLE 5.

### Average calculated bond lengths and angles with average experimental values

| | X-ray | MNDO | AM1 | PM3 |
|---|---|---|---|---|
| S-S | 2.058 (2) | 1.949 | 2.133 | 2.023 |
| S-C | 1.760 (4) | 1.690 | 1.687 | 1.760 |
| N-C | 1.385 (5) | 1.414 | 1.378 | 1.417 |
| C-C | 1.381 (6) | 1.412 | 1.403 | 1.397 |
| C-C-N | 121.2 (4) | 121.6 | 120.9 | 121.5 |
| S-C-C | 119.9 (3) | 120.6 | 120.2 | 120.6 |
| S-S-C | 103.8 (1) | 108.6 | 107.4 | 110.8 |
| C-C-C | 120.1 (4) | 119.9 | 120.2 | 120.1 |

### TABLE 6.

### The calculated energy depending on θ [C1-S1-S1'-C1']

| | E (kcal/mol) | | |
|---|---|---|---|
| θ (°) | MNDO | AM1 | PM3 |
| 0 | 55.04 | 57.48 | 68.44 |
| 30 | 53.68 | 55.77 | 66.35 |
| 60 | 51.60 | 53.05 | 63.14 |
| 90 | 50.59 | 52.06 | 62.3 |
| 120 | 50.96 | 53.13 | 64.74 |
| 150 | 51.80 | 54.89 | 67.97 |
| 180 | 52.35 | 55.97 | 69.38 |

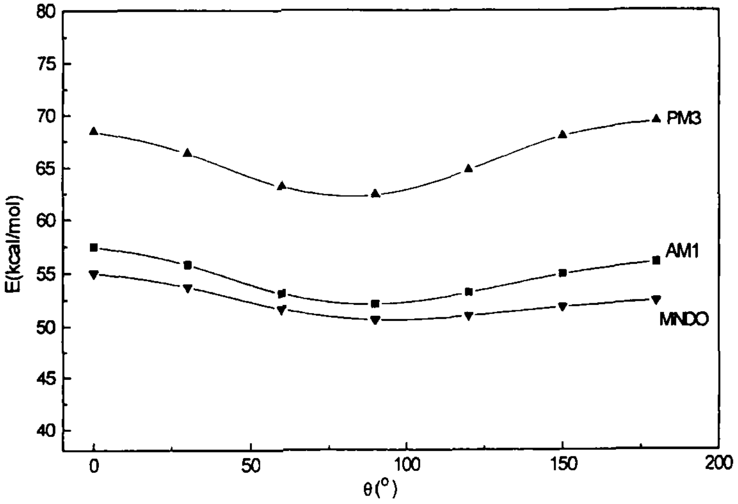

FIG. 2. The energy profiles for rotation about C1-S1-S1' -C1'.

## TABLE 7
## Hydrogen bond geometry

| D-H...A | D...A | D-H | H...A | <D-H...A | Symmetry |
|---|---|---|---|---|---|
| **Intramolecular** | | | | | |
| N1-H12...S1 | 3.004(4) | 0.95(4) | 2.739(2) | 94.51(7) | x,y,z |
| N1'-H11...S1' | 3.015(4) | 0.81(4) | 2.63(4) | 111(1) | x,y,z |
| **Intermolecular** | | | | | |
| C5-H5...C2' | 3.527(7) | 0.93(5) | 3.158(5) | 106(3) | 1+x,y,z |
| C5-H5...C1' | 3.472(7) | 0.93(5) | 3.101(5) | 106(3) | 1+x,y,z |
| C5'-H5'...C4 | 3.542(8) | 0.95(5) | 3.157(5) | 106(3) | x-1,y,z-1 |
| C4-H4...S1' | 3.554(5) | 0.89(5) | 3.320(5) | 98(3) | 1+x,y,z |

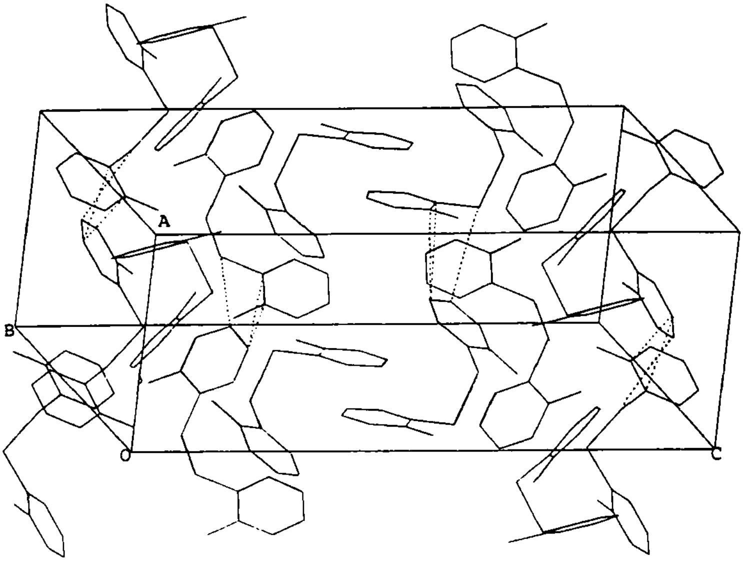

FIG. 3. Packing of the molecule in the crystal, viewed down the b axis.

bonds are in good agreement with only AM1 results and S-C bonds are well reproduced in PM3 results.

To determine the conformational energy profile, total energy was calculated as a function of the θ torsion angle about the S-S' bond. The calculated energy values depending on the θ are given in Table 6 and the energy profiles for rotation about C1-S1-S1'-C1' are shown in Figure 2. Minimum energy conformation from MNDO, AM1 and PM3 molecular orbital calculations has the torsion angle θ [ C1-S1-S1'-C1' ] near 90° which is in good agreement with the structural results. The energy barrier at 0° is due to the lone pair repulsion of sulphur atoms and interactions between NH... S and H(C6) ... S non-bonded atoms.

Though the length of S-S single bond distance 2.08 Å [18], it is appreciable smaller in the dibenzyl and diphenyl disulfide compounds (2,01 and 2,02 Å respectively) [19]. In these compounds the C-S-S-C angles are 92,1 and 96,2° respectively. According to Lee, a dihedral angle of 0° gives maximum repulsion between the non-bonding orbitals on the sulphur atoms. At 90° the overlap of d orbitals on the S atoms is a maximum. However in diamino diphenyl disulfide compound although dihedral angle is close to 90°, the length of S-S bond is 2,058 (2) Å and as is shown it is longer than above mentioned values. This can be a result of pπ-dπ interaction between the amino group and sulphur atom. There is also an inverse relationship exists between the S-S and C-S bond lengths. The mean S-$C_{sp^3}$ bond length is 1,81 Å [9]. In the title compound S1-C1 = 1,762 (4) and S1'-C1' = 1,759 (4) Å. This inverse relationship also can be shown in other disulfide compounds, e.g. S-S and C-S bond lengths are 1,997 Å, 1,805 Å in tetramethylthiuram disulfide [13] and 2,032 (2), 1,770 (4) Å in N,N' - bis ( 4-chlorobenzylidene )- 2,2'- diamino- diphenyl- disulfide.

The crystal structure is stabilized by H-bonding interactions. The intra molecular and inter molecular H-bonds are given in Table 7 and the packing diagram is shown in Figure 3. As is shown from Table 7 an intra molecular H-bond exists between the amin group and sulphur atom. NH...S is the most frequently occuring type of hydrogen bond involving a sulphur atom. The dithiosuccinimide and 2,2,3,3- tetramethyldithiosuccinimide molecules are similarly linked by pairs of NH...S hydrogen bonds [20].

Mean plane A (formed by atoms C1-C6) makes a dihedral angle of 32.3(3) with mean plane A'(formed by atoms C1'-C6'). S1 and N1 atoms deviate by -0.058(1) and 0.048(4) Å,respectively from plane A. The identical deviations of S1' atom from plane A' is 0.106(1) Å while there is no deviation of N1' from the same plane.

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