centered +59 ppm from external trimethylborane. The upfield shift from the conjugate acid is large, and indeed such a shift is characteristic of negatively charged boron.[10,11]

The smaller alternation of peak positions of adjacent CH groups of **4** relative to that of pentadienyl anions is consistent with a more even charge distribution in **4**. As expected from examination of classical resonance structures, the protons at C_4, C_2, and C_6 are more highly shielded than those at C_3 and C_5. That C_4 may have the greatest charge density is suggested by its highest field peak.

While spectra suggest significant aromatic properties for the borabenzene anion, further studies, now in progress, are necessary to better define this stabilization.

Acknowledgment. We wish to acknowledge partial support of this work by a Rackham Faculty Grant of the University of Michigan and to thank the National Science Foundation for a grant (No. GP-8345) to the University of Michigan for the purchase of an MS-9 mass spectrometer.

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(10) For a discussion of ^{11}B nmr spectra as a criterion of aromaticity in the borazarenes, see F. A. Davis, M. J. S. Dewar, and R. Dawes, *J. Amer. Chem. Soc.*, 90, 706 (1968).

(11) G. R. Eaton and W. N. Lipscomb, "Nmr Studies of Boron Hydrides and Related Compounds," W. A. Benjamin, New York, N. Y., 1969, pp 437–516, 562.

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The Barrier to Pyramidal Inversion in Acylphosphines[1]

Sir:

The amide functionality, due in part to its biological import, has been extensively studied. With regard to molecular structure and dynamics, amides are known to be planar or to possess low barriers (*ca.* 1 kcal/mol) to pyramidal inversion,[2] and relatively high (*ca.* 20 kcal/mol) torsional barriers[3] about the nitrogen–carbonyl bond. No comparable information is available for the congeneric structures formed by replacement of nitrogen by phosphorus or other group Va elements. We now report our finding that, in contradistinction to amides, the rate-limiting conformational exchange process in acylphosphines, as represented by acetylisopropylphenylphosphine (**1**), is pyramidal inversion. The magnitude of the barrier ($\Delta G^{\ddagger}_{110}$), *ca.* 19.4 kcal/mol, is markedly lower than that found for sundry acyclic diarylalkyl- and dialkylarylphosphines.[4]

The synthesis of **1** was accomplished by condensation of acetyl chloride with the sodium salt of isopropylphenylphosphine according to the procedure of Issleib and Priebe.[5] The crude reaction mixture was purified by chromatography (silica gel, benzene) followed by rapid distillation (kugelrohr, *ca.* 60° (0.02 mm)). The ir spectrum shows a low-frequency carbonyl stretch at *ca.* 1675 cm^{-1},[6] and the pmr spectrum (a *ca.* 20 v/v % solution in CF_2Cl_2 with *ca.* 1 v/v % tetramethylsilane) is consistent with the assigned structure: δ 7.9–7.2 (m, $C_6\mathit{H}_5$), 2.7–2.0 (m, $C\mathit{H}(CH_3)_2$), 2.0 (d, J_{PH} = 6.0 Hz, $C(O)C\mathit{H}_3$), 1.22 (q, J_{PH} = 17.8 Hz, J_{HH} = 6.8 Hz, $CH(C\mathit{H}_{3(A)})$), 0.80 (q, J_{PH} = 13.4 Hz, J_{HH} = 7.0 Hz, $CH(C\mathit{H}_{3(B)})$).

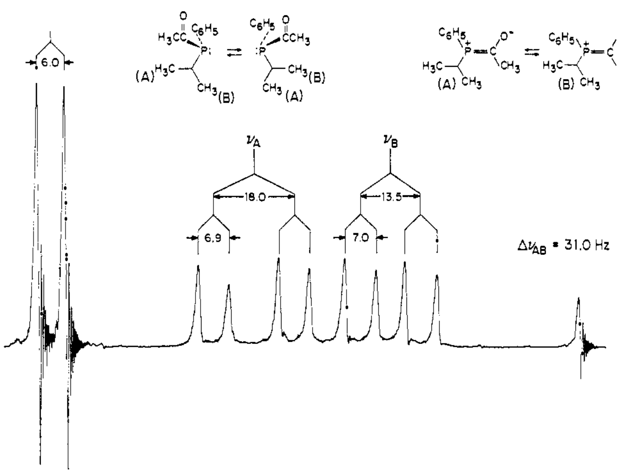
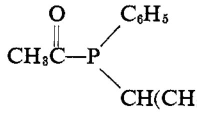
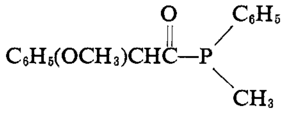


Figure 1. 60-MHz spectrum of the methyl region of **1** (*ca.* 25 v/v % solution in 1-bromonaphthalene with *ca.* 1 v/v % $(Si(CH_3)_3)_2$ as internal standard) at 45°.



$$CH_3C(=O)-P(C_6H_5)CH(CH_3)_2$$

1



$$C_6H_5(OCH_3)CHC(=O)-P(C_6H_5)CH_3$$

2

The methyl portion of the pmr spectrum of **1** in 1-bromonaphthalene (see Figure 1) is compatible with a conformationally restricted phosphine. The isopropyl methyl resonances exhibit a temperature dependence, broadening with increasing temperature to a coalescence at *ca.* 110°; further heating results in a quartet. The acetyl methyl signal remains as a sharp doublet over the entire range of temperature (45–150°). Substitution of the rate constant derived from the Gutowsky–Holm equation into the Eyring equation (assuming a transmission coefficient of unity)[7] yielded the above cited $\Delta G^{\ddagger}$. Cooling a sample of the phosphine (CF_2Cl_2 solvent) to *ca.* −100° produces only a severe broadening of all the resonances of **1**, while tetramethylsilane remains relatively sharp. However, no new resonances were observed.

These observations are accommodated by two alternative interpretations, suggested by analogy to related processes in phosphines and amides: either the phosphorus atom is pyramidal, and the interconversion is one of enantiomers, by inversion (limiting case I), or the phosphorus moiety is planar, and the interconversion is one of diastereomers, *i.e.*, cis and trans forms, by rotation (limiting case II); see Figure 1.

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(1) This work was supported by grants from the Air Force Office of Scientific Research (AF-AFOSR-1188-B) and the National Science Foundation (GP-22542).

(2) C. C. Costain and J. M. Dowling, *J. Chem. Phys.*, 32, 158 (1960).

(3) For a recent review, see W. E. Stewart and T. H. Siddall, III, *Chem. Rev.*, 70, 517 (1970).

(4) R. D. Baechler and K. Mislow, *J. Amer. Chem. Soc.*, **92**, 3090 (1970).

(5) K. Issleib and E. Priebe, *Chem. Ber.*, **92**, 3183 (1959).

(6) K. Issleib and O. Löw, *Z. Anorg. Allg. Chem.*, **346**, 241 (1966).

(7) The Gutowsky–Holm equation may justifiably be used[8] to obtain reliable values of $\Delta G^{\ddagger}$ in complex spin systems (at least in cases such as the present where the chemical shift is greater than the coupling constants). Trace impurities in the isopropyl region in concert with a relatively large chemical-shift difference (producing a very broad coalescence) rendered a complete line-shape analysis infeasible.

(8) K.-I. Dahlqvist and S. Forsén, *Acta Chem. Scand.*, **24**, 651 (1970).

In case I, the two methyl groups A and B within each isopropyl moiety are diastereotopic by internal comparison and become enantiotopic when pyramidal inversion is rapid on the nmr time scale. On the other hand, in case II, the two isopropyl groups, A and B, are diastereotopic by external comparison and become homotopic when rotation is rapid on the nmr time scale. Evidently, the collapse of the 8-line spectrum to a quartet at temperatures above 110° could correspond to the interchange of the environments of A and B by either process. However, that pyramidal inversion is the observed process may be deduced from two independent observations.

First, in case I the two interconverting isomers are enantiomers and are thus equally populated, whereas in case II they are diastereomers and are not expected to exist in a 1:1 ratio, nor in a ratio that is independent of temperature and solvent. The observation that the two sets of signals derived from A and B are of equal intensity over the whole temperature range and are independent of solvent thus speaks for case I.[9]

Second, the acetyl methyl groups in case I are enantiotopic, in case II diastereotopic, and under conditions of fast exchange become homotopic in both processes. One would thus expect, in the slow exchange limit, two resonances for case II and only one for case I. One resonance was observed,[10] and again the result is only compatible with case I.[11–14]

Ancillary evidence for the correctness of the assignment is provided by calculation. The CNDO/2 scheme has recently been parametrized[15] to reproduce, with a high degree of accuracy, barriers to pyramidal inversion for a wide variety of systems containing first- and second-row elements. Use of this scheme results in a barrier of 22 kcal/mol for acetyldimethylphosphine, in good agreement with that obtained for **1** by dnmr. Support for the accuracy of the experimental barrier derives from the observed coalescence of the $-OCH_3$ signals from the diastereomers of methyl (*O*-methylmandelyl)phenylphosphine (**2**). Coalescence (at *ca.* 100°, $\Delta\delta_{AB}$ 0.24 ppm) is between two uncoupled, unequally populated sites and a first-order rate constant is readily calculated.[16] The $\Delta G^{\ddagger}$ values determined for the interconversion of the diastereomers of **2** (in a 40:60 ratio) are 19.1 and 19.3 kcal/mol.

The low inversion barrier found for acylphosphines may be thought of as arising from enhanced $(p-p)\pi$ conjugation in the planar transition state, relative to the pyramidal ground state, of the phosphorus lone pair with the carbonyl group, producing, in effect, the contributing dipolar structures presented in Figure 1. The effect on the phosphorus–carbonyl torsional barrier is evidently considerably less than the corresponding effect in amides.

The contrast between the geometry (and conformational barriers) of amides and acylphosphines is accounted for by the significantly higher "intrinsic" inversion barrier of acyclic phosphines (30–36 kcal/mol)[4] as compared to amines (4–8 kcal/mol);[17] in structures differing only in the identity of the inverting center (N *vs.* P), it is far easier to flatten the nitrogen than the phosphorus pyramid.[18]

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[9] The utilizable temperature range was −75 to 90°. Below and above these temperatures broadening was too severe. The solvent for the low-temperature study (−100 to 45°) was CF_2Cl_2 while that for the higher temperatures (45–150°) was 1-bromonaphthalene. A 1:1 ratio was also observed at 45° in C_6D_6.

[10] The conditions were as in ref 9, except that the acetyl methyl remained as a sharp signal to 150°, the highest temperature employed.

[11] Nmr and ir evidence for conformational isomerism in acylphosphines have been presented,[12] but neither the nature of the interconversion (rotation *vs.* inversion) nor the barrier height was determined. The ir spectrum of trifluoroacetyldiphenylphosphine presented in this work[12] is not in accord with that published by Lindner and Kranz.[13]

[12] R. G. Kostyanovskii, V. V. Yakshin, and I. I. Chervin, *Dokl. Akad. Nauk SSSR*, 188, 366 (1969), and references cited therein.

[13] E. Lindner and H. Kranz, *Chem. Ber.*, 101, 3438 (1968).

[14] An interpretation based on the interconversion of rotational isomers in a pyramidally stable **1** is ruled out by the observed simplicity of the pmr spectrum.

[15] A. Rauk, J. D. Andose, W. G. Frick, R. Tang, and K. Mislow, unpublished work.

[16] H. Shanan-Atidi and K. H. Bar-Eli, *J. Phys. Chem.*, 74, 961 (1970).

[17] A. Rauk, L. C. Allen, and K. Mislow, *Angew. Chem., Int. Ed. Engl.*, **9**, 400 (1970).

[18] *Cf.* also, W. Egan, R. Tang, G. Zon, and K. Mislow, *J. Amer. Chem. Soc.*, **92**, 1442 (1970); R. D. Baechler and K. Mislow, *ibid.*, **93**, 773 (1971).

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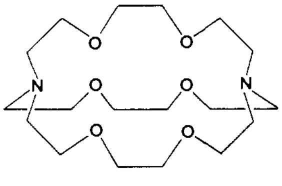
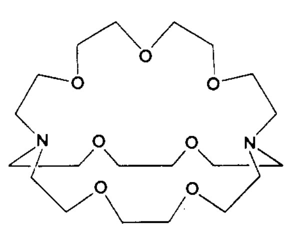
Crystal Structures of Two Barium Cryptates

Sir:

New types of metal–cation complexes known as cryptates[1,2] have recently been the subject of considerable interest. The crystal and molecular structures of ligand I and of the corresponding rubidium cryptate have already been reported.[3,4] We wish now to describe the structures of two complexes formed by barium thiocyanate with the ligands I and II. We started this study in order to compare the structures of alkali and alkaline-earth metal cryptates of different stabilities[5] and also to show the role of the water molecules present in the barium complexes of this type.



I: $C_{18}H_{36}N_2O_6$



II: $C_{20}H_{40}N_2O_7$

Suitable crystals of $[(I)Ba^{2+}][SCN^-]_2\cdot H_2O$ (denoted by A) and $[(II)Ba^{2+}][SCN^-]_2\cdot 2H_2O$ (denoted by B) were prepared by slow evaporation of methanol–butanol solutions of the ligands and barium thiocyanate in the ratio 1:1. Analytical results agree with the formulas given for the compounds.

A crystallizes in the orthorhombic system with a = 37.728 (11), b = 19.525 (5), c = 15.303 (3) Å; ρ_{obsd} = 1.57 ± 0.02, and ρ_{calcd} = 1.54 g cm^{-3} based on 16 formula species per cell. Diffraction symmetry and

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[1] B. Dietrich, J. M. Lehn, and J. P. Sauvage, *Tetrahedron Lett.*, 2885 (1969).

[2] B. Dietrich, J. M. Lehn, and J. P. Sauvage, *ibid.*, 2889 (1969).

[3] B. Metz, D. Moras, and R. Weiss, *Proc. Int. Conf. Coord. Chem., 13th, 1970*, **2**, 85 (1970).

[4] B. Metz, D. Moras, and R. Weiss, *Chem. Commun.*, 217 (1970).

[5] J. M. Lehn and J. P. Sauvage, to be published.