Organosulphur Phosphorus Acid Compounds. Part 1. *m*-Sulphophenylphosphonic Acid

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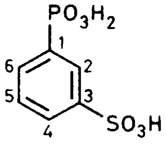
m-Sulphophenylphosphonic acid (**2**) is a high-temperature-melting (164 °C) and stable solid which has been synthesized from phenylphosphonic acid (**1**) and sulphur trioxide in the absence of solvent. Fractional precipitation of barium salts followed by ion exchange is a suitable procedure to isolate (**2**) from the reaction medium. The product has been characterized by i.r. and ^{31}P, ^{1}H, and ^{13}C n.m.r. spectroscopy.

To our knowledge the isolation of pure sulphophenylphosphonic acid has never been reported in the literature. Its formation has been previously inferred by interpretation of ^{31}P n.m.r. spectra of phenylphosphonic acid solutions in an excess of oleum.[1] Yang and Clearfield[2] obtained it as the mixed zirconium salt $Zr(HPO_4)_{1.1}(O_3PC_6H_4SO_3H)_{0.9}$, by sulphonation of zirconium phenylphosphonate phosphite with fuming sulphuric acid at 60 °C. No direct evidence of the aromatic substitution structure was given in both cases. The present investigation on the sulphonation of phenylphosphonic acid (**1**) to *m*-sulphophenylphosphonic acid (**2**) has been undertaken, in relation to previous work on the interaction of acid compounds and SO_3,[3-5] and in order to provide intermediates with polyfunctional acid groups[6] suitable for many uses in the fields of metal ion exchange, co-ordination chemistry, and Brønsted acid catalysis.[7,8]



(**2**)

Experimental

Phenylphosphonic acid (purity ⩾98%) was purchased from Fluka and used without further purification. All other reagents were C. Erba RPE products. Liquid SO_2 and freshly distilled SO_3 were obtained and handled as previously reported.[3-5] Sulphonation reactions were performed under N_2 with magnetic stirring.

Reaction in Liquid SO_2 *at a* SO_3:(**1**) *Mole Ratio of* 1.2:1.—Compound (**1**) (4.03 g, 25.5 mmol) was suspended in liquid SO_2 (40 cm^3) at −60 °C and the required amount of SO_3 added. Most (**1**) dissolves at this temperature. At −20 °C a precipitate formed. On raising the temperature under autogenous pressure, the precipitate turned into a viscous liquid (5 cm^3) at room temperature which contains the reagents and separates as a lower layer from the liquid SO_2 phase (*ca.* 40 cm^3). Two reactions were carried out under these conditions by maintaining the system at room temperature for 2 and 24 h respectively. At the end of the reaction the system was cooled to −30 °C and D_2O (1.5 cm^3) added. Upon evaporation of SO_2 at room temperature, the solution was either analysed by ^{31}P n.m.r. spectroscopy or worked up as described below to isolate the product.

Reaction in 1,2-*Dichloroethane at* SO_3:(**1**) *Mole Ratios of* 1.2 *and* 2.4:1.—At SO_3:(**1**) mole ratio 2.4:1, compound (**1**) (20.16 g, 127 mmol) in 1,2-dichloroethane (100 cm^3) was added with SO_3 (12.5 cm^3, 300 mmol) at 0 °C to yield a viscous liquid phase which does not mix with the solvent. The system was refluxed for 14 h whereupon the lower viscous layer was sampled and analysed by i.r. spectroscopy between AgCl plates. Complete conversion of compound (**1**) into (**2**) was shown by the absence of the band at 750 cm^{-1} typical of (**1**) and the presence of the band at 800 cm^{-1} typical of (**2**). At 1.2:1 mole ratio, compound (**1**) (20.16 g, 127 mmol) in 1,2-dichloroethane (100 cm^3) was added with SO_3 (6.2 cm^3, 150 mmol) and refluxed for 8 h. The i.r. spectra showed that (**1**) had not been sulphonated significantly.

Reaction in the Absence of Diluent at SO_3:(**1**) *Mole Ratio of* 1.2 *and* 2.4:1.—Compound (**1**) (20.2 g, 128 mmol) was added with the required amount of SO_3 to yield a viscous liquid phase, which was kept at room temperature or heated to 180 °C (Table 1) for several days. During this time, samples of the reaction mixtures were taken and either quenched with D_2O for ^{31}P n.m.r. analysis or placed as such (without any further treatment) between AgCl plates for analysis by i.r. spectroscopy. At the end of the reaction water was added to the whole reaction mixture to obtain a homogeneous aqueous solution, which was further worked up as described below.

Work up of the Reaction Mixture and Product Isolation.—The viscous phase from the sulphonation reaction (eventually separated from the diluent) was dissolved in water (200 cm^3), and concentrated HCl (10—20 cm^3) added. The solution was boiled and a 15% solution of $BaCl_2{\cdot}2H_2O$ added. Complete precipitation of free sulphuric acid (derived from unreacted SO_3 during sulphonation), as its barium salt, was achieved by digesting the precipitate in the mother-liquor at 80 °C for 4 h and filtering. More barium chloride reagent was added to the

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† *Non-S.I. unit employed:* mmHg ≈ 133 Pa.

filtrate which was processed repeatedly as above until the filtered mother-liquor yielded no precipitate by addition of barium chloride. The collected solid barium sulphate was washed with hot water until free of chloride ions and discarded. The mother-liquor and the collected washings were combined, concentrated to 100 cm^3, and extracted with Et_2O until the organic extract yielded no residue of phenylphosphonic acid by evaporation. The extracted mother-liquor was boiled again, brought to neutral pH by addition of $Ba(OH)_2 \cdot 8H_2O$, and filtered. Further fractions were precipitated by concentration of the filtrate and/or addition of EtOH. The fractions precipitated from the neutral mother-liquor contain the barium salts of (**2**) and of residual (**1**). Purity was checked by i.r. spectroscopy on the product as KBr pellets (absence of the band at 750 cm^{-1} and presence of the band at 800 cm^{-1}). Fractions which did not contain barium phenylphosphonate were collected and percolated through Dowex 50W-X8, H$^+$ form resin (Baker Chemical Co.) until barium free. The eluate was concentrated, decolourized on carbon, and evaporated in a rotary vacuum evaporator at 80 °C and *ca.* 15 mmHg until a solid residue was obtained. Further drying at 1 mmHg and 80 °C yielded solid sulphophenylphosphonic acid free of chloride ions. Products obtained in reactions where dephosphonation occurs may not solidify because of the presence of phosphoric acid. In this case, the product was dissolved in water again, brought to alkaline pH with $Ba(OH)_2 \cdot 8H_2O$, and concentrated until precipitation occurred. The filtered solid contains the barium salts of compound (**2**) and of H_3PO_4. The filtrate was percolated through the above ion-exchange resin and evaporated as above to obtain a solid product. Further drying of the product in a gravity convection oven at 115 °C for 1—2 weeks yielded anhydrous *m*-sulphophenylphosphonic acid. The yield of the anhydrous acid, recovered by this procedure, was 85—90% (mol/mol) of that determined in the reaction mixture by ^{31}P n.m.r. spectroscopy.

Product Yields by ^{31}*P N.M.R. Spectroscopy.*—The sample of the reaction mixture was dissolved in D_2O. The ^{31}P n.m.r. spectrum recorded immediately after the addition of D_2O exhibited sharp singlets at 17.5, 14.9, 8.5, 8.0, 7.7, 5.53, 5.20, and −0.2 p.p.m. With time, the relative intensities of the signals at 8.5—5.2 p.p.m. decreased rapidly, showing the presence of species which are not stable in water. It was observed that the decrease of the set of signals at 8.5—7.7 p.p.m. corresponded to the increase of the signal at 17.5 p.p.m. and the intensity decrease of the set at 5.5—5.2 p.p.m. corresponded to the increase of the signal at 14.9 p.p.m. A spectrum recorded after 8 h was stable and exhibited only the signals at 17.5 (**1**), at 14.9 (**2**) and, eventually, at −0.2 p.p.m. (H_3PO_4).[9] The signals in the stable spectrum were assigned based on the coincidence of the chemical shifts with those of authentic compounds. The unstable signals in D_2O ($5.2 \leqslant \delta$ p.p.m. $\leqslant 8.5$) could not be positively assigned. It is believed that these signals are associated with condensed species, which possibly contain P–O–P and/or P–O–S bonds and are hydrolysed in water to compound (**1**) and/or (**2**). However no identification of these species was possible by other techniques. The i.r. spectra of the reaction mixture contained very broad bands due to the overlapping of SO and PO vibrations. Investigation by Raman spectroscopy was also invalidated by the high fluorescence of the samples. Product yields [% (mol/mol), Table 1], relative to initial (**1**), were therefore calculated from the relative signal area ratios in the stable spectra: yield of (**2**) = $100\,A(\mathbf{2})/[A(\mathbf{1}) + A(\mathbf{2}) + A_{HP}]$ and yield of H_3PO_4 = $100\,A_{HP}/[A(\mathbf{1}) + A(\mathbf{2}) + A_{HP}]$, where $A(\mathbf{1})$, $A(\mathbf{2})$, and A_{HP} are the areas of the signals assigned to (**1**), (**2**), and H_3PO_4 respectively and measured in the spectrum recorded 8 h from the addition of D_2O to the n.m.r. sample of the reaction mixture.

Instruments.—Thermal gravimetric analysis (t.g.a.)–differential thermal analysis (d.t.a.) scans were performed in a Mettler TA 2000 C instrument, in 100 ml min^{-1} N_2, from ambient to 200 °C at 10 °C min^{-1}. Infrared spectra of solids (KBr pellets) and liquids (as films between AgCl plates) were recorded on a Perkin-Elmer 752 spectrometer, ^{1}H (at 200.13 MHz), ^{13}C (at 50.12 MHz), and ^{31}P (at 32.4 and 81.1 MHz) n.m.r. spectra on AC-200 WP-80 Bruker and on XL-200 Varian spectrometers. JMOD and two-dimensional spectra were measured using a standard pulse sequence[10] and microprograms from the Bruker library. All spectra were recorded in

Table 1. Product yields (% mol/mol)[a] in the reaction of phenylphosphonic acid (**1**) and SO_3 at SO_3:(**1**) mol ratio of 1.2 and 2.4:1

Mole ratio[b]	Reaction temperature (°C)	Reaction time, *t*	Sample number	Yield (**2**)	Yield H_3PO_4
1.2	16	0	8—1	9	
1.2	16	8 d	11—1	9	
1.2	115	50 min	8—2	12	
1.2	145	100 min	8—3	24	
1.2	180	12 h	8—4	63	6
1.2	180	24 h	8—5	63	13
1.2	180	5 d	9—1	64	24
1.2[c]	16	2 h	1—1	15[d]	
1.2[c]	16	24 h	1—2	24[d]	
2.4	16	24 h	10—2	30	
2.4	16	20 d	10—4	46	
2.4[e]	84	24 h		100[d]	

[a] Determined from ^{31}P decoupled n.m.r. spectra recorded at 32.4 MHz and 298 K as described in the Experimental section. [b] No solvent unless indicated otherwise. [c] In liquid SO_2. [d] N.m.r. spectrum not recorded, yield determined by i.r. spectroscopy. [e] In 1,2-dichloroethane.

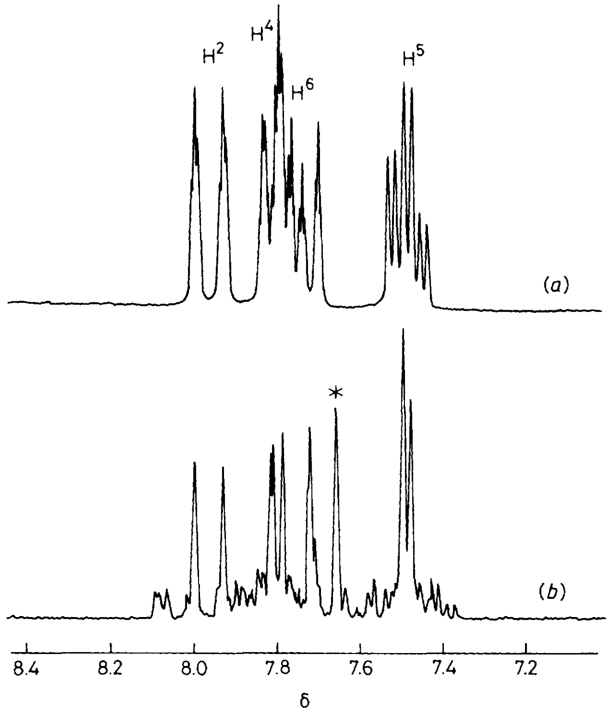

Figure 1. (*a*) Proton n.m.r. spectrum and (*b*) ^{1}H homodecoupled spectrum of compound (**2**) at 200.13 MHz. Asterisk indicates folding from signal due to water

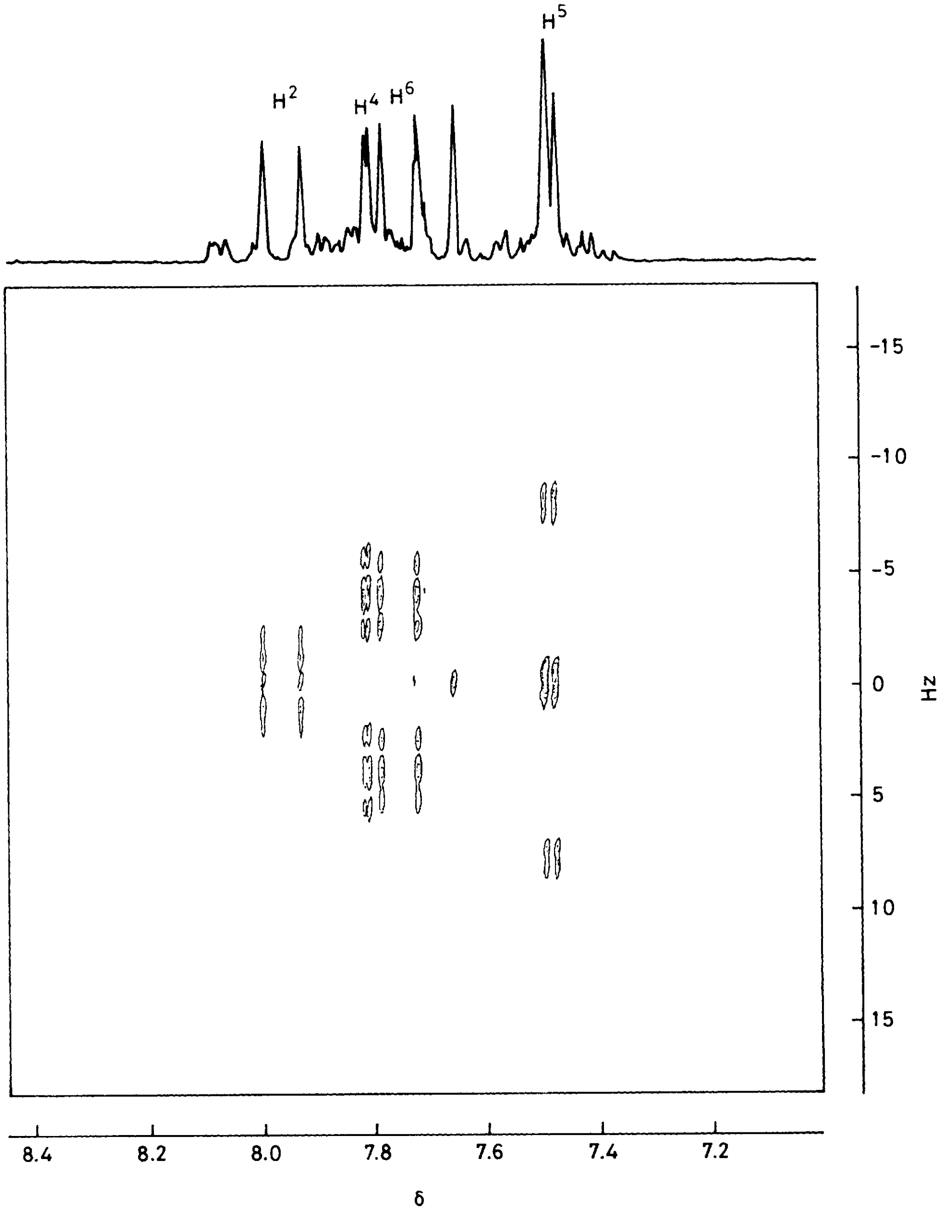

Figure 2. Counter plot of a two-dimensional ^{1}H COSY spectrum of compound (**2**) at 200.13 MHz; the corresponding one-dimensional spectrum is given in horizontal projection

D_2O at 298 K. Chemical shifts (δ) are in p.p.m. relative to $SiMe_4$ for ^{1}H and ^{13}C and to external 85% H_3PO_4 for ^{31}P; coupling constants (*J*) are in Hz.

Results and Discussion

The reaction between compound (**1**) and SO_3 has been performed either in the absence of solvent or in the presence of solvents (*i.e.* liquid SO_2 [3–5] and 1,2-dichloroethane [11]) which do not yield donor–acceptor complexes with SO_3 and, therefore, do not lower the reactivity of this reagent in sulphonation reactions. A viscous liquid phase was invariably obtained upon addition of SO_3 to solid (**1**) or to (**1**) suspended in SO_2 or 1,2-dichloroethane. When solvents were used the viscous phase separated as a bottom layer and was found to contain essentially the total amount of reagents. Experimental conditions and product yields are given in Table 1. It may be observed that in most cases only the monosulphonated product (**2**) is obtained. The yield of this product is a function of the SO_3 mol ratio and of the reaction temperature and time. It appears that, whereas at a mole ratio of 2.4:1 nearly quantitative conversion of (**1**) into (**2**) is obtained at 80 °C within 14 h, at 1.2:1 the reaction is very slow and has an upper temperature limit. At 180 °C a maximum yield of only 62—64% seems possible, very likely limited by the occurrence of slow dephosphonation.

The chemical composition of the anhydrous sulphonated product isolated from the reaction of (**1**) and SO_3 has been identified by correspondence of the elemental analysis data [C, 29.95; H, 3.10; P, 13.05; S, 13.25% (w/w)] and of the product acid equivalent concentration (12.40 H^+ mequiv./g, by titration with 0.1 mol dm^{-3} NaOH) with the theoretical values for structure (**2**) C, 30.25; H, 2.95; P, 13.00; S, 13.45% (w/w); 12.60 H^+ mequiv./g]. The product is a high-temperature melting and stable solid. The t.g.a.–d.t.a. scans in nitrogen showed no weight loss up to the highest temperature investigated (200 °C) and a

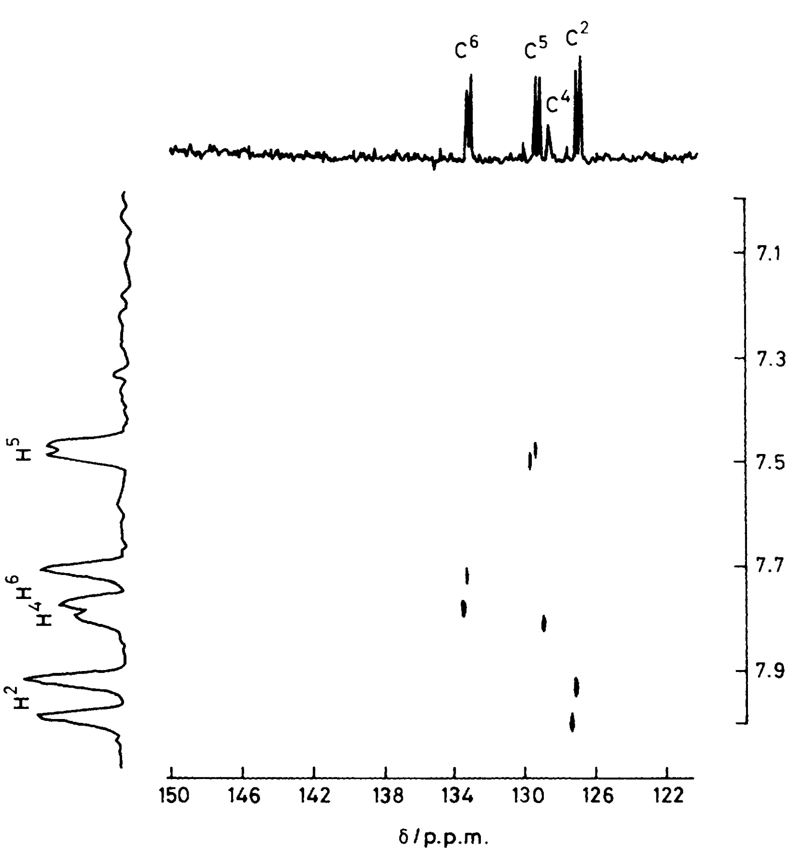

Figure 3. Counter plot of the two-dimensional ^{13}C–^{1}H correlation spectrum of compound (2); the one-dimensional ^{13}C–{^{1}H} spectrum is given in horizontal projection and the one-dimensional ^{1}H homodecoupled spectrum in vertical projection; cross peaks indicate C and H which are directly bonded

Table 2. N.m.r. data for *m*-sulphophenylphosphonic acid (2)

^{1}H$^{n\,a}$	H^2	H^4	H^5	H^6		
δ^b	7.96	7.82	7.48	7.75		
J/Hz	1.6^c 1.4^f	7.6^d 1.4^g	7.6^e			
J(HP^d)/Hz	13.7	1.7	3.6	13.0		
^{13}C^a	C^1	C^2	C^3	C^4	C^5	C^6
δ^b	132.20	127.26	142.81	128.92	129.57	133.39
J(CP)/Hz	132.3	12.0	14.8	2.6	14.5	10.3

[a] Protons and carbons numbered as in (2). [b] Chemical shift, p.p.m. from SiMe$_4$. [c] J(H^{2}H^4). [d] J(H^{4}H^5). [e] J(H^{5}H^6). [f] J(H^{2}H^6). [g] J(H^{4}H^6).

sharp endothermic peak starting at 164 °C. Melting of the product at this temperature was confirmed by visual observation in a Buchi melting-point apparatus.

Relative to the parent compound (1), the i.r. spectrum of (2) exhibited several distinct features. The C–C stretching[12] vibration band falls at 1 439 cm^{-1} for (1) and at 1 409 cm^{-1} for (2); the C–H out-of-plane bending[12] vibrations fall at 755, 711, and 692 cm^{-1} for (1) and at 800 and 680 cm^{-1} for (2). These bands appear very distinct also in the spectra of the raw reaction mixture and are useful to follow the course of the reaction. We have found for instance that the ratio (R) of the net absorbance of the band at 800 X(2) to that X(1) of the band at 755 cm^{-1} correlates well with the mole ratio of (2) to (1) (Y) as determined by ^{31}P n.m.r. spectroscopy, according to Beer's law: $R = aY + b$, where $a = 1.43$, $b = 0.11$, correlation coefficient = 0.9989, and $R = X(2)/X(1)$, where X = absorbance at the above corresponding wavelength − absorbance at 775 cm^{-1}.

The other bands, which were found in the spectra of the neat compounds (1) and (2), are mostly due to PO and SO vibrations. Specifically the S=O asymmetric and symmetric stretching bands[13] for (2) were distinctively observed at 1 235 and 1 045 cm^{-1}. However, if the acid is not anhydrous, considerable band broadening occurs in the 1 350—1 000 cm^{-1} region, due to increased hydrogen-bonding of the sulphonic and phosphonic functions.

N.m.r. spectroscopy provided definite evidence for the meta-disubstituted phenyl ring as shown in (2). The ^{1}H and ^{13}C n.m.r. data for this compound are reported in Table 2. In principle the monosulphonated phosphonic acid could have *ortho* (**A**), or *meta* (**B**), or *para* (**C**) disubstituted structures. Structure (**C**) is ruled out by the lack of symmetry observed both in the ^{1}H and ^{13}C n.m.r. spectra. The choice between (**A**) and (**B**) required a variety of one- and two-dimensional n.m.r. measurements. The interpretation of the ^{1}H n.m.r. spectrum (Figure 1) was not trivial due to the presence of overlapping multiplets and of ^{1}H–^{31}P couplings which further split each resonance. Two-dimensional Nuclear Overhauser Enhancement (NOESY) and correlation spectroscopy (COSY) ^{1}H n.m.r. spectra were not exhaustive, showing cross peaks between almost all sets of resonance. The result of the two-dimensional J resolved (JRES) experiment (Figure 2) is in contrast unambiguous and definitive. This method separates homonuclear couplings in the vertical dimension and shifts positive heteronuclear couplings (in our case H–P) in the horizontal dimension. The comparison between the JRES horizontal projection (Figure 2) and the ^{1}H n.m.r. spectrum of compound (2) (Figure 1) clearly identified the H–P and H–H couplings. The multiplicities of the four different protons were shown by taking vertical cross-sections of the JRES spectrum. Neglecting further splitting [J(HH) < 3 Hz] which arises from long-range couplings, we observe a triplet [J(HH) = 7.6 Hz] centred at δ 7.48, two doublets [J(HH) = 7.6 Hz] centred at δ 7.75 and 7.82, and a singlet centred at δ 7.96. These findings are consistent with structure (**B**); the assignment (Table 2) of the spectrum is therefore easily made. The $^{13}C-\{^1H\}$ n.m.r. spectrum of compound (**2**) consists of six doublets which indicate that all the carbons of the ring are coupled to the PO_3H_2 group. Quaternary carbons were identified by ^{13}C JMOD measurement and assigned: δ 132.20 (C^1) and 142.81 p.p.m. (C^3) by comparison with the ^{13}C n.m.r. spectrum of (**1**) [δ 132.69 (C^1), 133.09 (C^2), 131.35 (C^3), and 135.05 (C^4)]. Knowing the ^1H n.m.r. spectrum, the assignment of the methine carbons, as in Table 2, was unambiguously made from the two-dimensional C–H correlation spectrum; the cross peaks of the counter plot shown in Figure 3 indicate the C and H which are directly bonded. Since heteronuclear couplings are not removed, doubling of resonances and cross peaks relative to carbons and protons coupled to the PO_3H_2 group occur.

As further evidence for structure (**2**) (and against the *ortho* disubstituted structure), the ^{31}P coupled spectrum (recorded at 81.1 MHz) exhibited a triplet [^3J(PH) *ca.* 13.5 Hz] which indicates the presence of the two *ortho* protons with respect to the PO_3H_2 group. Since the *para* structure is ruled out by ^1H and ^{13}C n.m.r. measurements, this finding is consistent with the *meta* structure in which $J(P-H^2)$ and $J(P-H^6)$ are accidentally equivalent.

Acknowledgements

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