

formation. Spectral data allow assignment of provisional structures (17) and (18) to the remaining two compounds.

We have also isolated a polyacetylenic methyl ester (λ_{\max} 246, 258, 272, 289, 309, 331 nm) and a sterol ($C_{29}H_{48}O$), m.p. 161–163°, from these roots. The latter also occurs⁸ in *S. serotina* Ait. and its physical and spectral properties are very similar to a compound isolated⁹ from *Aplopappus heterophyllus* Blake. *S. elongata* Nutt. has been classified by some authors as a subspecies of *S. canadensis* L. However, since the latter has been shown to be devoid of acetylenes¹⁰ and to contain diterpenoids¹¹ which are markedly different from those reported in this communication, these plants are at least chemically distinct.

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- For previous communications in this series see: Anthonson, T., Henderson, M. S., Martin, A., McCrindle, R. and Murray, R. D. H. *Acta Chem. Scand.* **22** (1968) 351.
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NMR of Organophosphorus Compounds

Tri-3-thienylphosphine

H. J. JAKOBSEN and J. Aa. NIELSEN

Chemical Institute, University of Aarhus, DK-8000 Aarhus C, Denmark

As part of our studies on the determination of the magnitudes and signs of 1H - ^{31}P spin coupling constants in phosphorus substituted aromatic and heteroaromatic compounds we have recently analysed the NMR spectra of tri-2-thienylphosphine and some of its derivatives.¹

In this note we wish to report the analysis of the 1H NMR spectrum of the hitherto unknown 3-substituted isomer, tri-3-thienylphosphine (I), obtained by reaction of 3-thienyllithium with phosphorus tribromide. The proton magnetic resonance spectrum of (I) (Fig. 1) may be analysed as the ABCX part of an ABCX

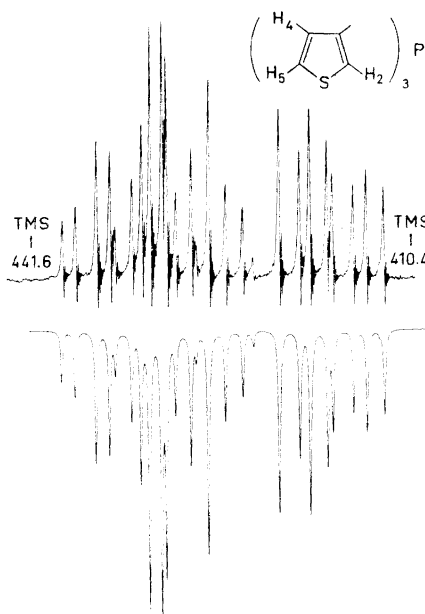


Fig. 1. Observed (above) and calculated (below) 60 MHz PMR spectrum of a 14% w/w degassed solution of tri-3-thienylphosphine in CCl_4 .

Table 1.

$\nu_2 = 428.614 \pm 0.007$;	$J_{24} = 1.220 \pm 0.011$;	$J_{3p-2} = 4.215 \pm 0.013$
$\nu_4 = 417.143 \pm 0.007$;	$J_{25} = 2.836 \pm 0.009$;	$J_{3p-4} = 2.579 \pm 0.012$
$\nu_5 = 434.096 \pm 0.007$;	$J_{45} = 4.917 \pm 0.010$;	$J_{3p-5} = 0.990 \pm 0.015$

spin system,² where X is the ³¹P nucleus and is thus showing up as a superposition of two ABC subspectra with identical sets of ¹H-¹H coupling constants and with effective chemical shifts $\nu_i^{\text{eff}} = \nu_i \pm J_{iX}$, where i=A, B, and C. The analysis was performed by assignment of the observed transitions to two ABC subenergy level diagrams using the technique of double quantum transitions as in our previous studies.^{1,3} These assignments were then used as input parameters for the iterative part of the computer programme LAOCOON II⁴ and two ABC parameter sets having identical ¹H-¹H coupling constants all with the same sign were obtained. The assignment of the effective chemical shifts to the protons in (I) was based on the known magnitudes of the ¹H-¹H coupling constants in thiophenes,⁵ and the ¹H-³¹P coupling constants were then obtained as the differences between the corresponding effective chemical shifts. Since the effective chemical shifts in one of the subspectra are all larger than the corresponding chemical shifts in the other, it is concluded that all ¹H-³¹P spin coupling constants carry the same sign, which is assumed to be positive.^{1,6} The analysis of the PMR spectrum of (I) was also carried out in a one-step iteration by combining the two ABC subenergy level diagrams into an ABCX energy level diagram followed by a renumbering of the transitions according to LAOCOON II as earlier described.¹ The NMR parameters (all in Hz; $\nu_0 = 60$ MHz; chemical shifts are referred to TMS as internal standard) resulting from the analysis are given in Table 1.

The ¹H-³¹P coupling constants in (I) are slightly smaller than the corresponding ¹H-¹H coupling constants in thiophene⁷ in contrast to some of the ¹H-³¹P coupling constants in tri-2-thienylphosphine.¹

A more detailed discussion of the spin coupling constants in these systems and in some of their phosphorus tetracoordinated derivatives will form part of a subsequent paper which will also include the energy level diagrams assigned from the double quantum transitions.

Experimental. The ¹H NMR spectra were recorded and calibrated with the aid of a Varian A-60 spectrometer, a General Radio low frequency oscillator, and a Hewlett-Packard frequency counter. The sample solution, 14 % w/w in CCl₄, was degassed and sealed off under vacuum. Line positions were taken as mean values of several measurements at a sweep rate of 0.05 Hz/sec and are believed to be correct at least to within 0.05 Hz. Computations were performed at N.E.U.C.C., Copenhagen on an IBM 7094 system. The r.m.s. error in line positions was 0.015 Hz.

Tri-3-thienylphosphine. 3-Thienyllithium was prepared from 109 g (0.67 mole) of 3-bromothiophene⁸ in 250 ml of anhydrous ether and 440 ml of 1.51 N (0.67 mole) butyllithium at -70°. 44 g (0.16 mole) of phosphorus tribromide in 100 ml of anhydrous ether was added dropwise to the reaction mixture at -70°. The reaction mixture was stirred for 2 h and then allowed to warm up to room temperature. After hydrolysis with a mixture of ammonium chloride and dilute hydrochloric acid the organic layer was separated, washed with sodium bicarbonate solution and dried. Distillation gave a fraction of a light yellow liquid which crystallized, b.p. 150-156°/0.2 mm Hg, yield 24.1 g (50 %). Recrystallization from a mixture of benzene and petroleum ether gave white crystals, m.p. 69-70°. (Found: C 51.46, H 3.43. Calc.: C 51.39; H 3.24).

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