$J_{PNCH} = 6.7$ 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 $-50 \pm 2°$. 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 $\Delta F^{\ddagger} =$ 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 ^{1}H 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 $-10 \pm 5°$, 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 $-46 \pm 3°$.

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 ^{1}H spectra. More detailed studies of these and related systems containing N–P and N–N bonds are being carried out.

Acknowledgment. We wish to thank the referees for constructive criticism of the first draft of the manuscript.

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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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(7) D. Felix and A. Eschenmoser, *Angew. Chem.*, **80**, 197 (1968); S. J. Brois, *J. Am. Chem. Soc.*, **90**, 508 (1968), and references therein.

(8) D. L. Griffith and J. D. Roberts, *ibid.*, **87**, 4089 (1965).

(9) M. Raban, *Chem. Commun.*, 1017 (1967).

(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).

(12) M. Raban, F. B. Jones, and G. W. J. Kenney, paper submitted for publication. We wish to thank Dr. Raban for informing us of this work.

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

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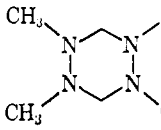
Conformational Equilibria and Equilibration of Tetramethylhexahydrotetrazine. Slow Nitrogen Inversion. N-Methyl Groups with a Preference for Axial Positioning[1]

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.

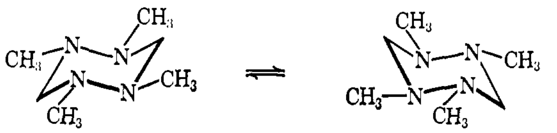
(2) E. Schmitz, *Ann.*, **635**, 73 (1960).

Table I. Spectral Parameters of N,N′,N″,N‴-Tetramethylhexahydrotetrazine in Cyclopropane Solution

	NCH_2N group	NCH_3 group
Chemical shift,[a] 37°	3.25	2.20
Chemical shift,[a] −87°	2.85 3.52	1.95 2.36
Relative chemical shift,[b] −87°	40.3	24.3
Geminal coupling constant,[b] −87°	11.6	
Coalescence temperature, deg	−24	−35
Free energy of activation at coalescence temperature, kcal/mole	11.8	11.6

[a] From protons of the cyclopropane used as solvent; in parts per million. [b] In hertz.

methyl groups (see Table I for a summary of the spectral data). The nonequivalence observed for the ring methylenes is indicative of slow ring inversion, for which somewhat similar examples have recently been reported with several six-membered rings containing N-methyl groups.[3] The 1:1 doublet obtained for the N-methyl groups rules out the possibility that **1** exists as a mixture of conformations **2** and **3** with equivalent equatorial methyl groups which are interconverted rapidly at room temperature and slowly at −87° by a ring inversion and four nitrogen inversions.



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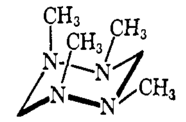
To account for the two equally intense N-methyl resonances, a conformation with two axial N-methyl groups and two equatorial methyl groups is required, and **4**, **5**, and **6** are the possibilities. It is likely that



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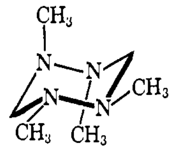

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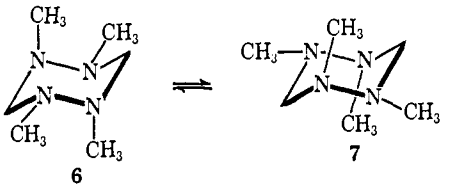
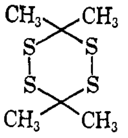


6 7

4 can be excluded because of the substantial 1,3 interaction between its axial methyl groups. A decision as to whether **5** or **6** is more favorable is less simple, but it seems reasonable to choose **6** on the basis that **6** has identical interaction between the members of each pair of vicinal N-methyl groups. Other grounds for favoring **6** over **5** will be presented elsewhere—the important point is that the unusual features of the low-temperature pmr spectrum of **1** to which we call attention here are independent of the choice between **5** and **6**.

An alternate conformation of a different kind is a boat-type arrangement which Bushweller[4] has recently reported to be important for duplodithioacetone (**8**). However, the mobility of boat-type conformations in the absence of bridging groups is likely to be much too great to permit observation of two kinds of methylene hydrogens and two kinds of methyl groups for **1** at −87°.



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For **6**, inversion of each of the four nitrogens gives conformation **7**, in which the axial and equatorial methyl groups have been interchanged but not the axial and equatorial methylene hydrogens. Clearly, observation of two N-methyl resonances at −87° means that the **6** $\rightleftarrows$ **7** equilibration which results by nitrogen inversion must also be slow at this temperature. Occurrence of slow nitrogen inversion in simple six-membered rings has only been reported previously for 4,4-difluoropiperidine[5] and in acid solutions.[6]

The free energies of activation corresponding to the coalescence points of the methyl and methylene signals are both about 11.7 kcal/mole. The methylene hydrogens only become equivalent on the nmr time scale when ring inversion is fast, so that the barrier to ring inversion is 11.7 kcal/mole. The N-methyl resonances are expected to coalesce when either ring inversion or nitrogen inversion is fast, so that the barrier to nitrogen inversion must be greater than or equal to 11.7 kcal/mole.

In summary, **1** is remarkable because two of its methyl groups prefer to occupy axial positions and because nitrogen inversion is relatively slow.

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(3) (a) N-Methylpiperidine: J. B. Lambert, R. G. Keske, R. E. Carhart, and A. P. Jovanovich, *J. Am. Chem. Soc.*, **89**, 3761 (1967); (b) N,N′-dimethylpiperazine: R. K. Harris and R. A. Spragg, *Chem. Commun.*, 314 (1966); (c) N,N′-dimethylhexahydropyrimidine: F. G. Riddell, *J. Chem. Soc.*, *B*, 560 (1967); (d) N,N′-dimethylpiperidazine: J. E. Anderson and J. M. Lehn, *Bull. Soc. Chim. France*, 2402 (1966); (e) N,N′,N″-trimethylhexahydrotriazine: J. M. Lehn, F. G. Riddell, B. J. Price, and I. O. Sutherland, *J. Chem. Soc.*, *B*, 387 (1967).

(4) C. H. Bushweller, *J. Am. Chem. Soc.*, **89**, 5978 (1967).

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(6) See the very recent work of J. J. Delpuech and M. N. Deschamps, *Chem. Commun.*, 1188 (1967), and J. L. Sudmeier and G. Occupati, *J. Am. Chem. Soc.*, **90**, 154 (1968). Some analogy to the present results can be found in bridged diaza ring systems; see J. E. Anderson and J. M. Lehn, *ibid.*, **89**, 81 (1967), and E. L. Allred, C. L. Anderson, R. L. Miller, and A. L. Johnson, *Tetrahedron Letters*, 525 (1967), and also in fused-ring compounds; see B. Junge and H. A. Staab, *ibid.*, 709 (1967).

(7) Harkness Fellow of the Commonwealth Fund of New York, 1966–1968.

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Evidence for a Concerted Mechanism for Allene Cycloaddition

Sir:

The Woodward–Hoffmann "selection rules" for electrocyclic reactions predict that concerted 2 + 2 cycloaddition should not be symmetry allowed from the ground state and that thermal cyclobutane-forming reactions must therefore proceed *via* multistep (*e.g.*, biradical) mechanisms.[1] The experimental support

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(1) R. Hoffmann and R. B. Woodward, *J. Amer. Chem. Soc.*, **87**, 2046 (1965).