

benzene layer, the solvent was evaporated to afford the crude oxide. The oxides crystallized from hexane, the *para* isomer as colorless needles, mp 122–123°, and the *meta* isomer as colorless needles, mp 101.5–103°.

Tris(fluorophenyl)methylphosphonium Iodide (IIIa). A sample of the phosphine in acetonitrile was heated under reflux overnight with excess methyl iodide. Removal of the solvent and methyl iodide left the crude salt which crystallized from ethanol-ether as colorless microcrystals, mp 306–307° (*para* isomer) and mp 212–213° (*meta* isomer).

Tris(fluorophenyl)-9-fluorenylphosphonium Bromide (IIIc). Equimolar quantities of the phosphine and 9-bromofluorene in acetonitrile solution were heated under reflux overnight. Removal of the solvent and crystallization of the solid residue from ethanol-ether afforded the pure colorless salts, mp 276–277° (*para* isomer) and mp 249–251° (*meta* isomer).

9-Fluorenylidene-tris(fluorophenyl)phosphoranes (IIIe). The salts (IIIc) were dissolved in ethanol then a few milliliters of 5% aqueous sodium hydroxide were added slowly. An immediate yellow pre-

cipitate formed which was filtered, washed with water then dried. The *para* isomer was recrystallized from benzene-hexane as fine yellow needles, mp 254–255°.

Anal. Calcd for $C_{31}H_{20}F_3P$: C, 77.48; H, 4.20; P, 6.45. Found: C, 77.90; H, 4.24; P, 6.40.

The *meta* isomer was recrystallized from benzene-hexane as thick yellow-orange needles, mp 194–195°.

Anal. Calcd for $C_{31}H_{20}F_3P$: C, 77.48; H, 4.20; P, 6.45. Found: C, 78.35; H, 4.52; P, 6.22.

Acknowledgment. We gratefully acknowledge the cooperation of Professor Taft and Dr. Rakshys in obtaining all of the ^{19}F nmr data and for continuing to communicate their results. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the National Research Council of Canada, for the support of this research.

The Electronic Properties of Tri-, Tetra-, and Pentacoordinate Phosphorus Substituents¹

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Abstract: Fluorine nuclear magnetic resonance shifts (and derived σ values) have been obtained for the families *m*- and *p*- $FC_6H_4PX_2$, *m*- and *p*- $FC_6H_4P(C_6H_5)_2X$, and *m*- and *p*- $FC_6H_4PF_4$. The effects of substitution at phosphorus can be described by the polar and resonance substituent parameters, σ_I and σ_R^0 . The results provide evidence of π acceptor orbitals on phosphorus in all families, in accord with proposed $\pi(p-d) C_{ar} \leftrightarrow P \leftrightarrow X$ interactions.

Substituent effects on chemical and physical properties have been treated in a number of aromatic systems as additive blends of polar (inductive) and π delocalization (resonance) effects.^{4–6} The polar effect is considered to arise as the consequence of the net polarization of the reaction (or detection) center by an interaction mechanism which does not require delocalization (transfer) of π charge between the substituent and the aromatic nucleus. The polar effect is characterized by the substituent parameter, σ_I , which is based upon polar effects measured at saturated carbon where, presumably, little or no transfer of π charge can occur.⁴

The π delocalization effect is considered to arise as the consequence of the effective polarization of the reaction (or detection) center which results from the transfer of π charge between substituent and the aromatic nucleus. The π delocalization effect is characteristic of the substituent but may also depend upon the nature of the aromatic or conjugating system. The substituent parameter σ_R^0 measures the π delocalization effect in systems in which the reaction center is effectively insulated from the aromatic nucleus.⁷ Other scales of the π delocalization effect, which are limited by reaction type, include⁸ $\sigma_R \equiv \sigma_p - \sigma_I$; $\sigma_R^+ \equiv \sigma_p^+ - \sigma_I$; and $\sigma_R^- \equiv \sigma_p^- - \sigma_I$.

These various substituent parameter scales are all based upon substitution at carbon. A critical test of the generality of the parameters and the treatment is provided by application to substitution at other atoms. In this paper the second row element phosphorus has been chosen to provide such a test. Evidence is obtained for the nature of the charge distribution which is associated with bonding at the phosphorus atom.

The effect of *meta* and *para* substituents on fluorine nuclear magnetic resonance (^{19}F nmr) shielding in

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(2) (a) Taken in part from the Ph.D. Thesis of J. W. Rakshys, University of California, Irvine, Calif., June 1967; (b) National Science Foundation Cooperative Graduate Fellow, 1965–1967.

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fluorobenzenes provide sensitive measures of σ parameters (especially of the σ_R scale) by virtue of the generalized correlations^{4d,9}

$$\int_H^{m-X} = (-7.10)\sigma_I + 0.60 \quad (1)$$

and

$$\int_{m-X}^{p-X} = -29.5\sigma_R^0 \quad (2)$$

The superscript to the shielding parameter,¹⁰ \int , refers to the specific substituent involved and the subscript indicates the fluorobenzene which is the internal reference standard (H, for example, refers to unsubstituted fluorobenzene).

For the substituent group of the general formula PX_2 , the group electronic properties may be anticipated to be a function of the polar and π delocalization effects of the component substituent, X. If the σ_I and σ_R^0 (or other) scales from carbon apply to phosphorus, a logical extension of the previous treatments suggests the relationships

$$\sigma_I(PX_2) = a_I\sigma_{I(X)} + b_I\sigma_{R(X)}^0 + C_I \quad (3)$$

and

$$\bar{\sigma}_R(PX_2) = a_R\sigma_{I(X)} + b_R\sigma_{R(X)}^0 + C_R \quad (4)$$

where $\bar{\sigma}_R$ is the "effective" σ_R value for the PX_2 substituent as obtained from the F nmr shielding.

Substitution of eq 3 and 4 in eq 1 and 2 gives

$$\int_H^{m-PX_2} = \rho_I^m\sigma_{I(X)} + \rho_R^m\sigma_{R(X)}^0 + C' \quad (5)$$

and

$$\int_H^{p-PX_2} = \rho_I^p\sigma_{I(X)} + \rho_R^p\sigma_{R(X)}^0 + C'' \quad (6)$$

Thus the measurement of the ^{19}F nmr shielding terms for $m\text{-}PX_2$ and $p\text{-}PX_2$ not only provides new σ values for PX_2 substituents (*i.e.*, σ_I , σ_R^0 , σ_m^0 , and σ_p^0), but it also provides the desired test of the applicability of σ_I and σ_R^0 values to substitution at phosphorus.

Experimental Section

1. Synthesis. a. P,P-Disubstituted Fluorophenylphosphines.

p-Fluorophenyldiphenylphosphine, mp 36–37°, and *m*-fluorophenyldiphenylphosphine, mp 56–58°, were prepared by treating the appropriate fluorophenylmagnesium bromide with chlorodiphenylphosphine in dry tetrahydrofuran as described for similar compounds.¹¹

p-Fluorophenyldichlorophosphine, bp 72° (3 mm), n_D^{25} 1.5704, and *m*-fluorophenyldichlorophosphine, bp 68–70° (1.3 mm), n_D^{25} 1.5721, were prepared by the method of Quinn and Humphrey.¹²

Anal. Calcd for $\text{C}_8\text{H}_4\text{Cl}_2\text{FP}$: C, 36.6; H, 2.15; F, 9.6; P, 15.8. Found for *meta*: F, 9.9; P, 15.8. Found for *para*: C, 36.8; H, 2.22; F, 10.1; P, 16.4.

p-Fluorophenyldifluorophosphine, bp 58° (40 mm), and *m*-fluorophenyldifluorophosphine, bp 47° (22 mm), n_D^{25} 1.4648, were prepared by method of Schmutzler.¹³ These phosphines contained 26 and

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14%, respectively, of the corresponding aryl tetrafluorophosphine (by ^{19}F nmr analysis on PF fluorines), probably from disproportionation¹³ during preparation. ^{19}F nmr for PF_2 groups (CCl_3F as solvent and calibrant, at infinite dilution) is as follows: $\delta_{\text{PF}^{meta}}$ 92.2 ppm, $J_{\text{PF}^{meta}} = 1182$ cps; $\delta_{\text{PF}^{para}}$ 90.4 ppm, $J_{\text{PF}^{para}} = 1074$ cps.

p-Fluorophenyldimethylphosphine, bp 49–50° (1 mm), and *m*-fluorophenyldimethylphosphine, bp 48–50° (1.5 mm), were prepared from the appropriate fluorophenyldichlorophosphine and methylmagnesium iodide according to the method of Ingold.¹⁴

p-Fluorophenylbis(trifluoromethyl)phosphine,¹⁵ bp 73° (60 mm), n_D^{25} 1.4277, and *m*-fluorophenylbis(trifluoromethyl)phosphine, bp 69° (60 mm) (crude material), were prepared by reaction of the fluorophenylmagnesium bromide with iodobis(trifluoromethyl)phosphine.¹⁶ The samples were purified by preparative gas chromatography (to remove fluorophenyl halide impurities) using a column packed with fluoroalkyl pyrometallite on Gas Chrom R 60–80.

Anal. Calcd for $\text{C}_8\text{H}_4\text{F}_7\text{P}$: C, 36.4; H, 1.53; F, 50.4. Found for *meta*: C, 36.4; H, 1.53; F, 49.9. Found for *para*: C, 36.6; H, 1.70; F, 50.1.

^{19}F nmr for CF_3 groups (CCl_3F as solvent and calibrant at infinite dilution) is as follows: $\delta_{\text{PCF}_3^{meta}}$ 54.0 ppm, $J_{\text{PF}^{meta}} = 82$ cps; $\delta_{\text{PCF}_3^{para}}$ 54.5 ppm, $J_{\text{PF}^{para}} = 81$ cps.

Higher boiling fractions, bp approximately 98° (20 mm), were identified as the corresponding bis(fluorophenyl)trifluoromethylphosphines [from diiodo(trifluoromethyl)phosphine impurity in the iodobis(trifluoromethyl)phosphine]. Samples for nmr measurement were purified by preparative gas chromatography (as above) and characterized by mass spectrometric analysis and relative intensities of ^{19}F and H nmr absorptions; ^{19}F nmr for CF_3 group (calibrated as above), $\delta_{\text{PCF}_3^{meta}}$ 55.9 ppm, $J_{\text{PF}^{meta}} = 76$ cps; $\delta_{\text{PCF}_3^{para}}$ 56.6 ppm, $J_{\text{PF}^{para}} = 76$ cps.

p-Fluorophenyldimethoxyphosphine, bp 75° (2.7 mm), and *m*-fluorophenyldimethoxyphosphine, bp 45° (0.7 mm), were prepared from methanol and the appropriate fluorophenyldichlorophosphine by a literature method.¹⁷

p-Fluorophenylbis(dimethylamino)phosphine, bp 83° (1.3 mm), and *m*-fluorophenylbis(dimethylamino)phosphine, bp 87° (0.2 mm), were prepared by treating the appropriate fluorophenyldichlorophosphine with dimethylamine following procedures described for similar compounds.¹⁸

m- and *p*-fluorophenyldicyanophosphine were prepared by treating a hexane solution of the appropriate fluorophenyldichlorophosphine with silver cyanide and refluxing the mixture overnight according to a method adapted from the work of Statts and Morgan.¹⁹ Both compounds were oils which could not be crystallized or distilled. Although the infrared spectra of both compounds contained a strong 4.65- μ absorption characteristic of a $-\text{CN}$ group, the substituent could be the isonitrile, $-\text{NC}$. The synthetic method could give either isomer, and there is no convenient method to distinguish between the two isomers.

b. m- and *p*-fluorophenylphosphorus tetrafluorides, bp 68° (90 mm) and 68° (77 mm), respectively, were prepared by the method of Schmutzler²⁰ from the corresponding fluorophenyldichlorophosphine and antimony trifluoride.

Anal. Calcd for $\text{C}_8\text{H}_4\text{F}_3\text{P}$: F, 47.7; P, 15.4. Found for *meta*: F, 47.2; P, 15.8. Found for *para*: F, 47.7; P, 15.4.

^{19}F nmr for P–F groups (calibrated as above) is as follows: $\delta_{\text{PF}^{meta}}$ 54.2 ppm, $J_{\text{PF}^{meta}} = 964$ cps; $\delta_{\text{PF}^{para}}$ 54.7 ppm, $J_{\text{PF}^{para}} = 954$ cps.

c. Fluorophenyl-Substituted Phosphonium Salts. *p*-Fluorophenyldiphenylmethylphosphonium iodide, mp 84–5°, and *m*-fluorophenyldiphenylmethylphosphonium iodide, mp 142–143°, were synthesized by treating the appropriate fluorophenyldiphenylphosphine in ether with a fivefold excess of methyl iodide. The salts precipitated from the ethereal solution and were recrystallized from a methanol–ether mixture.

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p-Fluorophenyltriphenylphosphonium iodide, mp 274–275°, and *m*-fluorophenyltriphenylphosphonium iodide, mp 253–255°, were prepared by the method of Horner.²¹

The $-P(C_6H_5)_2OH^+$ and $-P(C_6H_5)_2H^+$ compounds were formed by the protonation of the phosphine oxide and phosphine by the acidic medium. *p*-Fluorophenyldiphenylphosphine oxide, mp 134–135°, and *m*-fluorophenyldiphenylphosphine oxide, mp 133–136°, were prepared by oxidizing the appropriate phosphine with 10% hydrogen peroxide in acetone.

2. Nmr Calibrations. ¹⁹F nmr measurements were carried out at 25° with a Varian HA60 or A56-60 spectrometer, using techniques previously described.^{22,23} When spectrograde carbon tetrachloride or cyclohexane was used as solvent, the concentration of the phosphines was 0.10 M or less. Trichlorofluoromethane was also used as solvent (serves as internal calibrant); measurements were made at three concentrations (20, 10, 5%) and the chemical shift was obtained by extrapolation to infinite dilution. Results obtained in these two solvent systems have been shown to agree to within the ±0.04 ppm precision ascribed to the method.²³ The *m*- and *p*-FC₆H₄PX₂ and fluorophenylphosphorus tetrafluorides are listed in Table I. In Table II are listed values of the shielding effect parameter.

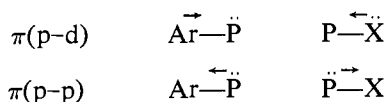
The fluorine nuclear magnetic resonance (¹⁹F nmr) shifts obtained for the P,P-disubstituted fluorophenylphosphines, *m*- and *p*-FC₆H₄PX₂, and fluorophenylphosphorus tetrafluorides are listed in Table I. In Table II are listed values of the shielding effect parameter.

$$\int_{m-P(C_6H_5)_2X}^{p-P(C_6H_5)_2X}$$

for tetracoordinate phosphorus substituents in the indicated solvents. Values of σ_R obtained from eq 2 are also given in Table II.

Discussion

Tricoordinate Phosphorus Substituents. At least four π interaction mechanisms must be considered for phosphorus in the ArPX₂ compounds, *i.e.*, $\pi(p-d)$ and $\pi(p-p)$ interactions for both the Ar-P and P-X bonds.^{24,25} The effective electron donation which accompanies these interactions is conveniently represented schematically



For the substituents involved in this study, we feel that $\pi(d-d)$ interaction in the P-X bond is not of sufficient significance to be considered.

The shielding of the *p*-X substituted fluorobenzene relative to its *meta* isomer as the internal standard \int_{m-X}^{p-X} has been proposed as a quantitative measure of the net delocalization of π charge (*cf.* eq 2).²⁶ This shielding

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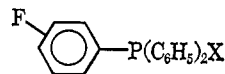
(26) (a) R. W. Taft, *J. Amer. Chem. Soc.*, **79**, 1045 (1957); (b) see ref 7; (c) see ref 9.

Table I. ¹⁹F Nmr Chemical Shifts of Fluorophenylphosphines^a *m*- and *p*-FC₆H₄PX₂, and Fluorophenylphosphorus Tetrafluorides, *m*- and *p*-FC₆H₄PF₄

Substituent	$\int_H^{m-PX_n}$	$\int_H^{p-PX_n}$	$\int_{m-PX_n}^{p-PX_n}$
P[N(CH ₃) ₂]	+0.63 ^c	+2.33 ^c	+1.70
P(CH ₃) ₂	+0.05 ^c	+1.40 ^c	+1.35
P(OCH ₃) ₂	-0.03 ^b	-1.94 ^b	-1.91
P(C ₆ H ₅) ₂	-0.64 ^b	-0.45 ^b	+0.19
P(CF ₃)(C ₆ H ₄ F) ^e	-2.29 ^d	-3.99 ^d	-1.70
PF ₂	-2.11 ^d	-8.30 ^d	-6.19
PCl ₂	-2.62, ^b -2.65 ^d	-7.37, ^b -7.42 ^d	-4.74
P(CF ₃) ₂	-3.12 ^d	-8.82 ^d	-5.70
P(CN) ₂	-4.65 ^b	-9.33 ^b	-4.68
PH ₂	...	-0.6 ^f	...
PF ₄	-2.62 ^d	-12.09 ^d	-9.47

^a In parts per million. Probable error is 0.04 ppm. ^b In CCl₄ solution. ^c In cyclohexane solution. A reaction occurs in CCl₄. However, shift is expected to apply to CCl₄ solution, *cf.* ref 4d. ^d At infinite dilution in CCl₃F solution. ^e Fluorine in fluorophenyl substituents has orientation of probe fluorophenyl. ^f Reported in 30% solution in FCCL₃ by H. Schindlbauer, *Chem. Ber.*, **100**, 3432 (1967).

Table II. Shielding and Derived Substituent Parameters for



<i>p</i> -Fluorophenyl-diphenylphosphine addend, X	Solvent	$\int_{m-P(C_6H_5)_2X}^{p-P(C_6H_5)_2X}$	$\bar{\sigma}_R$ for P(C ₆ H ₅) ₂ X
CH ₂	DMSO	-3.4	+0.12
O	CH ₂ Cl ₂	-4.3	+0.15
	CH ₃ OH	-4.7	+0.16
BCl ₃	CH ₂ Cl ₂	-4.7	+0.16
	H ₂ SO ₄	-7.4	+0.25
CH ₃ ⁺	CH ₂ Cl ₂	-7.1	+0.24
	H ₂ SO ₄	-7.4	+0.25
C ₆ H ₅ ⁺	CH ₂ Cl ₂	-7.6	+0.26
	H ₂ SO ₄	-8.3	+0.28
H ⁺	H ₂ SO ₄	-9.1	+0.31

term is positive (shift to higher field) if net π charge is delocalized to the benzene ring and negative if net π charge is delocalized from the ring to the substituent. From both theoretical considerations²⁴ and experimental data^{27,28} the accumulation of positive charge on phosphorus (resulting from electron withdrawal by X) will increase Ar-P and P-X $\pi(p-d)$ acceptor action and generally tend to decrease Ar-P $\pi(p-p)$ donor action.

The over-all trends exhibited by the present results (Table I) confirm these expectations. Thus values of $\int_{m-PX_2}^{p-PX_2}$ are positive for the P(NMe)₂ and P(CH₃)₂ substituents, corresponding to $\bar{\sigma}_R$ values of -0.06 and -0.05, respectively. That is, these substituents are weak but definite *net* π donors to the ring. On the other hand, values of $\int_{m-PX_2}^{p-PX_2}$ are negative for the PF₂ and P(CF₃)₂ substituents corresponding to $\bar{\sigma}_R$ values of +0.21 and +0.19, respectively. Thus, in spite of their "classical" saturated structures, these substituents are moderate *net* π electron acceptors from the ring. The existence of both *net* π donor and acceptor action within the series

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of substituents of general formula, PX_2 , is indeed compelling evidence that the above four kinds of π interaction mechanisms determine the resultant substituent effect.

The comparison of the following phosphorus PX_2 substituent effects with corresponding nitrogen NX_2 substituent effects adds substantial support to this conclusion (Table III).

Table III. Comparison of F Nmr Shielding Parameters for Nitrogen and Phosphorus Analogs^a

	$N(CH_3)_2$ ^b	$N(CF_3)_2$ ^c	$N(CN)_2$ ^d	$P(CH_3)_2$	$P(CF_3)_2$	$P(CN)_2$
$\int_H^{p-AX_2}$	+15.65	-3.19	+0.64	+1.40	-8.82	-9.33
$\int_H^{m-AX_2}$	-0.08	-2.86	-5.75	+0.05	-3.12	-4.65
$\int_{m-AX_2}^{p-AX_2}$	+15.57	-0.33	+6.39	+1.35	-5.70	-4.68

^a Units are in parts per million. ^b Reference 9. ^c F. S. Fawcett and W. A. Sheppard, *J. Amer. Chem. Soc.*, **87**, 4341 (1955). ^d Unpublished result.

Table IV. Substituent F Nmr Shifts for Methyl Derivatives of the First and Second Row Elements and Halogens^a

	CMe_3	NMe_2	OMe	F	$SiMe_3$	PMe_2	SMe	Cl
\int_H^{m-Y}	+0.45	-0.08	-1.05	-3.10	+0.85	+0.05	+0.40	-2.00
\int_{m-Y}^{p-Y}	+5.10	+15.98	+12.75	+9.90	-1.35	+1.35	+4.80	+5.20

^a Units are parts per million.

The positive value of $\int_{m-NX_2}^{p-NX_2}$ for the $N(CN)_2$ substituent must arise from lack of acceptor orbitals (presumably d) on N, coupled with a $\pi(p-p)$ donation of charge from N to the ring in spite of the strong inductive and conjugative interactions with N of the cyano substituents. For the $N(CF_3)_2$ substituent the value of $\int_{m-NX_2}^{p-NX_2}$ is effectively zero. Again, we have no acceptor orbitals but now the strong electron-withdrawing power of the CF_3 group coupled with a steric twisting²⁹ completely inhibits any $\pi(p-p)$ donation of charge density to the aromatic ring. The effect of the CF_3 and CN substituents (strongly electron withdrawing) on P is to coalesce the d orbitals²⁴ and make the $\pi(p-d)$ acceptor interaction of P with the ring predominant. The much smaller positive value of $\int_H^{p-AX_2}$ for $P(CH_3)_2$ than $N(CH_3)_2$ can be explained by Ar-P $\pi(p-d)$ acceptor action, which, however, is less effective when P is substituted by electron-donating substituents such as CH_3 . This possibility is not the only consideration since the $\pi(p-p)$ donation of electron density to the ring is probably more effective for nitrogen with $2p \rightarrow 2p$ than for phosphorus with $3p \rightarrow 2p$ because the larger size and more diffuse character of 3p relative to 2p and because the C-P bond is longer than C-N. These factors obviously complicate any attempt to quantitatively evaluate the extent of d orbital participation with phosphorus using nitrogen substituent

(29) The question of substituent effects on $X(CN)_n$ vs. $X(CF_3)_n$ will be discussed in detail in a forthcoming publication.

models. It is of interest to note that although values of $\int_H^{p-AX_2}$ are much more positive for $N(CH_3)_2$, $N(CF_3)_2$, and $N(CN)_2$ than for $P(CH_3)_2$, $P(CF_3)_2$, and $P(CN)_2$, respectively, the order is essentially reversed for values of $\int_H^{m-AX_2}$.³⁰ This result provides strong support for eq 1 since a reverse order is expected from the greater electronegativity of nitrogen relative to phosphorus.^{4d,30}

The shifts for substituents which are methyl derivatives of the first and second row elements and the halogens²⁶ further confirm this view (see Table IV).

In each row of substituents the *meta* shift follows the expected electronegativity sequence.³¹ The π delocalization effect parameter \int_{m-Y}^{p-Y} , is donor but with no regular pattern for the first row element substituents, as expected by $\pi(p-p)$ electron theory (of course, there is a regular sequence^{4d,9} $NH_2 > OH > F$). For the second row elements, the π electron effect changes from net donor to net acceptor within the sequence $Cl > SH > PH_2 > SiH_3$. This sequence is intelligible only in terms

that there is concomitant acceptor and donor interactions of the atomic centers with the benzene ring. The acceptor interaction is very probably $\pi(p-d)$, which increases in the order $Cl < SMe < PMe_2 < SiMe_3$.³²

For the PX_2 family of substituents, the measured net charge transfer to the benzene ring (the resultant of the Ar-P π interactions) is expected to be a function of the polar effects exerted by the X component substituents as well as a function of the P-X $\pi(p-d)$ and $\pi(p-p)$ inter-

(30) For CF_3 as substituent X, the *meta* shifts for $m-AX_2$ are similar but actually reversed. A $p-\pi$ interaction between the p electron on fluorine and the π system²³ should be more effective for $N(CF_3)_2$ than $P(CF_3)_2$ (because of differences in bond lengths) and could explain this apparent minor anomaly.

(31) Our interpretation of the basis for eq 1 should be made clear. There are good theoretical reasons to suppose that the F nmr substituent shielding effects are directly related to terms in the π charge density in the conjugating $2p_z$ orbital of fluorine and the σ charge density in the $2p_z$ orbital of fluorine [cf., M. Karplus and T. P. Das, *J. Chem. Phys.*, **34**, 1683 (1961), and F. R. Prosser and L. Goodman, *ibid.*, **38**, 374 (1963)]. In hydrocarbon solvents the π charge (\pm) which is delocalized from the ring to the substituent is nearly the same in both the *meta*- and *para*-substituted fluorobenzene.^{4d,9} The *para*-substituent shielding results imply that delocalization of π charge to the substituent in *meta*-substituted fluorobenzenes clearly must occur. The extent of the accumulation of π charge in even a strongly activating substituent is relatively small, however. Since this small amount of π charge may be expected to be distributed approximately in accord with the charge distribution in the "unperturbed" substituent, the substituent polar effect may be expected to follow (to useful quantitative approximation) the σ_I scale as determined at saturated carbon. Equation 1 is explained, therefore, as the consequence of the following conditions: (1) little or no substituent effect on the π charge density of the *m*-fluorine atom; (2) predominant control of the *m*-fluorine shift by the substituent polar effect on the fluorine σ charge density; (3) little or no effect on the polarity scale of delocalization of π charge to the substituent; and (4) little or no effect on the polarity scale resulting from the difference in hybridization of aliphatic and aromatic carbon.

(32) L. Goodman, private communication.

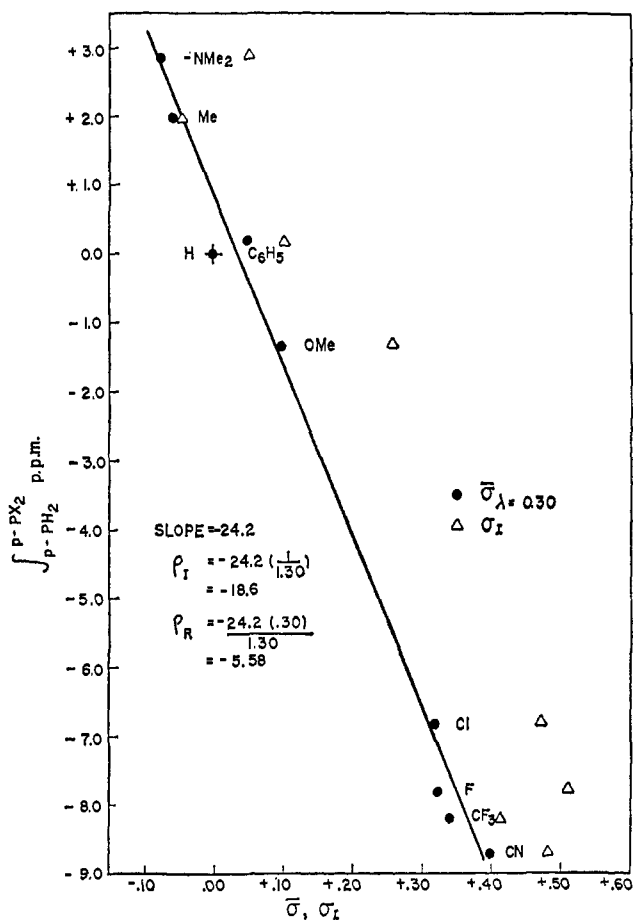


Figure 1. Correlation of the F nmr shielding effects for $p\text{-FC}_6\text{H}_4\text{PX}_2$ compounds by eq 6: shifts are given relative to the PH_2 substituent, the component substituent X is designated at each point; \circ , $\bar{\sigma}$ value for component substituent X based upon set with $\lambda = 0.30$; Δ , σ_I value for X.

actions. If the σ_I and σ_{R^0} scales of polar and π delocalization effects of X apply at phosphorus, the use of eq 5 and 6 will provide evidence for the relative magnitudes of these dependences.

Wells, Ehrenson, and Taft^{4e} have shown that the applicability of equations such as eq 5 and 6 may be usefully tested by demonstrating the precision and generality of a linear relationship between the measured quantity and a set of "blended" $\bar{\sigma}$ values, where

$$\bar{\sigma} \equiv \frac{\sigma_I + \lambda \sigma_{R^0}}{1 + |\lambda|} \quad \text{and} \quad \lambda \equiv \frac{\rho_R}{\rho_I}$$

If the plot of $\int_{\text{H}}^{m\text{-PX}_2}$ or $\int_{\text{H}}^{p\text{-PX}_2}$ vs. a unique σ set is judged to be of sufficient generality and precision to be significant, the slope of the plot, m , evaluates the parameters, *i.e.*

$$\rho_I = \frac{m}{1 + |\lambda|} \quad \text{and} \quad \rho_R = \frac{m\lambda}{1 + |\lambda|}$$

In Figure 1 a plot is given for the *para* shifts $\int_{p\text{-PH}_2}^{p\text{-PX}_2}$ vs. the $\bar{\sigma}$ set^{4e} for $\lambda = 0.30$ and similarly in Figure 2 for *meta* shifts $\int_{\text{H}}^{m\text{-PX}_2}$ vs. the $\bar{\sigma}$ set^{4e} for $\lambda = 0.60$. In Figure 1 the fluorine shifts are also shown plotted vs. σ_I ,

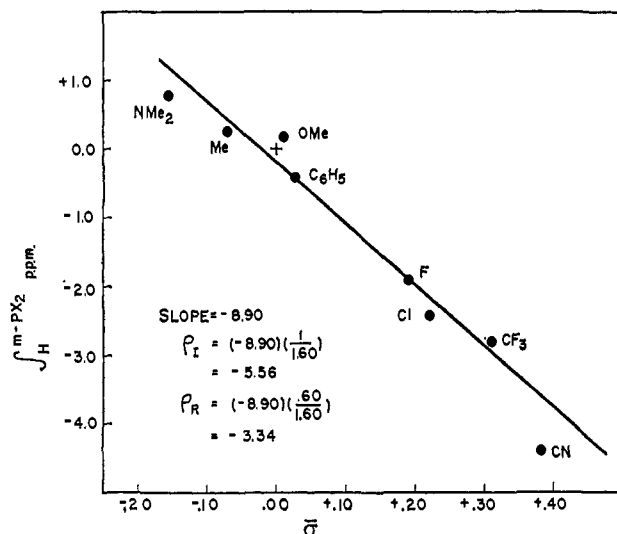


Figure 2. Correlation of the F nmr shielding effects for $m\text{-FC}_6\text{H}_4\text{PX}_2$ compounds by eq 5: shifts are given relative to fluorobenzene; $\bar{\sigma}$ value given is that for the component substituent X based upon set with $\lambda = 0.60$.

illustrating the much poorer precision of correlation when no $\sigma_{R(X)^0}$ dependence is allowed.

Equation 6 may be judged to be of useful precision and generality. The substituents, X, are of sufficient variety in their σ_I and σ_{R^0} properties to anticipate wide general applicability of eq 6. The standard deviation, $\text{sd} = 0.68$ ppm, is 11% of the rms (root mean square) of the data. The *para* shift range is 12 ppm (measured to ± 0.05 ppm). The precision is only slightly less favorable than that of other data which have been considered to be satisfactorily fitted by similar treatments.

Equation 5 is shown to apply (Figure 2) with similar statistics for the $\bar{\sigma}$ set with $\lambda = 0.60$. The point for $m\text{-P}(\text{CN})_2$ deviates (as shown), probably significantly. Because of this and the possible uncertainty in structure (*cf.* Experimental Section) this point was eliminated in obtaining the following statistics: $\text{sd} = 0.31$ ppm, which is 18% of the rms.

We conclude from these results that the σ_I and σ_{R^0} scales do apply to useful approximation for substitution at phosphorus. Thus important new evidence is provided regarding the preservation of integrity of the substituent structural unit. That is, the scales of polar and π delocalization effects are predominantly controlled by the nature of the substituent. Application of the present treatment to other second row elements, *e.g.*, Si and S, is clearly suggested.

For the *para* shifts $\int_{\text{H}}^{p\text{-PX}_2}$, the following parameters are obtained from eq 6.

$$\lambda^p = 0.30; \quad \rho_I^p = -18.6; \quad \rho_R^p = -5.58$$

$$\int_{\text{H}(\text{calcd})}^{p\text{-PH}_2} = C'' = +0.3$$

From the *meta* shift $\int_{\text{H}}^{m\text{-PX}_2}$, the corresponding parameters from eq 5 are

$$\lambda^m = 0.60; \quad \rho_I^m = -5.56; \quad \rho_R^m = -3.34$$

$$\int_{\text{H}(\text{calcd})}^{m\text{-PH}_2} = C' = -0.5$$

The distinct albeit secondary ρ_R values ($\lambda < 1$) from both eq 5 and 6 are also intelligible only on the basis that in the PX_2 substituents the phosphorus displays measurable π acceptor capacity. This conclusion is strongly supported by the results of a similar analysis of the ^{19}F nmr shifts obtained for substituents of the general formula CH_2X . In accord with the saturated nature of valences at the carbon atom (absence of acceptor orbitals), eq 5 and 6 are found to apply to CH_2X substituents with $\rho_R^m \cong \rho_R^p \cong 0$ ($\lambda = 0$). These equations

$$\int_{m-CH_3}^{m-CH_2X} = -3.72\sigma_{I(X)} \text{ and } \int_{p-CH_3}^{p-CH_2X} = -10.34\sigma_{I(X)}$$

are fitted with $sd = 0.57$ ppm, which is 23% of the rms of the data for the following X substituents: CH_3 , Cl, C_6H_5 , CN, $Si(CH_3)_3$, OH, NH_2 , CO_2H , and CF_3 . The sd is reduced to 0.46 ppm if the following small ρ_R terms are permitted

$$\int_{m-CH_3}^{m-CH_2X} = -3.71\sigma_{I(X)} + 0.06\sigma_{R(X)}^0$$

and

$$\int_{p-CH_3}^{p-CH_2X} = -9.87\sigma_{I(X)} + 2.11\sigma_{R(X)}^0$$

The values of λ^m and λ^p of zero, or less, for the CH_2X family are clearly consistent with the essential absence of acceptor orbitals at the carbon atom.

For substituents of the general formula COX , in which the carbon does possess a strong acceptor orbital, eq 5 and 6 do not apply with good precision. Best fit is achieved using σ_R instead of σ_R^0 values, giving $\lambda^m = 1.05$ and $\lambda^p = 1.19$. The sd is 1.19 ppm, which is 44% of the rms of the data for $X = CH_3$, Cl, C_6H_5 , CN, F, OC_2H_5 , $N(CH_3)_2$, and CF_3 . This poor precision is attributable to the inadequacy of either the σ_R^0 or the σ_R scale for description of the π delocalization effects of substituents substituted directly at the carbonyl carbon. In spite of this difficulty, λ^m and λ^p values for the COX family are clearly on the order of unity (*i.e.*, larger than the values for the PX_2 family).

From the comparison of these results for the PX_2 , CH_2X , and COX families, we conclude that acceptor orbital action of the phosphorus of PX_2 is clearly demonstrated. However, the ArP $\pi(p-d)$ acceptor action in PX_2 is frequently less effective than is $\pi(p-p)$ acceptor action for corresponding first row analogs, *e.g.*, COX . Corroborative evidence on this point is provided by comparison of the following ^{19}F nmr shielding effects of the BF_2 and PF_2 substituents. As expected by the above generalization, the π delocalization parameter, $\int_{m-AX_2}^{p-AX_2}$, is greater for BF_2 than PF_2 , in spite of the fact (expected by the electronegativity considerations) that the polar parameter, $-\int_H^{m-AX_2}$, is greater for PF_2 than BF_2 (Table V). It must be remembered, however, that the above generalization is subject to the important qualification that the $\pi(p-d)$ conjugation is not subject to the effects of steric twisting as is the $\pi(p-p)$ interaction.^{25g,k}

Barlow, Green, Haszeldine, and Higson³³ have re-

(33) M. G. Barlow, M. Green, R. N. Haszeldine, and H. G. Higson, *J. Chem. Soc., B*, 1025 (1966).

Table V. Comparison of F Nmr Shielding Parameters^a for BF_2 and PF_2 Substituents

Substituents	BF_2^b	PF_2
$\int_H^{m-AX_2}$	-0.54	-2.11
$\int_{m-AX_2}^{p-AX_2}$	-9.05	-6.19

^a Units are in parts per million. ^b P. Heffley, unpublished results in CH_2Cl_2 solution.

cently reported *m*- and *p*-fluorine shifts for a series of PX_2 substituents in pentafluorophenyl derivatives. Lawrenson³⁴ had previously found shifts in the pentafluorophenyl system to follow relationships of similar form of eq 1 and 2. Barlow, *et al.*, have correlated both the *m*- and *p*-fluorine shift results for PX_2 substituents ($X = N(CH_3)_2$, CH_3 , H, Cl, and F) with Hammett $\sigma_m(X)$ values. Since the σ_m values are well represented⁷ by the σ set for $\lambda \cong 0.50$, these data also may be taken to corroborate present results and conclusions.

Substitution of eq 5 into eq 1 with the evaluated parameters gives

$$\sigma_{I(PX_2)} = 0.78\sigma_{I(X)} + 0.47\sigma_{R(X)}^0 + 0.15 \quad (7)$$

Similarly eq 6 and 2 give

$$\bar{\sigma}_R(PX_2) = 0.44\sigma_{I(X)} + 0.08\sigma_{R(X)}^0 - 0.027 \quad (8)$$

Table VI summarizes the σ_I and $\bar{\sigma}_R$ values obtained from the present shielding results with the use of eq 1 and 2 and with eq 7 and 8. The only PX_2 substituent

Table VI. Substituent Parameters for P,P-Disubstituted Phosphino Groups

Group	σ_I (eq 1)	σ_I (eq 7)	$\bar{\sigma}_R$ (eq 2)	$\bar{\sigma}_R$ (eq 8)
$P[N(CH_3)_2]_2$	0.00	-0.05	-0.06	-0.05
$P(CH_3)_2$	+0.08	+0.06	-0.05	-0.06
$P(OCH_3)_2$	+0.09	+0.16	+0.06	+0.05
$P(C_6H_5)_2$	+0.17	+0.18	-0.01	0.00
PF_2	+0.38	+0.39	+0.21	+0.16
PCl_2	+0.45	+0.43	+0.16	+0.16
$P(CF_3)_2$	+0.50	+0.52	+0.19	+0.16
$P(CN)_2$	(+0.74)	+0.58	+0.16	+0.19

for which σ values are available from chemical equilibria (or rates) is the $P(C_6H_5)_2$ substituent. Schiemenz³⁵ has obtained from ionization constants of benzoic acids in 67% aqueous CH_3OH the σ_p value of +0.19. Baldwin, *et al.*,³⁶ from the same reaction carried out in 40% aqueous tetrahydrofuran have obtained the σ_p value of +0.03. The σ_p value obtained from the results in Table VI is +0.16 to +0.18 ($\sigma_p = \sigma_I + \bar{\sigma}_R$). This agreement appears satisfactory. Thus the tentative value of +0.68 based upon a correlation with ^{13}C nmr shifts³⁷ is untenable. However, the latter correlation has yielded σ_p values of +0.61 for PCl_2 and +0.33 for $P(OCH_3)_2$. The results in Table VI give σ_p values of +0.58-0.61 for PCl_2 and +0.15-0.21 for $P(OCH_3)_2$.

(34) I. J. Lawrenson, *J. Chem. Soc.*, 1117 (1965); *cf.* also ref 25h.

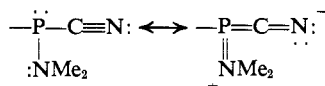
(35) G. P. Schiemenz, *Angew. Chem. Intern. Ed. Engl.*, 5, 595 (1966).

(36) R. A. Baldwin, M. T. Cheng, and G. D. Homer, *J. Org. Chem.*, 32, 2176 (1967).

(37) H. L. Retcofsky and C. E. Griffin, *Tetrahedron Lett.*, 18, 1975 (1966).

Equations 7 and 8 indicate that σ_I and δ_R values for the PX_2 group both increase as the σ_I and σ_R^0 values increase for the component substituent, X. However, there is an important discrimination in the relative dependencies upon $\sigma_{I(X)}$ and $\sigma_{R(X)^0}$. The appreciable $\sigma_{R(X)^0}$ dependence of $\sigma_{I(PX_2)}$ indicates that the P-X $\pi(p-d)$ delocalization of charge to phosphorus from X exerts a substantial influence on the polar property of PX_2 . The result is in accord with previous discussion^{4d,9} for the COX group, *i.e.*, the net charge density at phosphorus plays a dominant role in the polar effect of the PX_2 substituent. The very small $\sigma_{R(X)^0}$ dependence of $\delta_{R(PX_2)}$ indicates that the $\pi(p-d)$ P-X interaction (which according to eq 7 is moderately important) has only a very minor influence on the $\pi(p-d)$ Ar-P interaction. The $\pi(p-d)$ Ar-P interaction is indicated to be definitely present for all PX_2 substituents for which δ_R values of Table VI are positive. Consequently, the very small dependence of $\delta_{R(PX_2)}$ upon $\sigma_{R(X)^0}$ seems to be explained by the reasonable conclusion that different weakly interacting d orbitals on phosphorus are involved in the Ar-P $\pi(p-d)$ and the P-X $\pi(d-p)$ interactions. The δ_R for the COX substituent is relatively more dependent upon $\sigma_{R(X)}$ in accord with the fact that a single p_z orbital of carbon is involved in both the $\pi(p-p)$ Ar-C and $\pi(p-p)$ C-X interactions. For this reason, for example, an increase in the $\pi(p-p)$ C-X donor interaction would be expected to exert a relatively substantial decrease in the $\pi(p-p)$ Ar-C donor interaction.

For +R substituents in the PX_2 series, *e.g.*, CF_3 and CN, conjugation with the unshared electron pair of phosphorus in PX_2 could conceivably require the use of $\sigma_{R(X)^-}$ rather than $\sigma_{R(X)^0}$ parameters. However, the precision of fit with the latter is best, indicating that little such conjugation occurs in the PX_2 groups. This result does not preclude, however, conjugation of the following kind, which seems probable in view of the present results.



Tetracoordinate Phosphorus Substituents. In these compounds the Ar-P $\pi(p-p)$ ring acceptor interaction which is present in PX_2 groups is largely frozen out in σ bond formation (as, for example, in SiX_3 groups). Consequently, the Ar-P $\pi(p-d)$ ring donor interaction will be predominant in determining the substituent parameters for this class of substituent. However, similar relative dependences of the σ_I and δ_R parameters of the groups, say PR_2X and PX_2 , upon $\sigma_{I(X)}$ and $\sigma_{R(X)^0}$ is expected, *i.e.*, the shielding parameter $\int_{m-PR_2X}^{p-PR_2X}$ (and consequently δ_R) should depend substantially upon more on $\sigma_{I(X)}$ than $\sigma_{R(X)^0}$.

Listed in Table II are $\int_{m-PR_2X}^{p-PR_2X}$ parameters for a series of $P(C_6H_5)_2X$ substituents which may be considered to be derived from addends (X) to *m*- and *p*- $FC_6H_5P(C_6H_5)_2$ phosphines.

As anticipated, the shielding parameter $\int_{m-PR_2X}^{p-PR_2X}$ for all substituents is negative (δ_R positive), including the

powerful donor $X = CH_2^-$ addend (*i.e.*, in the phosphorus ylide). The presence of conjugatively acceptor orbitals on phosphorus for both Ar-P and P-X $\pi(p-d)$ interactions is thus confirmed for all of the members of the $P(C_6H_5)_2X$ family. Further, the over-all trends displayed in Table II are clearly in a qualitative "inductive order." That is, δ_R for $P(C_6H_5)_2X$ increases with increasing $\sigma_I(X)$. Similar results, which are in essentially quantitative agreement, have been obtained from *m*- and *p*-fluorine shifts for $(FC_6H_4)_3PX$ compounds.³⁸

We emphasize, therefore, that the observation of substituent effects in the "inductive" order for series, *e.g.*, PX_2 or PR_2X , does not permit the conclusion that there is no Ar-P $\pi(p-d)$ acceptor action by P.

A quantitative treatment for the substituents of Table II according to eq 5 and 6 is not possible, however, for the following reasons: σ_I values are not available for a number of the addend groups (X); solvent effects of unknown magnitude are involved; *meta* and *para* shifts are known to involve medium effects if substituents of different charge type are compared.³⁹

meta shifts have been obtained for $P(C_6H_5)_2O$ of -1.56 ppm in CCl_4 and -2.65 ppm in CH_3OH , which give by eq 1 σ_I values of $+0.30$ and $+0.46$, respectively. Combined with the δ_R values of Table II, δ_p values of $+0.42$ in CCl_4 and $+0.62$ in CH_3OH are obtained. From ionization of benzoic acids in aqueous organic solvents δ_p values for $P(C_6H_5)_2O$ of $+0.50$ ³⁵ and $+0.46$ ³⁷ have been reported. Schiemenz⁴⁰ has reported a $\sigma_{(p)^-}$ value of $+0.88$. The *meta* shift for $P(C_6H_5)_2OBCl_3$ in CH_2Cl_2 is -4.02 ppm giving $\sigma_I = +0.65$ and $\delta_p = +0.81$. The latter values may be compared with those obtained from *m*- and *p*-fluorine shifts⁴¹ for $C(C_6H_5)OBCl_3$ in CH_2Cl_2 , $\sigma_I = +0.62$ and $\delta_p = +1.21$.

Pentacoordinate Phosphorus Substituents. Our only example is $ArPF_4$ where the five bonds to phosphorus are considered to be covalent.⁴² The RPF_4 compounds (like PF_5) are considered to have a trigonal bipyramidal geometry with sp^3d bonding. As in the phosphonium substituents, the unshared p electrons on P are no longer available for $\pi(p-p)$ donation to the aromatic ring. The value of $\int_{m-PF_4}^{p-PF_4}$ of -9.47 (δ_R of 0.35) is the largest measured in the series of phosphorus substituents, indicating maximum Ar-P $\pi(d-p)$ interaction. Apparently, use of one d orbital in σ bonding does not inhibit use of the other d orbitals for Ar-P π interaction. Also the $\int_{m-AX_n}^{p-AX_n}$ value for PF_4 is comparable to that for BF_2 suggesting that under optimum conditions $\pi(p-d)$ donation from the ring can be made to approach $\pi(p-p)$ donation in its effectiveness. The σ_I value of PF_4 (0.45) is comparable to the values for PF_2 (0.39) and PCl_2 (0.44); the enhanced inductive effect from the two additional fluorines is probably offset because of geometrical con-

(38) A. W. Johnson and H. L. Jones, *J. Amer. Chem. Soc.*, **90**, 5232 (1968).

(39) J. W. Rakshys, Ph.D. Thesis, University of California, Irvine, Calif., June 1967.

(40) G. P. Schiemenz, *Angew. Chem. Intern. Ed. Engl.*, **5**, 129 (1966).

(41) R. G. Pews, Y. Tsuno, and R. W. Taft, *J. Amer. Chem. Soc.*, **89**, 2391 (1967).

(42) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 2nd ed, Interscience Publishers, Inc., New York, N. Y., 1966, Chapter 20.

siderations and because of a decrease in electronegativity of the phosphorus in the C-P bond due to decrease in s character through hybridization with p and d orbitals. Further studies of pentavalent phosphorus substituents are of interest. Substituents in such a series should conform to a relationship for $\sigma_{I(X)}$ and $\sigma_{R(X)}$ ⁰ dependencies similar to that noted above for the tetracoordinated phosphorus substituents.

phorus substituents are of interest. Substituents in such a series should conform to a relationship for $\sigma_{I(X)}$ and $\sigma_{R(X)}$ ⁰ dependencies similar to that noted above for the tetracoordinated phosphorus substituents.

Restricted Rotation in *t*-Butylcycloalkanes. Effect of Ring Size¹

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Abstract: The low-temperature (-130 to -160°) nmr spectra of the *t*-butyl protons in *t*-butylcycloalkanes (I-*n*, where *n* is the ring size) appear as 2:1 doublets, more or less well resolved, indicating restricted rotation. ΔF^\ddagger for the rotational barriers for I-5 to I-10 were found to vary from 6.0 to 7.8 kcal/mol in the following qualitatively understandable fashion: I-5 \sim I-6 < I-9 \sim I-10 \sim I-7 < I-8. Although a new interpretation of the nmr spectrum at low temperature of *t*-butylcyclooctane is presented, previous conclusions about the conformations of eight-membered rings are unchanged.

Nuclear magnetic resonance has been a valuable tool for the study of restricted rotation about the single bond joining two sp^3 hybridized carbon atoms.² Most of this work has involved fluorine resonance and highly substituted ethane derivatives.³ In our previous nmr work⁴ on *t*-butylcyclooctane (I-8), it had appeared that restricted rotation was not the explanation for changes which were observed in the *t*-butyl band at low temperatures. From more recent data discussed below, it is now apparent that these observed spectral changes are caused by rotation of the *t*-butyl group and that the observed rotational barriers for this type of rotation are affected markedly by ring size.

Results and Discussion

The room temperature nmr spectra of *t*-butylcycloalkanes show single sharp bands for the *t*-butyl protons and broad unresolved multiplets for the methylene protons.

In our earlier work⁴ on *t*-butylcyclooctane (I-8), it was found that the low-temperature nmr spectrum of the *t*-butyl group was a 2:1 doublet. At that time, this fact was not attributed to restricted rotation because (a) *t*-butylcyclohexane (I-6) did not show a similar change down to -150° and (b) the splitting in the

t-butyl band of I-8 was accompanied by distinct changes in the ring proton bands. Since rotation of the *t*-butyl group does not affect the chemical shift of the ring protons whereas a ring conformational change can affect the chemical shifts of both bands, the simplest hypothesis is that a ring conformational change is occurring rather than restricted rotation. However, the large splitting (14 Hz) observed in the *t*-butyl band at low temperatures is not in agreement with such a theory, and indeed was described as "puzzling" in the previous work. It is now apparent from our new data that I-6 is not a very good model for I-8 as far as restricted rotation is concerned (Table I) and that, by

Table I. Chemical Shift and ΔF^\ddagger Data for *t*-Butylcycloalkanes

Compd	T_c , ^a °C	<i>t</i> -Butyl chemical shift (τ) ^b	Separation of <i>t</i> -butyl doublet ^c ν_{AB} , Hz at 60 MHz	ΔF^\ddagger , ^d kcal/mol
I-5	Ca. -155	9.16	7	Ca. 6.0
I-6	Ca. -150	9.16 9.17 ^e	8 13 ^e	Ca. 6.3 ...
I-7	-126	9.19	11	7.4
I-8	-118	9.21	13.5	7.8
I-9	-130	9.15	10	7.3
I-10	Ca. -130	9.15	9	Ca. 7.3

^a Temperature of maximum spectral change. This corresponds roughly to the coalescence temperature for a completely resolved 2:1 doublet. ^b TMS = 10 ppm. These values are weighted average chemical shifts of the 2:1 doublets under the conditions given in Figure 1. ^c At temperatures given in Figure 1. ^d ΔF^\ddagger , the Gibb's free energy of activation for rotation of the *t*-butyl group about the $C_\alpha C_\beta$ bond by 120° in one direction, was calculated from absolute rate theory and rate constants obtained at T_c . Computer calculated spectra derived from these rate constants were in good agreement with experimental spectra in the two cases (I-5 and I-7) where this check was made. Because of varying reference line widths at different temperatures, the rate constants especially for I-5, I-6, and I-10 are only approximate; however, ΔF^\ddagger should be accurate to ± 0.1 kcal/mol for I-7, I-8, and I-9 and to ± 0.2 kcal/mol for I-5, I-6, and I-10. ^e 100 MHz. This spectrum was obtained by Y. Ogawa on a 4 H 100 spectrometer through the courtesy of Jeolco.

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