

# The Reactions of Triarylphosphines and Triarylsarsines with Chloramines B and T: Crystal and Molecular Structures of Triphenylarsine Oxide–Benzenesulphonamide (1 : 1) Hemi-acetone Solvate and Tri-*m*-tolylphosphine Oxide–Toluene-*p*-sulphonamide (1 : 1)

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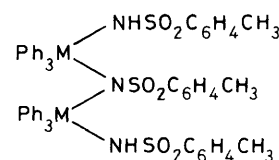
Triphenylarsine and triphenylphosphine react with chloramine-B, sodium *N*-chlorobenzene-sulphonamide, to yield products of composition  $C_{24}H_{22}NO_3SM$  [(3;  $M = As$ ) and 4;  $M = P$ ] and constitution  $Ph_3MO \cdot H_2NSO_2Ph$ . Crystals of (3)·0.5( $C_3H_6O$ ) are triclinic, space group  $P\bar{1}$  with  $a = 12.783(2)$ ,  $b = 13.016(2)$ ,  $c = 8.513(1)$  Å,  $\alpha = 97.40(1)$ ,  $\beta = 106.80(1)^\circ$ ,  $\gamma = 111.28(1)^\circ$  and  $Z = 2$ : the structure was refined from diffractometer data to an  $R$  value of 0.035. The structure consists of cyclic centrosymmetric aggregates in which two molecules of  $Ph_3AsO$  are linked to two molecules of  $PhSO_2NH_2$  via hydrogen bonds of type  $O \cdots H-N(SO_2Ph)-H \cdots O$ : the As–O distance is 1.655(1) Å and the two independent  $N \cdots O$  distances are 2.848(3) and 2.882(3) Å; the acetone from solution is disordered about an inversion centre. Crystals of (4)·0.5( $C_3H_6O$ ) are triclinic, space group  $P\bar{1}$ , and are isomorphous with those of (3)·0.5( $C_3H_6O$ ), with  $a = 12.712(5)$ ,  $b = 12.811(9)$ ,  $c = 8.481(3)$  Å,  $\alpha = 98.51(3)$ ,  $\beta = 105.31(3)$ ,  $\gamma = 111.81(5)^\circ$ . Tri-*m*-tolylphosphine reacts with chloramine-T, sodium *N*-chlorotoluene-*p*-sulphonamide, to yield a similar product (5) of constitution (3- $CH_3C_6H_4$ ) $_3PO \cdot H_2NSO_2C_6H_4-p-CH_3$ . Crystals of (5) are triclinic with  $a = 11.353(4)$ ,  $b = 13.694(5)$ ,  $c = 9.546(1)$  Å,  $\alpha = 76.16(2)$ ,  $\beta = 87.52(2)$ ,  $\gamma = 112.24(3)^\circ$  and  $Z = 2$ : the structure of (5) was refined from diffractometer data to an  $R$  value of 0.045. It consists of the same hydrogen-bonded array as (3), with  $N \cdots O$  distances of 2.882(2) and 2.931(2) Å.

The reactions between chloramine-T, sodium *N*-chlorotoluene-*p*-sulphonamide,  $CH_3C_6H_4SO_2NCl^-Na^+$ , and triarylphosphines and triarylsarsines provide a range of products. Under anhydrous conditions, the usual products are phosphinimines  $Ar_3P=NSO_2C_6H_4CH_3$  or arsinimines  $Ar_3As=NSO_2C_6H_4CH_3$ .<sup>1</sup> However, the trihydrate of chloramine-T can yield, with different phosphines, either the phosphinimine or a product which has been described as an hydroxysulphonamide  $Ar_3P(OH)NHSO_2C_6H_4CH_3$ ,<sup>1</sup> whereas triarylsarsines under these conditions were said generally to provide analogous hydroxysulphonamides.<sup>2</sup> Exceptions are triphenylphosphine and triphenylarsine which each react with chloramine-T trihydrate to yield products originally formulated<sup>1–3</sup> as (1). We have recently shown,<sup>4</sup> however, that these products are in fact 2:3 adducts of  $Ph_3MO$  and  $CH_3C_6H_4SO_2NH_2$  (2), in which the molecular aggregation is provided by hydrogen bonding.

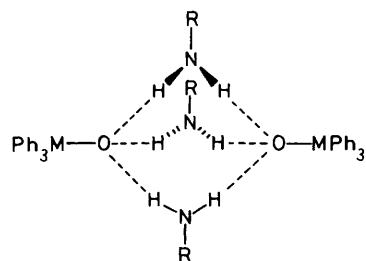
In contrast to the formation of (2) from  $Ph_3M$  ( $M = P, As$ ) and hydrated chloramine-T, the entirely analogous reaction of  $Ph_3As$  with hydrated chloramine-B, sodium *N*-chlorobenzene-sulphonamide,  $C_6H_5SO_2NCl^-Na^+$  is reported to yield the hydroxysulphonamide derivative (3), formulated<sup>2</sup> as  $Ph_3As(OH)NHSO_2C_6H_5$ . This is a formulation based upon five-co-ordinate arsenic. Here we report on a re-investigation of compound (3), and of the phosphorus analogue (4), including an *X*-ray crystal-structure determination for (3). We have also re-investigated the product (5) from the reaction between (*m*- $CH_3C_6H_4$ ) $_3P$  and hydrated chloramine-T, originally formulated<sup>1</sup> as the hydroxysulphonamide, (3- $CH_3C_6H_4$ ) $_3P(OH)NHSO_2C_6H_4-p-CH_3$ , containing five-co-ordinate phosphorus.

## Experimental

Compound (3) was prepared<sup>2</sup> by reaction of  $Ph_3As$  with



(1) a  $M = P$   
b  $M = As$



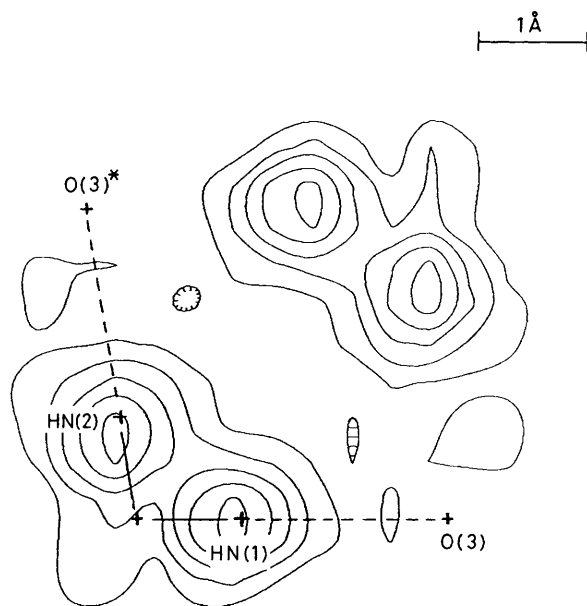
(2) a  $M = P$   
b  $M = As$  }  $R = CH_3C_6H_4SO_2$

$C_6H_5SO_2NCl^-Na^+$  in ethanol: the product was recrystallised from anhydrous acetone until its m.p. remained unchanged at 151–152 °C (lit.,<sup>2</sup> 151–153 °C) (Found: C, 59.8; H, 4.9; N, 2.7.  $C_{24}H_{22}AsNO_3S$  requires C, 60.1; H, 4.6; N, 2.9%;  $\delta_H(CD_2Cl_2)$  5.65 (s, br, 2 H,  $NH_2$ ), and 7.4–8.0 (m, 20 H, 4 ×  $C_6H_5$ ).

**Preparation of Compound (4).**—Triphenylphosphine (5.24 g, 0.02 mol) and chloramine-B (4.68 g, 0.022 mol) were each

**Table 1.** Details of data collection, and *R* values.

	(3)·0.5(C <sub>3</sub> H <sub>6</sub> O)	(5)
Crystal dimensions/mm	0.44 × 0.38 × 0.14	0.50 × 0.25 × 0.30
$\omega$ Scan width/°	0.6 + 0.35 tan $\theta$	0.6 + 0.35 tan $\theta$
$\theta$ Scan rate/° min <sup>-1</sup>	1–7	1–7
$2\theta_{\max}$ /°	54	54
Range of unique <i>h</i>	–16 → +16	0 → +14
<i>k</i>	0 → +16	–17 → +17
<i>l</i>	–10 → +10	–12 → +12
No. reflections measured	5 676	5 975
No. reflections unique	5 295	5 744
No. reflections observed	3 857	3 528
	[ $F_o^2 \geq 2\sigma(F_o^2)$ ]	[ $F_o^2 \geq 3\sigma(F_o^2)$ ]
<i>R</i>	0.035	0.045
<i>R<sub>w</sub></i>	0.045	0.062

**Figure 1.** Section of difference Fourier map in the O(3), N, O(3)<sup>l</sup> plane of compound (3) showing the location of hydrogen atoms bound to nitrogen; successive contour levels represent electron density of 0.1 e Å<sup>-3</sup>.

dissolved in hot ethanol (100 cm<sup>3</sup>): the solutions were mixed, and the solution refluxed for 1 h. The mixture was cooled, and filtered through Hyflosupercel; the solvent was removed to yield an oil which solidified upon standing overnight. The solid was recrystallised from CH<sub>2</sub>Cl<sub>2</sub>, m.p. 107–108 °C (Found: C, 66.4; H, 5.0; N, 3.1. C<sub>24</sub>H<sub>22</sub>NO<sub>3</sub>PS requires: C, 66.2; H, 5.1; N, 3.2%);  $\delta_{\text{H}}(\text{CD}_2\text{Cl}_2)$  5.64 (s, br, 2 H, NH<sub>2</sub>), and 7.4–7.9 (m, 20 H, 4 × C<sub>6</sub>H<sub>5</sub>);  $\delta_{\text{P}}(\text{CD}_2\text{Cl}_2)$  +28.8;  $\delta_{\text{C}}(\text{CD}_2\text{Cl}_2)$  126.6 (d), 129.4 (d), 132.7 (d), 143.1 (s), C<sub>6</sub>H<sub>5</sub>SO<sub>2</sub>; 129.9 (dd, *J*<sub>PC</sub> 12.1) 132.3 (dd, *J*<sub>PC</sub> 9.6), 132.4 (3, *J*<sub>PC</sub> small), and 132.9 (sd, *J*<sub>PC</sub> 99.1 Hz, C<sub>6</sub>H<sub>5</sub>P).

Compound (5) was prepared<sup>1</sup> by reaction of (*m*-CH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>)<sub>3</sub>P with CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>NCl<sup>+</sup>Na<sup>+</sup>·3H<sub>2</sub>O in ethanol: the product was recrystallised from ethanol, m.p. 97–98 °C, (lit.,<sup>1</sup> 98 °C) (Found: C, 68.8; H, 6.0, N, 2.8. C<sub>28</sub>H<sub>30</sub>NO<sub>3</sub>PS requires: C, 68.4; H, 6.2; N, 2.9%);  $\delta_{\text{H}}(\text{CD}_2\text{Cl}_2)$  2.37 (s, 9 H, *m*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>), 2.42 (s, 3 H, *p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>), 5.10 (s, br, 2 H, NH<sub>2</sub>), 7.20 and 7.80 (AB, *J* 8 Hz, 4 H, *p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>), and 7.2–7.7 (m, 12 H, *m*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>);  $\delta_{\text{P}}(\text{CD}_2\text{Cl}_2)$  +28.5. A product identical (m.p., microanalysis, <sup>1</sup>H and <sup>31</sup>P n.m.r.) to the foregoing was obtained by crystallising an ethanol solution containing equimolar quantities of (*m*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>)<sub>3</sub>PO and CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>NH<sub>2</sub>.

**X-Ray Crystallography.**—Crystals of compounds (3) and (4) suitable for X-ray examination were grown from acetone: crystals of compound (5) were grown from ethanol.

**Crystal Data.**—Compound (3)·0.5(C<sub>3</sub>H<sub>6</sub>O), C<sub>24</sub>H<sub>22</sub>AsNO<sub>3</sub>·S·0.5(C<sub>3</sub>H<sub>6</sub>O), *M* = 508.5, triclinic, *a* = 12.783(2), *b* = 13.016(2), *c* = 8.513(1) Å,  $\alpha$  = 97.40(1),  $\beta$  = 106.80(1),  $\gamma$  = 111.28(1)°, *V* = 1 219.4(8) Å<sup>3</sup>, space group *P* $\bar{1}$  (No. 2), *Z* = 2, *D<sub>c</sub>* = 1.39 g cm<sup>-3</sup>,  $\mu(\text{Mo-K}\alpha)$  = 15.0 cm<sup>-1</sup>,  $\lambda$  = 0.710 73 Å, *F*(000) = 524.

Compound (4)·0.5(C<sub>3</sub>H<sub>6</sub>O), C<sub>24</sub>H<sub>22</sub>NO<sub>3</sub>PS·0.5(C<sub>3</sub>H<sub>6</sub>O), *M* = 464.5, triclinic, *a* = 12.712(5), *b* = 12.811(9), *c* = 8.481(3) Å,  $\alpha$  = 98.51(5),  $\beta$  = 105.31(3),  $\gamma$  = 111.81(5)°, *V* = 1 189(3) Å<sup>3</sup>, space group *P* $\bar{1}$  (No. 2), *Z* = 2, *D<sub>c</sub>* = 1.30 g cm<sup>-3</sup>,  $\mu(\text{Mo-K}\alpha)$  = 2.2 cm<sup>-1</sup>, *F*(000) = 488. Crystals of (4)·0.5(C<sub>3</sub>H<sub>6</sub>O) diffracted very poorly and no crystal really suitable for data collection could be obtained.

Compound (5), C<sub>28</sub>H<sub>30</sub>NO<sub>3</sub>PS, *M* = 491.59, triclinic, *a* = 11.353(4), *b* = 13.694(5), *c* = 9.546(1) Å,  $\alpha$  = 76.16(2),  $\beta$  = 87.52(2),  $\gamma$  = 112.24(3)°, *V* = 1 318.9 Å<sup>3</sup>, space group *P* $\bar{1}$  (No. 2), *Z* = 2, *D<sub>c</sub>* = 1.24 g cm<sup>-3</sup>,  $\mu(\text{Mo-K}\alpha)$  = 2.0 cm<sup>-1</sup>,  $\lambda$  = 0.710 73 Å, *F*(000) = 520.

**Data Collection.**—Cell dimensions were determined by least-squares refinement using the setting angles for 25 reflections in the ranges 6° ≤  $\theta$  ≤ 19° for (3)·0.5(C<sub>3</sub>H<sub>6</sub>O), 4° ≤  $\theta$  ≤ 14° for (4)·0.5(C<sub>3</sub>H<sub>6</sub>O), and 9° ≤  $\theta$  ≤ 15° for (5). Intensity data for (3)·0.5(C<sub>3</sub>H<sub>6</sub>O) and (5) were collected at 21 °C using a CAD4 diffractometer with graphite-monochromated Mo-K $\alpha$  radiation, in the  $\omega/2\theta$  scan mode: details of crystal dimensions, numbers of reflections measured, and final *R* factors are in Table 1. Lorentz and polarisation corrections were applied. A numerical absorption correction was applied for (3): maximum and minimum transmission factors were 0.833 and 0.516.

**Structure Solution and Refinement.**—The structure of compound (3) was solved by Patterson methods, followed by difference Fourier syntheses. The structure of compound (5) was solved by direct methods: all the non-hydrogen atoms were located from the E-map: the remaining atoms were located in succeeding difference Fourier syntheses.

All non-hydrogen atoms were refined anisotropically. Hydrogen atoms bound to benzenoid carbon atoms were included in the refinement as riding atoms with *d*(C–H) = 0.95 Å: *B*<sub>iso</sub> was fixed at 6.0 Å<sup>2</sup> in (3) and 5.0 Å<sup>2</sup> in (5). For each methyl group in compound (5) the hydrogens appeared as a torus of electron density; they were allowed for by including six half-hydrogen atoms at 60° intervals around the torus. Hydrogen atoms bound to nitrogen, which were clearly visible in a difference map (see Figure 1), were also included in the refinement, constrained to lie on the N···O directions, with *d*(N–H) = 0.95 Å: *B*<sub>iso</sub> was 5.0 Å<sup>2</sup> in (3) and 4.0 Å<sup>2</sup> in (5). In compound (3) a molecule of acetone solvent was found to lie, disordered, over the centre of inversion at (0,  $\frac{1}{2}$ ,  $\frac{1}{2}$ ): the non-hydrogen atoms [OS, C(1)S, C(2)S, and C(3)S] were included in the calculations with site occupation factors 0.5 and fixed interatomic distances<sup>5</sup> *d*(C–O) = 1.211 Å and *d*(C–C) 1.513 Å, and were refined isotropically. A secondary extinction coefficient<sup>6</sup> refined to values of 4.29 × 10<sup>-7</sup> for compound (3), and 2.1 × 10<sup>-6</sup> for compound (5). Final *R* values are in Table 1.

Scattering factor data were taken from refs. 7–9. All calculations were performed on a PDP-11/73 computer using SDP-Plus.<sup>10</sup> Final refined atom co-ordinates for compounds (3) and (5) are given in Tables 2 and 3, and bond lengths and angles in Tables 4–6; perspective views of (3) and (5) showing the atom-numbering schemes are in Figures 2 and 3.

Tables of hydrogen-atom co-ordinates, temperature factors,

**Table 2.** Positional parameters for (3)·0.5(C<sub>3</sub>H<sub>6</sub>O) with esds in parentheses.<sup>a</sup>

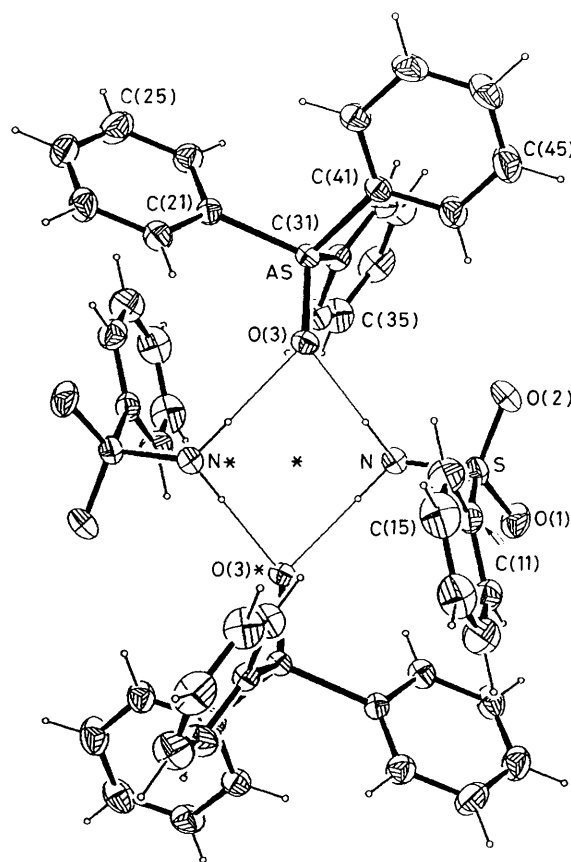
Atom	x	y	z
As	0.259 94(2)	0.272 63(2)	0.201 92(3)
S	-0.175 73(6)	0.132 93(6)	-0.034 9(1)
O(1)	-0.282 6(2)	0.090 0(2)	0.003 2(3)
O(2)	-0.101 7(2)	0.252 9(2)	0.018 0(3)
O(3)	0.146 6(2)	0.166 6(1)	0.045 3(2)
N	-0.091 9(2)	0.073 0(2)	0.046 7(3)
C(11)	-0.220 4(2)	0.090 4(2)	-0.258 7(4)
C(12)	-0.334 9(3)	0.009 2(3)	-0.356 5(4)
C(13)	-0.367 6(3)	-0.023 5(3)	-0.530 4(5)
C(14)	-0.287 9(4)	0.023 0(3)	-0.605 9(5)
C(15)	-0.175 4(4)	0.103 6(3)	-0.509 6(5)
C(16)	-0.139 5(3)	0.138 0(3)	-0.335 5(5)
C(21)	0.405 5(2)	0.254 6(2)	0.228 9(3)
C(22)	0.413 3(3)	0.195 1(2)	0.089 1(4)
C(23)	0.516 8(3)	0.179 1(3)	0.104 3(4)
C(24)	0.611 0(3)	0.222 8(3)	0.255 7(5)
C(25)	0.604 7(3)	0.283 1(3)	0.395 0(5)
C(26)	0.500 8(3)	0.298 3(3)	0.382 8(4)
C(31)	0.234 1(2)	0.276 6(2)	0.412 0(3)
C(32)	0.271 7(3)	0.378 7(3)	0.528 3(4)
C(33)	0.251 2(3)	0.377 1(4)	0.681 0(4)
C(34)	0.192 1(3)	0.275 5(4)	0.711 9(4)
C(35)	0.155 5(3)	0.175 0(3)	0.597 2(4)
C(36)	0.175 4(3)	0.174 6(3)	0.446 5(4)
C(41)	0.284 7(2)	0.419 2(2)	0.159 5(3)
C(42)	0.395 8(3)	0.494 3(2)	0.166 4(4)
C(43)	0.409 0(3)	0.599 3(3)	0.134 7(5)
C(44)	0.313 6(3)	0.628 1(3)	0.098 1(5)
C(45)	0.203 8(3)	0.553 7(3)	0.093 2(5)
C(46)	0.188 4(3)	0.448 6(3)	0.122 8(4)
OS	0.0586	0.5700	0.3850
C(1)S	0.0179	0.5174	0.4770
C(2)S	-0.0563	0.3895	0.4123
C(3)S	0.0597	0.5756	0.6639

<sup>a</sup> The acetone solvent molecule [OS, C(1)S, C(2)S, and C(3)S] was included in the calculations with fixed planar geometry; distances were C(sp<sup>2</sup>)-O 1.211 Å and C(sp<sup>2</sup>)-C(sp<sup>3</sup>) 1.513 Å. The molecule is disordered over a crystallographic centre of symmetry. The unique atoms were assigned 0.5 occupancy and their thermal parameters were refined isotropically.

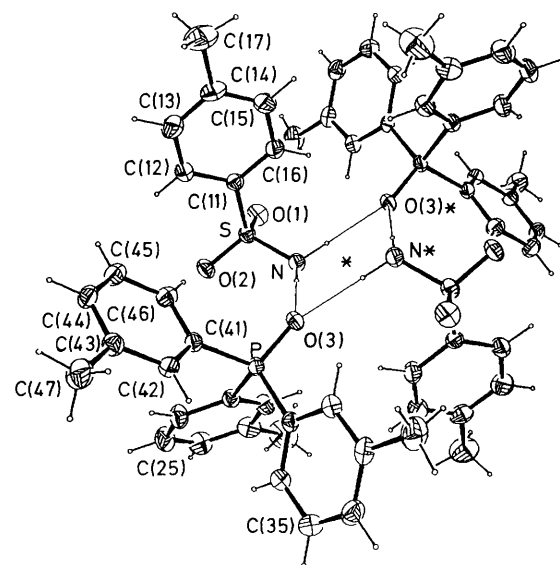
and torsional angles have been deposited at the Cambridge Crystallographic Data Centre.\*

## Results and Discussion

Compound (3) was readily prepared from triphenylarsine and the hydrated sodium salt of chloramine-B, C<sub>6</sub>H<sub>5</sub>SO<sub>2</sub>NCl<sup>-</sup>Na<sup>+</sup>·xH<sub>2</sub>O. The same product was obtained under a range of conditions, with composition and m.p. identical to those found by Mann<sup>2</sup> for the product obtained from similar reactions: hence there is no doubt that the compound obtained here is the same as that recorded by Mann. In solution in CD<sub>2</sub>Cl<sub>2</sub> the <sup>1</sup>H n.m.r. spectrum of (3) was simply a summation of the spectra of Ph<sub>3</sub>AsO and C<sub>6</sub>H<sub>5</sub>SO<sub>2</sub>NH<sub>2</sub>, while the i.r. spectrum of (3), recorded in a Nujol mull, differed from the sum of the spectra of Ph<sub>3</sub>AsO and C<sub>6</sub>H<sub>5</sub>SO<sub>2</sub>NH<sub>2</sub>, particularly in the NH stretching region. These observations suggest that, as with the products<sup>4</sup> of similar reactions<sup>1-3</sup> of Ph<sub>3</sub>P and Ph<sub>3</sub>As with chloramine-T, the product (3) is a specific compound containing a distinctive hydrogen-bonded array of Ph<sub>3</sub>AsO and C<sub>6</sub>H<sub>5</sub>SO<sub>2</sub>NH<sub>2</sub> molecules in a 1:1 molar ratio. The hydrogen-bonding in the



**Figure 2.** Perspective view of the molecule of (3) showing the atom-numbering scheme.



**Figure 3.** Perspective view of the molecule of (5) showing the atom-numbering scheme: for the sake of clarity, only three of the disordered hydrogen sites are shown for each methyl group.

solid state provides a solid-state spectrum different from that of the two components, but disruption of the hydrogen-bonding upon dissolution provides solution n.m.r. spectra which are simple summations of the spectra of the components. These deductions concerning (3) are entirely in accord with the results of our single-crystal X-ray analysis (see below).

\* For details of the CCDC deposition scheme, see 'Instructions for Authors' (1989), *J. Chem. Soc., Perkin Trans. 2*, in the January issue.

**Table 3.** Positional parameters for (5) with esds in parentheses.

Atom	x	y	z
S	0.310 91(6)	0.611 27(5)	0.373 22(6)
P	0.229 11(5)	0.234 92(5)	0.516 92(7)
O(1)	0.367 7(2)	0.721 1(2)	0.280 2(2)
O(2)	0.193 7(2)	0.535 3(1)	0.343 7(2)
O(3)	0.339 6(1)	0.333 7(1)	0.530 2(2)
N	0.415 6(2)	0.560 1(2)	0.369 5(2)
C(11)	0.279 4(2)	0.618 1(2)	0.552 2(3)
C(12)	0.155 5(2)	0.586 5(2)	0.615 5(3)
C(13)	0.131 8(3)	0.593 0(3)	0.754 5(4)
C(14)	0.230 0(3)	0.631 2(2)	0.832 8(3)
C(15)	0.353 5(3)	0.665 2(2)	0.766 4(3)
C(16)	0.379 4(3)	0.658 8(2)	0.627 6(3)
C(17)	0.203 5(4)	0.635 3(3)	0.986 2(4)
C(21)	0.184 1(2)	0.254 1(2)	0.336 6(3)
C(22)	0.279 3(3)	0.309 4(2)	0.217 2(3)
C(23)	0.249 7(3)	0.322 6(2)	0.076 0(3)
C(24)	0.123 0(3)	0.281 6(3)	0.058 0(3)
C(25)	0.027 7(3)	0.227 0(3)	0.175 1(3)
C(26)	0.057 2(2)	0.212 8(2)	0.314 4(3)
C(27)	0.352 8(5)	0.377 4(4)	-0.053 9(4)
C(31)	0.267 7(2)	0.116 3(2)	0.551 6(3)
C(32)	0.341 8(2)	0.102 1(2)	0.660 9(3)
C(33)	0.378 0(2)	0.014 0(2)	0.689 9(3)
C(34)	0.339 5(3)	-0.058 7(2)	0.604 4(4)
C(35)	0.266 9(3)	-0.045 3(2)	0.496 5(3)
C(36)	0.231 0(2)	0.041 9(2)	0.469 4(3)
C(37)	0.458 9(3)	0.000 8(3)	0.807 0(4)
C(41)	0.088 0(2)	0.203 4(2)	0.640 6(3)
C(42)	0.015 7(2)	0.100 8(2)	0.734 4(3)
C(43)	-0.094 0(2)	0.082 3(2)	0.825 7(3)
C(44)	-0.128 3(2)	0.169 6(2)	0.820 1(3)
C(45)	-0.057 0(2)	0.272 0(2)	0.729 4(3)
C(46)	-0.051 5(2)	0.290 3(2)	0.639 4(3)
C(47)	-0.173 3(3)	-0.029 8(3)	0.926 9(4)

In an entirely analogous reaction, triphenylphosphine reacted with hydrated chloramine-B to yield compound (4), whose composition was established by microanalysis as similar to that of (3). However the  $^{31}\text{P}$  n.m.r. spectrum in  $\text{CD}_2\text{Cl}_2$  solution showed no resonance which could be assigned to five-coordinate phosphorus, but only a single peak whose chemical shift was identical to that of  $\text{Ph}_3\text{PO}$ : indeed the  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{31}\text{P}$  spectra of compound (4) were all simply a summation of those of  $\text{Ph}_3\text{PO}$  and  $\text{C}_6\text{H}_5\text{SO}_2\text{NH}_2$  suggesting that, as for compound (3), compound (4) is a specific hydrogen-bonded adduct, here of  $\text{Ph}_3\text{PO}$  and  $\text{C}_6\text{H}_5\text{SO}_2\text{NH}_2$  in 1:1 molar ratio. X-Ray examination showed that crystals of (3)·0.5( $\text{C}_3\text{H}_6\text{O}$ ) and (4)·0.5( $\text{C}_3\text{H}_6\text{O}$ ) are isomorphous: the compounds (3) and (4) are thus isostructural.

It is interesting to note that while  $\text{Ph}_3\text{M}$  ( $\text{M} = \text{P}, \text{As}$ ) both react with hydrated chloramine-T to yield 2:3 hydrogen-bonded adducts,<sup>4</sup> ( $\text{Ph}_3\text{MO}$ )<sub>2</sub>( $\text{H}_2\text{NSO}_2\text{C}_6\text{H}_4\text{CH}_3$ )<sub>3</sub> (2),  $\text{Ph}_3\text{M}$  with hydrated chloramine-B give 1:1 adducts  $\text{Ph}_3\text{MO} \cdot \text{H}_2\text{NSO}_2\text{C}_6\text{H}_5$ . Such a change in composition as a result of a minor structural change in the sulphonamide component is repeated when minor change occurs in the  $\text{Ph}_3\text{M}$  portion. Mann<sup>1,2</sup> reported that the reactions of hydrated chloramine-T with triarylphosphines and triarylsines, other than  $\text{Ph}_3\text{P}$  or  $\text{Ph}_3\text{As}$ , all gave products formulated as  $\text{Ar}_3\text{M}(\text{OH})\text{NHSO}_2\text{C}_6\text{H}_3$ . Based upon the evidence described above, a more plausible formulation for all of these is  $\text{Ar}_3\text{MO} \cdot \text{H}_2\text{NSO}_2\text{C}_6\text{H}_4\text{CH}_3$ : we have demonstrated this for  $\text{Ar} = m\text{-CH}_3\text{C}_6\text{H}_4$  and  $\text{M} = \text{P}$ .

The reaction of ( $m\text{-CH}_3\text{C}_6\text{H}_4$ )<sub>3</sub>P with hydrated chloramine-T in ethanol gives a product (5), identical in composition and m.p. to that described by Mann.<sup>1</sup> The identical material can be obtained from ( $m\text{-CH}_3\text{C}_6\text{H}_4$ )<sub>3</sub>PO and  $\text{H}_2\text{NSO}_2\text{C}_6\text{H}_4\text{-}p\text{-CH}_3$ ,

**Table 4.** Molecular dimensions for (3)·0.5( $\text{C}_3\text{H}_6\text{O}$ ).

(a) Bond lengths/Å			
As—O(3)	1.655(1)	C(25)—C(26)	1.390(6)
As—C(21)	1.911(3)	C(31)—C(32)	1.379(4)
As—C(31)	1.908(3)	C(31)—C(36)	1.384(4)
As—C(41)	1.917(3)	C(32)—C(33)	1.400(6)
S—O(1)	1.426(2)	C(33)—C(34)	1.367(6)
S—O(2)	1.427(2)	C(34)—C(35)	1.359(5)
S—N	1.598(3)	C(35)—C(36)	1.378(5)
S—C(11)	1.770(3)	C(41)—C(42)	1.380(4)
C(11)—C(12)	1.378(3)	C(41)—C(46)	1.382(5)
C(11)—C(16)	1.382(5)	C(42)—C(43)	1.387(5)
C(12)—C(13)	1.378(5)	C(43)—C(44)	1.366(6)
C(13)—C(14)	1.359(6)	C(44)—C(45)	1.371(5)
C(14)—C(15)	1.358(4)	C(45)—C(46)	1.376(5)
C(15)—C(16)	1.376(5)	O(3)—N	2.848(3)
C(21)—C(22)	1.384(4)	O(3I) <sup>a</sup> —N	2.882(3)
C(21)—C(26)	1.381(3)	HN(1)—N	0.95
C(22)—C(23)	1.385(5)	HN(2)—N	0.95
C(23)—C(24)	1.361(4)	HN(1)—O(3)	1.90
C(24)—C(25)	1.375(6)	HN(2)—O(3I) <sup>a</sup>	1.93
(b) Bond angles/°			
O(3)—As—C(21)	109.5(1)	C(22)—C(23)—C(24)	120.2(4)
O(3)—As—C(31)	111.7(1)	C(23)—C(24)—C(25)	120.6(4)
O(3)—As—C(41)	112.5(1)	C(24)—C(25)—C(26)	120.0(3)
C(21)—As—C(31)	108.7(1)	C(21)—C(26)—C(25)	119.4(3)
C(21)—As—C(41)	107.4(1)	As—C(31)—C(32)	121.3(2)
C(31)—As—C(41)	106.9(1)	As—C(31)—C(36)	119.0(2)
O(1)—S—O(2)	119.3(2)	C(32)—C(31)—C(36)	119.8(3)
O(1)—S—N	108.3(2)	C(31)—C(32)—C(33)	119.1(3)
O(1)—S—C(11)	106.8(1)	C(32)—C(33)—C(34)	120.2(4)
O(2)—S—N	106.7(1)	C(33)—C(34)—C(35)	120.5(4)
O(2)—S—C(11)	107.0(2)	C(34)—C(35)—C(36)	120.3(3)
N—S—C(11)	108.3(2)	C(31)—C(36)—C(35)	120.1(3)
S—C(11)—C(12)	120.4(3)	As—C(41)—C(42)	121.2(3)
S—C(11)—C(16)	119.8(2)	As—C(41)—C(46)	118.3(2)
C(12)—C(11)—C(16)	119.8(3)	C(42)—C(41)—C(46)	120.5(3)
C(11)—C(12)—C(13)	119.5(4)	C(41)—C(42)—C(43)	119.0(3)
C(12)—C(13)—C(14)	120.6(3)	C(42)—C(43)—C(44)	120.4(3)
C(13)—C(14)—C(15)	119.9(4)	C(43)—C(44)—C(45)	120.3(3)
C(14)—C(15)—C(16)	121.1(4)	C(44)—C(45)—C(46)	120.2(4)
C(11)—C(16)—C(15)	119.1(3)	C(41)—C(46)—C(45)	119.6(3)
As—C(21)—C(22)	118.1(2)	O(3)—HN(1)—N	180
As—C(21)—C(26)	121.8(3)	O(3I) <sup>a</sup> —HN(2)—N	180
C(22)—C(21)—C(26)	120.1(3)	N—O(3)—N(1) <sup>a</sup>	80.5(1)
C(21)—C(22)—C(23)	119.7(2)	O(3)—N—O(3I) <sup>a</sup>	99.5(1)

<sup>a</sup> The roman numeral refers to the equivalent position, -x, -y, -z.

and has a composition corresponding to a 1:1 adduct of these components. The  $^{31}\text{P}$  n.m.r. spectrum of a solution in  $\text{CD}_2\text{Cl}_2$  shows only one resonance, identical with that of ( $m\text{-CH}_3\text{C}_6\text{H}_4$ )<sub>3</sub>PO: as with compound (4) the  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{31}\text{P}$  n.m.r. spectra of (5) are a simple summation of those of the two constituents in 1:1 molar ratio. The hydrogen-bonded character of (5) was also established by a single-crystal X-ray analysis (see below).

#### Crystal and Molecular Structures of (3)·0.5( $\text{C}_3\text{H}_6\text{O}$ ) and (5).—

The crystal structure of (3)·0.5( $\text{C}_3\text{H}_6\text{O}$ ) reveals a structural unit (Figure 2) containing two molecules of  $\text{Ph}_3\text{AsO}$  and two molecules of  $\text{PhSO}_2\text{NH}_2$  connected by hydrogen bonding as shown schematically below [formulae (3)–(5)]. The structure is shown in perspective in Figure 2. The array (3) lies across a centre of inversion so that the two oxygen atoms and the two nitrogen atoms of the hydrogen bonded system are strictly coplanar, with N...O distances of 2.848(3) and 2.882(3) Å. All of the hydrogen bonds are contained in this central  $\text{O}_2\text{N}_2$  core,



**Table 5.** Molecular dimensions for (5).

## (a) Bond lengths/Å

S—O(1)	1.430(2)	C(23)—C(24)	1.367(4)
S—O(2)	1.435(2)	C(23)—C(27)	1.496(5)
S—N	1.594(3)	C(24)—C(25)	1.365(4)
S—C(11)	1.762(3)	C(25)—C(26)	1.371(4)
P—O(3)	1.494(2)	C(31)—C(32)	1.391(4)
P—C(21)	1.803(3)	C(31)—C(36)	1.386(4)
P—C(31)	1.798(3)	C(32)—C(33)	1.389(4)
P—C(41)	1.794(2)	C(33)—C(34)	1.393(5)
C(11)—C(12)	1.368(3)	C(33)—C(37)	1.497(5)
C(11)—C(16)	1.379(4)	C(34)—C(35)	1.367(5)
C(12)—C(13)	1.372(5)	C(35)—C(36)	1.375(5)
C(13)—C(14)	1.376(4)	C(41)—C(42)	1.383(3)
C(14)—C(15)	1.369(4)	C(41)—C(46)	1.398(4)
C(14)—C(17)	1.500(5)	C(42)—C(43)	1.391(4)
C(15)—C(16)	1.375(4)	C(43)—C(44)	1.383(4)
C(21)—C(22)	1.379(3)	C(43)—C(47)	1.507(3)
C(21)—C(26)	1.381(3)	C(44)—C(45)	1.368(3)
C(22)—C(23)	1.389(4)	C(45)—C(46)	1.374(4)

## (b) Bond angles/°

O(1)—S—O(2)	119.2(1)	C(22)—C(23)—C(24)	118.3(3)
O(1)—S—N	107.2(1)	C(22)—C(23)—C(27)	121.4(3)
O(1)—S—C(11)	107.8(1)	C(24)—C(23)—C(27)	120.3(3)
O(2)—S—N	107.4(1)	C(23)—C(24)—C(25)	121.2(3)
O(2)—S—C(11)	106.6(1)	C(24)—C(25)—C(26)	120.4(3)
N—S—C(11)	108.4(1)	C(21)—C(26)—C(25)	119.9(2)
O(3)—P—C(21)	112.0(1)	P—C(31)—C(32)	118.4(2)
O(3)—P—C(31)	111.4(1)	P—C(31)—C(36)	122.3(2)
O(3)—P—C(41)	111.8(1)	C(32)—C(31)—C(36)	119.3(3)
C(21)—P—C(31)	106.6(1)	C(31)—C(32)—C(33)	121.1(3)
C(21)—P—C(41)	106.3(1)	C(32)—C(33)—C(34)	117.8(3)
C(31)—P—C(41)	108.4(1)	C(32)—C(33)—C(37)	120.3(3)
S—C(11)—C(12)	120.2(2)	C(34)—C(33)—C(37)	121.9(3)
S—C(11)—C(16)	120.3(2)	C(33)—C(34)—C(35)	121.5(3)
C(12)—C(11)—C(16)	119.5(3)	C(34)—C(35)—C(36)	120.2(3)
C(11)—C(12)—C(13)	119.8(3)	C(31)—C(36)—C(35)	120.1(3)
C(12)—C(13)—C(14)	121.7(3)	P—C(41)—C(42)	124.4(2)
C(13)—C(14)—C(15)	117.8(3)	P—C(41)—C(46)	116.2(2)
C(13)—C(14)—C(17)	121.5(3)	C(42)—C(41)—C(46)	119.4(2)
C(15)—C(14)—C(17)	120.7(3)	C(41)—C(42)—C(43)	121.1(3)
C(14)—C(15)—C(16)	121.5(3)	C(42)—C(43)—C(44)	117.9(2)
C(11)—C(16)—C(15)	119.7(3)	C(42)—C(43)—C(47)	121.0(3)
P—C(21)—C(22)	119.1(2)	C(44)—C(43)—C(47)	121.0(3)
P—C(21)—C(26)	121.9(2)	C(43)—C(44)—C(45)	121.8(3)
C(22)—C(21)—C(26)	119.0(2)	C(44)—C(45)—C(46)	120.2(3)
C(21)—C(22)—C(23)	121.2(3)	C(41)—C(46)—C(45)	119.6(2)

**Table 6.** Hydrogen bond dimensions for (5).

## Bond distances/Å

N...O(3)	2.882(2)
N...O(31)	2.931(2)
HN(1)...O(3)	1.93
HN(2)...O(31)	1.98

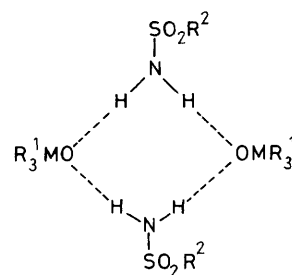
## Bond angles/°

O(31)...N...O(3)	101.9(1)
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The roman numeral I refers to the atom at equivalent position 1 - x, 1 - y, 1 - z.

and there are no close intermolecular contacts between different units of (3). Similarly, there are no close contacts between (3) and the disordered molecule of acetone of solvation.

The As—O distance refined to a value of 1.655(1) Å, typical of those found in adducts between Ph<sub>3</sub>AsO and weak acids.<sup>11–16</sup> and is little different from the values found for isolated arsine



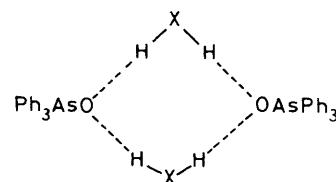
(3) R<sup>1</sup> = R<sup>2</sup> = Ph; M = As

(4) R<sup>1</sup> = R<sup>2</sup> = Ph; M = P

(5) R<sup>1</sup> = *m*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>; R<sup>2</sup> = *p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>; M = P

oxides.<sup>12,17</sup> The torsional angles, O—As—C—C, of the three independent phenyl rings in the Ph<sub>3</sub>AsO fragment are 26.4°, 35.5°, and 54.5°, whose mean, 38.3°, is close to the value of 40° deduced<sup>18</sup> from the analysis of the observed conformations of a wide range of Ph<sub>3</sub>PO derivatives.

It is of interest to compare the different patterns of hydrogen bonding which occur when Ph<sub>3</sub>AsO forms adducts with acids of different strengths. With very strong acids, the cation [(Ph<sub>3</sub>AsO)<sub>2</sub>H]<sup>+</sup> is formed, which contains very strong, and probably symmetrical hydrogen bonds O—H—O, characterised by O...O distances of 2.44 Å or less,<sup>19–21</sup> with the strong acids HX (X = Cl, Br) again strong, but necessarily asymmetric, hydrogen bonds O—H—X are formed, which were represented<sup>22</sup> as Ph<sub>3</sub>As—O<sup>1+</sup>—H<sup>0.5-</sup>—X<sup>0.5-</sup>. With medium weak acids, such as H<sub>2</sub>SeO<sub>3</sub><sup>14,15</sup> and phenols,<sup>13,16</sup> weak and very asymmetric hydrogen bonds AsO...H—OR are formed. In each of these categories, a single hydrogen bond is formed by each Ph<sub>3</sub>AsO fragment. With very weak acids, Ph<sub>3</sub>AsO forms more than one hydrogen bond: with water<sup>11,12</sup> or PhSO<sub>2</sub>NH<sub>2</sub>, as here, each Ph<sub>3</sub>AsO unit forms two hydrogen bonds, providing the centrosymmetric parallelogram structure (6), while with *p*-



(6) X = O or NSO<sub>2</sub>Ph

CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>NH<sub>2</sub>,<sup>4</sup> each Ph<sub>3</sub>AsO unit forms three equivalent hydrogen bonds, providing structure (2b).

The crystal structure of (5) reveals the same centrosymmetric unit as found for (3)·0.5(C<sub>3</sub>H<sub>6</sub>O) (Figure 3). The structure of (*m*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>)<sub>3</sub>PO does not appear to have been previously reported, although that of (*o*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>)<sub>3</sub>PO has:<sup>23</sup> the (*m*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>)<sub>3</sub>PO fragment in compound (5) adopts a conformation of approximate threefold symmetry with torsional angles O—P—C—C of 38.2°, 39.5°, and 50.5° (mean 42.7°), again close to the value of 40° deduced<sup>18</sup> to be the energy minimum. The P—O distance 1.494(2) Å is identical with those found in both Ph<sub>3</sub>PO and the 2:3 adduct (2a),<sup>4</sup> but is significantly longer than the mean 1.474(3) Å found<sup>23</sup> in (*o*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>)<sub>3</sub>PO. The two independent N...O distances in (5) are 2.882(2) and 2.931(2) Å: the corresponding distances in (2a) are<sup>4</sup> 2.946(3) and 2.957(3) Å, indicating that in (5) where there are only two hydrogen bonds formed by each Ar<sub>3</sub>PO fragment, as against three in (2a), the individual hydrogen bonds are marginally

stronger than those in (2a): on the other hand, the hydrogen bonds in (3) are shorter and stronger than those in (5).

The present structure determination for compound (5) means that all three classes of product<sup>1</sup> from the reactions of chloramine-T with triarylphosphines have now been structurally characterised: these comprise phosphinimines, such as  $\text{Ph}_3\text{P}=\text{NSO}_2\text{C}_6\text{H}_4\text{CH}_3$ <sup>24</sup> and the 2:3 and 1:1 adducts, typified by (2a) and (5), formed between  $\text{Ar}_3\text{PO}$  and  $\text{H}_2\text{NSO}_2\text{C}_6\text{H}_4\text{CH}_3$ .

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