Determination of Chemical Shifts by Heteronuclear Magnetic Triple Resonance: the Nature of the Phosphorus–Selenium Bond in Organophosphorus Selenides

By W. McFarlane* and D. S. Rycroft

(*Chemistry Department, Sir John Cass School of Science and Technology, City of London Polytechnic, Jewry Street, London* E.C.3)

Summary A novel heteronuclear triple resonance technique is used to obtain ^{77}Se chemical shifts in organophosphorus selenides, and to show that the dipolar form of the phosphorus–selenium link is predominant.

ORGANOPHOSPHORUS SELENIDES can be represented either as the dipolar form (I), or as (II) in which there is d_π–p_π bonding between phosphorus and selenium. It is probable that each form contributes to some extent to the resonance hybrid.[1] We now report (Table) ^{77}Se chemical shifts and ^{31}P–^{77}Se coupling constants obtained by triple and double resonance respectively which indicate that the dipolar form (I) predominates.

R_3P^+–Se^- (I) $\qquad$ $R_3P{=}Se$ (II)

Except in Ph_2HPSe, the coupling $J(^{77}Se\cdots H)$ in these molecules is zero, so standard ^1H–$\{^{77}Se\}$ double-resonance experiments cannot be used to determine the selenium resonance frequency, and hence the ^{77}Se chemical shift.[2] However, ^1H–$\{^{31}P\}$ double-resonance experiments involving irradiation of the ^{77}Se satellites in the ^{31}P spectrum can be used to collapse selectively parts of the proton doublet arising from molecules containing ^{77}Se ($I = \frac{1}{2}$, abundance $= 7{\cdot}5\%$). In this way two ^{31}P frequencies [separated by $^1J(^{31}P–^{77}Se)$] can be determined, and the the effect of irradiating at one of these frequencies is illustrated in the Figure (b). Simultaneous irradiation at appropriate ^{77}Se

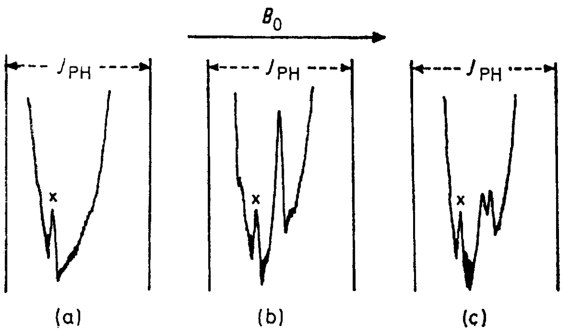

FIGURE. *Region between the components of the* P–H *doublet in the* 60 MHz *proton spectrum of* $(MeO)_3PSe$ *at high gain. The vertical lines give the positions of the unperturbed components of the doublet and the asymmetry is due to incorrect phase adjustment.* (a) *Normal single resonance spectrum. The peak marked "x" arises from an impurity.* (b) *With irradiation at the frequency of the low-field* ^{77}Se *satellite of the* ^{31}P *resonance.* (c) *As for* (b) *but with simultaneous irradiation at the frequency of the high-field line in the* ^{77}Se *spectrum.*

TABLE. *N.m.r. parameters of organophosphorus selenides*

Compound	$J(^{31}P\cdots H)$ (Hz)	$^1J(^{31}P–^{77}Se)$ (Hz)	Ξ (^{31}P) (Hz)[a]	δ (^{31}P) (p.p.m.)[b]	Ξ (^{77}Se) (Hz)[a]	δ (^{77}Se) (p.p.m.)[c]
Me_3PSe	− 13·2	−648	40,481,114	8·01	19,067,041	−235
Ph_2HPSe	+461·2[d]	−740	40,481,018	5·64	19,064,869	−349
$(Me_2N)_3PSe$	+ 11·7	−805	40,484,101	81·78	19,064,544	−366
$(MeO)_3PSe$	+ 14·3	−963	40,483,926	77·46	19,063,966	−396

[a] The Ξ-value is the resonant frequency corrected to a polarising field strength in which Me_4Si gives a proton resonance of exactly 100 MHz. [b] To low field of 85% H_3PO_4. [c] Relative to Me_2Se: the negative sign indicates a shift to high field. [d] This refers to $^1J(^{31}P–H)$.

resonant frequencies then gives a splitting[3] of connected ^{31}P transitions which is 'transferred'[4] to the proton spectrum by the action of the r.f. field at the ^{31}P resonant frequency. Thus an observable result is obtained as shown in (c) of the Figure, and the ^{77}Se chemical shift may be calculated.

The trend shown by $^1J(^{31}P–^{77}Se)$ as the electronegativity of the groups attached to phosphorus is increased is consistent with increased inductive electron withdrawal leading to greater *s*-character for the phosphorus hybrid orbital used to form the P–Se sigma bond, and/or greater effective nuclear charge of the phosphorus atom.[5] Studies of ^{77}Se chemical shifts in a wide range of compounds have shown that these move to higher field (*i.e.* more negative values) as the groups attached to selenium become more electropositive.[6] In particular the only class of compounds known to give shifts at as high field as −200 p.p.m. are the alkyl selenide anions RSe^- (typical ^{77}Se chemical shifts are $MeSe^-$, −332; Me_2Se, 0; Me_3Se^+, 253; Me_2Se_2, 275; Me_2SeO, 812 p.p.m.). Thus it appears that in the organophosphorus selenides the selenium bears a negative charge and this is consistent with their formulation as the dipolar form (I). p_π–d_π bonding between selenium and phosphorus will reduce this charge and so should decrease the selenium magnetic shielding; this effect will be greatest in Me_3PSe in which there is no competition for the phosphorus *d* orbitals. However, in $(MeO)_3PSe$ the *p* orbitals of the oxygen atoms will compete very effectively with those of selenium and the contribution from structure (II) will be very small indeed, so that the ^{77}Se nucleus is very highly shielded as is observed. The behaviour of Ph_2HPSe and $(Me_2N)_3PSe$ will be intermediate.

We conclude that the dipolar form (I) makes the major contribution to the P–Se bond in an organophosphorus selenide, but that the contribution from (II) is significant, especially when the other groups cannot form π-bonds with the phosphorus atom.

We thank the S.R.C. for financial support.

(*Received, 24th May* 1972; *Com.* 894.)

---

[1] R. F. Hudson, 'Structure and Mechanism in Organo-phosphorus Chemistry, Academic Press, London, ch. 3, 1965.
[2] W. McFarlane, *Ann. Rev. N.M.R. Spectroscopy*, 1968, **1**, 135.
[3] R. Freeman and W. A. Anderson, *J. Chem. Phys.*, 1962, **37**, 2053.
[4] R. Freeman and B. Gestblom, *J. Chem. Phys.*, 1967, **47**, 1472.
[5] W. McFarlane, *Quart. Rev.*, 1969, **23**, 187.
[6] W. McFarlane and R. J. Wood, *J.C.S. Dalton*, 1972, 1397.