these conditions reactive halides, such as methyl iodide, benzyl chloride, ethyl bromoacetate and chloromethyl methyl ether, react completely in 0.5–2 hr. Less reactive halides, such as ethyl iodide, require days for complete reaction. The reaction can be accelerated in tetrahydrofuran by increasing the sodium cobalt tetracarbonyl concentration.

Acylcobalt Tricarbonyl Triphenylphosphines from Acylcobalt Tetracarbonyls.—A 10–50% excess of a 1.0 M triphenylphosphine solution in ether is added at 0° to an ethereal solution of acylcobalt tetracarbonyl prepared by either of the procedures above. Reaction is complete in a few minutes to a few hours as indicated by both gas evolution and the infrared spectrum. The reaction mixture is evaporated *in vacuo* below room temperature to remove excess halide, the crystalline yellow or orange residue is taken up in ether or tetrahydrofuran, centrifuged and concentrated to a small volume. Addition of n-pentane often leads to the separation of a small amount of amorphous solid. This is removed by centrifuging, the clear solution is cooled to −80°; more n-pentane is added and the crystals are separated. Two or three low-temperature recrystallizations from a mixture of ether, tetrahydrofuran or methylene chloride and n-pentane yield a pure product. All manipulations are carried out under nitrogen.

Acylcobalt Tricarbonyl Triphenylphosphines from Alkyl Halides.—Alkyl halide is reacted with sodium cobalt tetracarbonyl as described above at 0°, except that a 10–50% excess of triphenylphosphine in ether is added before the alkyl halide and the reaction is carried out under nitrogen. Completion is indicated by disappearance of the 5.3-μ band. The product is isolated in the same fashion as described above.

Reaction of Acetylcobalt Tetracarbonyl with Triphenyl Phosphite.—Acetylcobalt tetracarbonyl was prepared from 15 ml. of 0.07 M sodium cobalt tetracarbonyl and 1.0 ml. of methyl iodide in ether at 0° under CO. In 1 hr. 1.09 mmoles (104% of theory) of CO was absorbed. The addition of 0.5 ml. (1.9 mmoles) of triphenyl phosphite resulted in the evolution of 1.11 mmoles (106% of theory) of gas in 1.3 hr. The carbonyl spectrum was identical with that of the corresponding triphenylphosphine complex. No attempt was made to isolate the complex.

Reaction of Methylcobalt Tetracarbonyl with Ethylenebis-(diphenylphosphine).—No reaction occurred between 15 ml. of 0.07 M sodium cobalt tetracarbonyl in ether and 2.5 ml. of 0.5 M ethylenebis-(diphenylphosphine)[17] in tetrahydrofuran in 30 minutes at 0°. Addition of 0.5 ml. of methyl iodide led to the formation of a pale yellow solution, but there was no change in gas volume in 2 hr. at 0°. The infrared spectrum was very similar to that of acetylcobalt tricarbonyl triphenylphosphine (bands at 4.85, 5.10 and 5.90 μ). Warming the solution to 25° led to a very slow evolution of gas and the appearance of two new infrared bands at 5.2 and 6.15 μ. After standing at room temperature for several days, the solvent was evaporated and an attempt was made to recrystallize the reddish, crystalline product from tetrahydrofuran-n-pentane at −80°. Each attempt led to the formation of an insoluble yellow-red solid. The crude material had infrared bands at 5.05 (m), 5.20 (vs) and 6.15 (s) μ.

Cyanomethylcobalt Tricarbonyl Triphenylphosphine (IX). —Ethereal solutions of sodium cobalt tetracarbonyl (30 ml. of 0.07 M) and chloroacetonitrile (3.0 ml. of 1 M) were mixed and stirred at 0° for 2.25 hr. under one atmosphere of CO; 7 ml. of gas was evolved. The infrared spectrum showed coördinated CO bands at 4.88 (vs), 4.98 (s) and 5.05 (vs) μ, but no carbonyl band at 5.8 μ. Addition of 3.0 ml. of 1 M triphenylphosphine in ether at 0° led to gas evolution. After standing overnight at 0° the cold solution was evaporated to dryness and the residue was extracted with methylene chloride. Addition of ether and cooling to −80° yielded a yellow, crystalline powder. Recrystallization once more from methylene chloride–ether gave a product which decomposed at about 120° without melting.

The infrared spectrum in carbon tetrachloride had bands at 3.40 (w), 3.49 (vw), 4.51 (w), 4.86 (vw), 5.02 (s), 6.74 (w), 6.98 (w), 7.65 (w), 7.96 (w), 8.41 (w), 9.10 (s), 9.30 (w), 9.70 (w), 9.98 (w), 11.12 (w) and 14.6 (m) μ.

Anal. Calcd. for $C_{23}H_{17}O_3NPCo$: C, 62.04; H, 3.85. Found: C, 61.64; H, 3.95.

Conformation of Organophosphorus Compounds. I. Proton Magnetic Resonance Studies of Some Phosphinates, Phosphinic Acids, Phosphinyl Chlorides and Phosphonyl Dichlorides[1]

BY T. H. SIDDALL, III, AND C. A. PROHASKA

A number of alkylphosphonyl dichlorides and alkylarylphosphinic acids, -phosphinyl chlorides and -phosphinates were synthesized and their proton nuclear magnetic resonance spectra were obtained. Some of the compounds that contain a benzene ring attached to the phosphorus atom show a doubling of the proton resonances of the alkyl groups in the molecule. A theory is advanced to explain this doubling in terms of preferred rotational isomers.

Introduction

There have been a number of studies of hindered rotation by use of nuclear magnetic resonance,[2,3] but no reports have been made of previous studies involving the phosphorus bonds in organophosphorus compounds. Preliminary results of the present investigation were reported elsewhere.[4] In that communication it was pointed out that phenyl-substituted organophosphorus compounds in three categories showed a doubling of certain of the proton resonances. This doubling of resonances was attributed to hindered rotation around phosphorus bonds. A benzene ring in a molecule in this situation serves as an internal probe to indicate the relative position of other substituents in the molecule. Because of the diamagnetic anisotropy of the benzene ring, protons of other groups, if they are close to the ring, will resonate at a different value of the applied magnetic field than will otherwise identical protons that are far from the ring. Protons in the plane of the ring will resonate at a lower applied field, while protons axial to the ring will resonate at a higher applied field.
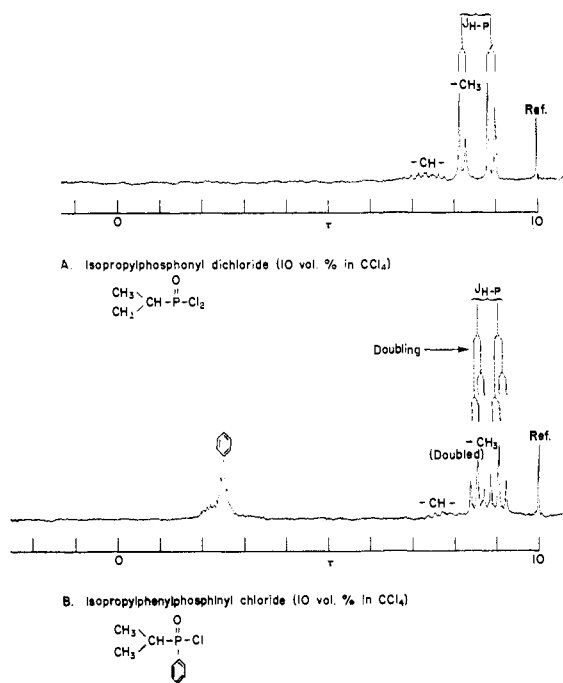
(1) The information contained in this article was developed during the course of work under contract AT(07-2)-1 with the U. S. Atomic Energy Commission.

(2) (a) J. J. Drysdale and W. D. Phillips, *J. Am. Chem. Soc.*, **79**, 319 (1957). (b) P. M. Nair and J. D. Roberts, *ibid.*, **79**, 4565 (1957).

(3) J. A. Pople, W. G. Schneider and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., New York, N. Y., 1959.

(4) T. H. Siddall, C. A. Prohaska and W. E. Shuler, *Nature*, **190**, 903 (1961).

A. Isopropylphosphonyl dichloride (10 vol. % in CCl₄)

B. Isopropylphenylphosphinyl chloride (10 vol. % in CCl₄)

Fig. 1.

The purpose of this paper is to report a more complete investigation of the conformation of compounds of the first category

$$R_2 — \underset{\underset{R_3}{|}}{\overset{\overset{R_1}{\diagdown}}{C}} — \underset{\underset{X}{|}}{\overset{\overset{O}{\parallel}}{P}} — Y$$
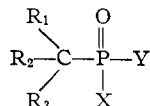
The R's are limited to the hydrogen atom, alkyl groups or the benzene ring; Y may either be –OH, –Cl, –OCH₃ or –OCH₂CH₃; while X is either –Cl or a benzene ring.

Experimental

The alkylphosphonyl dichlorides were made by the method of Kinnear and Perren[5] and were purified by vacuum distillation. The phosphinic acids were made by the method of Biddle, Kennedy and Williams.[6] None of several attempts to prepare the phosphinyl chloride directly by partial hydrolysis of the reaction mixture were successful. Complete hydrolysis was always obtained except with *t*-butylphenylphosphinyl chloride, and it was necessary to react phosphinic acids with thionyl chloride in order to obtain the phosphinyl chlorides. Isobutylphenylphosphinyl chloride was made *via* the addition of isobutyl Grignard to an excess of phenylphosphonyl dichloride. One attempt to make this compound by the method of Biddle, Kennedy and Williams led only to the formation of *t*-butylphenylphosphinyl chloride as might be expected from the work of Kinnear and Perren. Phosphinates were obtained in moderate yield either by (1) esterifying the phosphinyl chloride in the presence of pyridine or (2) esterifying directly the reaction mixture of arylphosphonous dichloride, aluminum chloride and alkyl chloride (or bromide equally well) in a solution of dichloromethane. The phosphinates and phosphinyl chlorides were purified by vacuum distillation and the phosphinic acids by crystallizing several times from appropriate solvents.

The measurements of proton resonances were made with a Varian Associates Model 4300B high resolution nuclear magnetic resonance spectrometer at a frequency of 40 mc. Sidebands were introduced by modulating the sawtooth

(5) A. M. Kinnear and E. A. Perren, *J. Chem. Soc.*, 3437 (1952).

(6) P. Biddle, J. Kennedy and J. L. Williams, *Chem. and Ind.* (London), 1481 (1957).
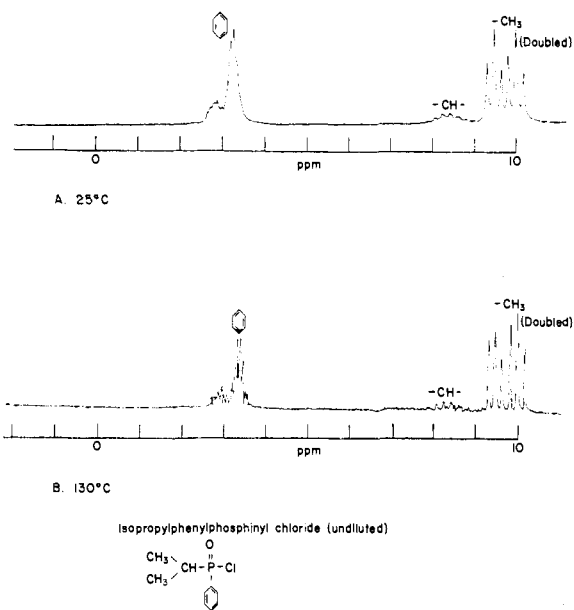
A. 25°C

B. 130°C

Isopropylphenylphosphinyl chloride (undiluted)

Fig. 2.

sweep voltage with a modified Hewlett–Packard 200 CD audio oscillator, and the separation of these sidebands was measured to ±0.1 c.p.s. with a Berkeley 7370 Universal EPUT and Timer. Spectra were obtained for the pure compound, if it were a liquid at room temperature, and for a 10% (by volume) solution of the compound in CCl₄ or CDCl₃. Chemical shifts, spin coupling constants and resonance doubling were measured for these solutions at room temperature (25 ± 1°). Spin coupling and resonance doubling were also measured for some pure compounds at 25 and 140°.

The 10% solution of each compound, which also contained 1% tetramethylsilane as an internal reference, was placed in a 3-mm. i.d. inner sample tube. This inner tube was then placed in a 5-mm. o.d. outer sample tube and the annular space between the two tubes was filled with benzene as an external reference. The modulating frequency was adjusted so that the first sideband of the internal reference appeared just below the low field portion of the spectra, and the first sideband of the external reference appeared above the internal reference. The τ (defined as parts per million (p.p.m.), referred to the value τ = 10.00 for the tetramethylsilane internal reference) values were measured by linear interpolation of these spectra. In addition, the location of major peaks was measured by the method of Arnold and Packard[7] as modified by Dailey and Shoolery.[8] Chemical shifts measured by either method were the same ±0.5 c.p.s. (0.013 p.p.m.). The spin–spin coupling constants are believed to be accurate to ±0.2 c.p.s. (0.005 p.p.m.).

Results

The results of the proton magnetic resonance measurements are given in Table I. Typical spectra are given in Figs. 1–3. (A complete set of spectra will be sent to the Chemical and Petroleum Research Laboratory for publication in the catalogs of the Manufacturing Chemists Association Research Project.) Table I shows that, in certain compounds, the proton resonances are doubled. Further, the doubled resonances remain doubled even at elevated temperatures. As illustrated in Figs. 1–3 the components of a doubled resonance have about equal intensity. This is particularly

(7) J. T. Arnold and M. E. Packard, *J. Chem. Phys.*, **19**, 1608 (1951).

(8) B. P. Dailey and J. N. Shoolery, *J. Am. Chem. Soc.*, **77**, 3977 (1955).

TABLE I
PROTON RESONANCE DATA

	R₁	R₂	R₃	X	Y	Proton resonance doubling of β terminal methyl group[d]	$J_{H\alpha-H\beta(CH_3)}$	$J_{H\alpha-H\beta(CH_2)}$	$J_{H\alpha-P}$	$J_{H\beta-P}$
Methylphenylphosphinyl chloride	-H	-H	-H	-C₆H₅	-Cl	b	b	b	14.1	b
Ethylphosphonyl dichloride	-H	-H	-CH₃	-Cl	-Cl	None	6–8	b	14.2	30.0
Ethylphenylphosphinyl chloride	-H	-H	-CH₃	-C₆H₅	-Cl	None	6–8	b	12.1	22.1
Isopropylphosphonyl dichloride	-H	-CH₃	-CH₃	-Cl	-Cl	None	6.1–6.7	b	12 ± 1	27.6
Isopropylphenylphosphinyl chloride	-H	-CH₃	-CH₃	-C₆H₅	-Cl	6.2–7.1	6.2–7.1	b	c	20.6
Isopropylphenylphosphinic acid	-H	-CH₃	-CH₃	-C₆H₅	-OH	None	5.4–7.1	b	c	17.0
Methyl isopropylphenylphosphinate	-H	-CH₃	-CH₃	-C₆H₅	-OCH₃	5.6–7.0	5.6–7.0	b	c	17.3
Ethyl isopropylphenylphosphinate	-H	-CH₃	-CH₃	-C₆H₅	-OC₂H₅	5.5–7.0	5.5–7.0	b	c	17.1
t-Butylphosphonyl dichloride	-CH₃	-CH₃	-CH₃	-Cl	-Cl	None	b	b	b	24.8
t-Butylphenylphosphinyl chloride	-CH₃	-CH₃	-CH₃	-C₆H₅	-Cl	None	b	b	b	17.7
t-Butylphenylphosphinic acid	-CH₃	-CH₃	-CH₃	-C₆H₅	-OH	None	b	b	b	15.7
2-Butylphosphonyl dichloride	-H	-CH₃	-C₂H₅	-Cl	-Cl	None	c	c	c	c
2-Butylphenylphosphinyl chloride	-H	-CH₃	-C₂H₅	-C₆H₅	-Cl	a	7.1	6.1–8.0	c	20.0
Isobutylphenylphosphinyl chloride	-H	-H	-C₃H₇	-C₆H₆	-Cl	a		c	c	c
3-Amylphenylphosphinyl chloride	-H	-C₂H₅	-C₂H₅	-C₆H₅	-Cl	a		c	c	c
1-Phenylethylphenylphosphinic acid	-H	-CH₃	-C₆H₅	-C₆H₆	-OH	None	7.4	b	18.6	16.8
Methyl 1-phenylethylphenylphosphinate	-H	-CH₃	-C₆H₅	-C₆H₅	-OCH₃	5.3–6.5	7.2	b		17.1

a Too complex for first order analysis. b Molecule does not contain protons in the appropriate group (β-methyl, β-methylene, protons on a α-carbon atom, etc.), hence this column not applicable. c The data were not sufficient to determine this coupling constant. d These values, in cycles per second, are for alkyl groups attached directly to the phosphorus atom.

well illustrated in Fig. 3B by the resonances of the protons of the methoxy group. The four resonances are nearly equal. The differences in height are probably caused by the presence of the overlapping –CH– resonances, so that if the latter could be subtracted, the four –CH₃ resonances would become nearly equal.

A. 1-phenylethylphenylphosphinic acid (10 vol. % in CDCl₃)

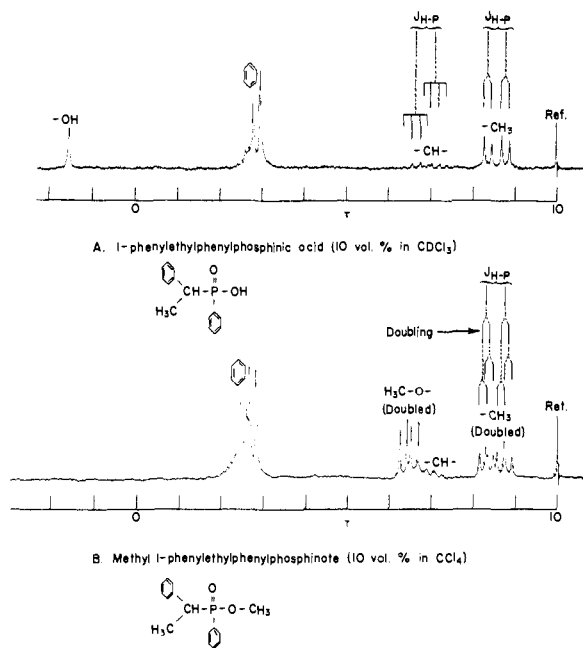B. Methyl 1-phenylethylphenylphosphinate (10 vol. % in CCl₄)

Fig. 3.

The compounds, 2-butylphenylphosphinyl chloride, isobutylphenylphosphinyl chloride and 3-amylphenylphosphinyl chloride, were synthesized. However, the spectra were all too complex and had too much second-order character for even a qualitative analysis.

Discussion

The data in Table I permit certain inferences to be drawn as to the manner of rotation around the carbon-to-phosphorus bond. First, there is considerable evidence that rotation around this bond is rapid,[3] with the mean lifetimes of isomers being milliseconds or less. There is no evidence that need be interpreted in terms of slow rotation. Second, where steric considerations suggest that one of the three rotational isomers could be much more stable than the other two, the proton resonances indicate that these molecules do indeed spend most of the time at a preferred angle of rotation. The reasons for these two conclusions are given in the following paragraphs.

The behavior of the proton resonances of the compounds in Table I as a function of temperature is indicative that resonance doubling, when it occurs, is not a result of slow rotation. Slow rotation would give rise to two rotational isomers of relatively long lifetimes, each with its own set of resonances. In general, doubled signals arising from such a slow rotation collapse into a single signal at elevated temperatures.[3] Well before such doublets collapse the apparent resolution of the doublets becomes poor. The doubled resonances of the compounds listed in Table I are not only maintained up to 130°, but the spectra are apparently much better resolved at 130° than at 25°.[9] Such behavior could be expected from two discrete rotational isomers only if they coexisted in equal amounts over a wide temperature range (ΔH between isomers approximately zero) and a very large energy barrier existed between them.

Further evidence in favor of rapid rotation is obtained from the spectrum of t-butylphenylphosphinyl chloride. If rotation were slow and isomers of long life existed, the methyl protons would exhibit a doubled set of resonances. For each isomer there would be two methyl groups near the benzene ring and one farther away. Two sets of resonances for the methyl protons would result, with one set having twice the in-

(9) See Fig. 2 as an example. Most of these compounds are quite viscous at room temperature, and the apparent increased resolution at elevated temperatures is undoubtedly due to the decrease in viscosity.
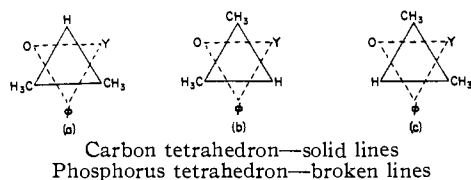
Carbon tetrahedron—solid lines
Phosphorus tetrahedron—broken lines

Fig. 4.—Rotational isomers of 2-propyl compounds.

Carbon tetrahedron—solid lines
Phosphorus tetrahedron—broken lines

Fig. 5.—Isomers of methyl 1-phenylethylphenylphosphinate
and 1-phenylethylphenylphosphinic acid.

tensity of the other. However, only a single set of resonances is observed. Since the alpha carbon atom is attached to three identical methyl groups, no preferred angle of rotation is to be expected during rotation and consequently no resonance doubling occurs with rapid rotation. A similar situation is also obtained with methylphenyl-phosphinyl chloride. However, it might be argued that rapid rotation is to be expected in this case from steric considerations and that no extrapolation should be made to compounds with larger substituents on the alpha carbon atom.

None of the resonances of ethylphenylphos-phinyl chloride are doubled. This observation is consistent with the view that in this molecule there is also rapid rotation around the carbon-to-phosphorus bond. In such a case, even with one preferred rotational isomer, there can be only one set of resonances for the methyl protons. The single methyl group cannot at the same time be both far from and near to the benzene ring. The lack of doubling for the resonances of the protons attached to the alpha carbon atom is subject to several interpretations: (1) there is a single preferred isomer, and this is the one with the methyl group between the chlorine and oxygen; (2) there is rapid exchange between two preferred isomers neither of which is the isomer of alternative (1); or (3) there are no preferred isomers. The fact that the methyl proton resonances are not doubled could also be due to no preferred isomers. This possibility cannot be excluded on the basis of the present data.

For 2-propylphenylphosphinyl chloride (Fig. 1), its esters, and methyl 1-phenylethylphenyl-phosphinate (Fig. 3), the resonances of the methyl protons are always doubled, but those of the protons attached to the alpha carbon atom are never doubled. Figure 4 gives diagrams of the rotational isomers of the 2-propyl compounds. It is clear, if either (b) or (c) is the more stable isomer, that doubled resonance could occur. In either situation there is one methyl group that spends most of its time near the benzene ring, while the other is farther from the ring most of the time. It might be expected that (b) is the preferred isomer since it places a minimum of large groups of atoms in close proximity to each other.

The compound, 2-propylphenylphosphinic acid, e.g., the compound where Y in Fig. 4 is –OH, does not exhibit doubled resonances. A simple explanation, though perhaps not the only explanation, is that the phosphoryl oxygen and the OH group are too nearly the same size. As a consequence (b) and (c) of Fig. 4 are of approximately equal stability. This being so, then on the average the methyl groups would spend about the same amount of time near to and far from the benzene
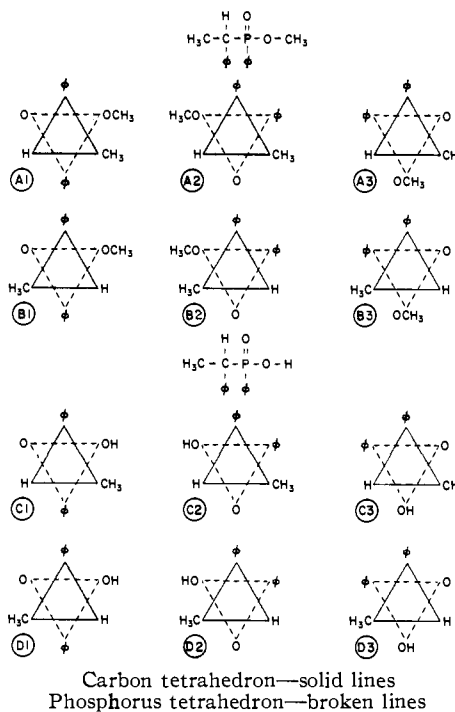
ring. Their average magnetic environments would not differ and only one set of signals would result. The proton resonance of the OH group is not doubled. This lack of spin–spin coupling between the phosphorus and the OH proton implies that this proton is bonded to both oxygens or rapidly exchanging between them. In either case, the phosphoryl oxygen and the OH group would be equivalent.

With methyl 1-phenylethylphenylphosphinate it can be inferred that (A3) is the preferred rotational isomer of one diastereoisomer and (B1) of the other. The spectrum of this compound is shown in Fig. 3 and the rotational isomers are shown in Fig. 5. Since there are two asymmetric atoms (the alpha carbon atom and the phosphorus atom) there are two pairs of enantiomorphs (A and B in the Fig. 5), the enantiomorphs from different pairs being diastereoisomers. The methyl and methoxy proton signals to be expected from the various isomers are given in Table II. From

TABLE II

SIGNALS FROM ROTATIONAL ISOMERS

Methyl signal		Methoxy signal	
High field[a]	Low field[b]	High field[a]	Low field[b]
A1	B2	A1	A3
B1	A3	B1	B3
A2		A2	
B3		B2	

[a] Protons close to benzene ring. [b] Protons far from benzene ring.

this compilation of signals it can be shown that A3 and B1 must be the preferred isomers. This result follows since it is only by the combination of A3 and B1 that high and low field signals can be obtained for both types of protons. Also it is to

be noted that the ring signals appear to be doubled. This is consistent with the choice of isomers. Further, since high and low field signals are equally intense, the diastereoisomers are about equally abundant.

The failure of the protons of 1-phenylethylphenylphosphinic acid to exhibit doubled resonances, as with 2-propylphenylphosphinic acid, may be ascribed to near equivalence of the oxygen atom and OH group. Another possible explanation, of course, is that there are no preferred rotational isomers in these compounds. This possibility cannot be excluded on the basis of the present data. It seems unlikely, however, if the phosphinic esters and phosphinyl halides do have a preferred rotational isomer that the corresponding phosphinic acids would not have such an isomer.

Aside from implications as to rotational isomerism, some of these compounds show spectral peculiarities that are of interest in themselves. Since the alpha and beta protons have only a small chemical shift between them, the spectra are not entirely first order but have considerable second-order character. However, the protons on the beta carbon atoms are coupled quite strongly

to the phosphorus atom. The high field halves of the spectra for the beta protons are much cleaner, and more similar to first-order spectra, than those of the low field half. Further, both the apparent coupling constant (J) between alpha and beta protons and the additional resonance doubling described above are different in the two halves of the spectra. Data for these coupling constants for a number of these compounds are compiled in Table I. The values for the coupling constant are based on only a first-order analysis of the spectrum, hence these values are only approximate.

It is plausible that this difference in the spectra is basically the same type of phenomenon as that seen as a result of C^{13} coupling to protons.[10] The combination of phosphorus to proton coupling and ordinary chemical shift may tend to cancel or to add in producing an over-all chemical shift. In the low field half of the spectra, the effective over-all shift is very small and the spectra are strongly second order. In the high field half, the over-all shift is larger and the spectra have approximate first-order character.

(10) A. D. Cohen, N. S. Sheppard and J. J. Turner, *Proc. Chem. Soc.* (London), 118 (1958).

Chemistry of Boranes. III.[1] The Infrared and Raman Spectra of B₁₂H₁₂⁻ and Related Anions

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RECEIVED JANUARY 3, 1962

The infrared and Raman spectra of the borohydride anion, B₁₂H₁₂⁻, have been determined and found to be in complete agreement with predictions for a regular icosahedral structure, I_h, with equivalence of the boron and hydrogen sets and no B–H–B bridge bonds. The infrared and Raman fundamentals have been assigned with the aid of exchange deuteration. The Raman spectra of halogenated borohydride anions consist of single strong lines because of accidental cancellation of all but the out-of-phase breathing vibration.

Introduction

Molecular aggregates with regular icosahedral (I_h) symmetry amenable to vibrational analysis are rare. The regular icosahedral structure has been assigned to the anion B₁₂H₁₂⁻ by the X-ray investigations of Wunderlich and Lipscomb.[2] Hence, we have determined the infrared and Raman spectra of this anion, B₁₂H₁₂⁻, for comparison with group theoretical predictions of the number and depolarization of Raman lines and the number and Raman coincidence of infrared fundamental absorption bands.

Discussion

The tables of Jahn and Teller[3] indicate that the anion, B₁₂H₁₂⁻, in point group, I_h, should give two strongly polarized Raman lines of symmetry species, A_g, one line from the set of symmetrically equivalent boron atoms and the other from the hydrogen set; four depolarized Raman lines of

species H_g; and three infrared absorption fundamentals of species F_{1u}. The character table describing the molecular vibrations of the regular icosahedron is given in reference texts.[4]

The infrared and Raman data for the B₁₂H₁₂⁻ anion (Fig. 1) are in good agreement with the above predictions of group theory for a regular icosahedral structure. For discussion purposes, the observed frequencies (ν_n in cm.⁻¹) for B₁₂H₁₂⁻ are presented below in the form of the Teller–Redlich product ratios[5] of the three active symmetry species for approximately 90% conversion to B₁₂D₁₂⁻, as:

Species A_g (Raman active)

$$\left(\frac{2518}{1912}\right)_1^2 \times \left(\frac{743}{716}\right)_{\nu_2}^{\nu^2} = \left(\frac{M_D}{M_H}\right)\left(\frac{M_B}{M_B}\right)$$

$$1.73 \quad \times \quad 1.08 \quad = \quad 1.87 \quad (vs.\ 2)$$

(1) Paper II, W. H. Knoth and E. L. Muetterties, *J. Inorg. Nuclear Chem.*, **20**, 66 (1961).

(2) J. A. Wunderlich and W. N. Lipscomb, *J. Am. Chem. Soc.*, **82**, 4427 (1960).

(3) H. A. Jahn and E. Teller, *Proc. Roy. Soc.* (London), **161A**, 228 (1937).

(4) *Cf.* E. B. Wilson, Jr., J. C. Decius and P. C. Cross, "Molecular Vibrations," McGraw–Hill Book Co., New York, N. Y., 1955, p. 330. (An error is noted in the character for C_5 in species H, which should be +1 instead of 0.)

(5) *Cf.*, G. Herzberg, "Infrared and Raman Spectra," D. Van Nostrand Co., 1945, p. 232.