Related literature. We have been concerned with the chemistry of molecules containing the S_2PR_2 moiety and have reported the chemistry and structures of molecules where this group is bound to a metal ion (Pinkerton, Schwarzenbach & Spiliadis, 1987) and on the dimers formed when the anion is oxidized (Gallacher, 1989; Gallacher & Pinkerton, 1989). As we have indicated previously (Pinkerton & Terrill, 1988), there are few reported structures of the parent dithio acids or of the uncomplexed salts, which makes discussion of small variations in the geometry of metal compounds difficult.

The current structure contains two molecules in the asymmetric unit; however, they are essentially identical. The phosphorus atoms are tetrahedral with identical P—S bond distances as expected for a delocalized anion. The P—S bond lengths [1·989 (1)– 1·995 (2) Å] are significantly longer than the analogous values for the few known structures: 1·96(1)Å (identical by symmetry) in $KS_2P(OMe)_2$ (Coppens, McGillavry, Hovenkamp & Douwes, 1962); 1·965 (6), 1·974 (6) Å in $[Me_2NH_2][S_2P(OC_3H_7)_2]$ (Kalinin, Andrianov & Struchkov, 1979); 1·945 (2), 1·969 (2) Å in $KS_2P(CH_2Ph)_2$ (Hazel & Collin, 1972); 1·944 (3), 1·954 (3) Å in $[Ph_4As][S_2P(OMe)_2]$ (Pinkerton & Terrill, 1988). This is easily attributed to the inductive effect of the substituents at phosphorus, alkyl *versus* alkoxy or aromatic. The latter two structures indicate a possible small asymmetry in the PS_2 moiety, but much less than that expected for P—S and P=S bonds, *e.g.* P—SH =

2·077 (1) and P=S = 1·954 (1) Å in $Ph_2P(S)SH$ (Krebs & Henkel, 1981); P—S = 2·076 (2)–2·158 (2), P=S = 1·900 (2)–1·940 (3) Å for a series of thiophosphoryl disulfides (Gallacher, 1989). The S—P—S valence angle is larger than ideal [117·66 (6), 117·36 (7)°] owing to S···S steric interactions in agreement with a range of 116·6 (3)–120·1 (1)° for the anions cited above. The disulfides have a wider range of S—P—S angles [103·8 (1)–115·96 (4)°]; however, these are additional steric considerations here because of the variety of torsion angles about the disulfide bond.

The geometry of the tetraphenylarsonium cations is unremarkable.

References

Coppens, P., McGillavry, C. H., Hovenkamp, S. G. & Douwes, H. (1962). *Acta Cryst.* **15**, 765–769.
Fair, K. (1989). *MOLEN. An Interactive Intelligent System for Crystal Structure Analysis, User Manual.* Enraf–Nonius, Delft, The Netherlands.
Gallacher, A. C. (1989). MS Thesis, Univ. of Toledo, USA.
Gallacher, A. C. & Pinkerton, A. A. (1989). Am. Crystallogr. Assoc. Meet., Seattle, Abstract PA73, p. 96.
Hazel, J. P. & Collin, R. L. (1972). *Acta Cryst.* **A28**, 2279–2287.
Kalinin, A. E., Andrianov, V. G. & Struchkov, Yu. T. (1979). *Izv. Akad. Nauk SSSR Ser. Khim.* pp. 783–786.
Krebs, B. & Henkel, G. (1981). *Z. Anorg. Allg. Chem.* **475**, 143–155.
Pinkerton, A. A., Schwarzenbach, D. & Spiliadis, S. (1987). *Inorg. Chim. Acta*, **128**, 283–287, and references therein.
Pinkerton, A. A. & Terrill, N. J. (1988). *Acta Cryst.* **C44**, 567–568.

Stereochemical Studies of Oligomers. XXVII.*
Reinvestigation of the Structure of 4,4'-Diaminodiphenyl Sulfone

By Gabriele Bocelli and Andrea Cantoni

Centro di Studio per la Strutturistica Diffrattometrica del CNR, Viale delle Scienze, 43100 Parma, Italy

Abstract. $C_{12}H_{12}N_2O_2S$, $M_r = 248·30$, orthorhombic, $P2_12_12_1$, $a = 8·078$ (2), $b = 25·589$ (3), $c = 5·772$ (1) Å, $V = 1193·1$ Å^3, $Z = 4$, $D_x = 1·38$ g cm^{-3}, $\lambda(Cu\ K\alpha) = 1·5418$ Å, $\mu = 23·01$ cm^{-1}, $F(000) = 520$, room temperature, $R = 0·046$ for 1252 reflections with $I \geq 2\sigma(I)$. The structure of the title compound, which plays an important role in the synthesis of epoxide resins, was redetermined in order to provide more precise geometrical information than available in Dickinson, Stewart & Ammon [*J. Chem. Soc. Chem. Commun.* (1970), pp. 920–921] ($R = 0·12$, with average e.s.d.'s in bond lengths and angles of 0·01 Å and 0·8°, respectively).

Experimental. Specimen approximately 0·2 × 0·8 × 0·9 mm, Siemens AED single-crystal diffractometer equipped with an IBM PS2/30 personal computer, unit cell from a least-squares fit to 28 reflections

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* Part XXVI: Bocelli & Cantoni (1989).

Table 1. *Atomic fractional coordinates* $(\times 10^4)$ *and* U_{eq} *values* $(\text{Å}^2 \times 10^4)$

	x	y	z	U_{eq}*
S	9190 (1)	1245 (1)	6261 (2)	435 (3)
O1	9359 (4)	1196 (1)	3754 (5)	581 (10)
O2	10533 (3)	1063 (1)	7700 (6)	584 (9)
N1	2914 (5)	270 (1)	9361 (8)	540 (13)
N2	8052 (7)	3490 (1)	8271 (9)	643 (15)
C1	7374 (5)	921 (1)	7109 (7)	392 (11)
C2	7339 (5)	640 (2)	9206 (7)	461 (12)
C3	5864 (6)	414 (2)	9906 (8)	474 (12)
C4	4421 (5)	479 (1)	8646 (7)	399 (11)
C5	4490 (5)	758 (2)	6547 (8)	454 (13)
C6	5951 (5)	975 (1)	5800 (7)	452 (11)
C7	8865 (4)	1910 (1)	6868 (6)	376 (10)
C8	9416 (5)	2121 (2)	8944 (8)	482 (13)
C9	9175 (6)	2645 (2)	9413 (7)	533 (14)
C10	8330 (5)	2962 (1)	7840 (7)	458 (12)
C11	7788 (6)	2744 (2)	5758 (8)	518 (13)
C12	8053 (5)	2222 (2)	5264 (8)	482 (12)

* Hamilton (1959).

$(11\cdot3 \leq \theta \leq 28\cdot6^\circ)$. Intensities measured in the θ range 2–70° following a modified version (Belletti, Cantoni & Pasquinelli, 1988) of the Lehmann & Larsen (1974) profile-analysis method. One standard reflection monitored every 50 measurements showed no decrease in intensity, intensities corrected for Lorentz and polarization effects. Absorption was treated by the method of Walker & Stuart (1983) with a program written by Ugozzoli (1987). A total of 1368 reflections were measured (index range: h 0/9, k 0/31, l 0/7), 1253 having $I \geq 2\sigma(I)$ were considered observed and used in the refinement. Structure solved by direct methods with *SHELX76* (Sheldrick, 1976), full-matrix least-squares refinement, initially with isotropic thermal parameters and then with anisotropic ones. H atoms were obtained from a difference Fourier map and refined isotropically. One reflection was omitted because of very poor agreement with calculations, $\sum w\Delta F^2$ minimized. The highest peak in the final ΔF map was $0\cdot24$ e Å^{-3}, 202 parameters refined, final $R = 0\cdot046$, $wR = 0\cdot047$, $w = 0\cdot7106/(\sigma^2 F + 0\cdot000724 F^2)$. Atomic scattering factors were taken from *SHELX76*.

All calculations were performed on an IBM PS2/80 personal computer with the *CRYSRULER* package (Rizzoli, Sangermano, Calestani & Andreetti, 1987).

Table 1 lists atomic fractional coordinates and equivalent isotropic thermal parameters of heavy atoms; Table 2 summarizes bond distances, bond angles and selected torsion angles of the molecule, which is depicted in Fig. 1.*

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* Lists of structure factors, anisotropic thermal parameters of heavy atoms and H-atom coordinates with their isotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53027 (9 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Bond distances* (Å), *bond angles* (°) *and selected torsion angles* (°)

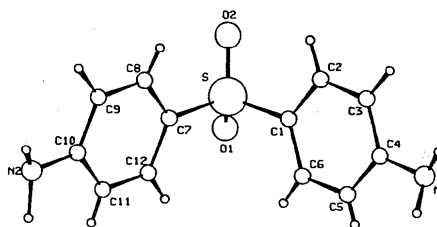|			
S—O1	1·459 (3)	C3—C4	1·384 (6)
S—O2	1·443 (3)	C4—C5	1·407 (6)
S—C1	1·755 (4)	C5—C6	1·374 (6)
S—C7	1·757 (4)	C7—C8	1·388 (6)
N1—C4	1·392 (6)	C7—C12	1·387 (6)
N2—C10	1·392 (4)	C8—C9	1·382 (7)
C1—C2	1·408 (6)	C9—C10	1·396 (6)
C1—C6	1·383 (6)	C10—C11	1·395 (6)
C2—C3	1·385 (7)	C11—C12	1·383 (7)
C1—S—C7	106·1 (1)	N1—C4—C5	119·0 (3)
O2—S—C7	108·1 (1)	C4—C5—C6	120·6 (4)
O2—S—C1	108·4 (1)	C1—C6—C5	120·2 (3)
O1—S—C7	107·2 (1)	S—C7—C12	119·7 (2)
O1—S—C1	108·3 (1)	S—C7—C8	120·1 (2)
O1—S—O2	118·2 (1)	C8—C7—C12	120·3 (3)
S—C1—C6	119·7 (2)	C7—C8—C9	120·1 (3)
S—C1—C2	119·9 (3)	C8—C9—C10	120·4 (4)
C2—C1—C6	120·3 (3)	N2—C10—C9	121·8 (3)
C1—C2—C3	118·8 (3)	C9—C10—C11	118·8 (3)
C2—C3—C4	121·4 (4)	N2—C10—C11	119·4 (3)
N1—C4—C3	122·3 (3)	C10—C11—C12	121·0 (4)
C3—C4—C5	118·7 (3)	C7—C12—C11	119·4 (3)
O1—S—C1—C6	−42·1 (4)	C1—S—C7—C8	95·0 (3)
O2—S—C1—C6	−171·6 (3)	C1—S—C7—C12	−84·9 (3)
C7—S—C1—C6	72·6 (3)	O1—S—C7—C8	−149·5 (3)
O1—S—C1—C2	142·6 (3)	O1—S—C7—C12	30·7 (4)
O2—S—C1—C2	13·2 (3)	O2—S—C7—C8	−21·1 (4)
C7—S—C1—C2	−102·6 (3)	O2—S—C7—C12	159·1 (3)

Fig. 1. Projection of the molecule with the numbering scheme.

Related literature. This structure is related to that of its hydrate derivative (Bel'skii, Chernikova, Rotaru & Kruchinin, 1983), to 4,4′-diaminodiphenylmethane (Bel'skii, Rotaru & Kruchinin, 1983) and to sulphathiazole II (Kruger & Gafner, 1971). An intermolecular hydrogen bond [H1N1···O2^i = 1·99 (6) Å, N1—H1N1···O2^i = 160 (5)°; (i) $x - 1$, y, z] was found.

References

BELLETTI, D., CANTONI, A. & PASQUINELLI, G. (1988). *Gestione on Line di Diffrattometro a Cristallo Singolo Siemens AED con Sistema IBM PS2/30.* Internal Report 1/88. Centro di Studio per la Strutturistica Diffrattometrica del CNR, Parma, Italy.

BEL'SKII, V. K., CHERNIKOVA, N. YU., ROTARU, V. K. & KRUCHININ, M. M. (1983). *Kristallografiya,* **28,** 690–694.

BEL'SKII, V. K., ROTARU, V. K. & KRUCHININ, M. M. (1983). *Kristallografiya,* **28,** 695–698.

BOCELLI, G. & CANTONI, A. (1989). *Acta Cryst.* C45, 1660–1661.

DICKINSON, C., STEWART, J. M. & AMMON, H. L. (1970). *J. Chem. Soc. Chem. Commun.* pp. 920–921.

HAMILTON, W. C. (1959). *Acta Cryst.* **12,** 609–610.

KRUGER, G. J. & GAFNER, G. (1971). *Acta Cryst.* B27, 326–333.

LEHMANN, M. S. & LARSEN, F. K. (1974). *Acta Cryst.* A30, 580–589.

RIZZOLI, C., SANGERMANO, V., CALESTANI, G. & ANDREETTI, G. D. (1987). *J. Appl. Cryst.* 20, 436–439.

SHELDRICK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.

UGOZZOLI, F. (1987). *Comput. Chem.* 11(2), 109–120.

WALKER, N. & STUART, D. (1983). *Acta Cryst.* A39, 158–166.

Stereochemical Studies of Oligomers. XXVIII.*
4,4′-Bis(p-aminophenoxy)diphenyl Sulfone

BY GABRIELE BOCELLI

Centro di Studio per la Strutturistica Diffrattometrica del CNR, Viale delle Scienze, 43100 Parma, Italy

AND CORRADO RIZZOLI

Istituto di Strutturistica Chimica, Università di Parma, Viale delle Scienze, 43100 Parma, Italy

Abstract. $C_{27}H_{20}N_2O_4$, $M_r = 436.47$, monoclinic, $P2_1/c$, $a = 21.442$ (3), $b = 9.954$ (2), $c = 9.934$ (2) Å, $\beta = 94.69$ (4)°, $V = 2113.2$ Å^3, $Z = 4$, $D_x = 1.37$ g cm^{-3}, λ(Cu $K\alpha$) = 1.5418 Å, $\mu = 7.17$ cm^{-1}, $F(000) = 912$, room temperature, final $R = 0.057$ for 3308 reflections with $I \geq 2\sigma(I)$. The molecule adopts a butterfly conformation with the C—S—C angle [107.6 (2)°] comparable with that [106.1 (1)°] observed in 4,4′-diaminodiphenyl sulfone [Bocelli & Cantoni (1990). *Acta Cryst.* C46, 2257–2259]. The dihedral angles between the individual planar rings A—B, A—C, A—D, B—C, B—D and C—D are 98.3 (1), 28.0 (1), 50.9 (1), 70.7 (1), 42.5 (1) and 77.3 (1)°, respectively. Intermolecular contacts < 2.5 Å are: N1⋯H27^i = 2.48 (4), O4⋯H20^{ii} = 2.49 (3) and C23⋯H1N2^{iii} = 2.40 (3) Å [(i) $-x$, $-y$, $-z$; (ii) x, $-y-\frac{1}{2}$, $z+\frac{1}{2}$; (iii) x, $-y+\frac{1}{2}$, $z+\frac{1}{2}$].

Experimental. Colorless prismatic crystal approximately $0.32 \times 0.57 \times 0.67$ mm, diffraction data collected on a Siemens AED single-crystal diffractometer equipped with an IBM PS2/30 personal computer, unit-cell parameters obtained from a least-squares fit to the angular values of 29 reflections ($11.3 \leq \theta \leq 44.3°$) accurately centred on the diffractometer, reflections measured using a modified version (Belletti, Cantoni & Pasquinelli, 1988) of the Lehmann & Larsen (1974) method. One standard reflection monitored every 50 measurements showed no decrease in intensity. Intensities corrected for Lorentz and polarization effects but not for absorption. A total of 4486 reflections collected (index range): h $-26/26$, k $0/12$, l $0/12$) in the θ range 3–70°; 4102 independent ($R_{int} = 0.015$) and 3326 with

$I \geq 2\sigma(I)$ considered observed. Structure solved by direct methods with *SHELX76* (Sheldrick, 1976), anisotropic block-matrix least-squares refinement, H atoms found from a difference Fourier map refined with isotropic temperature factors. $\sum w\Delta F^2$ minimized, unit weights, 14 reflections omitted because they were probably affected by extinction. The highest peak in the final ΔF map was 0.35 e Å^{-3}, final R

Table 1. *Atomic fractional coordinates* ($\times 10^4$) *and* U_{eq} *values* (Å$^2 \times 10^4$)

	x	y	z	U_{eq}*
S	2504 (1)	668 (1)	2993 (1)	548 (2)
O1	−85 (1)	2162 (2)	1214 (2)	697 (8)
O2	3840 (1)	−1260 (2)	−1571 (2)	667 (7)
O3	2779 (1)	1922 (2)	3436 (2)	758 (8)
O4	2487 (1)	−418 (3)	3946 (2)	709 (8)
N1	−2292 (2)	220 (4)	3075 (4)	790 (13)
N2	5033 (2)	2159 (2)	−4998 (3)	714 (10)
C4	1722 (1)	1011 (3)	2397 (3)	487 (8)
C5	1596 (1)	2070 (3)	1504 (3)	632 (10)
C6	987 (2)	2421 (3)	1133 (3)	649 (11)
C7	499 (1)	1723 (3)	1654 (3)	513 (7)
C8	619 (1)	650 (3)	2521 (3)	518 (8)
C9	1233 (1)	289 (3)	2885 (3)	508 (8)
C10	−613 (1)	1585 (3)	1750 (3)	555 (9)
C11	−772 (1)	1934 (3)	3016 (3)	598 (10)
C12	−1331 (1)	1467 (3)	3464 (3)	603 (10)
C13	−1715 (1)	645 (3)	2647 (3)	573 (9)
C14	−1549 (2)	285 (4)	1407 (3)	680 (11)
C15	−988 (2)	763 (4)	939 (3)	639 (10)
C16	2896 (1)	107 (3)	1616 (3)	477 (7)
C17	3242 (1)	1020 (3)	921 (3)	590 (9)
C18	3558 (1)	589 (3)	−157 (3)	580 (10)
C19	3533 (1)	−739 (3)	−521 (3)	506 (8)
C20	3194 (1)	−1654 (3)	158 (3)	592 (9)
C21	2873 (1)	−1234 (3)	1233 (3)	555 (9)
C22	4150 (1)	−374 (3)	−2403 (3)	539 (9)
C23	4758 (1)	5 (3)	−2063 (3)	570 (9)
C24	5056 (1)	847 (3)	−2926 (3)	559 (8)
C25	4749 (1)	1287 (2)	−4140 (3)	513 (8)
C26	4136 (1)	851 (3)	−4460 (3)	578 (9)
C27	3841 (1)	38 (3)	−3594 (3)	601 (9)

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* Part XXVII: Bocelli & Cantoni (1990).

* Hamilton (1959).