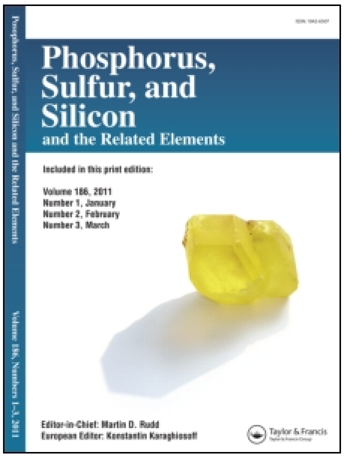

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ORGANOSULPHUR PHOSPHORUS ACID COMPOUNDS. PART 5.† BIPHENYL-4,4′-DIPHOSPHONO-2,6,2′-TRISULPHONIC ACID

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Biphenyl-4,4′-diphosphono-2,6,2′-trisulphonic acid is obtained in the reaction of 4,4′-biphenyldiphosphonic acid and SO_3 in the absence of solvent at 270°C under autogeneous pressure. The product is isolated from the reaction mixture as barium salt and obtained in free acid form by ion-exchange. Its structure is established by ^1H, ^{31}P and ^{13}C n.m.r. spectroscopy.

Key words: Sulphonation; biphenyldiphosphono-polysulphonic acids; biphenyl-4,4′-diphosphono-2,6,2′-trisulphonic acid; organosulphur phosphorus polyacids.

INTRODUCTION

Biphenyldiphosphono-polysulphonic acids, $H_2O_3PC_6H_{4-n}(SO_3H)_nC_6H_{4-n'}\text{-}(SO_3H)_{n'}PO_3H_2$ (**I**), are not well known. Yet, these compounds are desirable intermediates for the preparation of pillared biphenylphosphonates with improved ion-exchanging capacity to use in chemical separation and acid catalysis.[5]

So far, disulphonated zirconium phosphate 4,4′-biphenyldiphosphonate, $Zr(HPO_4)[O_3PC_6H_3(SO_3H)\text{-}C_6H_3(SO_3H)PO_3]_{0.5}$ (**II**), is the only known example of a product containing structure **I** ($n = n' = 1$). The diphosphonate (**II**) was obtained from zirconium phosphate 4,4′-biphenyldiphosphonate and fuming sulphuric acid at 60°C. The empirical formula was derived on the basis of its titration curve and of the weight reduction at 225°C.[6]

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†Previous work: Part I,[1] Part II,[2] Part III,[3] Part IV.[4]

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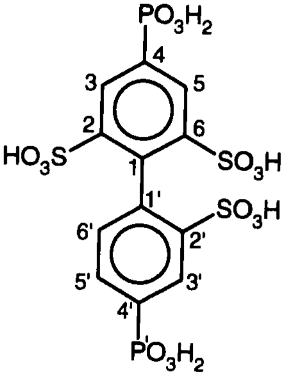
The fact that monosulphonation at the phenyl ring deactivated by the —PO_3H_2 substituent could occur under relatively mild conditions was confirmed by us in the reaction of benzenephosphonic acid and SO_3 to benzenephosphono-3-sulphonic acid.[1] Disulphonation to benzenephosphono-3,5-disulphonic acid[3] however required very drastic conditions: i.e. 5–13 moles excess of liquid SO_3 as solvent-reagent at 180–240°C for 13–35 days. The synthesis of biphenyl-4,4′-diphosphono-2,6,2′-trisulphonic acid (**III**) is now reported hereinafter. To our knowledge, this is the first example of a compound with structure **III** being isolated and characterized in free acid form.

RESULTS AND DISCUSSION

Sulphonation of 4,4′-biphenyldiphosphonic acid in liquid SO_3 as solvent-reagent at 270°C (see Experimental) yielded the trisulphonic acid (III).



III

The proposed structure for **III** was in agreement with the elemental analytical data and with the product n.m.r. spectra (Tables I and II): five one-proton resonance absorptions in the ^1H spectrum, five methine and seven quaternary carbon resonances in the ^{13}C spectrum, and two ^{31}P signals of equal intensities. The fact that, in 4,4′-biphenyldisphonic acid, one phenyl ring is disulphonated and the other is only monosulphonated may indicate that further substitution in the latter is sterically hindered.

Thermal analyses showed for the product 15% weight loss between 80 and 150°C (corresponding to loss of one out of three SO_3 moles), no further weight loss up to 300°C, and more weight loss starting above this temperature. No melting could be assessed either by DTA scans and by visual observation in a Büchi melting-point apparatus.

The biphenyl-4,4′-diphosphono-2,6,2′-trisulphonic acid structure was the only one out of all other possible isomeric structures to fit the splitting pattern of the ^1H n.m.r. spectrum recorded in D_2O (Table I): i.e. four resonance absorptions which exhibited splitting due to PH coupling over three bonds (^3J = 10.2–12.3 Hz) and two absorptions which showed ortho HH coupling (J = 6.0–6.9 Hz). Splitting of ^1H resonance absorptions due to PH coupling was assessed from ^{31}P

TABLE I

^1H and ^{31}P magnetic resonance data[a] for biphenyl-4,4′-diphosphono-2,6,2′-trisulphonic acid (**III**), and for benzenephosphono-3-sulphonic acid (**IV**)[b] and benzenephosphono-3,5-disulphonic acid (**V**):[c] chemical shifts (δ, p.p.m.) and coupling constants (*J*, Hz) in D_2O, CD_3OD (Mtl) and $(CD_3)_2SO$ (DMSO)

		Protons[e] in **III**					^{31}P nuclei[f] in **III**	
Slv[d]	δ or *J*	H5′	H3′	H3	H5	H6′	P	P′
D_2O	δ	7.99	8.12	8.22	8.47	8.88		12.0
D_2O	*J*(PH)	12.0	12.3	10.2	11.5	n.m.[g]		
D_2O	*J*(HH)	6.0				6.9		
Mtl	δ	8.17[h]	8.22[h]	8.27[h]	8.80	9.38	9.9[i]	10.5[l]
Mtl	*J*(PH)	n.m.[g]	n.m.[g]	n.m.[g]	9.4			
Mtl	*J*(HH)	n.m.[g]				5.50		
DMSO	δ	8.06[m]	8.06[m]	8.06[m]	8.58	9.39	10.1	10.6
DMSO	*J*(PH)	n.m.[g]	n.m.[g]	n.m.[g]	11.5			
DMSO	*J*(HH)	n.m.[g]				5.4		
		Protons[e] in **IV**					^{31}P nucleus in **IV**	
		H6	H2			H5		P′
D_2O	δ	7.75	7.96			7.48		14.9
D_2O	*J*(PH)	13.0	13.7					
D_2O	*J*(HH)					7.6		
		Protons[e] in **V**					^{32}P nucleus in **V**	
				H6	H2		P	
D_2O	δ			8.03	8.03		12.3	
D_2O	*J*(PH)			15.1	15.1			

[a] Obtained at 200.1 MHz (^1H) and at 80.961 MHz (^{31}P) by XL 200 Varian spectrometer; chemical shifts relative to external TMS for ^1H and to external 85% w/w H_3PO_4 for ^{31}P.

[b] Data from Reference 1.

[c] Unpublished data by the authors.

[d] Solvent (Slv).

[e] Protons numbered as bonded carbons in structure drawing; protons in **IV** and **V** are reported in the same column of the proton having the same position relatively to the acid substituents in **III**.

[f] For **III**, phosphorus nuclei are identified as P in the disulphonated ring and P′ in the monosulphonated ring; in D_2O one broad band for both P and P′ is observed, with width at half height = 202 Hz; for convenience, phosphorus nuclei in **IV** and **V** are identified as the corresponding nuclei in **III**.

[g] Not measured due to signal broadness.

[h] Broad band exhibiting three absorption maxima.

[i] Coupled with H3 and H5 proton signals in the two-dimensional $^1H—^{31}P$ correlation spectrum.

[l] Coupled with H3′ and H5′ proton signals in the two-dimensional $^1H—^{31}P$ correlation spectrum.

[m] Broad band exhibiting one absorption maximum.

TABLE II

^{13}C magnetic resonance data[a] for compounds **III**, **IV** and **V** in D_2O: chemical shift (δ, p.p.m.)[b] value, with subscript indicating signal relative intensity[c] for compound **III**; PC coupling constant (*J*) in Hz

δ or *J*	Carbons[d] in disulphonated phenyl ring of **III**					
	C6	C2	C4	C1	C3	C5
δ	142.8_2	141.4_2	138.7_1	133.4_3	138.7_6	129.2_6
J	13.4	15.6	177	n.o.[e]	12.2	12.2
	Carbons[d] in **V**					
	C3	C5	C1	C4	C6	C2
δ	143.7	143.7	132.5	125.8	129.8	129.8
J	14.8	14.8	182	n.o.[e]	10.9	10.9
	Carbons[d] in monosulphonated phenyl ring of **III**					
	C5′	C2′	C6′	C4′	C1′	C3′
δ	139.8_6	139.2_2	132.1_6	134.2_1	134.5_3	126.7_6
J	10.7	16.2	13.1	182	n.o.[e]	10.9
	Carbons[d] in **IV**					
	C6	C3	C5	C1	C4	C2
δ	133.4	142.8	129.6	132.2	128.9	127.3
J	10.3	14.8	14.5	132	2.6	12.0

[a] Obtained at 50.288 MHz by varian XL 200 spectrometer; coupling constants for **III** were measured both in the ^1H coupled and decoupled ^{13}C spectra. In the ^1H coupled ^{13}C spectrum HC coupling constants were as follows: $^1J_{HC}$ for C3, C5, C3′, C5′ = 166–173 Hz, $^3J_{HC}$ for C3, C5, C3′, C5′, C2′ = 7.6 Hz; $^3J_{HC}$ for C1 and C1′ were not measured, but the band width at half height was 15–16 Hz; C1 and C6 signals remained unchanged upon ^1H coupling and decoupling. C4 and C4′ signals were low and broad in the ^1H decoupled ^{13}C spectrum and could not be picked out in the ^1H coupled spectrum. N.m.r. data reported in the Table were measured in the ^1H decoupled ^{13}C spectrum.

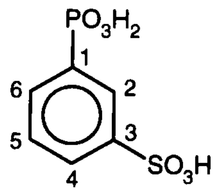
[b] Relative to external TMS.

[c] For **III**, C4 and C4′ signals were significantly broader than C6, C2 and C2′.

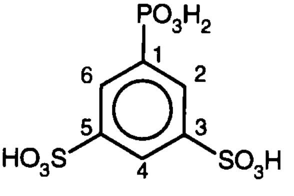
[d] Carbons numbered as in structure drawing; carbons in **IV** and **V** are reported in the same column as the carbon having the same position relatively to the carbons bonded to phosphorus and sulphur in **III**.

[e] Not observed.

coupled and decoupled ^1H spectra. Resonance absorptions were generally broad, with resolution depending on the solvent. ^1H and ^{13}C spectra were better resolved in D_2O than in CD_3OD or in $(CD_3)_2SO$; ^{31}P spectra, on the contrary, were better resolved in CD_3OD or in $(CD_3)_2SO$ (two sharp ^{31}P signals) than in D_2O (one broad signal). Specific coupling between H3 or H5 with the phosphorus in the disulphonated ring (P), and between H3′ or H5′ with the other phosphorus (P′), was thus assessed by two-dimensional ^{31}P—^1H correlation spectroscopy in CD_3OD. The order of ^{31}P chemical shifts (δP′ > δP) in methanol and in dimethylsulfoxide is the same as observed for benzenephosphono-3-sulphonic acid (**IV**) and benzenephosphono-3,5-disulphonic acid (**V**) in D_2O. Assignments of ^1H resonance absorptions in CD_3OD were performed following the order of the chemical shifts assigned in D_2O. Assignments of ^1H and ^{13}C signals (Table I) in D_2O were based on the values of the coupling constants and of the chemical shifts observed for compound **III**, and on the comparison with the n.m.r. data previously reported for the acids (**IV**)[1]



IV



V

and (V).[3] These compounds formally represent the two phenyl rings in **III**, except for the carbons in para to the —PO_3H_2 which are bonded to each other in compound **III**. It may be observed that for **III** the differences between proton chemical shifts are larger than in **IV** and in **V**; also, the most deshielded proton in compound **III** is the proton (H6′) in meta to the SO_3H group of the monosulphonated ring, whereas in **IV** the same proton (H5) is the most shielded.[1] Another significant difference is the inequalities of chemical shift which are observed in **III**, i.e. $\delta H_3 \neq \delta H5$, $\delta C3 \neq \delta C5$ and $\delta C2 \neq \delta C6$, and not in compound **V** for the pairs of nuclei in the corresponding relative positions (i.e. $\delta H6 = \delta H2$, $\delta C6 = \delta C2$ and $\delta C5 = \delta C3$). A possible explanation for observing a signal pattern contrary to symmetry considerations may be that in **III** the electron-withdrawing effects of the two —SO_3H substituents bonded at C2 and C6 were not equal; the —SO_3H groups in the symmetrically substituted ring could differ in polarization or ionization state, with one sulphonic function being possibly involved in H-bonding or ionic interactions with the third —SO_3 function at C2′. Other effects may derive from the reciprocal orientation of the two phenyl rings. The above mentioned dependence of the spectral pattern resolution on the nature of the solvent indicates that solute-solvent interactions are also significant for the state of ionization and/or solution conformation of compound **III**. Whereas these aspects may offer further scope for specific investigation, the results of this work confirm previous findings[3,4] that aromatic sulphonation in liquid SO_3 as solvent-reagent is an easy synthetic tool to obtain organosulphur phosphorus polyacids.

EXPERIMENTAL

Analyses and Physical Measurements. Elemental carbon analyses were performed by the microanalytical laboratory of the Dipartimento di Chimica Organica e Industriale dell'Universitá di Milano. Phosphorus was analyzed spectrophotometrically as molybdate, after mineralization of the sample with concentrated HNO_3.[8] Sulphur was determined gravimetrically as $BaSO_4$, after incineration of the sample with Eska mixture.[9] Thermal analyses were performed in a Mettler TA 2000 C instrument under N_2 (100 ml/min) and scanning at 10°C/min. N.m.r. spectra were recorded under conditions reported in Tables I and II.

Preparation of biphenyl-4,4'-diphosphono-2,6,2'-trisulphonic acid (**III**). Authentic[7] 4,4'-biphenyldiphosphonic acid (14.0 g) was caused to react with freshly distilled[1] SO_3 (19.6 ml) in a sealed glass bottle at 270°C for 25 days. Afterwards, most unreacted SO_3 was eliminated by distillation and any residual amount was precipitated as $BaSO_4$ by addition of water, aqueous HCl and excess $BaCl_2$ to the reaction mixture. Concentration of the sulfate free solution in a rotary vacuum evaporator allowed to precipitate excess $BaCl_2$ (6.8 g) and, successively, a second fraction of organic barium salt (22.9 g). This latter material was dissolved in water, after addition of 5% w/w aqueous HCl. The solution was then ion-exchanged on Dowex 50W-X8, H^+ form resin to remove barium ions. Evaporation of the eluate and drying of the solid residue over silica gel at room temperature for 10 weeks gave 9.0 g of product **III**, $C_{12}H_{12}O_{15}P_2S_3$ (554.34), found: C 26.0, P 10.7, S 17.2% w/w; theor.: C 26.0, P 11.2, S 17.4% w/w.

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