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Peak doubling in the nuclear magnetic resonance spectra of certain organophosphorus esters—II.* The role of hydrogen bonding

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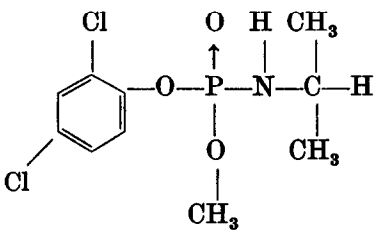
Abstract—We have extended our investigations of the peak doubling phenomenon observed in the nuclear magnetic resonance (NMR) spectra of certain organophosphorus esters. Double resonance experiments have confirmed that the doubling of NMR resonances is due to magnetic non-equivalence and has supported our contention that the doubling results from the presence of rotational conformers.

It has also been shown that hydrogen bonding is not an important contributor to the doubling phenomenon.

INTRODUCTION

A NUMBER of theories to explain the phenomenon of doubling of nuclear magnetic resonances (NMR) have been advanced during the past decade. These include partial bond hybridization [1], hindered rotation [2, 3], stereochemical non-equivalence of geminal protons [4] and rotational conformation [5]. A recent publication has ascribed the doubling of resonances to enhancement of asymmetry effects by intermolecular hydrogen bonding [6]. This has prompted us to report our findings on similar compounds, which clearly indicate that hydrogen bonding does not play a necessary role in peak doubling.

GARRISON *et al.* [6] report that methyl 2,4-dichlorophenyl *iso*propyl phosphoroamidate (1), displays unusual doubling of the NMR signals of the *iso*propyl moiety. They demonstrated that the doubling was actually a chemical shift difference by obtaining the spectrum at two different frequencies.



(1)

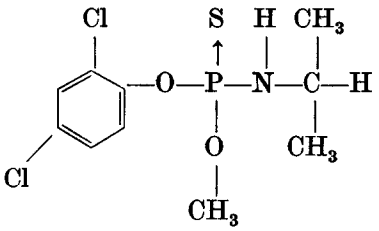
Their study of the i.r. spectra of (1) in which concentrations were varied from 0.007 molar to 1.4 molar showed that the hydrogen bound phosphoramide N—H

* For Part I see: R. V. JARDINE, A. H. GRAY and J. B. REESOR, *Can. J. Chem.* **47**, 35 (1969).

[1] H. FINEGOLD, *J. Am. Chem. Soc.* **82**, 2641 (1960).
[2] H. S. GUTOWSKY and C. H. HOLM, *J. Chem. Phys.* **25**, 1228 (1956).
[3] J. J. DRYSDALE and W. D. PHILLIPS, *J. Am. Chem. Soc.* **79**, 319 (1957).
[4] J. S. WAUGH and F. A. COTTON, *J. Phys. Chem.* **65**, 562 (1961).
[5] R. V. JARDINE, A. H. GRAY and J. B. REESOR, *Can. J. Chem.* **47**, 35 (1969).
[6] A. W. GARRISON, L. H. KEITH and A. L. ALFORD, *Spectrochim. Acta* **25A**, 77 (1969).

signal increased in intensity and width at 3205 cm^{-1}. NMR signals over a similar concentration range showed that the methyl group of the *iso*propyl function changed from a doublet to an apparent triplet. This was interpreted as a doubling of the signal.

In contrast, measurements carried out under a variety of conditions on the thio analogue, methyl 2,4-dichlorophenyl *iso*propylphosphoramidothionate, Zytron (2), did not exhibit doubling of the *iso*propyl methyl groups. The authors

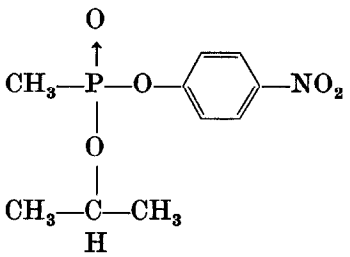


(2)

therefore concluded that the observed doubling of the spectra of the oxygen analogue could be ascribed to hydrogen bonding, a phenomena not observed in the corresponding thio analogue, due to the inability of the sulphur atom to form hydrogen bonds.

RESULTS AND DISCUSSION

In a previous paper [5] we have discussed the doubling of the *iso*propyl resonances of *iso*propyl *p*-nitrophenyl methylphosphonate (3) and



(3)

attributed this effect to the presence of rotational conformers, in which the alkoxyl group occupies 'up' and 'down' orientation with respect to the phosphoryl moiety.

Further experimentation has continued to support our conclusions. Heteronuclear double irradiation of the phosphorus atom of (3) clearly showed that the doubling observed was not due to long range coupling. In these experiments decoupling of the phenyl protons *ortho* to the P—O-group, the methine proton and the P—CH_3 protons was observed. However, signals attributed to the CH_3 groups of the *iso*propyl moiety remained unchanged (Fig. 1).

Homonuclear double resonance experiments on 3 have strengthened the evidence. In this compound the β methyl protons of the isopropyl moiety appear as two doublets centered at $\tau = 8.73$ ($J_{H-H} = 6.0$ Hz) and $\tau = 8.66$ ($J_{H-H} = 6.0$). The methine proton of this group is an apparent sixteen line spectrum centered at $\tau = 5.10$ (Fig. 2).

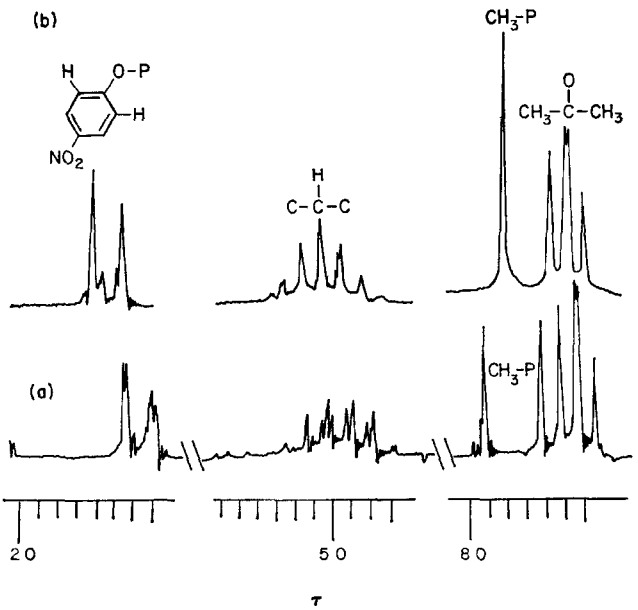


Fig. 1(a). Partial nuclear magnetic resonance spectrum of *iso*propyl *p*-nitrophenyl methylphosphonate, 3, obtained in deuterochloroform; (b). Irradiation of the phosphorus atom.

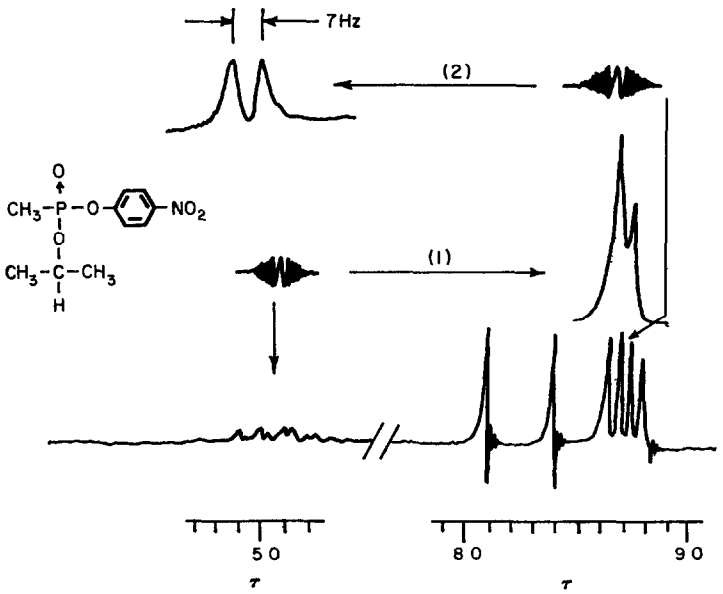


Fig. 2. Partial nuclear magnetic resonance spectrum of *iso*propyl *p*-nitrophenyl methylphosphonate: (1) Irradiation of the methine region; (2) Irradiation of the β methyl region.

The β methyl protons of *iso*propyl *p*-nitrophenyl methylphosphonate may be regarded as superposed AB_6, $A'B_6'$ spin systems, while the methine region consists of superposed A_6BX, $A_6'B'X$ spin systems. Irradiation of the methine proton resulted in collapse of the β methyl doublets into *two* singlets, separated by 4.0 Hz, demonstrating a difference in magnetic environment.

Irradiation of the β methyl region reduced the methine spin system into superposed BX, $B'X$ spins. The $BX(B'X)$ representing coupling of this proton with phosphorus. The small chemical shift difference between B and B′ signals is not discernible due to the width of the signals (Fig. 2).

The *iso*propyl moiety of the uranyl nitrate complex of 1 may be regarded as composed of the elements A_6B and A_6BX (Fig. 3). Irradiation of the β methyl doublet results in collapse of the methine multiplet into a doublet, $J_{P-H} = 7.0$ Hz. Conversely, irradiation of the methine region reduces the β methyl doublet into a singlet (Fig. 3).

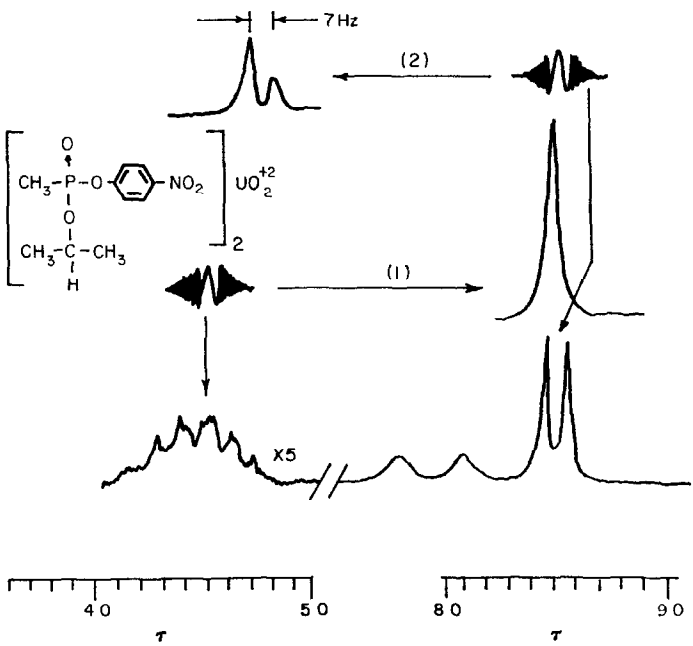
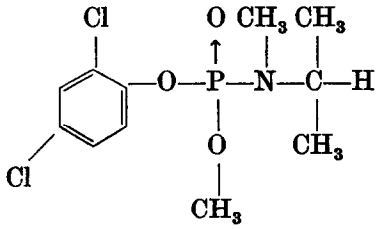


Fig. 3. Partial nuclear magnetic resonance spectrum of *iso*propyl *p*-nitrophenyl methylphosphonate, uranyl nitrate complex; (1) Irradiation of the methine region; (2) Irradiation of the β methyl region.

We believe that the doubling reported by GARRISON *et al.* [6] for (1), to be an analogous case, and that their claim of hydrogen bonding as an important contributor to the phenomenon is overstated. We therefore returned to a investigation of compounds relating to Garrison's work.

Direct evidence that hydrogen bonding is not an important contributor to doubling of resonances was obtained from the homologue (4) methyl 2,4-dichlorophenyl

methyl*iso*propylphosphoroamidate. This compound, in



(4)

which hydrogen bonding is precluded, exhibited doubling of the *iso*propyl methyl groups (Fig. 4). A 25% solution of methyl 2,4-dichlorophenyl methyl*iso*propylphosphoroamidate, 4, in acetone revealed two doublets centered at $\tau = 8.87$ ($J_{H-H} = 6.5$ Hz) and $\tau = 8.89$ ($J_{H-H} = 6.5$ Hz). The difference in chemical shift, in this case, being 1.25 Hz. Treatment of this compound with uranyl nitrate results in a complex, displaying in its n.m.r. spectrum only one *iso*propyl doublet centered at

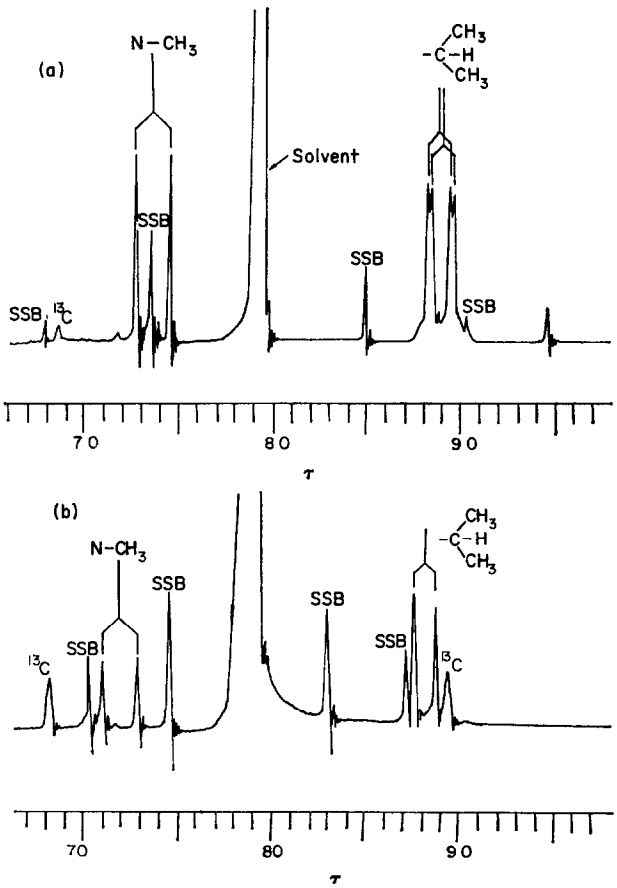


Fig. 4a. Partial nuclear magnetic resonance spectrum of methyl 2,4-dichlorophenyl methyl*iso*propylphosphoroamidate obtained in acetone; b. Uranyl nitrate complex.

$\tau = 8\ 81 (J_{H-H} = 6\ 5$ Hz) Fig. 4. We therefore ascribe this resonance doubling to the presence of rotational conformers.

Furthermore, in our hands, Zytron* displayed doubling of the *iso*propyl methyl resonances. A 25% solution of Zytron in deuterochloroform revealed an apparent doublet at $\tau = 8.85$ ($J_{H-H} = 6.3$ Hz) on a 60 MHz spectrometer, but when the spectrum was expanded to 250 Hz and a slow sweep employed, resplitting of the resonances could be clearly ascertained The difference in chemical shift obtained under these conditions is 0.6 Hz A spectrum obtained on a 100 MHz spectrometer revealed a similar doublet, resplit by 0.6 Hz. It would appear, therefore, that the resplitting of resonances in Zytron is due to long range phosphorus coupling. This interpretation is consistent with the work of FINEGOLD [7] who has demonstrated that thio analogues of a number of organophosphorus compounds are more sensitive to long range coupling and display larger coupling than the corresponding oxygen analogues.

From these studies we have obtained additional support for our explanation of the peak doubling phenomenon observed for certain organophosphorus compounds, and shown that hydrogen bonding does not play an important role in the doubling of resonances. Phosphonothionates may also engage in peak doubling, however in the compounds cited resplitting of resonances was found to be due to long range phosphorus coupling.

EXPERIMENTAL

N.m.r. spectra were determined on a Varian Associates spectrometer model A-60 modified to A-60A specifications. The spectrometer is equipped with a Varian model V-6058A homonuclear decoupler and a Nuclear Magnetic Resonance Specialties heteronuclear decoupler model HD-60. A 100 Hz spectrum was obtained on a Varian Associates model HA-100. Spectra were obtained from 25% w/v solutions in deuterochloroform or acetone using tetramethylsilane (TMS) as internal standard. On pertinent spectra the field was swept in both directions.

Gas chromatographic analysis was carried out on a Varian 1800 instrument using a 3 ft × $\frac{1}{8}$ in. stainless steel column packed with 8% OV225 100/120 mesh on gaschrom Q. The detector was a Melpar FPD 200 in conjunction with a dual pen recorder so that a specific signal for phosphorus could be obtained. The column temperature was 143°C with a carrier gas flow rate of 35 ml/min and an injection volume of 0.1λ.

Thin layer chromatographic (TLC) analysis was carried out on Eastman Chromagram sheets (silica gel) using benzene as developing solvent. Spots were visualized with iodine vapour.

Methyl 2,4-*Dichlorophenyl Methyl*iso*propylphosphoramidate*, 7

2,4-Dichlorophenylphosphorodichloridate was obtained in 72% yield by the method of MAGUIRE and SHAW [8]. Treatment of this dichloridate with one molar equivalent of methanol in methylene dichloride yielded 68% of methyl 2,4-dichlorophenyl phosphorochloridate, a colourless oil, b.p. 88–91°/0.02 mm. The required

* The authors thank Dr. T. Haagsma of Dow Chemical Co., Sarnia, Ontario, for a generous supply of methyl 2,4-dichlorophenyl *iso*propylphosphoramidothionate, "Zytron".

[7] H. FINEGOLD, *Ann. N.Y. Acad. Sci.* **70**, 875 (1958).
[8] M. H. MAGUIRE and G. SHAW, *J. Chem. Soc.* 1479 (1953).

amidate was obtained by treatment of methyl 2,4-dichlorophenyl phosphorochloridate, 27.5 g (0.1 mole) in 100 ml methylene chloride with 7.3 g (0.1 mole) methyl-*iso*propylamine in 100 ml methylene chloride containing 5 ml triethylamine. Following the exothermic reaction the products were stirred for ½ hour and then refluxed 1 hour. The methylene chloride was evaporated *in vacuo* and the product washed successively with water (2 × 100 ml) and saturated sodium bicarbonate (2 × 100 ml). The resulting product was then taken up in chloroform and dried with sodium sulfate. The chloroform was evaporated and the remaining oil distilled to yield 20 g (64%) of a light yellow oil, b.p. 120–124°/0.03 mm. *Anal.* Calcd. for

$$C_{11}H_{16}Cl_2NO_3P;$$

H, 5.17; Cl, 22.49; N, 4.49; P, 9.92. Found: H, 5.06; Cl, 22.38; N, 4.42, P, 9.94.