Molecular Conformation of *S*-4-Nitrophenyl *OO*-Diphenyl Thiophosphate: *X*-Ray Crystal Structure Analysis

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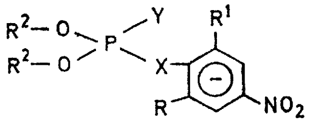
The crystal structure of the title compound has been determined from three-dimensional data by direct methods. Crystals are monoclinic, space group $P2_1/c$, with $Z = 4$ in a unit cell of dimensions: $a = 10{\cdot}826(2)$, $b = 20{\cdot}325(7)$, $c = 8{\cdot}139(2)$ Å, $\beta = 105{\cdot}4(1)°$. The structure was refined by least-squares to a final R of 0·13. The conformation of the molecule in the solid state is consistent with e.p.r. measurements in solution and is not such as to suggest π-bonding on the basis of symmetry considerations.

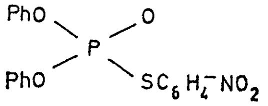
THE geometry of roughly tetrahedral groupings, *e.g.* SO_4^{2-}, PO_4^{2-}, and ClO_4^-, allows for the possibility of π-bonding between $2p$ orbitals of the ligand atoms and empty central-atom $3d$ orbitals.[1] Evidence for π-bonding has been sought in spectroscopic, structural, stability, and reaction-rate data,[2] although its extent and importance remains an open question.[3] The conformations of phosphate esters have been discussed by Collin [4] in terms of π-bonding. Since that time the crystal structures of several phosphate esters have been solved and a number of generalizations made which do not seem to provide clear evidence for conformational constraints imposed by bonding. Nevertheless, it remains of interest to understand the conformations of phosphate esters since this type of compound has considerable biological significance.

E.s.r. hyperfine coupling constants of phosphorus have been determined by Gulick [5] in a series of nitroaromatic anion radicals of the type (I), where X and Y are either



(I)

sulphur or oxygen atoms and R, R¹, and R² are alkyl or aryl groups. The results have been interpreted in terms of an hyperconjugative mechanism for the transmission of spin density from the nitroaromatic ring to the phosphorus atom. It appears that steric effects influence the ^{31}P coupling constant in as much as bulky R groups constrain the nitroaromatic ring to lie more-or-less normal to the Y–P–X plane, thus placing the π-electron system



(II)

of the ring ideally for interaction with phosphorus $3d$ orbitals. For the radical (II) of *S*-4-nitrophenyl *OO*-diphenyl thiophosphate the coupling constant is particularly large, and it is conjectured that (*a*) the favoured geometry is optimal for hyperconjugation, despite the absence of bulky groups R, (*b*) the P–S–C angle is small, thus bringing the phosphorus close to the ring π-orbitals, and (*c*) there is some conjugation through the sulphur atom. We have determined the structure of this compound to investigate these points and to elucidate further the nature of preferred conformations of phosphate esters. Since very little is known structurally about thiophosphate esters it was also interesting to see if replacement of an oxygen by a sulphur atom introduced any significant new factor governing the conformation of the molecule.

EXPERIMENTAL

Crystal Data.—$C_{18}H_{14}O_5NSP$, $M = 387{\cdot}35$. Monoclinic, $a = 10{\cdot}826(2)$, $b = 20{\cdot}325(7)$, $c = 8{\cdot}139(2)$ Å, $\beta = 105{\cdot}4(1)°$, $U = 1726$ Å^3, $D_c = 1{\cdot}47$, $Z = 4$, $D_m = 1{\cdot}47$, $F(000) = 200$. Space group $P2_1/c$. Mo-K_α radiation, $\lambda = 0{\cdot}71069$ Å; μ(Mo-K_α) = 3·08 cm^{-1}.

Space group and approximate cell dimensions were determined by Weissenberg and precession photography, with rotation about the *b* and *c* axes. A crystal for which absorption was negligible was mounted with its needle axis parallel to the ϕ axis of an automatic four-circle Hilger and Watts diffractometer. The needle axis corresponded to the *c* axis of the cell. Cell parameters were refined from angle measurements of 12 reflections. A total of 1991 non-zero unique reflection intensities were obtained from 2θ—ω scan measurements by use of Mo-K_α radiation, and a scintillation counter with pulse-height discrimination. Because of decrease in the intensities of the standard reflections with time, portions of the data were re-collected by use of another crystal. Data were scaled by use of the standard reflections.

All calculations were performed on a CDC 6500 computer with local modifications of the '*X*-Ray' system of programmes,[6a] and the plotting programme ORTEP.[6b] Scattering factors were taken from ref. 7. The structure was solved by direct methods. 339 $|E|$ values were $>1{\cdot}3$; a choice of three origin-defining reflections was made on the

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[6] (*a*) J. M. Stewart, G. J. Kruger, M. L. Ammon, C. Dickinson, and S. R. Hall, Technical Report TR 192 of the Computer Science Center, University of Maryland, 1972; (*b*) C. K. Johnson, 'ORTEP: A Fortran Thermal-ellipsoid Plot Program for Crystal Structure Illustrations,' Report ORNL 3794, Oak Ridge National Laboratory, Tennessee, 1970.

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basis of their large $|E|$ values and the large number of sign combinations into which they entered:

h	k	l	$\|E\|$
3	5	3	3·47
6	8	$\bar{3}$	3·15
2	17	$\bar{1}$	2·95

These, along with the 75 largest $|E|$ values as generators produced finally 317 phased reflections by the use of Σ_2 relationships. An E map calculated on these reflections showed clearly 20 out of the 25 atom positions. Calculation of structure factors gave a conventional R of 0·46. The remaining atoms were located by means of an F_o map. Refinement was by least squares, the function minimized being $\Sigma(|F_o| - K|F_c|)^2$, with anisotropic temperature factors for all atoms. Several weighting schemes were tried but none resulted in better refinement than that with all reflections assigned unit weight, except for ten having $F_o \ll F_c$, which were assigned zero weight. The best value of R obtained was 0·13 over all 1991 reflections. This high value was considered to be due to errors in the data resulting from deterioration of the crystals during data collection. The weak, high-angle reflections which took the longest to measure were the most adversely affected. Weighting analysis showed that they had by far the greatest R.

TABLE 1

Atomic positions (fractional co-ordinates), with estimated standard deviations in parentheses

Atom	X	Y	Z
S	−0·3481(04)	0·0972(02)	−0·1242(07)
P	−0·2348(04)	0·0887(02)	0·1208(07)
O(1)	−0·3392(11)	0·0686(05)	0·2174(18)
O(2)	−0·1535(10)	0·0236(05)	0·1326(19)
O(3)	−0·1530(11)	0·1449(06)	0·1910(20)
O(4)	0·0951(14)	0·1975(07)	−0·4987(24)
O(5)	0·1025(12)	0·0916(07)	−0·5397(21)
N	0·0617(14)	0·1409(09)	−0·4798(24)
C(01)	−0·2233(13)	0·1116(08)	−0·2247(22)
C(02)	−0·1648(17)	0·1737(08)	−0·2162(27)
C(03)	−0·0689(16)	0·1840(08)	−0·2982(26)
C(04)	−0·0412(14)	0·1318(08)	−0·4000(22)
C(05)	−0·0986(14)	0·0694(07)	−0·4107(24)
C(06)	−0·1194(15)	0·0600(08)	−0·3278(25)
C(11)	−0·4081(15)	0·1091(07)	0·2950(22)
C(12)	−0·3795(18)	0·1748(08)	0·3336(28)
C(13)	−0·4497(20)	0·2095(09)	0·4265(26)
C(14)	−0·5472(20)	0·1777(11)	0·4837(36)
C(15)	−0·5756(18)	0·1106(11)	0·4395(33)
C(16)	−0·5043(16)	0·0748(09)	0·3487(24)
C(21)	−0·1937(14)	−0·0387(08)	0·0720(24)
C(22)	−0·1307(16)	−0·0684(09)	−0·0246(27)
C(23)	−0·1605(18)	−0·1347(09)	−0·0818(29)
C(24)	−0·2520(19)	−0·1690(10)	−0·0122(31)
C(25)	−0·3130(18)	−0·1375(09)	0·0917(38)
C(26)	−0·2848(17)	−0·0704(09)	0·1534(33)

TABLE 2

Bond lengths (Å), with estimated standard deviations in parentheses

P–S	2·052(7)	O(1)–C(11)	1·372(22)
P–O(1)	1·592(15)	O(2)–C(21)	1·385(19)
P–O(2)	1·579(12)	N–O(4)	1·228(23)
P–O(3)	1·464(12)	N–O(5)	1·246(24)
S–C(01)	1·780(18)	N–C(04)	1·443(26)
Ph rings C–C	1·317(29)—1·474(30)		
Mean	1·410(83)		

Final atomic parameters are in Table 1, bond distances and angles in Tables 2 and 3, and intramolecular distances in Table 4. Final observed and calculated structure factors and atomic thermal parameters are listed in Supplementary Publication No. SUP 21037 (3 pp.).*

TABLE 3

Bond angles (deg.), with estimated standard deviations in parentheses

S–P–O(1)	100·49(49)	P–S–C(01)	97·45(53)
S–P–O(2)	107·98(59)	P–O(1)–C(11)	128·20(1·06)
S–P–O(3)	117·23(64)	P–O(2)–C(21)	128·82(95)
O(1)–P–O(2)	102·28(70)	O(4)–N–O(5)	123·97(1·96)
O(1)–P–O(3)	116·23(85)	O(4)–N–O(4)	117·66(1·72)
O(2)–P–O(3)	111·12(64)	O(5)–N–O(4)	118·00(1·59)
Ph, ring, internal	111·12(2·11)—124·10(2·16)		

TABLE 4

Intramolecular contacts (Å), with estimated standard deviations in parentheses

P · · · C(11)	2·668(20)	O(1) · · · O(3)	2·596(18)
P · · · C(21)	2·675(17)	O(1) · · · C(16)	2·317(25)
S · · · O(1)	2·817(16)	O(2) · · · O(3)	2·510(16)
S · · · O(2)	2·950(12)	O(2) · · · C(22)	2·316(23)
S · · · O(3)	3·017(14)	O(4) · · · O(5)	2·184(21)
S · · · C(06)	2·749(21)	O(4) · · · C(04)	2·288(25)
O(1) · · · O(2)	2·469(19)	O(5) · · · C(04)	2·308(24)

RESULTS AND DISCUSSION

The ligands are disposed around the phosphorus atom in roughly tetrahedral geometry. The molecule adopts an extended configuration in the crystal with all phenyl rings approximately parallel, the perpendicular distance between the nearest rings being 3·5 Å. A projection of half the contents of the unit cell down the unique b axis is shown in Figure 1 and an ORTEP plot in Figure 2 shows the molecular conformation. The phosphoryl bond length is 1·46(1), and the two ester P–O bonds are equal at 1·58(1) Å. Relatively few P–S distances have been measured, but the value for bridging sulphurs in the phosphorus cage compounds with sulphur and oxygen is 2·11 Å as compared to a terminal P–S distance of 1·85—1·95 Å, depending on the electronegativities of other atoms bonded to phosphorus.[8] The P–S distance in potassium *OO*-dimethyl phosphorodithioate is 1·96 Å.[9] Our value [2·052(7) Å] indicates very little multiple-bond nature, though one may not rule out a small reduction in length, with respect to a normal single bond, due to a conjugative mechanism. The S–C distance [1·78(2) Å] represents a normal single bond.

The O–P–O and O–P–S bond angles range from 100 to 117°. In agreement with other phosphate ester structures, the X–P–Y angles involving the esterified atoms are the smallest. The angles subtended at the ester oxygens are 128°, which is a rather large value in comparison to those of other structures. Bond angles at sulphur are known to attain smaller values than the corresponding angles in oxygen compounds. The present P–S–C angle is 97°.

The phosphorus atom lies almost directly over the plane of the nitroaromatic group, and this together with the small angle at sulphur may account for the very large

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* See Notice to Authors No. 7 in *J.C.S. Perkin II*, 1973, Index issue.

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phosphorus hyperfine coupling constant for the radical anion.[5] The agreement between the molecular conformation observed for the solid state and that conjectured from e.s.r. results for solutions suggests that the former is due largely to intramolecular interactions rather than to crystal packing forces.

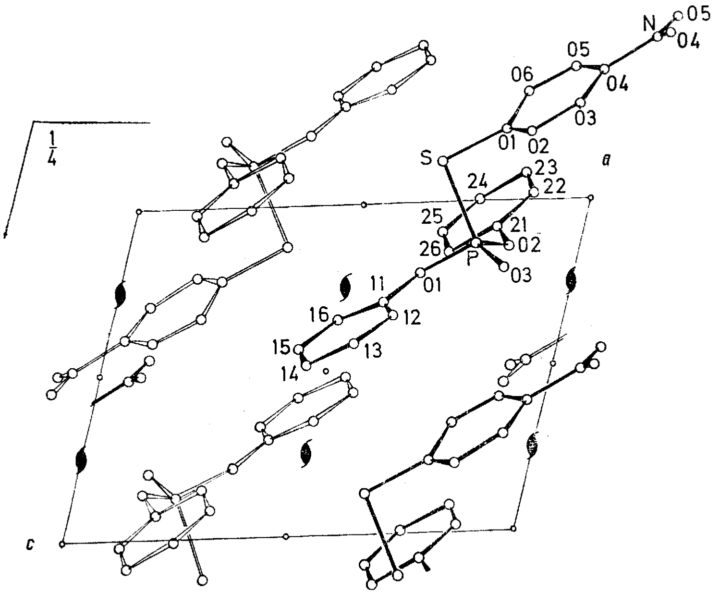

FIGURE 1 Projection of half the contents of the unit cell along the unique *b* axis

As in other nitro-aromatic compounds,[10] the nitro-group is rotated a few degrees out of the plane of the phenyl ring.

The angles between the P–O(3) bond and the normals to the planes P–O(1)–C(11), P–O(2)–C(21), and P–S–C(01) are 41, 86, and 58·5°. Thus atoms O(3)–P–O(2)–C(21) are almost coplanar. This coplanarity is one of the most consistent features of phosphate ester structures.[11] In six structures [11-16] the greatest deviation of any atom from the best plane through O=P–O–C is 0·07 Å.

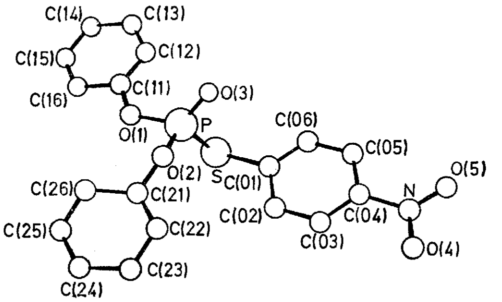

FIGURE 2 ORTEP drawing of one molecule showing the molecular conformation and numbering system used in the analysis

These data might be interpreted as allowing for a large degree of overlap between phosphorus 3*d* and oxygen 2*p* orbitals, assuming approximate *sp*^{2} hybridization of the oxygen orbitals. The other ester groupings, however, are not usually very well oriented for large overlap, and there appear to be no consistent length differences between various P–O(ester) bonds.

Methyl pinacol phosphate [11] is unusual in that the methyl carbon lies on the same side of the O–P bond as the phosphoryl oxygen rather than in a '*trans*'-arrangement as in the other structures. Bertrand *et al.*[11] felt that this was evidence for π bonding, but further structural work appears to have provided little support of the idea. As Trueblood *et al.*[17] point out, the planarity of the four atoms may reflect nothing more than the usual tendency to assume a staggered conformation.

In the parent compound of (II), looking in turn along the O(1)–P, O(2)–P, and S–P bonds, the O(1)–C(11), O(2)–C(21), and S–C(01) bonds lie almost exactly staggered with respect to two bonds radiating from the phosphorus. This geometry, and the equality of the ester P–O bond lengths, lend support to Trueblood's point of view.

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