The Reactions of Triphenylphosphine and Triphenylarsine with Chloramine-T, Sodium *N*-Chlorotoluene-*p*-sulphonamide: Crystal and Molecular Structure of Triphenylphosphine Oxide–Toluene-*p*-sulphonamide (2/3)

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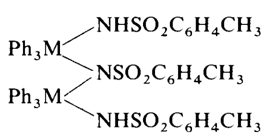
Triphenylphosphine and triphenylarsine react with chloramine-T, sodium *N*-chlorotoluene-*p*-sulphonamide, to yield products of composition $C_{57}H_{57}N_3O_8S_3M_2$ [(**1**; M = P) and (**2**; M = As)] and constitution $(Ph_3MO)_2(H_2NSO_2C_6H_4CH_3)_3$. Crystals of (**1**) are trigonal, space group *R*3, with a = 18.648(2), c = 27.527(5) Å, and Z = 6. The structure was refined from diffractometer data to an *R* value of 0.033. The structure consists of hydrogen-bonded aggregates of $(Ph_3PO)_2(H_2NSO_2C_6H_4CH_3)_3$, having overall 3-fold rotational symmetry, in which three sulphonamide groups link two Ph_3PO molecules *via* O ··· H–N(R)–H ··· O hydrogen bonding (R = $SO_2C_6H_4CH_3$), with P–O distances of 1.490(3) and 1.494(3) Å and N ··· O distances of 2.946(3) and 2.957(3) Å. Crystals of (**2**) are isomorphous with (**1**), having a = 18.813(3), c = 27.356(6) Å.

Many years ago, Mann and his colleagues studied the reactions of the sodium salt of chloramine-T, sodium *N*-chlorotoluene-*p*-sulphonamide trihydrate $CH_3C_6H_4SO_2NCl^-Na^+\cdot3H_2O$, with triphenylphosphine[1] and with triphenylarsine.[2,3] Amongst the product were two similar compounds, (**1**) from Ph_3P and (**2**) from Ph_3As, formulated on the basis of analytical data as $C_{57}H_{53}N_3O_6S_3M_2$ (M = P or As) for which the constitution (**3**) was suggested.[1,2]



(**3**) **a**; M = P
b; M = As

If substantiated, the constitution (**3**) would be of great interest as it contains two five-co-ordinate phosphorus [in (**3a**)] or arsenic atoms [in (**3b**)] bonded to the same nitrogen atom. Here we report a re-investigation of compounds (**1**) and (**2**), including an *X*-ray crystal-structure determination for (**1**).

Experimental

Samples of $Ph_3PNNNSO_2C_6H_4CH_3$ (δ_P + 28.4 p.p.m.) and $Ph_3PNSO_2C_6H_4CH_3$ (δ_P + 14.7) were prepared by literature methods.[4,5]

Compound (**1**) was prepared[1] by reaction of Ph_3P with $CH_3C_6H_4SO_2NCl^-Na^+\cdot3H_2O$ in ethanol: the product was repeatedly recrystallised from anhydrous benzene until its m.p. was unchanged at 138 °C (lit.,[1] 138 °C) {Found: C, 63.9; H, 5.4; N, 3.9. $C_{57}H_{57}N_3O_8P_2S_3$ requires C, 64.0; H, 5.4; N, 3.9; $C_{57}H_{53}N_3O_6P_2S_3$ [*cf.* ref. (1)] requires C, 66.2; H, 5.2; N, 4.1%}. $\delta_H(CD_2Cl_2)$ 2.38 (s, 9 H, CH_3), 5.70 (s, br, 6 H, NH_2), 7.21 and 7.72 (AB, *J* 8 Hz, 12 H, $-C_6H_4-$), and 7.4—7.6 (m, 30 H, C_6H_5), $\delta_P(CD_2Cl_2)$ +29.2 p.p.m.

Compound (**2**) was prepared[2] by reaction of Ph_3As with $CH_3C_6H_4SO_2NCl^-Na^+\cdot3H_2O$ in water: the product was repeatedly recrystallised from CH_2Cl_2 until its m.p. was unchanged at 176 °C (lit.,[2,3] 176 °C) {Found: C, 59.7; H, 4.9; N, 3.6. $C_{57}H_{57}As_2N_3O_8S_3$ requires C, 59.1; H, 5.0; N, 3.6. $C_{57}H_{53}As_2N_3O_6S_3$ [*cf.* refs (2) and (3)] requires: C, 61.0; H, 4.8; N, 3.8%}; $\delta_H(CD_2Cl_2)$ 2.39 (s, 9 H, CH_3), 5.98 (s, br, 6 H, NH_2), 7.24 and 7.75 (AB, *J* 8 Hz, 12 H, $-C_6H_4-$), and 7.4—7.8 (m, 30 H, C_6H_5).

X-Ray Crystallography.—Crystals of compounds (**1**) and (**2**) suitable for *X*-ray examination were grown from solutions in CH_2Cl_2. Prior to *X*-ray analysis, the crystals of (**1**) were re-examined (m.p., microanalysis, ^1H and ^{31}P n.m.r.) to ensure that they were of the same material as the crystals obtained earlier from benzene: they were identical in all respects.

Crystal Data.—Compound (**1**), $C_{57}H_{57}N_3O_8P_2S_3$, M = 1 070.25, trigonal, a = 18.648(2), c = 27.527(5) Å, V = 8 289.7 Å^3, space group *R*3 (no. 148), Z = 6, D_c = 1.29 g cm^{-3}, μ(Mo-K_α) = 2.4 cm^{-1}, λ = 0.710 73 Å, $F(000)$ = 3 372.

Compound (**2**), $C_{57}H_{57}As_2N_3O_8S_3$, M = 1 158.08, trigonal, a = 18.813(3), c = 27.356(6) Å, V = 8 387 Å^3, space-group *R*3 (no. 148), Z = 6, D_c = 1.38 g cm^{-3}, $F(000)$ = 3 588.

Data Collection for (**1**).—A crystal of dimensions 0.20 × 0.20 × 0.40 mm was used. Cell dimensions were determined by least-squares refinement using the setting angles of 25 reflections in the range 12° $\leqslant \theta \leqslant$ 14°. Intensity data were collected at 21 °C using a CAD4 diffractometer with graphite-monochromated Mo-K_α radiation, in the $\omega/2\theta$ scan mode; ω-scan rate 1—4° min^{-1}; ω-scan width = $(0.6 + 0.35 \tan\theta)$°; the maximum value of 2θ was 54°. 5 483 Reflections were measured, of which 3 486 were unique, and 1 512 had $F \geqslant 3\sigma(F)$. Lorentz and polarisation corrections, but no absorption corrections were made.

Structure Solution and Refinement for (**1**).—The structure was solved by direct methods, followed by difference Fourier syntheses. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms bound to carbon were included in the refinement, as riding atoms with d(C–H) = 0.95 Å, and B_{iso} = 5.0 Å^2. The methyl hydrogens appeared as a torus of electron density and 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

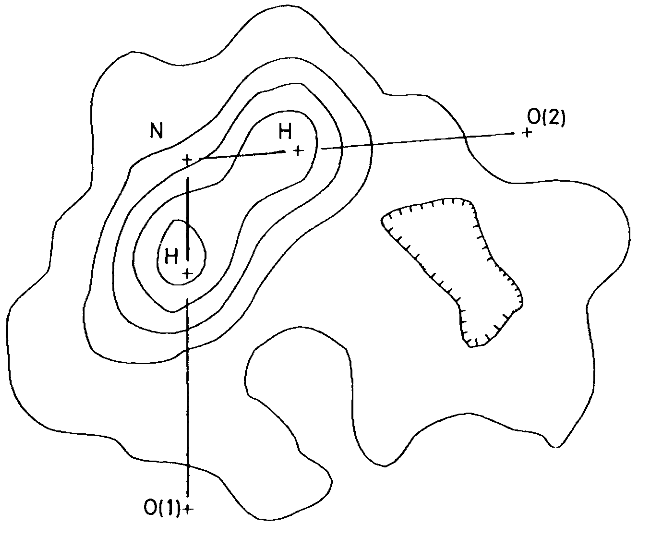


Figure 1. Section of difference Fourier map in the O(1), N, O(2) plane showing the location of the hydrogen atoms bound to nitrogen: successive contour levels represent electron density increments of 0.1 e Å^{-3}

Table 1. Positional parameters and their estimated standard deviations[a]

Atom	x	y	z	B/Å^2
S	0.182 42(4)	0.003 04(4)	0.249 35(3)	4.20(2)
P(1)	0	0	0.117 48(5)	3.11(2)
P(2)	0	0	0.382 74(5)	2.79(2)
O(1)	0	0	0.171 62(11)	3.62(6)
O(2)	0	0	0.328 46(11)	3.37(5)
O(11)	0.204 3(1)	−0.021 9(1)	0.293 57(8)	5.47(6)
O(12)	0.204 3(1)	−0.017 8(1)	0.204 03(8)	5.34(6)
N	0.084 0(1)	−0.037 7(1)	0.249 77(9)	4.19(6)
C(11)	−0.085 8(2)	0.007 0(2)	0.093 5(1)	3.47(7)
C(12)	−0.163 7(2)	−0.046 1(2)	0.111 5(1)	5.52(9)
C(13)	−0.231 5(2)	−0.042 1(2)	0.094 7(2)	6.7(1)
C(14)	−0.221 2(2)	0.016 2(2)	0.061 0(1)	6.6(1)
C(15)	−0.145 2(2)	0.068 4(2)	0.043 1(1)	6.3(1)
C(16)	−0.077 4(2)	0.064 0(2)	0.059 1(1)	4.90(8)
C(21)	−0.092 7(1)	−0.007 6(1)	0.407 0(1)	2.83(6)
C(22)	−0.091 5(1)	0.044 0(2)	0.443 3(1)	3.71(7)
C(23)	−0.165 1(2)	0.033 9(2)	0.461 9(1)	4.61(8)
C(24)	−0.239 2(2)	−0.026 8(2)	0.443 9(1)	4.65(8)
C(25)	−0.241 1(2)	−0.077 4(2)	0.407 5(1)	4.67(8)
C(26)	−0.168 4(2)	−0.068 3(2)	0.389 0(1)	3.93(7)
C(31)	0.228 4(2)	0.111 6(2)	0.251 4(1)	3.92(7)
C(32)	0.236 0(2)	0.151 2(2)	0.294 7(1)	5.10(9)
C(33)	0.274 9(2)	0.236 6(2)	0.296 1(1)	5.6(1)
C(34)	0.307 7(2)	0.283 8(2)	0.254 9(1)	5.07(9)
C(35)	0.297 8(2)	0.242 5(2)	0.212 0(1)	5.9(1)
C(36)	0.258 0(2)	0.157 6(2)	0.209 9(1)	5.29(9)
C(37)	0.353 8(2)	0.376 3(2)	0.257 6(2)	7.4(1)

[a] The co-ordinates of the entire complex are obtained from the above list by applying symmetry transformations $-y, x - y, z$ and $-x + y, -x, z$. Anisotropically refined atoms are given in the form of the isotropic-equivalent thermal parameter defined as:

$$4/3[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab\cos\gamma\, B_{12} + ac\cos\beta\, B_{13} + bc\cos\alpha\, B_{23}]$$

(Figure 1), were also included in the refinement, constrained to lie on the N···O directions, with d(N–H) = 0.95 Å and B_{iso} = 5.0 Å^2. A secondary extinction coefficient[6] refined to a value of 1.2 × 10^{-6}. The weighting scheme $w = 1/\sigma^2(F_o)$ gave final R and R_w values of 0.033 and 0.044, with 221 refined parameters.

Scattering factor data were taken from refs (7)—(9). All calculations were performed on a PDP-11/73 computer using SDP-Plus.[10]

Table 2. Molecular dimensions

(*a*) Bond lengths/Å

S–O(11)	1.433(2)	C(22)–C(23)	1.385(4)
S–O(12)	1.426(2)	C(23)–C(24)	1.369(3)
S–N	1.597(2)	C(24)–C(25)	1.363(5)
S–C(31)	1.760(3)	C(25)–C(26)	1.377(5)
P(1)–O(1)	1.490(3)	C(31)–C(32)	1.371(4)
P(1)–C(11)	1.795(3)	C(31)–C(36)	1.371(4)
P(2)–O(2)	1.494(3)	C(32)–C(33)	1.381(5)
P(2)–C(21)	1.791(3)	C(33)–C(34)	1.376(4)
C(11)–C(12)	1.377(4)	C(34)–C(35)	1.372(5)
C(11)–C(16)	1.373(4)	C(34)–C(37)	1.496(5)
C(12)–C(13)	1.383(6)	C(35)–C(36)	1.373(4)
C(13)–C(14)	1.368(6)	N···O(1)	2.946(3)
C(14)–C(15)	1.349(4)	N···O(2)	2.957(3)
C(15)–C(16)	1.379(5)	H(1)···O(1)	2.00
C(21)–C(22)	1.382(4)	H(2)···O(2)	2.01
C(21)–C(26)	1.385(3)		

(*b*) Bond angles (°)

O(11)–S–O(12)	119.2(2)	C(14)–C(15)–C(16)	120.2(3)
O(11)–S–N	106.6(1)	C(11)–C(16)–C(15)	120.8(3)
O(11)–S–C(31)	106.9(1)	P(2)–C(21)–C(22)	122.4(2)
O(12)–S–N	107.1(1)	P(2)–C(21)–C(26)	118.7(2)
O(12)–S–C(31)	107.5(1)	C(22)–C(21)–C(26)	118.9(3)
N–S–C(31)	109.2(2)	C(21)–C(22)–C(23)	120.2(2)
O(1)–P(1)–C(11)	111.6(1)	C(22)–C(23)–C(24)	120.0(3)
C(11)–P(1)–C(11)[a]	107.3(1)	C(23)–C(24)–C(25)	120.2(3)
O(2)–P(2)–C(21)	111.84(9)	C(24)–C(25)–C(26)	120.3(2)
C(21)–P(2)–C(21)[a]	107.0(1)	C(21)–C(26)–C(25)	120.4(3)
P(1)–O(1)···N	136.9(1)	S–C(31)–C(32)	120.5(2)
N···O(1)···N[a]	72.6(1)	S–C(31)–C(36)	120.3(2)
P(2)–O(2)···N	137.1(1)	C(32)–C(31)–C(36)	119.2(3)
N···O(2)···N[a]	72.2(1)	C(31)–C(32)–C(33)	119.9(3)
P(1)–C(11)–C(12)	118.2(3)	C(32)–C(33)–C(34)	121.6(3)
P(1)–C(11)–C(16)	123.3(2)	C(33)–C(34)–C(35)	117.3(3)
C(12)–C(11)–C(16)	118.5(3)	C(33)–C(34)–C(37)	120.8(3)
C(11)–C(12)–C(13)	120.3(3)	C(35)–C(34)–C(37)	121.9(3)
C(12)–C(13)–C(14)	120.0(3)	C(34)–C(35)–C(36)	121.9(3)
C(13)–C(14)–C(15)	120.1(4)	C(31)–C(36)–C(35)	120.2(3)

[a] Refers to equivalent position $-y, x - y, z$.

Final refined atom co-ordinates are given in Table 1, and bond lengths and angles in Table 2. A perspective view, showing the atom-numbering scheme, is given in Figure 2.

Tables of hydrogen atom co-ordinates, anisotropic temperature factors, and torsional angles have been deposited at the Cambridge Crystallographic Data Centre.*

Results and Discussion

Compound (**1**) was readily prepared from triphenylphosphine and the hydrated sodium salt of chloramine-T, $CH_3C_6H_4SO_2NCl^-Na^+\cdot3H_2O$, under a wide range of conditions. The same product was always obtained, with a melting point identical with that found by Mann[1] for the product obtained from similar reactions. There is no doubt, on the basis of the original evidence,[1] that the compound obtained here is the same as that recorded by Mann.[1]

Microanalysis of (**1**), however, was repeatedly consistent with an empirical formula $C_{57}H_{57}N_3O_8P_2S_3$, rather than with the formula $C_{57}H_{53}N_3O_6P_2S_3$ proposed by Mann:[1] these

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* For details of the deposition of material at the Cambridge Crystallographic Data Centre see 'Instructions for Authors (1988), *J. Chem. Soc., Perkin Trans. 2*, 1988, issue 1, p. xviii, paragraph 5.6.3.

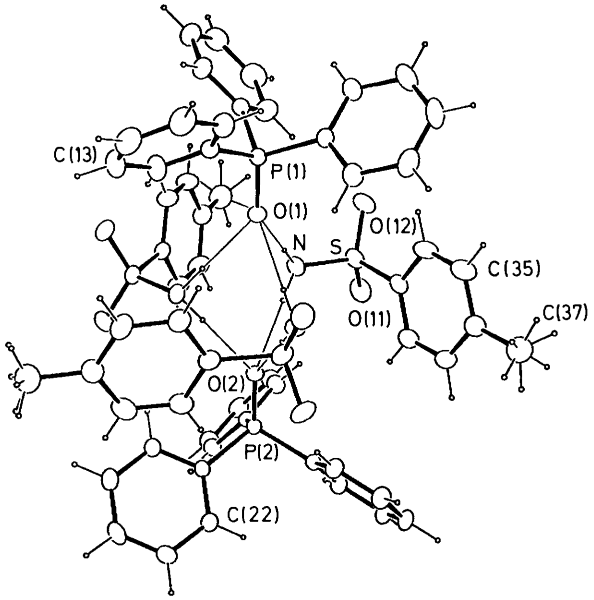


Figure 2. Perspective view of the molecule of (1) showing the atom-numbering scheme.

formulations differ by H_4O_2. In solution in CD_2Cl_2, the ^{31}P n.m.r. spectrum showed no signal which could be assigned to the five-co-ordinate phosphorus atom expected from the molecular structure (3),[1] but rather showed only a single resonance at δ_P +29.2 (relative to 85% H_3PO_4), identical with the chemical shift of Ph_3PO, also in CD_2Cl_2. At the same time, the ^1H n.m.r. spectrum of (1), in CD_2Cl_2 showed clear evidence of NH_2 groups, as a broad singlet at δ 5.70, with an integral corresponding to one NH_2 group per $CH_3C_6H_4$ group: these data suggest the presence of Ph_3PO and $CH_3C_6H_4SO_2NH_2$ fragments in CD_2Cl_2 solution. In fact, the ^1H n.m.r. spectrum of (1) in CD_2Cl_2 was simply a summation of the individual spectra of Ph_3PO and $CH_3C_6H_4SO_2NH_2$; this ^1H n.m.r. spectrum was found to be identical in all aspects with that of a mixture of Ph_3PO and $CH_3C_6H_4SO_2NH_2$, in a molar ratio of 2:3, prepared by grinding the anhydrous solids together, without heating, before dissolution.

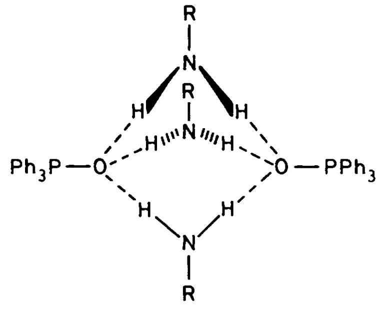
Despite the identity of the solution n.m.r. spectra of (1) and a 2:3 molar mixture of Ph_3PO and $CH_3H_4SO_2NH_2$, the infra-red spectra of crystalline samples (measured in Nujol mulls) of (1) and of a 2:3 mixture of Ph_3PO and $CH_3C_6H_4SO_2NH_2$, were different, especially in the NH stretching region, although the spectrum of the solid mixture was itself simply the summation of the spectra of the individual components.

These spectral observations can be explained if (1) is a specific compound containing a distinctive hydrogen-bonded array of Ph_3PO and $CH_3C_6H_4SO_2NH_2$ molecules in a molar ratio of 2:3. Such hydrogen-bonding in the solid state would provide a solid-state infra-red spectrum different from the sum of the component spectra, but upon dissolution would be disrupted to give unperturbed Ph_3PO and $CH_3C_6H_4SO_2NH_2$, so providing the observed solution n.m.r. spectra. These deductions concerning the nature of (1), based upon analytical and spectroscopic evidence, were fully substantiated by a single-crystal *X*-ray analysis of (1) (see below).

The arsenic compound (2) was similarly prepared according to the published procedure[2,3] and had a melting point identical with that recorded by Mann.[2,3] Its microanalysis was more consistent with the formula $C_{57}H_{57}As_2N_3O_8S_3$ than with $C_{57}H_{53}As_2N_3O_6S_3$, although not definitive: however, the ^1H n.m.r. spectrum in CD_2Cl_2 solution was a simple summation of the spectra of Ph_3AsO and $CH_3C_6H_4SO_2NH_2$ in a molar ratio of 2:3. *X*-Ray examination of crystals of (2) showed them to be isomorphous with crystals of (1). Compounds (1) and (2) are thus clearly isostructural.

It is interesting to note that the calculated analytical figures for $C_{57}H_{57}M_2N_3O_8S_3$ and $C_{57}H_{53}M_2N_3O_6S_3$, for both M = As and P, differ by more than the usual limits of acceptable error only for carbon and oxygen. Mann recorded[1–3] that both compounds (1) and (2) gave consistently low analytical values for carbon: he quoted no figure for (1),[3] but for (2) gave[2] a value of 58.76% for carbon, which is in fact much closer to the value (59.1%) required by the formulation $C_{57}H_{57}As_2N_3O_8S_3$ established here than to that (61.0%) required by his preferred formulation $C_{57}H_{53}As_2N_3O_6S_3$. It is not easy to see why these incorrect formulations for (1) and (2), which are still quoted in contemporary literature,[11] were chosen, particularly since both (1) and (2) can be produced by the direct interaction in solution of $CH_3C_6H_4SO_2NH_2$ and either Ph_3PO [to form (1)],[3] or Ph_3AsO [to form (2)].[2]

Crystal and Molecular Structure of (1).—The crystal structure of (1) both confirms the composition $C_{57}H_{57}N_3O_8P_2S_3$, and reveals a structural unit consisting of two molecules of Ph_3PO and three molecules of $CH_3C_6H_4SO_2NH_2$ connected by hydrogen-bonds as indicated schematically in (4): the structure is shown in perspective in Figure 2. The phosphorus and oxygen atoms lie on a crystallographic 3-fold symmetry axis; the whole array (4) thus has exact 3-fold rotational symmetry and it also has approximate 3/*m* symmetry. All of the hydrogen bonds are contained within the central O_2N_3 core of the array (4), the exterior of which consists only of phenyl and 4-methylphenyl groups: hence there are no close intermolecular contacts, other than the interior hydrogen bonds, and the forces between the units (4) correspond to normal van der Waals interactions.



(4) R = $CH_3C_6H_4SO_2$

Each oxygen atom of the Ph_3PO fragments forms three essentially linear hydrogen bonds of type O···H–N (see Figure 1), with N–H···O distances of 2.946(3) Å which by symmetry are equivalent. If it is assumed that, as usual, the oxygen atom requires a lone pair of electrons in order to act as the proton acceptor in each hydrogen bond O···H–N, then this can only be achieved if the Ph_3PO fragments exist substantially in the dipolar form $Ph_3P^+–O^-$ rather than in the doubly bonded form $Ph_3P=O$. Despite this, the PO distances [1.490(3) and 1.494(3) Å], are the same, within experimental error, as those in Ph_3PO itself[12] and in the adducts of Ph_3PO with HF,[13] $(CO_2H)_2$,[14] and C_6F_5OH,[15] in each of which adducts the oxygen of the Ph_3PO forms only a single hydrogen bond. In all of these hydrogen bonds, P–O···H–X (X = N, O, or F) the O···H distance is long and the H–X distance short. Only in the presence of hydrogen bonds of type P–O–H···X, as found for example in Ph_3POHCl,[16] is the PO distance significantly longer, 1.517(2) Å in Ph_3POHCl,[16] than in Ph_3PO, 1.493(2) Å.[12]

The two independent molecules of Ph_3PO, each having 3-fold rotational symmetry, exhibit torsional angles O–P–C–C of 129.7° ($\equiv -50.3°$) and 48.3° respectively: the conformation of the Ph_3PO fragments observed here is thus very close to the mininum-emergy conformation (3-fold symmetry, torsional angle = 40°) deduced[17] from analysis of the observed conformations of a wide range of Ph_3PO derivatives.

The structure of the $CH_3C_6H_4SO_2NH_2$ fragment does not appear to have been determined, although structures of its derivation are plentiful. That of $C_6H_5SO_2NH_2$ has been determined[18] as a complex with the crown ether 18-crown-6: these two sulphonamide structures are very similar, and differ significantly only in the S–C bond distance: 1.760(3) Å found here in the toluenesulphonamide and 1.782(3) Å found[18] in the benzenesulphonamide.

The analytical and spectroscopic data for (**1**) and (**2**) on the one hand, and the *X*-ray analysis of (**1**) on the other, together with the isomorphous character of (**1**) and (**2**) show definitely that the constitution (**3**) is an inappropriate description for the products of the reactions between Ph_3P or Ph_3As and chloramine-T. Alternative approaches to structure (**3**) (M = P) involving reactions of $CH_3C_6H_4SO_2NH_2$ with either $Ph_3P{=}NSO_2C_6H_4CH_3$ or $Ph_3P{=}NNNSO_2C_6H_4CH_3$ have so far proved to be unsuccessful: in every case the reaction products are simple mixtures of $CH_3C_6H_4SO_2NH_2$ and $Ph_3P{=}NSO_2C_6H_4CH_3$ showing no evidence of any intermolecular interaction, even in the solid state.

Acknowledgements

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