ŁANGOWSKA, K. & WIEWIÓROWSKI, M. (1977). *Bull. Acad. Pol. Sci. Ser. Sci. Chim.* **25**, 757–763.
LEHMANN, M. S. & LARSEN, F. K. (1974). *Acta Cryst.* A**30**, 580–584.
MAŁUSZYŃSKA, H., HOSER, A. & KAŁUSKI, Z. (1979). *Acta Cryst.* B**35**, 970–973.
MAŁUSZYŃSKA, H., KAŁUSKI, Z. & WIEWIÓROWSKI, M. (1987). In preparation.
MAŁUSZYŃSKA, H. & OKAYA, Y. (1977*a*). *Acta Cryst.* B**33**, 3049–3054.
MAŁUSZYŃSKA, H. & OKAYA, Y. (1977*b*). *Acta Cryst.* B**33**, 3889–3891.
SHELDRICK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.
SKOLIK, J., ŁANGOWSKA, K. & WIEWIÓROWSKI, M. (1971). *Bull. Acad. Pol. Sci. Ser. Sci. Chim.* **20**, 383–390.
SKOLIK, J., ŁANGOWSKA, K. & WIEWIÓROWSKI, M. (1974). *Bull. Acad. Pol. Sci. Ser. Sci. Chim.* **23**, 215–222.
SKRZYPCZAK-JANKUN, E., HOSER, A., KAŁUSKI, Z. & PERKOWSKA, A. (1980). *Acta Cryst.* B**36**, 1517–1520.
SKRZYPCZAK-JANKUN, E. & KAŁUSKI, Z. (1978). *Acta Cryst.* B**34**, 2651–2653.
SRIVASTAVA, S. N. & PRZYBYLSKA, M. (1969). *Acta Cryst.* B**25**, 1651–1659.

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4,4′-Biphenyldithiol

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Abstract. $C_{12}H_{10}S_2$, $M_r = 218{\cdot}3$, monoclinic, $P2_1/c$, $a = 11{\cdot}858$ (3), $b = 7{\cdot}462$ (1), $c = 6{\cdot}049$ (1) Å, $\beta = 96{\cdot}45$ (2)°, $V = 531{\cdot}9$ (2) Å^3, $Z = 2$, $D_x = 1{\cdot}36$ (1) g cm^{-3}, λ(Cu $K\alpha$) = 1·54178 Å, μ(Cu $K\alpha$) = 39·95 cm^{-1}, $F(000) = 228$, $T = 292$ K, $R = 0{\cdot}055$ for 548 unique reflections. The molecule is positioned on a centre of symmetry in the crystal and consequently the two phenyl rings are restricted by symmetry to be coplanar. There are slight deformations of the phenyl rings similar to those observed in biphenyl.

Introduction. Despite the considerable interest in aryl–sulfuric and alkyl–aryl–sulfuric compounds and their importance in the chemistry of polymers there are very few data describing their molecular and crystal structures. The present paper on the structure of 4,4′-biphenyldithiol [hereinafter referred to as (I)], a sulfuric derivative of biphenyl, is a continuation of our X-ray diffraction studies on this group of compounds (Andreetti, Garbarczyk & Królikowska, 1981; Garbarczyk, 1984). Our main interest connected with (I) concerned the planarity of the molecule and the way the S substituents influence the phenyl fragments, compared with the molecule of biphenyl.

Experimental. Crystals of (I) were obtained by slow evaporation of a cyclohexane solution oversaturated at 353 K. The crystal selected for data collection was a colourless prism of dimensions 0·12 × 0·07 × 0·05 mm. The crystallization proved to be very difficult and a number of crystallization techniques and different solvents were tried. The crystal used was the only specimen obtained which was suitable for X-ray investigation. It was mounted on a Syntex $P2_1$ diffractometer; graphite-monochromated Cu $K\alpha$ radiation was used. The unit-cell parameters were determined by a least-squares fit to 15 automatically centred reflections ($21{\cdot}0 \leq 2\theta \leq 71{\cdot}5°$). The θ–2θ scan technique with a variable scan speed (2·1 to 29·3° min^{-1}) was applied. Two control reflections were monitored after each 50 intensity measurements and showed no systematic variation in intensity. Up to $2\theta = 115{\cdot}0°$ 850 reflections were measured, with index ranges h −12/12, k 0/8, l 0/6. The background and integrated intensity for each reflection were calculated according to the profile-analysis method of Lehmann & Larsen (1974). Of 729 unique reflections ($R_{\rm int} = 0{\cdot}035$) 548 reflections had $I \geq 1{\cdot}96\,\sigma_I$ and were used in the structure refinement. Only Lp corrections were applied. The structure was solved using *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). After the non-hydrogen atoms were refined ansiotropically, all the H atoms, except for H at S(1), were located from a ΔF map. They were included in the refinement with isotropic temperature factors. An electron density peak was observed in the ΔF map at 1·32 Å from S(1) and could be considered to correspond to the hydrogen of the SH group. However, all attempts to refine this hydrogen were unsuccessful and finally it was excluded from the atom list. The function minimized was $\sum w(|F_o| - |F_c|)^2$, where $w = 1/[\sigma^2(F_o) + 0{\cdot}000170F_o^2]$. The final discrepancy indices were $R = 0{\cdot}0552$, $wR = 0{\cdot}0614$ and $S = 1{\cdot}4$. For all the parameters the final Δ/σ was smaller than 0·06, the max. and min. peaks on the final ΔF map were 0·22 and −0·23 e Å^{-3}.

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The final atomic parameters are listed in Table 1.[*] Most of the calculations were performed with program *SHELX*76 (Sheldrick, 1976) on a RIAD-32 computer, scattering factors were from *International Tables for X-ray Crystallography* (1974).

Table 1. *Final fractional coordinates and equivalent isotropic thermal parameters of non-hydrogen atoms*

$U_{eq} = (U_{11}U_{22}U_{33})^{1/3}$.

	x	y	z	U_{eq}(Å^2)
S(1)	0·5925 (1)	0·0324 (2)	0·2964 (3)	0·085
C(1)	0·9440 (3)	0·0022 (5)	0·0423 (7)	0·047
C(2)	0·9280 (4)	0·0824 (6)	0·2443 (7)	0·053
C(3)	0·8225 (4)	0·0910 (6)	0·3221 (8)	0·058
C(4)	0·7271 (4)	0·0200 (6)	0·1989 (8)	0·058
C(5)	0·7410 (4)	−0·0634 (7)	−0·0034 (9)	0·064
C(6)	0·8468 (4)	−0·0726 (6)	−0·0765 (8)	0·058

Discussion. The site of the molecule of (I) in the crystal, a special position of a centre of inversion, restrains the two phenyl rings of the molecule to be coplanar. The same result was reported for the very similar structure of biphenyl, the molecule of which was also located on a centre of inversion in the crystal lattice (Trotter, 1961; Hargreaves & Rizvi, 1962; Charbonneau & Delugeard, 1976, 1977). At the same time much evidence has been provided that the molecule of biphenyl is non-planar in the gas phase, in solution or in the melt (Karle & Brockway, 1944; Bastiansen & Trætteberg, 1962; Schmid & Brosa, 1972; Barrett & Steele, 1972). We could not find any reports of similar investigations for (I). Most recently Brock & Minton (1986) have compared over 90 crystal structures of biphenyl derivatives without *ortho* substituents and found that most biphenyl conformations have the phenyl rings at an angle of about 36°. The phenyl rings of (I) are, within experimental error, almost perfectly planar themselves: the largest distance to the best least-squares plane fitted to the independent carbon atoms is 0·011 (5) Å for C(6). χ^2 for this plane equals 15·6. Atom S(1) is 0·016 (2) Å out of this plane.

Fig. 1 shows a view of the molecule of (I); bond distances, valency angles and torsion angles are given in this drawing. The endocyclic valency angles at C(1) and C(4) are smaller than 120°, while C(1)—C(2)—C(3) and C(1)—C(6)—C(5) are wider; the other two endocyclic valency angles, C(2)—C(3)—C(4) and C(4)—C(5)—C(6), have values close to 120° (see Fig. 1). Similar deformations of the phenyl ring, but somewhat smaller in magnitude, were reported for biphenyl (Charbonneau & Delugeard 1977). These authors pointed out the large libration of the biphenyl molecule about its long axis at 293 K. This libration can considerably affect the values of the bond lengths and valency angles of the phenyl ring.

The distance between H(2) and H(6′) is 2·02 (6) Å which is commensurate with the close contact of unbonded H atoms (Ramachandran & Sasisekharan, 1968). The H(2)···H(6′) distance calculated for the model of the molecule with regular phenyl rings is 1·80 Å (Charbonneau & Delugeard, 1977).

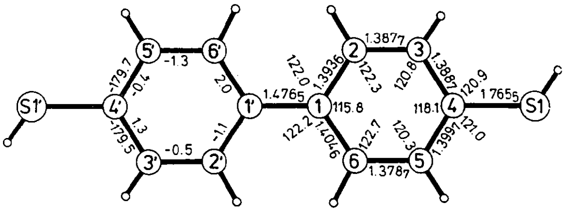

Fig. 1. A perspective view of the molecule of (I) with bond distances (Å) and valency and torsion angles (°) for non-hydrogen atoms. The e.s.d.'s for the valency angles range from 0·3 to 0·4°, for the torsion angles from 0·4 to 0·5°.

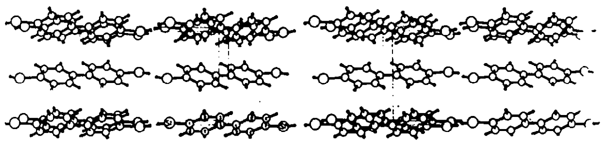

Fig. 2. A stereoscopic view of the unit-cell contents (Motherwell & Clegg, 1978).

A stereodiagram of the unit-cell contents is shown in Fig. 2. Only van der Waals contacts are observed between the molecules.

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References

Andreetti, G. D., Garbarczyk, J. & Królikowska, M. (1981). *Cryst. Struct. Commun.* **10**, 789–792.

Barrett, R. M. & Steele, D. (1972). *J. Mol. Struct.* **11**, 105–108.

Bastiansen, O. & Trætteberg, M. (1962). *Tetrahedron*, **17**, 147–154.

Brock, C. P. & Minton, R. P. (1986). Pre-Meeting Symposium on Organic Crystal Chemistry, Poznań-Rydzyna, 1–4 August 1986. Collected Abstracts, 39.

Charbonneau, G.-P. & Delugeard, Y. (1976). *Acta Cryst.* B**32**, 1420–1423.

Charbonneau, G.-P. & Delugeard, Y. (1977). *Acta Cryst.* B**33**, 1586–1588.

Garbarczyk, J. (1984). *Makromol. Chem.* **185**, 2033–2041.

Hargreaves, A. & Rizvi, S. H. (1962). *Acta Cryst.* **15**, 365–372.

International Tables for X-ray Crystallography. (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

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[*] Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44218 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Karle, I. L. & Brockway, L. O. (1944). *J. Am. Chem. Soc.* **66**, 1974.

Lehmann, M. S. & Larsen, F. K. (1974). *Acta Cryst.* A**30**, 580–584.

Main, P., Fiske, S. J., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson, M. M. (1980). *MULTAN*80. *A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.

Motherwell, W. D. S. & Clegg, W. (1978). *PLUTO*. Program for plotting molecular and crystal structures. Univ. of Cambridge, England.

Ramachandran, G. N. & Sasisekharan, V. (1968). *Adv. Protein Chem.* **23**, 283.

Schmid, E. D. & Brosa, B. (1972). *J. Chem. Phys.* **56**, 6267–6268.

Sheldrick, G. M. (1976). *SHELX*76. Program for crystal structure determination. Univ. of Cambridge, England.

Trotter, J. (1961). *Acta Cryst.* **14**, 1135–1140.

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Structure of 1,2-Dipiperidinoethane Mono-*N*-oxide Trihydrate

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Abstract. *N*-(2-Piperidinoethyl)piperidine *N*-oxide trihydrate, $C_{12}H_{24}N_2O.3H_2O$, $M_r = 267{\cdot}1$, monoclinic, $P2_1/n$, $a = 13{\cdot}696\,(2)$, $b = 7{\cdot}5819\,(5)$, $c = 14{\cdot}721\,(2)$ Å, $\beta = 99{\cdot}10\,(1)°$, $V = 1509{\cdot}5\,(3)$ Å^3, $Z = 4$, $D_x = 1{\cdot}17$ Mg m^{-3}, $\lambda(\mathrm{Cu}\,K\alpha) = 1{\cdot}54178$ Å, $\mu = 0{\cdot}71$ mm^{-1}, $F(000) = 592$, $T = 292$ K, $R = 0{\cdot}044$ for 1570 observed reflexions. The overall conformation of the molecule is similar to that of the *transoidal* form characteristic of the bis-*N*-oxide derivative: the piperidine rings are in a chair form, the $-CH_2-$ substituents at the N atoms are equatorial, the C—N—C—C torsion angles around the exocyclic N—C bonds are characteristic of *gauche* and *trans* conformations at both N atoms, the *N* substituents at the C—C bridge are *trans*. The water molecules play distinctly different roles in the structure. One forms only two H bonds (as a donor) with water molecules, one participates in two O(*W*)—H···O(*W*) interactions and in a relatively weak O(*W*)—H···N(2) hydrogen bond and the third one accepts two H bonds from water molecules and forms two relatively strong H bonds with *N*-oxide O atoms. Being involved in two H bonds, the *N*-oxide O atom is a much more active H-bond acceptor than the amino N atom which accepts only one, relatively weak, H bond.

Introduction. This paper continues the studies on the derivatives of 1,1′-ethylenebispiperidine (PEtP) in the aspects of their conformation and H bonding in the crystalline state. The $PEtP(NO)_2$ molecule [1,1′-ethylenebis(piperidine 1-oxide)] and its diprotonated cation [in $PEtP(NO)_2.2HClO_4$] were found to be crystallographically centrosymmetric in their crystal structures (Jaskólski, Kosturkiewicz, Mickiewicz-Wichłacz & Wiewiórowski, 1979; Jaskólski, 1982). It was concluded from those structures that in the $PEtP(NO)_2$ skeleton the piperidine rings maintain their chair conformations, the O atoms are axial and the diaminoethylene bridge has a *gauche*$^+$-*trans*-*gauche*$^-$ conformation (O—N—C—C—N—O). This conformation was termed '*transoidal*' as it has the *N*-oxide O atoms on the ends of the N—C—C—N bridge *trans* oriented. However, the monoprotonated $PEtP(NO)_2H^+$ cation [in $PEtP(NO)_2.HClO_4$; Jaskólski, Gdaniec & Kosturkiewicz, 1982; Jaskólski, Olovsson, Tellgren & Mickiewicz-Wichłacz, 1982] turned out to be *cisoidal* with the two N—O groups bridged by a very short intramolecular O···H···O hydrogen bond [2·426 (3) Å] and with appreciable deformation in the N—C—C—N bridge owing to internal strain. A similar situation was found in the monoprotonated mono-*N*-oxide analog [$PEtP(NO).HClO_4.H_2O$; Jaskólski & Kosturkiewicz, 1984] where the $PEtP(NO)H^+$ cation is *cisoidal* with a very short intramolecular O···H···N hydrogen bond [2·551 (4) Å]. It was, therefore, of interest to investigate if the mono-*N*-oxide free-base PEtP(NO) molecule will also adopt a conformation similar to that of $PEtP(NO)_2$. This paper reports the X-ray crystal structure of $PEtP(NO).3H_2O$.

Experimental. Hygroscopic crystals (elongated plates) from water. Crystal 0·25 × 0·3 × 0·4 mm covered with thin film of vaseline and mounted on a Syntex $P2_1$ diffractometer, Cu $K\alpha$ radiation. Cell parameters from least-squares treatment of setting angles of 15 reflexions ($8{\cdot}2 \leq 2\theta \leq 31{\cdot}3°$). θ:2θ profiles measured for 2214 unique $+h+k\pm l$ reflexions with $2\theta \leq 115°$ [$\sin\theta/\lambda$ (max.) $= 0{\cdot}547$ Å^{-1}; $0 \leq h \leq 14$, $0 \leq k \leq 8$, $-16 \leq l \leq 15$], profile analysis according to Lehmann & Larsen (1974). No significant intensity variation (<2·7%) for two standard reflexions measured every 1·5 h. No

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