complexes are present over the entire temperature range of contact shift measurements (240–360°K). Active [(+,+), (−,−)] and *meso* (+,−) diastereoisomers are generated by the two asymmetric ligand centers; as in other cases[9,13] their pmr signals are clearly resolved and identifiable by preparation of active isomers from resolved amines. Thermodynamic data for comparison, obtained by a procedure described[9] using β-H signals and hyperfine coupling constants ($a_{\beta H}$) from the R = *t*-Bu complexes, are presented in Table I. Two important conclusions applicable within and below the temperature interval of measurement emerge for the pairs A–D compared: (i) $\Delta F_S - \Delta F_O = \Delta\Delta F > 0$, demonstrating that *sulfur effects greater stabilization of planar stereochemistry than oxygen;* (ii) $|\Delta\Delta H| > |T\Delta\Delta S|$, indicating that inequalities in stereochemical populations are due to enthalpy rather than entropy effects. On the basis of arguments developed elsewhere,[8] differences in metal–ligand bonding in the two stereoisomers are considered principally responsible, with a large extent of π bonding in the planar thio complexes a plausible source of the stability differences. Comparison of experimental and calculated spin densities, currently underway, should serve to establish relative degrees of π bonding in the tetrahedral O, S stereoisomers. Finally, conclusions i and ii are unchanged by comparisons in $CDCl_3$ solutions, the following $\Delta\Delta F = \Delta\Delta H - T\Delta\Delta S$ relationships having been obtained for the indicated pairs: A, 5060 − 12.0*T;* B, 3960 − 11.5*T;* C, 3900 − 8.0*T;* D, 3250 − 7.2*T.*

Table I. Thermodynamics of the Planar–Tetrahedral Structural Conversion of Nickel(II) Complexes **2** (X = O, S) in Carbon Tetrachloride Solution[a]

	Pair	Isomer	ΔH, cal/mole	ΔS, eu	$\Delta F^{323°}$,[b] cal/mole	$N_t^{323°}$ [b]
A	$Ni(Amp\text{–}PhHH)_2$	active	−320	3.06	−1310	0.89
	$Ni(Amp\text{–}SPhHH)_2$		3580	11.4	−98	0.54
B	$Ni(Amp\text{–}PhHH)_2$	*meso*	399	4.70	−1120	0.85
	$Ni(Amp\text{–}SPhHH)_2$		2910	11.4	−784	0.77
C	$Ni(\textit{sec}\text{-}Bu\text{–}PhHH)_2$	active	892	5.98	−1040	0.83
	$Ni(\textit{sec}\text{-}Bu\text{–}SPhHH)_2$		3490	10.1	221	0.41
D	$Ni(\textit{sec}\text{-}Bu\text{–}PhHH)_2$	*meso*	1230	6.82	−969	0.82
	$Ni(\textit{sec}\text{-}Bu\text{–}SPhHH)_2$		3120	9.98	−106	0.54

[a] Data calculated from measured proton contact shifts (240–360°K) and eq 3 in ref 9 using $a_{\beta H}$ (X = O) = −0.884 G (from $Ni(\textit{t}\text{-}Bu\text{–}PhHH)_2$) and $a_{\beta H}$ (X = S) = −0.717 G (from $Ni(\textit{t}\text{-}Bu\text{–}SPhHH)_2$). [b] Given at the indicated temperature for comparison with data in ref 9.

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[14] National Science Foundation Predoctoral Fellow 1966 to present.

Restricted Rotation Around Phosphorus–Nitrogen Bonds[1]

Sir:

We wish to report the first measurement of a rotational barrier around a P–N bond. The ^1H nmr spectrum of chloro(dimethylamino)phenylphosphine (**1**), $C_6H_5P(Cl)N(CH_3)_2$, displayed the expected doublet in the methyl region at ambient temperature with J_{PNCH} = 12.6 Hz and τ 7.4.[2] On cooling, the methyl doublet broaded (Figure 1b) and eventually coalesced. Below −60° (Figures 1d, e) two clearly defined doublets developed. At −80° the low-field doublet (τ 7.22) had J_{PNCH} = 19.2 Hz and the high-field doublet (τ 7.75) had

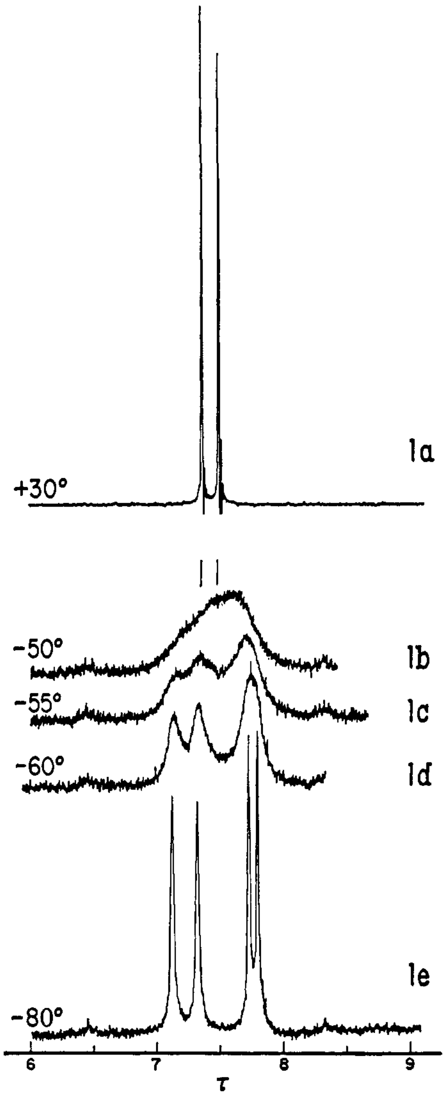

Figure 1.

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[1] This work was supported by the Air Force Office of Scientific Research, through Grant No. AF-AFOSR-1050-67, and the Robert A. Welch Foundation.

[2] All spectra were measured by Mr. E. J. Burshnick on a Varian Associates HA-100 spectrometer equipped with a calibrated variable-temperature accessory. Approximately 15% solutions of the (dialkylamino)phosphines in CCl_3F were sealed *in vacuo* along with a few per cent TMS as internal standard. Chloro(dibenzylamino)phenylphosphine was dissolved in $CDCl_3$ (5% solution) with CH_2Cl_2 internal standard.

$J_{PNCH} = 6.7$ Hz.[3] The coupling constant of the doublet at ambient temperature is the average of the low-temperature values.

When these experiments were repeated with saturation at the phosphorus frequency,[4] the ambient temperature singlet gradually broadened and separated into two singlets as the temperature was lowered. The coalescence temperature was −50 ± 2°. The separation of the doublets was measured as a function of temperature between −50 and −65°, yielding an approximate value of 12 kcal mol^{-1} for the rotational barrier of the P–N bond.[5] At the coalescence temperature $\Delta F^{\neq} = 10.5$ kcal mol^{-1} (from the Eyring equation).

The above data could also be interpreted in terms of a barrier to pyramidal inversion of the nitrogen atom. High barriers to inversion have been reported for aziridines[6] and N-haloaziridines[7] where the nitrogen atom is constrained in a three-membered ring.

In noncyclic systems the presence of a hetero atom directly bonded to the nitrogen atom has been alleged to substantially increase the inversion barrier. However, in some of these cases, *e.g.*, the spectra of N-benzyl-N,O-dimethylhydroxylamine[8] and N,N-dibenzyltrichloromethanesulfenamide,[9] the interpretation of the spectra in terms of a N-hetero atom rotational barrier has not been rigorously excluded.

The interpretation of our results in terms of P–N bond restricted rotation is supported by the following additional experiments.

(i) Below −50° the methyl region in the ^1H spectrum of chloro(diisopropylamino)phenylphosphine (II), $PhP(Cl)N[CH(CH_3)_2]_2$, was that expected for four nonequivalent methyl groups (doublets at τ 8.55, 8.63, 8.89, and 9.17, with $J_{HCCH} = 6.4$ Hz). On warming, coalescence occurred at −10 ± 5°, and the ambient temperature spectrum consisted of a pair of doublets at τ 8.71 and 8.91. The diastereotopic character[10] of the isopropyl methyl groups in the ambient-temperature spectrum results from the chiral center at phosphorus.[11]

(ii) Analogous changes were noted with ^{31}P-irradiated spectra of (dibenzylamino)chloro(phenyl)phosphine (III), $C_6H_5P(Cl)N(CH_2C_6H_5)_2$, with a coalescence temperature of the benzyl methylene groups at −46 ± 3°.

The increase of coalescence temperature with increasing bulk of the nitrogen substituent is opposite to the trend expected on the basis of nitrogen inversion.[6] A similar argument has been invoked very recently to interpret the spectra of a series of sulfenamides in terms of hindered S–N bond rotation.[12]

Rotational barriers of ∼12 kcal mol^{-1} in P–N bonds are too large to be attributed to conformational effects of the kind operating in compounds such as ethane or methylamine. Further, this interaction seems unlikely to be of pπ–dπ type, because such π bonding would not be expected to lead to hindered rotation.[13] On this basis it might seem reasonable to attribute the barrier to a lone-pair–line-pair interaction, and, if so, to anticipate barriers of comparable magnitude in analogous derivatives of hydrazine. Kosuya and Kojuma[14] have claimed that the barrier in hydrazine itself is only 3.15 kcal mol^{-1}. However, this was a microwave determination based on an assumed form of the potential function and may therefore be subject to errors of uncertain magnitude. Other reported measurements refer to hydrazones,[15] triazines,[16] and tetrazines,[17] *i.e.*, compounds in which one of the nitrogen atoms forms a π bond; the barriers in such cases would be very different from those in simple hydrazines.

The related aminophosphines $RP(Cl)N(CH_3)_2$, R = CF_3 and CH_3, and the aminoarsine $C_6H_5As(Cl)N(CH_3)_2$ displayed similar low-temperature ^1H spectra. More detailed studies of these and related systems containing N–P and N–N bonds are being carried out.

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[3] Recent work with a cyclic phosphine indicates that the magnitude of J_{PCH} is sensitive to the stereochemical environment: D. Gagnaire, J. B. Robert, and J. Nerrier, *Chem. Commun.*, 819 (1967). Presumably a similar effect is operative here.

[4] Saturation at the phosphorus frequency was achieved using a NMR Specialties HD-60B heteronuclear decoupler. We wish to thank Dr. B. Shoulders for assistance with these experiments.

[5] Using the method described by J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co. Inc., New York, N. Y., 1959, p 224. More accurate values from line-shape calculations for this and related compounds will be presented in the full publication.

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[10] See K. Mislow and M. Raban in "Topics in Stereochemistry," Vol. 1, N. L. Allinger and E. L. Eliel, Ed., Interscience Division of John Wiley and Sons, Inc., 1967, p 1, for terminology.

[11] Considerably higher temperatures are required for inversion at phosphorus. See J. B. Lambert and D. C. Mueller, *J. Am. Chem. Soc.*, 88, 3669 (1966).

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[18] On leave of absence from the Queen's University of Belfast, N. Ireland.

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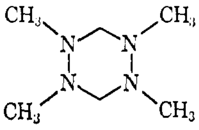
Conformational Equilibria and Equilibration of Tetramethylhexahydrotetrazine. Slow Nitrogen Inversion. N-Methyl Groups with a Preference for Axial Positioning[1]

Sir:

The ambient-temperature pmr spectrum of N,N′,-N′′,N′′′-tetramethylhexahydrotetrazine[2] (1) at 60 MHz shows two sharp peaks of relative intensity 1:3, as would be expected for rapid conformational inversion. However, at −87°, the methylene resonance appears as an AB quartet while there is a 1:1 doublet for the



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[1] Supported by the National Science Foundation.

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