Nuclear Magnetic Resonance Spectroscopy. Hindered Rotation about the Carbon–Phosphorus Bond in *tert*-Butyldichlorophosphine[1]

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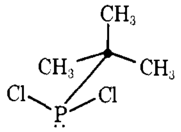
Abstract: The barrier to rotation about the C–P bond in *tert*-butyldichlorophosphine has been derived from a line-shape analysis of the proton nmr spectrum as a function of temperature. The $^3J_{PCCH}$ coupling constants are different for the two kinds of methyl protons. This difference suggests an influence of the bond orientation about the phosphorus–carbon bond on $^3J_{PCCH}$ for three-coordinate phosphorus compounds.

Although many nmr studies have been made of barriers to rotation about bonds connecting first-row elements,[3] much less has been done with the corresponding barriers for bonds in which one or both of the atoms is a second-row element. As far as phosphorus is concerned, the principal research has been on substances with P–N bonds.[4] For P–C bonds, the reported barriers are for CH_3–P rotations and come from microwave, infrared, and Raman spectroscopy. These barriers (in kilocalories per mole) are, as expected, rather small: CH_3PH_2(g), 1.96 (microwave);[5a] $(CH_3)_2PH$(g), 2.22 (microwave);[5b] $(CH_3)_3P$(g), 2.6 (microwave);[5c] $(CH_3)_3P$(s), 3.58 (infrared, Raman);[5d] CH_3PCl_2(s), 3.4 (infrared);[5e] CH_3POCl_2(s), 4.4 (infrared);[5e] CH_3POF_2(s), 3.6 (infrared);[5e] and CH_3PSCl_2(s), 3.2 (infrared).[5e] The effect of steric hindrance across a P–C bond is anticipated, because of its greater length (1.87 Å, predicted from the sum of the covalent-bond radii), to be less than across a C–C bond. To investigate this point and to find out whether there are unexpected factors involved in determining rotational barriers about P–C bonds, we have investigated the change with temperature of the proton nmr spectrum of *tert*-butyldichlorophosphine. It has been possible to determine the barrier to rotation as well as the stereochemical dependence of the $^3J_{PCCH}$ coupling.

The proton spectrum of *tert*-butyldichlorophosphine (used as received from Strem Chemicals), as a 4% solution in vinyl chloride and recorded with a Varian A56/60 spectrometer equipped with a V6040 temperature controller, is shown as a function of temperature in Figure 1. The temperature controller dial was calibrated with the aid of thermocouple readings made on a nonspinning sample of vinyl chloride. The uncertainty in temperature is estimated to be ±2°.

At higher temperatures, the methyl proton resonances are a doublet ($^3J_{PCCH}$ = 15.6 Hz). When the temperature is reduced to the point where rotation becomes slow on the nmr time scale, the lines broaden and finally split below about −140° into three peaks in approximately the ratio 3:2:1. We assume here that the change in spectrum arises from slow interconversion of staggered conformations **1** in line with other evidence for this kind of favored conformation for phosphorus compounds.[5a,6]



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The perhaps unexpected changes in line shapes which occur on lowering the temperature can be accounted for as follows. In the first place, the chemical-shift difference between the two methyls gauche to the phosphorus lone pair and the methyl trans is about 8 Hz at the lowest temperature. The coupling $^3J_{PCCH}$(g) = 21 Hz is substantially larger than $^3J_{PCCH}$(t) = 5.2 Hz, where g refers to the coupling to phosphorus with the lone pair gauche and t with the lone pair trans. Provided that the $^4J_{HCCCH}$ couplings between protons on the nonequivalent methyls are negligible, the observed low-temperature spectrum arises as shown in Figure 2.

A total line-shape analysis has been carried on by the method of "effective chemical shifts"[7] using the DNMR3 program[8] of the change in spectra with temperature on the assumption that the relaxation of phosphorus is slow compared to the rates of interconversion of the isomers. With this assumption, it is possible to treat **1** as a mixture of two isomers differing only in the spin state (α or β) of the phosphorus. The calculated spectra as a function of rate of rotation are also given in Figure 1. In the calculation T_2, the line width, in absence of interconversion, was estimated from the line widths of the solvent resonances. A least-squares fit

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[2] On leave of absence from the University of Grenoble (France).

[3] *Cf.* J. P. Lowe, *Progr. Phys. Org. Chem.*, **6**, 1 (1968), and H. Kessler, *Angew. Chem., Int. Ed. Engl.*, **9**, 219 (1970).

[4] (a) M. P. Simmonin, J. J. Basselier, and C. Charrier, *Bull. Soc. Chim. Fr.*, 3544 (1967); (b) A. H. Cowley, M. J. S. Dewar, and W. R. Jackson, *J. Amer. Chem. Soc.*, **90**, 4185 (1968); **92**, 5206 (1970); (c) T. T. Bopp, M. D. Havlicek, and J. W. Gilje, *ibid.*, **93**, 3051 (1971); (d) J. E. Bissey, H. Goldwhite, and D. E. Rowsell, *Org. Magn. Resonance*, **2**, 81 (1970).

[5] (a) T. Kojima, E. L. Breig, and C. C. Lin, *J. Chem. Phys.*, **35**, 2139 (1961); (b) R. Nelson, *ibid.*, **39**, 2382 (1963); (c) D. R. Lide, Jr., and D. E. Mann, *ibid.*, **29**, 914 (1958); (d) J. R. Durig, S. M. Craven, and J. Bragin, *ibid.*, **53**, 38 (1970); (e) J. R. Durig and J. M. Casper, *J. Phys. Chem.*, **75**, 1956 (1971).

[6] L. S. Bartell and L. O. Brockway, *J. Chem. Phys.*, **32**, 512 (1960); L. S. Bartell, *ibid.*, **32**, 832 (1960).

[7] (a) G. Klose, *Ann. Phys.*, **9**, 262 (1962); (b) P. T. Narashimhan and M. T. Rogers, *J. Chem. Phys.*, **34**, 1049 (1961); (c) F. J. Weigert, M. B. Winstead, J. I. Garrels, and J. D. Roberts, *J. Amer. Chem. Soc.*, **92**, 7359 (1970).

[8] G. Binsch, *ibid.*, **91**, 1304 (1969).

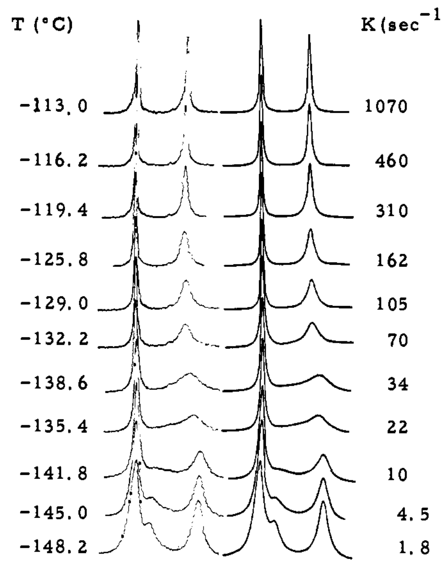

Figure 1. Observed and calculated 60-MHz proton spectra of *tert*-butyldichlorophosphine in vinyl chloride at various temperatures.

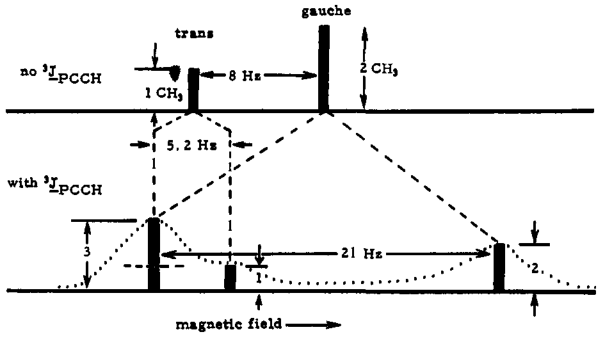

Figure 2. Chemical shifts and couplings which account for the observed low-temperature spectrum of **1**. The upper stick plot is the one expected if the phosphorus were decoupled from the protons.

of the variation of k to the Eyring equation (Figure 3) affords $\Delta G^{\ddagger} = 6.5$ kcal/mol (160°K), $\Delta H \sim 6.5$ kcal/mol, and $\Delta S \approx -3$ eu.

The barrier to rotation in **1** is substantially smaller than the $\Delta G^{\ddagger}$ of 11 kcal/mol found for $(CH_3)_3CCCl_2CH_3$.[9] This seems to be the result of the greater length of P–C as compared to C–C bonds, with the consequently smaller steric interactions between the substituent groups. No interference is expected from inversion at phosphorus which, in combination with partial rotations, would make the methyl groups equivalent[10] because, in general, inversion at phosphorus is slow.

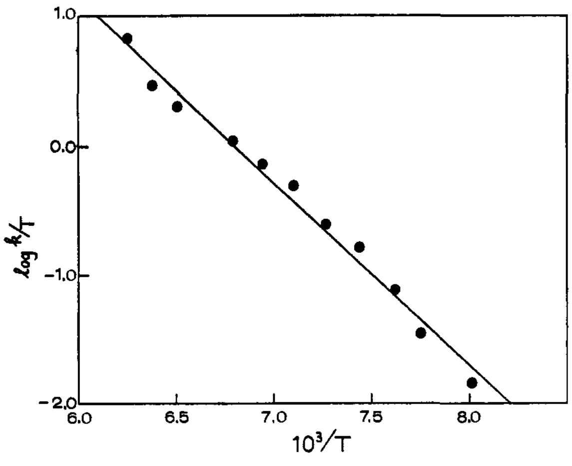

Figure 3. Eyring plot of the rate of rotation around the P–C bond of *tert*-butyldichlorophosphine.

However, the possibility that the barrier which we ascribe to slow rotation may actually be more or less of a mixture of $\Delta G^{\ddagger}$ for chlorine exchange[11] and $\Delta G^{\ddagger}$ for rotation was not ruled out, although it is hardly expected from the earlier studies[11] that the rates would be as reproducible and fast at $-120°$ if halogen exchange were involved. To the extent that chlorine exchange does occur, the experimental $\Delta G^{\ddagger}$ becomes a lower limit of $\Delta G^{\ddagger}$ for rotation.

No evidence for slow rotation about the P–C bonds was obtained in studies of the low-temperature nmr spectra of di-*tert*-butylchlorophosphine, dimethylphenylphosphine, or *tert*-butyldichlorophosphine oxide.[12] The latter compound is particularly surprising in this connection, and further research will be required to determine whether this is a result of a very low barrier to rotation or accidental equivalence of the methyl-group chemical shifts.

That the $^3J_{PCCH}$ coupling at room temperature (15.6 Hz) is equal to $(2\,^3J_{PCCH}(g) + {}^3J_{PCCH}(t))/3$ shows that $J(g)$ and $J(t)$ have the same sign—probably positive, judging from other cases where the signs of $^3J_{PCCH}$ couplings have been determined.[13] That $J(g) > J(t)$ is in accord with findings with other three-coordinate phosphorus compounds.[4b,14] A Karplus-like relationship[15] has been proposed to account for the angular dependence of the $^3J_{PCCH}$ coupling in tetracoordinated phosphorus compounds. For *tert*-butyldichlorophosphine, the two different kinds of methyl groups observed at low temperature should have reasonably comparable P–C–C–H

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(9) (a) A. Rieker and H. Kessler, *Tetrahedron Lett.*, 1227 (1969); (b) B. L. Hawkins, W. Bremser, S. Borcic, and J. D. Roberts, *J. Amer. Chem. Soc.*, **93**, 4472 (1971).

(10) *Cf.* S. Brownstein, E. C. Horswill, and K. U. Ingold, *ibid.*, **92**, 7217 (1970), for an illustration as to how inversion and rotation can become entangled with amines.

(11) (a) B. Fontal and H. Goldwhite, *Tetrahedron*, **22**, 3275 (1966); (b) R. H. Cox, M. G. Newton, and B. S. Campbell, *J. Amer. Chem. Soc.*, **93**, 528 (1971).

(12) Kindly supplied by Professor H. Goldwhite of the California State College at Los Angeles.

(13) (a) W. A. Anderson, R. Freeman, and C. A. Reilly, *J. Chem. Phys.*, **39**, 1518 (1962); (b) S. L. Manatt, G. L. Juvinall, R. I. Wagner, and D. D. Elleman, *J. Amer. Chem. Soc.*, **88**, 2689 (1966); (c) J. P. Albrand, D. Gagnaire, and J. B. Robert, *J. Mol. Spectrosc.*, **27**, 428 (1968); (d) C. Schuman, H. Dreeskamp, and O. Stelzer, *J. Chem. Soc. D*, 619 (1970).

(14) (a) L. D. Quin and T. P. Barket, *J. Amer. Chem. Soc.*, **92**, 4303 (1970); (b) J. P. Albrand, D. Gagnaire, M. Picard, and J. B. Robert, *Tetrahedron Lett.*, 4592 (1970); (c) A. H. Cowley, M. J. S. Dewar, W. R. Jackson, and W. B. Jennings, *J. Amer. Chem. Soc.*, **92**, 1085 (1970); (d) J. Nelson, R. Spratt, and B. J. Walker, *J. Chem. Soc. D*, 1509 (1970).

(15) (a) C. Benezra and G. Ourisson, *Bull. Soc. Chim. Fr.*, 1825 (1966); (b) C. Benezra, S. Nšeič, and G. Ourisson, *ibid.*, 1140 (1967).

dihedral angles. If this is the case, the large difference in the ${}^3J_{PCCH}$ couplings suggests that this kind of coupling in three-coordinate phosphorus compounds may have an angular dependence which is rather more complicated than a simple Karplus-type relationship, because account will have to be taken of the orientation about the P–C bond as has already been proposed for ${}^2J_{PCH}$ couplings,[16] and is well known for nitrogen compounds.[17]

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(16) (a) D. Gagnaire, J. B. Robert, and J. Verrier, *Chem. Commun.*, 819 (1967); (b) J. P. Albrand, D. Gagnaire, J. M. Martin, and J. B. Robert, *Bull. Soc. Chim. Fr.*, 40 (1969).

(17) *Cf.* R. L. Lichter and J. D. Roberts, *J. Amer. Chem. Soc.*, **93**, 5218 (1971), and references cited therein.

Nitrogen-15 Magnetic Resonance Spectroscopy. XV. Natural-Abundance Spectra. Chemical Shifts of Hydrazines[1]

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Abstract: The ${}^{15}N$ resonances of the methylhydrazines and some phenylhydrazines have been determined at the natural-abundance level of ${}^{15}N$. The chemical shifts for the methyl compounds were interpretable in terms of deshielding α and β effects. The β shift, -24.4 ppm, is substantially larger than that found for amine ${}^{15}N$ (-18.2 ppm) or hydrocarbon cmr resonances (-9.7 ppm), and an explanation is offered in terms of possible steric influences. Although the ${}^{15}N$ shifts of the phenylhydrazines also change with structure, the data are so far insufficient to allow derivation of substituent parameters. Nonetheless, the effects of substitution appear to be less systematic than for the alkylhydrazines. The cmr chemical shifts of the methylhydrazines have been measured. While the shifts do not correlate with the ${}^{15}N$ shifts, they can be expressed in terms of deshielding β and shielding γ effects comparable to those found for hydrocarbons and alcohols.

A number of ${}^{15}N$ chemical shifts of amines at the natural-abundance level have recently been reported[2] and were shown to be subject to structural influences which parallel to a substantial degree those which determine carbon chemical shifts. Hydrogen bonding was also suggested as a possible contributing factor to the shifts, although no explicit isolation of its effect could be adduced. As an adjunct to that work, we have measured the chemical shifts of the methylhydrazines and a few phenylhydrazines, and report here the effect of substituents on the nitrogen chemical shifts of this type of molecule.

Results

The ${}^{15}N$ chemical shifts of the methylhydrazines, obtained with complete proton noise decoupling,[3] are given in Table I. The resonances of the unsymmetrical hydrazines were assigned in part on the basis of the upright or inverted disposition of the signal, which may be taken as an indication of the presence or absence of a nuclear Overhauser effect (NOE).[4] Consistent with the assignments is the observation that those nitrogen atoms bearing protons were in general detectable after many fewer scans than the fully substituted atoms. Correlating with the difficulty experienced in detecting resonances of tertiary amines in natural abundance,[2,5] this result is very likely attributable to longer relaxation times for these nuclei.[6] Because neither of these criteria is definitive, it is of interest to consider briefly other possible bases for assignment. The early successful identification of carbon resonances derives in large part from analysis of spectral patterns arising from spin–spin coupling to directly bonded protons.[7] Subsequent derivation of substituent parameters then allowed characterization of resonances of more com-

Table I. ${}^{15}N$ Chemical Shifts of Hydrazine and Its Methyl Derivatives[a]

	$\delta_{N\text{-}1}$, ppm		$\delta_{N\text{-}2}$, ppm
H_2NNH_2		328.7[b]	
CH_3NHNH_2	321.9[b]		299.4[b]
$(CH_3)_2NNH_2$	316.6[c]		275.3[b]
$CH_3NHNHCH_3$		300.5[c]	
$(CH_3)_2NNHCH_3$	301.6[c]		279.2[b]
$(CH_3)_2NN(CH_3)_2$[d]		271.5[b]	

[a] With respect to external $H^{15}NO_3$, error ~0.3 ppm. [b] Inverted signal. [c] Upright signal. [d] Contaminated with about 30% 1,1,2-trimethylhydrazine, for which the N-2 chemical shift was 279.9 ppm.

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(2) Part XIV: R. L. Lichter and J. D. Roberts, *J. Amer. Chem. Soc.*, **94**, 2495 (1972).

(3) (a) F. J. Weigert, M. Jautelat, and J. D. Roberts, *Proc. Nat. Acad. Sci. U. S.*, **60**, 1152 (1968); (b) L. F. Johnson and M. E. Tate, *Can. J. Chem.*, **47**, 63 (1969).

(4) (a) R. L. Lichter and J. D. Roberts, *J. Amer. Chem. Soc.*, **93**, 3200 (1971); (b) R. A. Cooper, R. L. Lichter, and J. D. Roberts, paper in preparation.

(5) J. P. Warren and J. D. Roberts, unpublished results.

(6) W. M. Litchman, Abstracts, 161st National Meeting of the American Chemical Society, Los Angeles, Calif., March 29, 1971, No. PHYS-010.

(7) (a) See, *e.g.*, D. M. Grant and E. G. Paul, *J. Amer. Chem. Soc.*, **86**, 2984 (1964); (b) J. D. Roberts, F. J. Weigert, J. I. Kroschwitz, and H. J. Reich, *ibid.*, **92**, 1338 (1970).