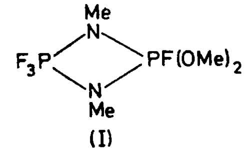
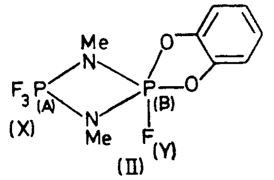
Preparative and Nuclear Magnetic Resonance Studies of Diazadiphosphetidines. Part VIII.† 2,2,2,4-Tetrafluoro-1,3-dimethyl-4-*o*-phenylenedioxy-1,3-diazadiphosphetidine

By **Robin K. Harris** * and **Mohamed. I. M. Wazeer**, School of Chemical Sciences, University of East Anglia, Norwich NR4 7TJ
Ottfried Schlak and **Reinhard Schmutzler**, Lehrstuhl B für Anorganische Chemie, der Technischen Universität, 33 Braunschweig, Pockelsstrasse 4, Germany

The preparation and mass spectrum of the title compound containing a chelating catechol substituent are described. The $^{31}P-\{^1H\}$ and $^{19}F-\{^1H\}$ n.m.r. spectra have been analyzed, and the results indicate that the single fluorine attached to the chelated phosphorus atom is basically equatorial rather than axial.

DURING attempts to prepare 2,2,2,4-tetrafluoro-4,4-dimethoxy-1,3-dimethyl-1,3-diazadiphosphetidine, (I),[1] it was thought to be of interest to combine the two oxygen functions into a ring system, and to study the nature and temperature dependence of the n.m.r. spectra of spirophosphoranes, such as (II). The synthesis of (II) was accomplished by the reaction of 2,2,2,4,4,4-hexafluoro-1,3-dimethyl-1,3-diazadiphosphetidine[2] with dilithium catecholate.

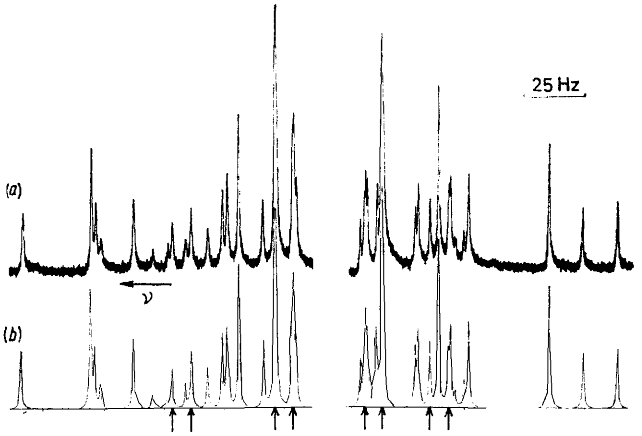

(I)



(II)

RESULTS AND DISCUSSION

N.m.r. Studies.—The structure of (II) was fully characterized by n.m.r. spectroscopy. The proton-decoupled ^{19}F (Figure) and ^{31}P n.m.r. spectra were highly second-order in nature because of the very small chemical-shift difference between the two types of fluorine nucleus. However, a complete analysis was feasible on the basis of an ABX_3Y spin system using the iterative computer program UEA NMR ITR.[3] Values for the ^{31}P chemical shifts and for J_{PP} were obtained by inspection of the $^{31}P-\{^1H\}$ spectrum. It also proved



94.155 MHz $^{19}F-\{^1H\}$ noise-decoupled n.m.r. spectrum of (II) at ambient probe temperature (*ca.* 35 °C): (*a*), observed, (*b*), computed using the parameters given in the text. The vertical arrows mark the positions of lines in the DD sub-sub-spectra of the x_3y subspectra. The two most intense peaks in the computed spectrum are not shown to their full height

---

† Part VII, R. K. Harris and M. I. M. Wazeer, preceding paper.

[1] R. K. Harris, M. I. M. Wazeer, O. Schlak, and R. Schmutzler, *J.C.S. Dalton*, 1974, 1912.

[2] R. Schmutzler, *J.C.S. Dalton*, 1973, 2687.

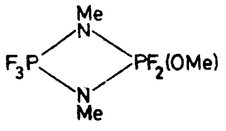
[3] R. B. Johannesen, J. A. Ferretti, and R. K. Harris, *J. Mag. Res.*, 1970, **3**, 84.

possible to pick out an x_3y subspectrum in the $^{19}F-\{^1H\}$ spectrum, thus giving $^4J_{FF}$. The final computed fluorine spectrum (from iterating to observed ^{19}F lines only) is shown in Figure (*b*), and the parameters derived are as follows (the signs of the coupling constants assume $^1J_{PF}$ is negative):

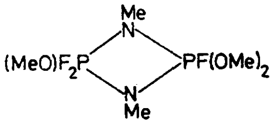
$\delta_F(X)$	−78.50 p.p.m.	$\delta_F(Y)$	−78.59 p.p.m.
$\delta_P(A)$	−69.4 p.p.m.	$\delta_P(B)$	−51.7 p.p.m.
$^1J_{PF}(AX)$	−917.5 Hz	$^1J_{PF}(BY)$	−981.0 Hz
$^3J_{PF}(AY)$	24.7 Hz	$^3J_{PF}(BX)$	29.7 Hz
$^4J_{FF}$	7.8 Hz	$^2J_{PP}$	196.5 Hz

The r.m.s. error from fitting 36 observed ^{19}F lines to 56 computed ones was 0.316 Hz. The values for $\Delta\nu_P$ and J_{PP} were not allowed to vary during the iteration.

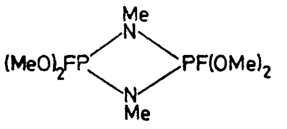
The above parameters may be compared with those for the methoxydiazadiphosphetidines[1] (III)—(V). Some of the data are unremarkable. For instance, the values of δ_F, δ_P, and $^1J_{PF}$ for the PF_3 group of (II) are close to the corresponding values for (III) (−78.24 p.p.m., −68.1 p.p.m., and −909.7 Hz, respectively). Other parameters for (II), such as $\delta_F(Y)$ and $^1J_{PF}(BY)$ are considerably different from the analogous data for (IV) [δ_F 74.71 p.p.m. and $^1J_{PF}$ −797.6 Hz for the $PF(OMe)_2$ group] and (V) (δ_F −73.50 p.p.m. and $^1J_{PF}$ −779.5 Hz). These observations only make sense if F_Y is not axial (assuming a roughly trigonal bipyramidal structure), as would be normal for the only fluorine atom of a phosphorane, but equatorial. In fact, at low temperature, n.m.r. spectra for (IV) show[1] that the two fluorines of the $PF_2(OMe)$ group are non-equivalent, with δ_F −85.0 p.p.m. and $^1J_{PF}$ −949 Hz for one (assumed equatorial) and δ_F −68.9 p.p.m. and $^1J_{PF}$ −805 Hz for the other (assumed axial). It is, in fact, generally understood that axial fluorines are less shielded than equatorial fluorines, and that $|^1J_{PF}(ax)| < |^1J_{PF}(eq)|$, so the data for (II) are qualitatively as expected for an equatorial fluorine. This is not altogether surprising since if F_Y were axial for (II) there would be considerable strain induced in the five-membered ring involving the chelating catechol group. With F_Y equatorial the ring can be formed with one oxygen atom axial and one equatorial, involving less strain in the ring. Since the apicophilicity of oxygen does not differ very much from that of fluorine, the preferred conformation minimises ring strain. There will still, of course, be some ring strain causing deviations from a strictly trigonal bipyramidal geometry, and this is probably indicated by the value of $\delta_F(Y)$, which is not as negative as expected by comparison with (IV) and (V), and that of $|^1J_{PF}(BY)|$, which is even higher than that for the equatorial group in (III) (though this may be simply a substituent effect). The conclusions regarding the equatorial character of the fluorine atom in (II) parallel those reported earlier[4-6] for certain other phosphorus compounds with ligands in a spiro arrangement, *viz.* (VI)—(VIII). All three of these molecules have larger values of $|^1J_{PF}|$ and ^{19}F resonances at lower frequency than expected for axial fluorines. In the case of (VIII) *X*-ray studies[6] have established that the geometry at phosphorus is between a trigonal bipyramid and a tetragonal bipyramid in the solid state.



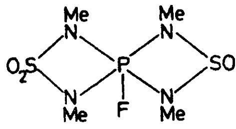
(III)



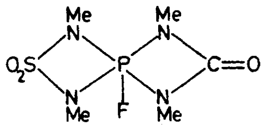
(IV)



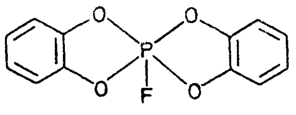
(V)



(VI)



(VII)



(VIII)

The value of J_{PP} for (II) is somewhat above that predicted (188.2 Hz) for (I) on the basis of multiplicative substituent parameters,[1] but this may be because the parameter used for the $PF(OMe)_2$ group is that for an axial fluorine. The result of 7.8 Hz for $^4J_{FF}$ in (II) is probably reasonable; that between two axial fluorines for (IV) and (V) is *ca.* 0, the axial–equatorial value for (IV) is 9.2 Hz, and there is no properly attested value for the equatorial–equatorial interaction. The two values of $^3J_{PF}$ for (II) are as anticipated from the data for the methoxydiazadiphosphetidines presented earlier.[1] The value of $\delta_P(B)$ for (II) may be compared with −71.8 p.p.m. for the corresponding group of (IV) and −70.6 p.p.m. for (V). The considerable discrepancies in this parameter are probably attributable to the nature of the catechol group and to the ring strain in (II) rather than to the equatorial position of the fluorine.

The signs of the coupling constants for (II), reported above relative to a negative sign for $^1J_{PF}$, are almost certainly correct. Due to the pronounced second-order nature of the spectra it is doubtful whether any other sign combination would give an acceptable fit. In any

---

[4] M. Becke-Goehring and H. Weber, *Z. anorg. Chem.*, 1969, **365**, 185.

[5] (*a*) G. O. Doak and R. Schmutzler, *Chem. Comm.*, 1970, 476; (*b*) G. O. Doak and R. Schmutzler, *J. Chem. Soc.* (*A*), 1971, 1295.

[6] H. Wunderlich, D. Mootz, R. Schmutzler, and M. Wieber, *Z. Naturforsch*, 1974, **29b**, 32.

case, the signs are all well established for the diazadiphosphetidines, and the present results are consistent with the earlier ones.[1,7] No significant change was observed in the ^{19}F–{^{1}H} spectrum of (II) from ambient probe temperature down to −80 °C. This perhaps reinforces the idea that the fluorine is equatorial (or at least that there is only a small energy required to place it equatorial), since the preferred axial position for the fluorine atom of the $PF(OMe)_2$ group in (III) introduces a considerable rigidity at the other phosphorus.[1]

The 100 MHz ^{1}H n.m.r. spectrum of (II) was recorded at ambient probe temperature. The C_6H_4 protons gave a complex band *ca.* 1.7 p.p.m. to high frequency of the CH_2Cl_2 signal. The NMe protons gave a triplet 2.54 p.p.m. to low frequency of the CH_2Cl_2 signal. The triplet structure arises from (P,H) coupling, J_{PH} 13.5 Hz. It is surprising that the coupling to the two phosphorus nuclei appears to be equal; ^{1}H–{^{19}F} double resonance improved the resolution but failed to show any difference in the splittings due to J_{PH}. It is unlikely that this effect is due to deceptive simplicity. The single resonance NMe triplet in the ^{1}H spectrum showed further ill-resolved structure due to (F,H) coupling ($|^{4}J_{FH}|$ *ca.* 0.5 Hz). The fact that the ^{19}F spectrum is strongly coupled implies that the effect of (F,H) coupling on the ^{1}H spectrum is probably to give deceptive simplicity. Integration of the ^{1}H spectrum showed that signal areas were in the ratio 4.0 : 5.9 for aromatic : aliphatic protons. The sign of $^{3}J_{PH}$ was confirmed as opposite to that of $^{1}J_{PF}$ for (II) by ^{1}H–{^{19}F} partial-decoupling experiments. Since the fluorine nuclei are closely coupled, but $^{1}J_{PF}$ is large, it is relatively easy to irradiate only half the spectrum shown in the Figure and to observe the effect on the outer lines of the ^{1}H triplet, thus correlating regions of the ^{19}F and ^{1}H spectra due to the $\alpha\alpha$ (or $\beta\beta$) ^{31}P spin states.

The ^{1}H spectrum shows there is a single type of NMe group. Compound (II) is therefore subject to rapid pseudo-rotation on the n.m.r. timescale at room temperature, which makes the two N–P bonds to a given phosphorus equivalent. This implies that the two P–O bonds are also equivalent, and they therefore have a character that is 50% axial and 50% equatorial. The pseudo-rotation situation is, in fact, analogous to that for (III), except that the roles of F and O at the substituted phosphorus are reversed.

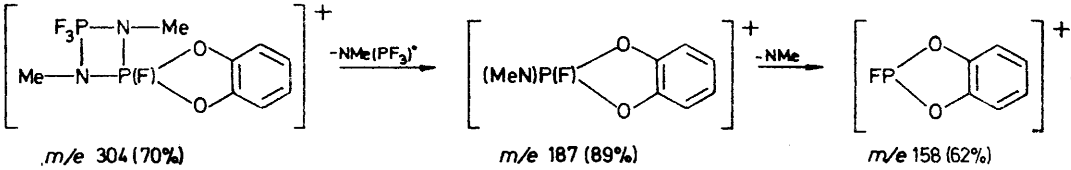
EXPERIMENTAL

N.m.r. Spectra.—The ^{19}F–{^{1}H} and ^{31}P–{^{1}H} spectra at 94.155 and 40.5 MHz, respectively, were recorded using Varian HA100 and XL100 n.m.r. spectrometers as described earlier, with proton-noise decoupling.[1,7] The compound was dissolved in CH_2Cl_2–CD_2Cl_2, and $CFCl_3$ was added to provide a field-frequency lock and a reference for the ^{19}F work. Chemical shifts are reported with respect to $CFCl_3$ and external 85% H_3PO_4 for ^{19}F and ^{31}P resonances, respectively, with positive δ values implying that the sample resonates to high frequency of the reference. The ^{31}P shifts were calculated indirectly, as outlined previously.[1] The 100 MHz n.m.r. spectrum of the same sample was recorded using the HA100 spectrometer in the frequency-sweep mode. The ^{1}H–{^{19}F} work was carried out using the circuitry described earlier.[1]

Mass Spectrometry.—The mass spectra of symmetrical fluorodiazadiphosphetidines are known[8] to exhibit a characteristic fragmentation pattern, the main decomposition path in equation (1) being followed (where

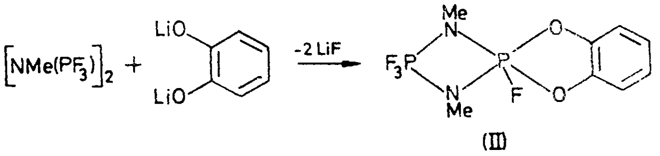
$$[M]^{+\cdot} \longrightarrow \left[\frac{M}{2}+1\right]^{+}, \left[\frac{M}{2}-1\right]^{+} \qquad (1)$$

$\left[\frac{M}{2}+1\right]^{+}$ is usually the most abundant fragment). Analogous behaviour was not found for compound (II). The fragmentation pattern observed may be rationalized, formally, as a decomposition into two 'monomeric' species. The following characteristic fragments were observed in the 70 eV mass spectrum of (II): *m/e* 116 (9); 117 (2); 118 (5); 186 (100); 187 (89); and 188 (10%).* Decomposition in accord with equation (2) is indicated from the metastable peaks. At 15 eV the mass spectrum revealed characteristic signals only for $[M]^{+\cdot}$ (*m/e* 304, 100%) and for *m/e* 187 (17%). The mass spectra of (II) at 70 and 15 eV were obtained on a Hitachi RMU-6L instrument.



(2)

Preparation of 2,2,2,4-*Tetrafluoro*-1,3-*dimethyl*-4-o-*phenylenedioxy*-1,3-*diazadiphosphetidine*, (II).—The reaction was conducted in a two-necked flask (250 cm³) fitted with a pressure-equalizing dropping funnel and a reflux condenser, topped by a drying tube. With careful exclusion of moisture, 8.2 g (0.128 mol) of $LiBu^n$ (54.7 g of a 15% solution in hexane) was added dropwise with magnetic stirring over 90 min to catechol (7.05 g, 0.064 mol) in



(II)

---

* 1 eV ≈ 1.60 × 10^{-19} J, 1 Torr = (101 325/760) Pa.

[7] R. K. Harris, M. Lewellyn, M. I. M. Wazeer J. R. Woplin, R. E. Dunmur, M. J. C. Hewson, and R. Schmutzler, *J.C.S. Dalton*, 1975, 61.

[8] O. Schlak, R. Schmutzler, and I. K. Gregor, *Org. Mass. Spectrometry*, 1974, **9**, 582.

diethyl ether (60 cm^3). The LiBu was transferred by means of a hypodermic syringe which was rinsed out with diethyl ether (20 cm^3). The reaction mixture was stirred for another 24 h at room temperature and for 2 h at reflux. The cooled reaction mixture was then transferred to the dropping funnel by inverting the apparatus, and so was added dropwise with stirring over 2 h at −80 to −40 °C to a solution of $[NMe(PF_3)]_2$ (15.0 g, 0.064 mol) in diethyl ether (50 cm^3).[2] After stirring for a further 24 h (at room temperature) and 2 h reflux, the solid product that had formed was filtered through a closed sintered-glass funnel system, and the filtrate was distilled in a short-path still. Between 77 (1.0) and 74 °C (0.6 Torr), 10.4 g [53% as (II)] of a colourless liquid were obtained which solidified on cooling. After two redistillations, the product was obtained, b.p. 71 °C (0.9 Torr), m.p. 47—48 °C (Found: C, 31.65; H, 3.3; N, 9.1. Calc. for $C_8H_{10}F_4N_2O_2P_2$: C, 31.6; H, 3.3; N, 9.2%). The product could also be sublimed at 40 °C (bath temperature) and 0.05 Torr.

We thank Dr. K. M. Worvill for assistance with the computations, the Commonwealth Scholarship Commission for a scholarship (to M. I. M. W.), Dr. D. Habel, Metallgesellschaft AG, Langelsheim/Harz, Germany, for generous supplies of n-butyl-lithium, Dr. I. K. Gregor, School of Chemistry, University of New South Wales, Kensington, N.S.W., Australia, for the mass-spectral data, and Deutsche Forschungsgemeinschaft and Fonds der Chemischen Industrie for support. The international collaboration which is essential to this project was made possible through the support of the N.A.T.O. Scientific Affairs Division.

[5/923 *Received* 15*th May*, 1975]