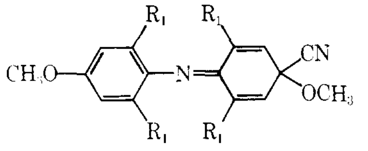
agents is an attractive route to new compounds. As an example, with tetraethylammonium cyanide the product of oxidation of **1a** is isolated with a yield near 90% and a similar compound is obtained from **1d.** These products result from the addition of one cyanide ion to the nitrenium ion **6** as indicated by satisfactory elemental analyses and mass molecular weights. Their spectroscopic and electrochemical properties[12] suggest the structure **8.** The reaction stops at the first stage without rearomatization but simple aromatic substitution has been observed for monosubstituted diphenylamines during anodic oxidation in methanolic sodium cyanide solutions.[13] A recent study proposed a route to aryl nitrenium ions *via* an electron reaction between aminyl radicals formed during the deoxygenation of aryl nitroxydes radicals by trialkyl phosphites in alcohol solutions.[14] It should be pointed out that anodic oxidation of arylamines can be used as an independent route to arylnitrenium species prepared from *N*-chloroarylamines following Gassman's work.[15]



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Moreover, **1a** allows, for the first time with an aromatic amine, the estimation of the formal potential $E_4° = -0.26$ V of the redox couple Ar_2N^+–$Ar_2N·$ which lies lower than the value $E_1° = 0.035$ V for the couple $Ar_2NH^{+·}$–Ar_2NH. This fact has some implications regarding the pathways involved in anodic coupling reactions of various diphenylamines.[4]

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(5) For a similar study with compounds bearing a NH group, see G. Cauquis, A. Deronzier, and D. Serve, *J. Electroanal. Chem.*, **47,** 193 (1973).

(6) The epr spectrum is a triplet 1:1:1 ($g = 2.0038$) with $a_N = 7.65$ G, in agreement with $a_N = 8.2$ or 8.08 G measured[7] for a spectrum of **7a** chemically produced in a benzene solution of **1a.**

(7) (a) B. G. Pobedimskii, A. L. Buchachenko, and M. B. Neiman, *Russ. J. Phys. Chem.*, **42,** 748 (1968); (b) F. A. Neugebauer and S. Bamberger, *Chem. Ber.*, **107**, 2362 (1974).

(8) Its conditions of isolation and properties will be given later.[4] This compound gives a very stable cation radical with a epr spectrum erroneously attributed to a tetraarylhydrazinium radical cation.[7a]

(9) Steric hindrance around the nitrogen nucleus does not seem to be the main factor since there is a strong decrease in the stability of the Ar_2N^+ ion in going from **6**a to **6**d.

(10) Here only remains the problem of the absorption of the cation **6c** because its spectrum is not obtained by conventional spectroscopy in the presence of 2,6-lutidine. Nevertheless, a spectroelectrochemical study with specular reflectance suggests that the dication **3c** and the cation **6c** have nearly the same band between 640 and 670 nm in the visible part of the absorption spectrum (A. Bewick and D. Serve, unpublished results, Southampton University, 1973).

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(12) From **1d** only one product is isolated (mp 98°; ir (KBr) $\nu_{C\equiv N}$ 2225 cm^{-1} (w); uv_{max} (CH_3CN) 245, 425 nm) but **1a** gives a mixture of the para and ortho cyano derivatives as will be discussed elsewhere.[4] The structure **8** is supported by the results of a comparative study of the cyano derivatives and of **5a.** Anodic oxidation of all these compounds produces a cation radical characterized by a large a_N value near 13 G in the epr spectrum.

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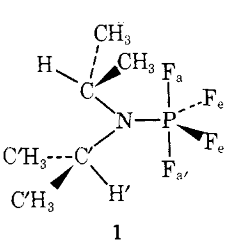
A Dynamic Nuclear Magnetic Resonance Study of Diisopropylaminotetrafluorophosphorane. Ground State Geometry and Barriers to Fluxional Processes

Sir:

Substituted derivatives of phosphorus pentafluoride are of interest because they can exhibit several stereochemical processes. For example, in the case of aminofluorophosphoranes of the type $R_1R_2NPF_4$ or $[R_1R_2N]_2PF_3$ these processes comprise: (a) fluorine positional interchange, (b) rotation around the nitrogen–phosphorus bond(s), (c) pyramidal inversion at nitrogen, and (d) rotation around the N–C bonds of the $-NR_1R_2$ moieties. At this point quantitative information regarding these stereochemical features is very sparse and, in fact, limited to one measurement[1] of the barrier to process *a* in $(CH_3)_2NPF_4$ and one measurement[2] of the barrier to process *b* in $(H_2N)_2PF_3$. The present paper describes the measurement of the barriers to processes *a* and *d* and an estimation of a lower limit for the barrier to process *b* in the title compound.

Diisopropylaminotetrafluorophosphorane (**1**) was prepared[3] by both the thermal decomposition[4] of the adduct $[(CH_3)_2CH]_2NH·PF_5$ and by the liquid phase reaction[5] between $[(CH_3)_2CH]_2NSi(CH_3)_3$ and PF_5. For the dynamic nmr (dnmr) experiments, **1** was dissolved in various halomethane solvents ($HCCl_2F$, $HCClF_2$, F_2CCl_2, $DCCl_3$, and CCl_3F) at a substrate concentration of *ca.* 2 *M*.

Above −20° all the stereochemical processes (a, b, c, and d) are rapid on the nmr time scale since (i) the isopropyl methyl (doublet, τ 8.68, $J_{HCCH} = 6.75$ Hz) and methine protons (overlapping doublet of heptets, τ 6.11, J_{PNCH} (average) = 26.5 Hz, $J_{HCCH} = 6.68$ Hz) are equivalent in the ambient temperature ^1H spectrum (Figure 1a), (ii) the methyl (singlet, +103.6 ppm[6]) and methine (singlet, +75.5 ppm) carbon atoms are equivalent in the ambient temperature ^{13}C spectrum, (iii) the ambient temperature ^{19}F spectrum consists of a doublet (+60.3 ppm,[6] $J_{PF} = 868$ Hz) thereby indicating that the axial and equatorial fluorine environments are being averaged, and (iv) the −20° ^{31}P spectrum (Figure 1b) is a quintet of triplets centered at +65.8 ppm[6] with $J_{PF} \simeq 870$ and J_{PNCH} (average) $\simeq$ 26 Hz.



1

On cooling from ambient temperature to −110°, the ^{19}F spectrum of **1** changes from a doublet to a set of five triplets possessing an intensity ratio 1:1:1:3:2 (Figure 1c). If, as is usually found,[7] the equatorial ^{19}F resonances appear at higher field, this is consistent with the ground state structure in which the equatorial fluorines are equivalent but the axial fluorines are chemical shift nonequivalent due to the different orientations of the isopropyl groups, *i.e.*, $F_{a'}$ +47.7,[8] F_a +58.8,[8] and F_e +68.0 ppm, and $J_{PF_{a'}} = 800$, $J_{PF_a} = 793$, $J_{PF_e} = 934$ Hz, and $J_{F_aPF_e} = J_{F_{a'}PF_e} = 74$ Hz. The observed intensity ratio results from overlap of the low field component of the F_e resonance with the high field component of one of the F_a resonances.

Further confirmation of this structure is provided by the low temperature ^1H and ^{13}C spectra of **1**. The fact that the −90° ^1H spectrum (Figure 1d) of the isopropyl methyl region consists of an overlapping doublet of doublets ($\tau \simeq 8.7$, $J_{HCCH} \simeq 7.5$ Hz; $\tau \simeq 8.8$, $J_{HCCH} \simeq 7.0$ Hz)[9] clearly indicates that the methyl groups have become chemical shift nonequivalent. This nonequivalence is also apparent in the −80° ^{13}C spectrum of **1** which exhibits two singlet[10] resonances (+103.2 and +105.2 ppm[6]) in the methyl region. The deduction that the chemical shift nonequivalence arises from chemical shift differences *between isopropyl groups* rather than between the methyl groups of a particular isopropyl moiety follows from the fact that the −80° ^{13}C spectrum of **1** exhibits two resonances (+73.5 and +77.5 ppm) in the methine region. The −90° ^1H spectrum of **1** in the methine region consists of three multiplets in an intensity ratio 2:1:1 (Figure 1d). The separation of the high field pair of multiplets corresponds to the doublet spacing which is observed in the low temperature ^{31}P spectra (*vide infra*) and consequently is assigned[11] to methine H ($\tau \simeq 6.5$, $J_{PNCH} = 43.5$ Hz). The multiplet of area 2 ($\tau \simeq 5.9$) is assigned to methine H′. Both sets of multiplets are complex on account of poorly resolved coupling from the nonequivalent isopropyl methyl protons.

The low temperature ^{31}P spectra also proved to be informative. On cooling from −20 to −100° the ^{31}P spectrum of **1** changes from a quintet of triplets (Figure 1b) to a quintet of doublets (Figure 1e). This indicates that while fluorine positional exchange is still rapid; N-C bond rotation[12] has become sufficiently slow on the nmr time scale that only one of the isopropyl methine protons exhibits a measurable coupling to phosphorus. Further cooling arrests the fluorine positional exchange since the −120° ^{31}P spectrum consists of 36 lines (Figure 1f) centered at +65.9 ppm.[6] The observed coupling constants were essentially the same as those which were measured from the spectra of other nuclei. The only additional coupling which was measured is $J_{PNCH'} \simeq 8$ Hz.[11]

Analysis of the ^{13}C spectra at the coalescence temperature of −63° by means of the Gutowsky-Holm relationship[13] yields a barrier of $\simeq 10$ kcal/mol for process *d*.[12] Similarly, the barrier to process *a* was determined to be $\simeq 7.5$ kcal/mol by analysis of the ^{19}F spectra at the coalescence temperature of −92°. As in the case of $(H_2N)_2PF_3$,[2] processes *a* and *b* appear to be inextricably coupled; hence the barrier for process *a* also represents a lower limit to the barrier for process *b*.

Other interpretations of the foregoing data were considered and rejected. For example, the possibility of the coexistence of different isomers of **1** is eliminated by the fact that there is only one ^{31}P resonance. Likewise, the possibility of a pyramidal rather than a planar (or time-averaged planar) nitrogen geometry for **1** is eliminated by the fact that the nonequivalence of the low temperature methine ^{13}C resonances would demand nonequivalence of the low temperature equatorial fluorines. Furthermore, planar nitrogeneous geometry appears to be a consistent feature of several N-P compounds.[14] Finally the possibility of a square pyramidal ground state structure[15] for **1** seems unlikely because the chemical shift and coupling constant values are in close agreement with the data for numerous trigonal bipyramidal

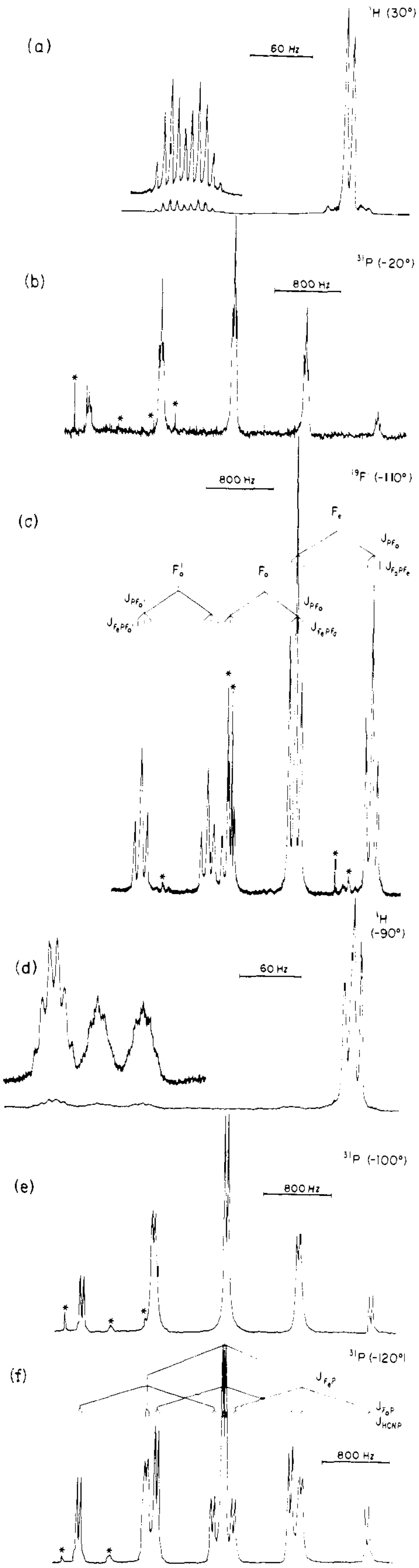


Figure 1. Nmr spectra of $(i\text{-}C_3H_7)_2NPF_4$ (**1**): (a) ambient temperature ^1H spectrum at 60 MHz; (b) −20° ^{31}P spectrum at 40.5 MHz; (c) −110° ^{19}F spectrum at 94.1 MHz; (d) −90° ^1H spectrum at 100 MHz; (e) −100° ^{31}P spectrum at 40.5 MHz; (f) −120° ^{31}P spectrum at 40.5 MHz. Only 18 lines are discernible in this spectrum. However, under higher resolution an additional doublet splitting of ~8 Hz is detectable on each of the peaks shown here. The asterisks in (b), (c), (e), and (f) denote spinning side bands or trace impurities.

phosphoranes.[1,16] Nevertheless it is worth noting that at this point characteristic nmr parameters have not been established for the square pyramidal phosphorane geometry.[17]

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(9) More accurate measurement of the chemical shifts and coupling constants was precluded by the fact that the resonances overlap.

(10) Note that no ^{31}P–N–^{13}C coupling is observed. The two-bond ^{31}P–C–^{13}C coupling constant is very small (<0.1 Hz) in $CH_2 = CHP(O)Cl_2$ (W. Althoff and R. Schmutzler, private communication). These very small or zero coupling constants are due presumably to the facility with which two-bond phosphorus couplings undergo sign changes; see, *e.g.*, S. L. Manatt, G. L. Juvinall, R. I. Wagner, and D. D. Elleman, *J. Amer. Chem. Soc.*, **88**, 2689 (1966); A. R. Cullingworth, A. Pidcock, and J. D. Smith, *Chem. Commun.*, 89 (1966); G. Mavel, *Progr. Nucl. Magn. Resonance Spectrosc.*, 1, 251 (1966); W. McFarlane, *Chem. Commun.*, 58 (1967); D. Gagnaire, J. B. Robert, and J. Verrier, *Chem. Commun.*, 819 (1967); E. J. Boros, R. D. Compton, and J. G. Verkade, *Inorg. Chem.*, **7**, 165 (1968); C. J. Jameson, *J. Amer. Chem. Soc.*, **91**, 6232 (1969); J. R. Schweiger, A. H. Cowley, E. A. Cohen, P. A. Kroon, and S. L. Manatt, *J. Amer. Chem. Soc.*, **96**, 7122 (1974).

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Synthesis of a Triazole Homo-C-nucleoside

Sir:

With pseudouridine[1] as its first member, the group of compounds known as C-nucleosides has steadily increased.[2] Each of the compounds has biological properties of considerable importance and interest. Although a variety of syntheses are reported, practically all have been partial, involving D-ribose or some other sugar in some way.[3] We now wish to describe a stereospecific total synthesis approach, independent of natural ribose, which has furnished a new homo-C-nucleoside, and which promises to open a way to other related compounds.

The starting point is the readily accessible tetrachlorobicyclo compound **1**,[4] which on reduction with lithium aluminum hydride in the presence of lithium hydride loses three of its four chloro groups to give 3-chloro-8-oxabicyclo-[3.2.1]octa-2,6-diene (**2**)[5] in 80% yield. The expectation that the double bond in **2** that carries the chloro group ($\Delta^{2(3)}$) would be less readily attacked by electrophilic reagents than the unsubstituted double bond ($\Delta^{6(7)}$) was realized when diolefin **2** was found to react smoothly and selectively with osmium tetroxide–hydrogen peroxide and acetone to give the desired glycol (in the form of its isopropylidene derivative **3**) as the only product in 70% yield (Scheme I).

We have formulated adduct **3** with the oxygen substituents cis exo rather than cis endo for two reasons. First, examination of a Dreiding scale model of substrate **2** reveals that the exo side of the double bond offers more room for approach of the bulky reagent than the endo side. Second, a model of exo compound **3** has a dihedral angle between H-6 and the bridgehead H-5 measuring close to 90°. The same is true of the dihedral angle between H-7 and the bridgehead H-1. Accordingly, there should be minimal nuclear magnetic resonance coupling between H-5 and -6 as well as between H-1 and -7,[6] so that the quartet expected from the spin-spin coupled cis protons at positions 6 and 7 should ap-

Scheme I