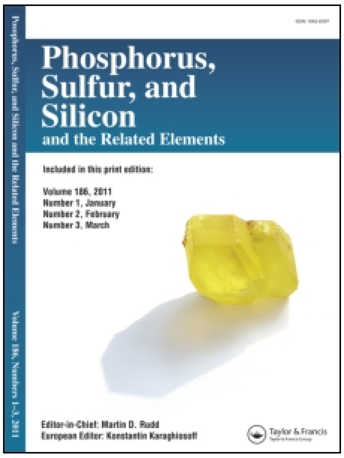

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NMR STUDY OF PHOSPHORUS-CARBON AND PHOSPHORUS-NITROGEN BONDS IN ALKYL-AND MONO-N-SUBSTITUTED AMINOTRIARYLPHOSPHONIUM SALTS

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NMR STUDY OF PHOSPHORUS-CARBON AND PHOSPHORUS-NITROGEN BONDS IN ALKYL- AND MONO-N-SUBSTITUTED AMINOTRIARYLPHOSPHONIUM SALTS[1]

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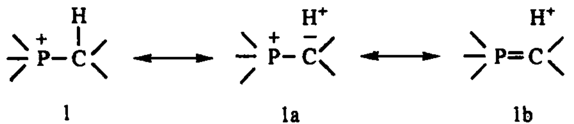
^{1}H, ^{13}C, and ^{31}P NMR spectra of a series of alkyltriarylphosphonium salts, $(p\text{-}XC_6H_4)_3\overset{+}{P}R\ I^-$ (R = Me, CH_2CMe_3, and CH_2SiMe_3; X = H, Me, OMe, and NMe_2) are reported. Their chemical shifts and coupling constants, $^1J_{PC}$ and $^2J_{PH}$, are rationalized in terms of hyperconjugative π bonding between the α C—H bonds and 3*d* orbitals of phosphorus. NMR including ^{15}N spectra of $Ph_3\overset{+}{P}NHR\ BF_4^-$, where R = H, Me, CMe_3, NH_2, and NMe_2, have also been determined. Relative changes in their parameters are discussed in the light of interaction between the lone pair of nitrogen and *d* orbitals of phosphorus, and compared vs. those due to hyperconjugative π bonding in the alkyltriarylphosphonium salts. Temperature effects on their spectra are reported and interpreted in terms of changes in bonding around phosphorus as a result of inversion at the α nitrogen.

Key words: Phosphorus-carbon, phosphorus-nitrogen, X-ray, NMR, phosphonium salts.

INTRODUCTION

Although several NMR studies of alkylphosphonium salts have been reported,[2–6] ^{1}H, ^{13}C, and ^{31}P chemical shifts and their coupling constants, $^1J_{PC}$ and $^2J_{PH}$, have not been fully understood in terms of bonding. Especially the role of hyperconjugative interaction of their α C—H bonds with the 3*d* orbitals has not been explored. Such an interaction would imply ylid (**1a** ↔ **1b**) as one of the contributing structures:



1 1a 1b

The difficulty has been that even in free ylids the question of bonding is not yet settled. The only agreement is that phosphonium cation stabilizes the negative charge on the ylid carbon using its $3d_{xy}$ or $3d_{xz}$ orbitals.[7] Ylids have been conventionally represented as a hybrid of polar and non-polar structures. The non-polar structure involves $p\pi$-$d\pi$ bonding, requiring change in hybridization of phosphorus from sp^3 to sp^3d. However, Dixon[8] has recently concluded from *ab initio* calculations that the ylid structure is essentially polar, in which the negative charge on its carbon is stabilized by 'back-bonding' to the 3*d* orbitals of phosphorus or σ^* orbitals of P—R bonds.

In the absence of any theoretical work, NMR data of alkylphosphonium salts would help in understanding their bonding. In this paper, we report such a study using the following phosphonium salts:

$$(p\text{-}XC_6H_4)_3\overset{+}{P}\text{—}R\quad I^- \qquad R = CH_3,\ CH_2C(CH_3)_3,\ \text{and}\ CH_2Si(CH_3)_3$$

$$X = H,\ CH_3,\ OCH_3,\ \text{and}\ N(CH_3)_2$$

The *p*-substituents on the phenyl rings provide a sensitive electronic probe to monitor changes in the NMR parameters, resulting from the changes in bonding around phosphorus. In addition, NMR spectra of a series of mono-substituted aminophosphonium salts:

$$Ph_3\overset{+}{P}\text{—}NHR\quad BF_4^- \quad R = H,\ CH_3,\ C(CH_3)_3,\ NH_2,\ N(CH_3)_2$$

have been determined for comparison with those of the alkylphosphonium salts.

RESULTS AND DISCUSSION

Alkyltriphenylphosphonium Salts

In Table I are listed the pertinent ^{1}H, ^{13}C, and ^{31}P NMR spectral data of some alkyltriphenylphosphonium salts. We will discuss these data first relative to what has been described in the literature.

The α carbon is deshielded with increasing substitution on the α or β carbon. This deshielding is primarily a result of the substitution as it also occurs in the corresponding alkanes.[9] A plot of the α ^{13}C chemical shifts in alkyltriphenylphosphonium salts vs. those in the corresponding alkanes is shown in Figure 1. Its slope

TABLE I

^{1}H, ^{13}C, and ^{31}P NMR data of $(C_6H_5)_3\overset{+}{P}R\ I^-$

	α Protons			Carbon-13			
				P-C (Alk)		P-C (Ar)	
R	δ_H ppm	$^2J_{PH}$ Hz	$\delta_{^{31}P}$, ppm	δ, ppm	J, Hz	δ, ppm	J, Hz
CH_3	3.16	13.2	22.10, 21.1[a]	11.5, 11.4[a]	57.4, 57.1[a]	118.69, 118.8[a]	88.5, 88.6[a]
CH_2CH_3[b]	3.66	12.2	26.53	17.03	50.6	117.16	83.7
$CH(CH_3)_2$[c]	--	--	31.3[a]	21.5[a]	47.0[a]	117.5[a]	83.1[a]
$C(CH_3)_3$	--	--	35.6[a]	35.3[a]	42.5[a]	117.1[a]	80.1[a]
$CH_2CH_2CH_3$	3.59	12.5	24.30, 24.1[a]	24.17	48.2	117.27	90.1
$CH_2CH(CH_3)_2$	3.56	12.8	23.45	30.83	46.5	118.36	86.2
$CH_2C(CH_3)_3$	3.82	12.9	20.0	35.6	44.5	120.25	84.5

[a] Data from ref. 5.

[b] CH_3 : δ_H = 1.40 ppm ; $^3J_{PH}$ = 19.6 Hz ; $^3J_{HH}$ = 7.4 Hz; δ_C = 6.37 ppm; $^2J_{PC}$ = 3.8 Hz.

[c] Phosphonium bromide.

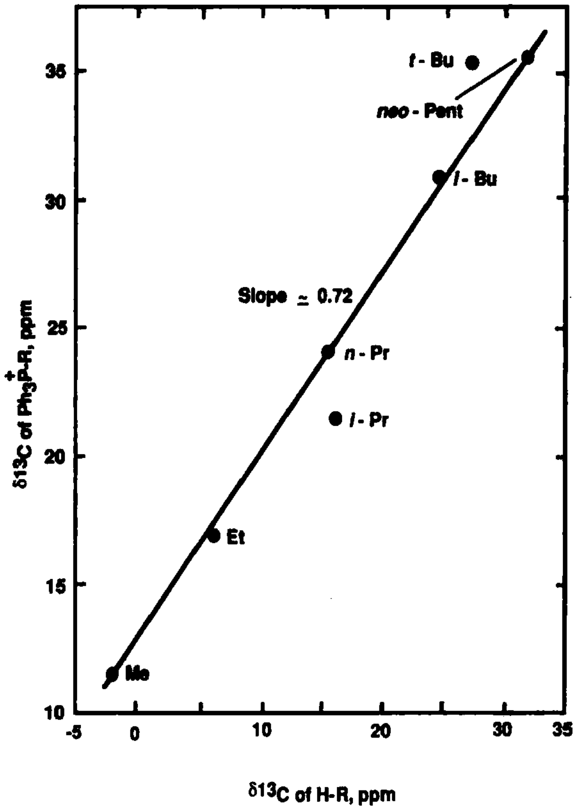


FIGURE 1 Plot of ^{13}C chemical shifts of the carbons directly bonded to phosphorus in $(C_6H_5)_3\overset{+}{P}—R$ X^- vs. those in the corresponding alkanes, H-R (from Reference 9).

TABLE II

^1H and ^{31}P NMR data of $(p\text{-}XC_6H_4)_3\overset{+}{P}R$ I^-

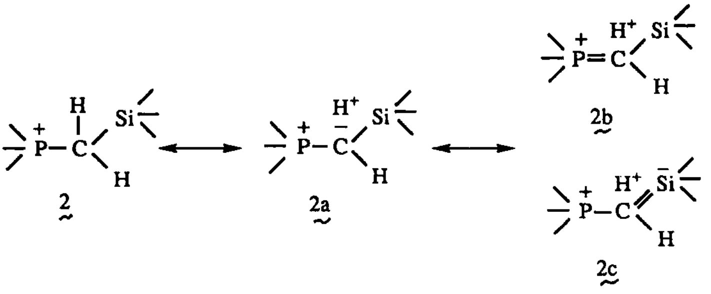
			α Protons			
No.	R	X	δ_H ppm	$^2J_{PH}$ Hz	$J_{^{13}C—H}$	$\delta_{^{31}P}$ ppm
6	CH_3	H	3.16	13.2	134.0	22.10
7		CH_3	3.01	13.2	133.6	20.85
8		OCH_3	2.92	13.1	133.4	19.37
9		$N(CH_3)_2$	2.54	13.0	132.5	16.49
10	$CH_2C(CH_3)_3$	H	3.82	12.9	128.0	19.95
11		CH_3	3.63	12.9	127.4	18.95
12		OCH_3	3.50	12.8	—	17.67
13		$N(CH_3)_2$	3.02	12.8	126.2	15.12
14	$CH_2Si(CH_3)_3$	H	3.14	18.4	[a]	24.85
15		CH_3	2.97	18.2	[a]	23.68
16		OCH_3	2.88	18.1	[a]	22.11
17		$N(CH_3)_2$	2.37	17.7	[a]	19.17

[a] Coupling not observed due to interference from absorptions of the phosphonium salts hydrolysis products, $(p\text{-}XC_6H_4)_3\overset{+}{P}CH_3$ I^-.

of less than 1.0 indicates that the presence of quaternary phosphorus actually has a shielding effect on the α carbon, presumably due to hyperconjugative interaction. The isopropyl carbon is more shielded because its secondary structure would result in more effective hyperconjugative π bonding with phosphorus. The *t*-butyl carbon, on the other hand, is deshielded as it has no α C—H bond to participate in hyperconjugation. Typically, olefinic carbons (sp^2) are deshielded relative to those of their saturated analogs.[10] However, the ylid carbon of $Ph_3P{=}CH_2$ is more shielded than its phosphonium salt.[11] This is obviously due to the polar nature of the ylid bond,[12] which concentrates the negative charge preferentially on the α carbon. Lumbroso *et al.*[13] have estimated from dipole moment measurements that the above ylid has 55% ionic character in its PC bond.

The phosphorus atom of ylids is also usually more shielded than that of the corresponding phosphonium salts,[14] as it can receive electrons from the negative carbon through its *d* orbitals. Therefore, hyperconjugative π bonding in alkylphosphonium salts should also provide shielding to phosphorus. On the contrary, as the hyperconjugative interaction increases with substitution at the α carbon, i.e., R = CH_3, C_2H_5, and $CH(CH_3)_2$, phosphorus gets deshielded (Table I). Schweizer and co-workers[5] have attributed this to the steric effect of the alkyl groups. But when substitution occurs at the β carbon, phosphorus gets more shielded, probably due to the hyperconjugative interaction being stronger than the steric effect.

In (trimethylsilyl)methylphosphonium salts, phosphorus is strongly deshielded vs. that in the corresponding neopentylphosphonium salts (Table II). This is either due to the steric bulk of Me_3SiCH_2 vs. Me_3CCH_2, or the electron withdrawing effect resulting from $p\pi$(C)-$p\pi$(Si) bonding shown by the contributing structure **2c** below:



Relationship between ${}^1J_{PC}$ (or ${}^1J_{PN}$) and ${}^2J_{PH}$

In organometallic systems, linear relationships have been shown between ${}^1J_{MC}$ and ${}^2J_{MH}$, where M = ${}^{117,119}Sn$, ${}^{207}Pb$, ${}^{199}Hg$, ${}^{195}Pt$, etc.[15] Such relationships are actually expected from the Fermi contact term of these coupling constants; a simplified version of which can be written for ${}^1J_{PC}$ as follows[16]:

$$ {}^1J_{MC} \propto \gamma_M \gamma_C \alpha^2_{MC} \alpha^2_{CM} \left(\frac{Z^*_M}{n_M}\right)^3 \left(\frac{Z^*_C}{n_C}\right)^3 \Delta E^{-1} \qquad (1) $$

where γ's are nuclear magnetogyric ratios, α^2_{MC} and α^2_{CM} are the fractional *s* characters of the orbitals of M and C, respectively, and Z^*_M and Z^*_C are their effective nuclear charges, n is the quantum number of the period to which the atom belongs, and ΔE is the average energy approximation term. A similar expression can be written for $^2J_{PH}$; and it can be shown from these equations that, when Fermi contact is the main mechanism of coupling, a plot of $^1J_{MC}$ vs. $^2J_{MH}$ passes through the origin. No such relationship, however, is apparent between $^1J_{PC}$ and $^2J_{PH}$ of the alkylphosphonium salts. While $^1J_{PC}$ values in the methyl and neopentyl phosphonium salts change significantly (Table III), their $^2J_{PH}$ remain practically unchanged in each series (Table II). On the other hand, in mono-N-substituted aminotriphenylphosphonium salts, $^1J_{PN}$ and $^2J_{PH}$ (data of **18**, **19**, and **22** in $CDCl_3$, see Table IV) show an approximate linear relationship which, on extrapolation, passes through the origin indicating that Fermi contact is the main mechanism of their coupling.

The failure of a similar relationship in alkylphosphonium salts can be explained from the hyperconjugative π bonding. Such bonding decreases the *s* character of the P—C bond due to change in hybridization of the phosphorus atom from sp^3 to sp^3d. Further, it would favor more *p* character in the α C—H bonds. Both these hybridizational changes would have opposite effect on $^2J_{PH}$[17]; and, consequently, cancel each other in the methyl and neopentyl phosphonium salts. As hyperconjugative π bonding decreases with electron donating *p*-substituents on the phenyl rings (*vide infra*), the *s* character of the P—C bond increases resulting in the corresponding increase in $^1J_{PC}$ values.

In (trimethylsilyl)methylphosphonium salts, there is discernible decrease in $^2J_{PH}$ with electron donating *p*-substituents on the phenyl rings, suggesting that the effect of change in hybridization at the α carbon is more dominant than that at the phosphorus atom. Further, their $^2J_{PH}$ values are much larger (18.4–17.7 Hz) than those of the corresponding neopentylphosphonium salts (~12.8 Hz). Actually, they

TABLE III

^{13}C and ^{29}Si NMR data of $(p\text{-}XC_6H_4)_3\overset{+}{P}R\ I^-$

		Substituent		δ, ppm			J, Hz			δ, ppm				J, Hz		
No.	R	X	δ_C ppm	C_1	C_2	C_3	PC_1	PC_2	PC_3	C_4	C_5	C_6	C_7	PC_4	PC_5	PC_6
6	CH_3	H	--	11.52	–	--	57.4	--	--	118.69	133.21	130.53	135.25	88.5	10.9	12.8
7		CH_3	21.88	11.69	–	--	58.3	--	--	115.66	133.01	131.14	146.32	90.8	10.9	13.1
8		OCH_3	56.25	12.34	–	--	59.6	--	--	109.78	135.06	116.25	164.65	97.0	12.3	14.0
9		$N(CH_3)_2$	40.04	12.27	–	--	62.0	--	--	102.98	133.79	112.30	153.46	101.3	12.1	13.6
10	$\overset{1}{C}H_2\overset{2}{C}(\overset{3}{C}H_3)$	H	--	35.56	33.15	31.88	44.5	4.9	7.3	120.25	133.87	130.40	134.78	84.5	10.0	12.4
11		CH_3	21.59	35.44	32.82	31.71	46.6	4.6	7.1	116.28	133.49	130.91	145.81	86.6	10.3	13.0
12		OCH_3	55.91	35.54	32.38	31.32	48.8	–4.9	–6.1	109.67	135.12	115.63	163.90	92.8	11.6	13.4
13		$N(CH_3)_2$	40.05	36.64	32.03	31.41	52.7	4.4	6.7	102.70	134.30	111.94	153.02	97.6	12.4	13.3
					^{29}Si			PSi								
14	$\overset{1}{C}H_2Si(\overset{3}{C}H_3)_3$	H	--	10.15	3.31	0.81	44.7	5.8	[b]	120.86	[a]	130.34	134.81	86.4	[a]	12.6
15		CH_3	21.93	10.46	3.09	0.84	44.6	5.9	[b]	117.86	133.18	130.99	145.85	90.1	9.9	12.4
16		OCH_3	56.18	11.27	2.83	0.82	47.6	5.7	[b]	111.82	135.25	115.96	164.25	95.2	12.1	14.3
17		$N(CH_3)_2$	40.05	11.71	2.21	0.80	50.0	5.6	[b]	104.80	133.88	112.03	153.17	100.5	12.0	13.9

[a] Absorptions overlapped those of its hydrolysis product, $Ph_3\overset{+}{P}CH_3\ I^-$.

[b] No coupling was observed.

TABLE IV

^1H, ^{13}C, ^{15}N, and ^{31}P NMR data of $Ph_3\overset{+}{P}NHR\ BF_4^-$

			α Protons			δ, ppm				J, Hz			Nitrogen-15	
No.	R	Temp °C	δ_H ppm	$^2J_{PH}$ Hz	$\delta_{^{31}P}$ ppm	C_4	C_5	C_6	C_7	PC_4	PC_5	PC_6	δ, ppm[a]	J_{PN}, Hz
18	H	30	5.61	3.5	37.01	122.79	133.09	129.68	134.54	103.5	11.9	13.7	-354.00	0.0
		-50	5.61	3.5	37.63	122.19	132.82	129.50	134.49	103.5	11.9	13.7	---	---
19	CH_3[b]	30	5.49	8.6	40.27	120.54	133.27	130.14	135.07	103.2	11.0	13.4	-365.87	6.1
		-50	5.35	11.0	40.51	119.63	133.07	129.93	135.09	103.5	11.0	13.7	---	---
20	$\overset{2}{C}(\overset{3}{C}H_3)_3$[c]	30	5.41	7.2	32.40	122.59	133.54	129.86	134.74	102.6	11.0.	13.7	-326.96	d
		-50	5.32	8.2	32.45	121.75	133.23	129.70	134.67	102.6	11.0	13.7	---	--
21	NH_2[e]	30	7.09	25.8	40.39	120.19	133.78	129.89	135.13	103.5	11.0	13.7	f, (-330.36)[g]	f, (4.3)[g]
		-50	6.94	31.1	40.92	119.41	133.59	129.79	135.17	104.4	11.9	13.7	---	---
22	$N(CH_3)_2$[h]	30	6.94	35.0	34.92	120.43	133.99	129.78	135.15	104.4	11.0	13.8	-293.71, (-291.22)[g]	11.3, (6.1)[g]
		-50	6.79	36.3	35.27	119.46	133.74	129.66	135.14	104.4	11.0	12.8	---	---

[a] From external reference of $\overset{+}{N}H_4\ \overset{-}{NO_3}$ (^{15}N).

[b] $\delta_C = 26.33$ ppm ; $^2J_{PC} \cong 0.0$ Hz.

[c] $\delta_{C(2)} = 56.30$ ppm; $^2J_{PC} \cong 0.0$ Hz. $\delta_{C(3)} = 31.77$ ppm; $^3J_{PC} = 3.7$ Hz.

[d] Broad, unresolved peak.

[e] Spectra recorded on ~0.02M solution ($CDCl_3$). $\delta_N = (-324.89$ ppm$)^g$; $^2J_{PN} = (14.0$ Hz$)^g$.

[f] Not determined in $CDCl_3$ because of very low solubility.

[g] Values in parentheses are in DMSO-d_6 solutions (~0.5M).

[h] $\delta_C = 49.00$ ppm ; $^3J_{PC} = 4.6$ Hz. $\delta_N = (-310.99$ ppm$)^g$; $^2J_{PN} = (14.7$ Hz$)^g$.

are the largest $^2J_{PH}$ observed for any phosphonium salt of $Ph_3\overset{+}{P}CH_2R$ structure.[22] This is probably because of the change in hybridization of the α C—H bonds due to the silicon atom.

Relationship between $^2J_{PC}$ and $^2J_{PH}$

Weigert and Roberts[23] related two-bond phosphorus-carbon and phosphorus-proton coupling constants in alkylphosphonium salts by:

$$^2J_{PC} = \alpha\ ^2J_{PH} \tag{2}$$

where α is a constant. Equation 2 was derived from equations similar to Equation 1 written for $^2J_{PH}$ and $^2J_{PC}$. The average energy approximation usually holds for hydrocarbons, and $\alpha = 0.3$, 0.4, and 0.61 for sp^3, sp^2, and sp hybridized carbons, respectively.[24] This also appears to apply to alkylphosphonium salts. For example, the α value for $Ph_3\overset{+}{P}C_2H_5\ I^-$ is 0.31, which is consistent with the essentially single bond between phosphorus and carbon. On the other hand, the α values for the neopentylphosphonium salts, calculated from the $^2J_{PH}$ and $^2J_{PC}$ data given in Tables II and III, range from 0.34 to 0.38, indicating partial double bond character of their PC bonds. In (trimethylsilyl)methylphosphonium salts, where α corresponds to the $^2J_{PSi}/^2J_{PH}$ ratio, its values are ~0.32.

The X-ray structure of neopentyltriphenylphosphonium iodide shows the cation to exist in two independent ion pairs in the asymmetric unit (Figure 2) with PCC angles of 120.3° and 124° (Table II), indicating a strong steric effect of the neopentyl

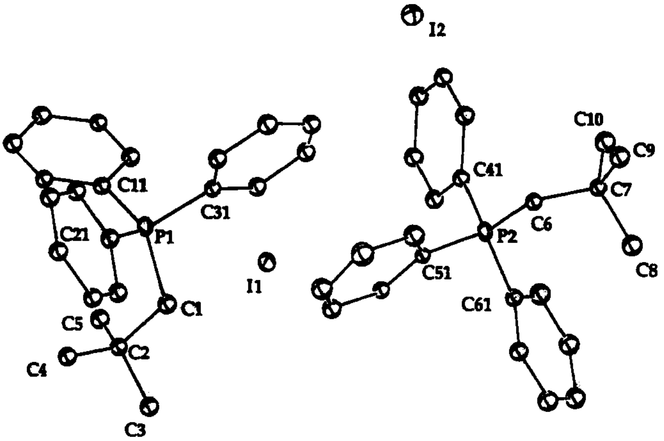


FIGURE 2 ORTEP drawing of $(C_6H_5)_3\overset{+}{P}{-}CH_2C(CH_3)_3\ I^-$ with numbering of atoms.

group on the hybridization of its α carbon. These angles ($\sim sp^2$) would impart more p character to the C—H bonds, or reduce their s character (see $^{13}C{-}H$ coupling constants[21] in Table II), thereby resulting in more effective hyperconjugative π bonding in the neopentyl vs. methyl phosphonium salts.[25] the PC bond of $Ph_3\overset{+}{P}{-}CH_2CMe_3\ I^-$ is still longer, 1.822 Å and 1.787 Å, than that of $Ph_3\overset{+}{P}{-}CH_3\ I^-$ (1.786 Å)[27]; obviously due to the steric effect of the neopentyl group.

p-Substituted Triarylphosphonium Salts

In these compounds both phosphorus and the directly bonded carbon are more shielded with the electron donating p-substituents on the phenyl rings: $NMe_2 >$ OMe > Me > H (Tables II and III). Linear relationships are shown between ^{31}P chemical shifts and Hammett's substituent constants, σ_p (Figure 3). The alkyl carbon, on the other hand, gets deshielded. Consequently, with electron donating substituents on the phenyl rings, the hyperconjugative π bonding decreases, resulting in the deshielding of the alkyl α carbon. Furthermore, both $^1J_{PC_{Alk}}$ and $^1J_{PC_{Ar}}$ increase with the decrease in the π bonding, presumably due to the increase in the s character of the phosphorus orbitals bonding to the alkyl as well as aryl carbons. Actually, linear relationships exist between these coupling constants (Figure 4). The slope of the neopentyl line is about twice that of methyl series, obviously due to the stronger hyperconjugative π interaction in the neopentyl compounds and, therefore, more pronounced effect of the substituents. The situation in (trimethylsilyl)methylphosphonium salts is intermediate between the neopentyl and methyl salts.

Another effect of the change in bonding around phosphorus is on the ^{13}C chemical shifts of the aryl carbons directly bonded to phorphorus. For example, the directly-bonded aryl carbons of $Ph_3\overset{+}{P}CH_3\ I^-$ are more shielded than that of $Ph_3\overset{+}{P}{-}CH_2CMe_3\ I^-$. Consequently, due to less hyperconjugative π interaction in the methyl salt, its phosphorus is more positive and, therefore, resonance structures like **3a** make a greater contribution than in the neopentyl salt. The partial negative charge on the directly bonded aryl carbon results in its shielding.

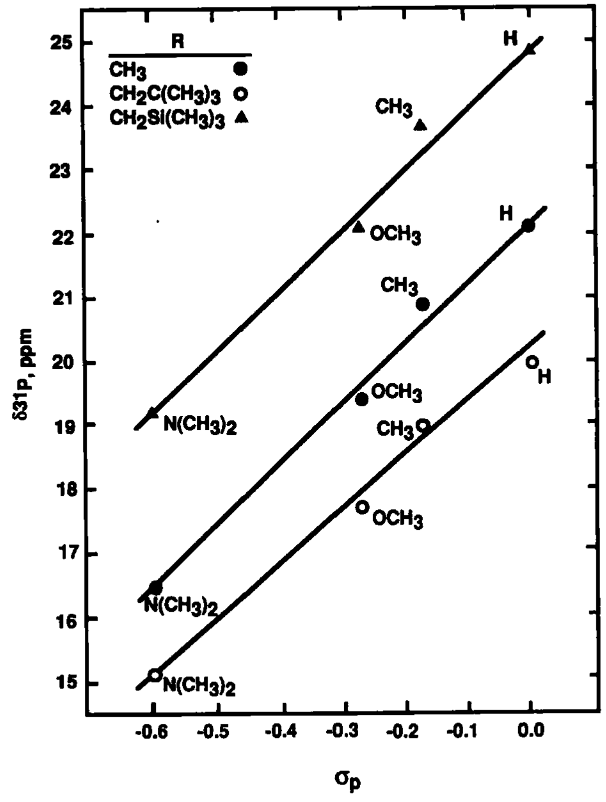
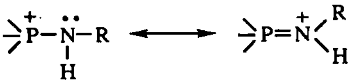


FIGURE 3 Plots of ^{31}P chemical shifts vs. Hammett's substituent constants (σ_p) in $(p\text{-}XC_6H_4)_3\overset{+}{P}$—R
I

3 3a

Mono-N-substituted Aminotriphenylphosphonium Tetrafluoroborates

Their NMR data are listed in Table IV. Tetrafluoroborates were used instead of halides to avoid any complication due to hydrogen bonding between NH and the anions.[28] It is known from phosphorus-nitrogen bond measurements that the nitrogen lone pair of aminophosphonium salts has considerable overlap with the 3*d* orbitals of phosphorus,[29]



4 4a

which would make the nitrogen more planar in the ground state. It appears from the $^2J_{PH}$ data that the planarity of α nitrogen and, hence, its lone pair interaction

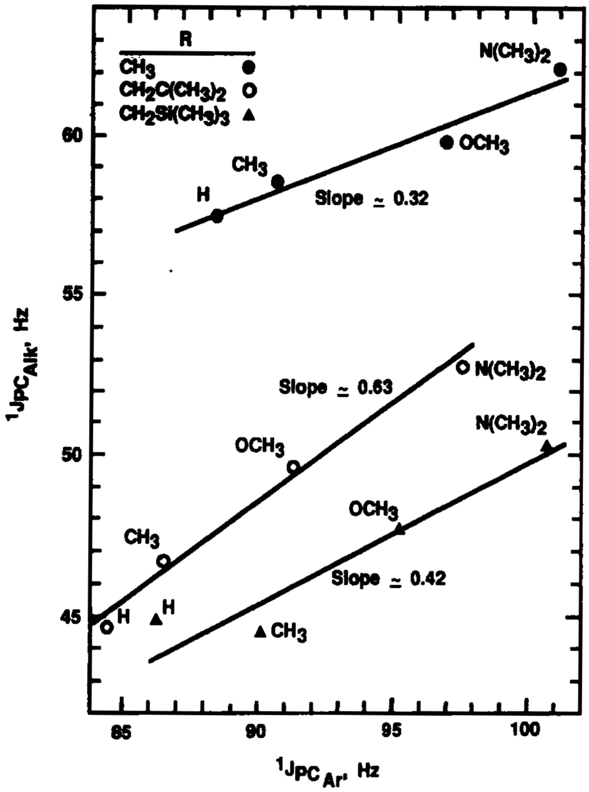
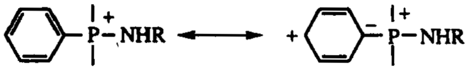


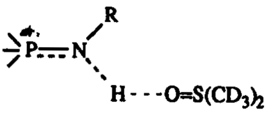
FIGURE 4 Plots of $^1J_{PC_{Alk}}$ vs. $^1J_{PC_{Ar}}$ in $(p\text{-XC}_6H_4)_3\overset{+}{P}\text{—R I}^-$.

with the *d* orbitals of phosphorus increase in the order: P = H > *t*-Bu > Me > NH_2 > NMe_2. With more pyramidal α nitrogen, i.e., less *s* or more *p* character in the N—H bonds, $^2J_{PH}$ increases, presumably more in the negative direction, in a fashion very similar to $^2J_{PH}$ in alkylphosphonium salts with the decrease in the *s* character of their C—H bonds.[17] $^1J_{PN}$ increases roughly in the same order as $^2J_{PH}$. Phosphorus gets deshielded as it becomes more positive due to the decrease in pπ-dπ interaction. The aryl carbons directly bonded to phosphorus, on the other hand, are more shielded on account of greater contributions by structures like **5a**.



5 5a

The phosphorus-nitrogen coupling, $^1J_{PN}$, shows high sensitivity toward solvent. For example, its values decrease in DMSO-d_6 vs. those in $CDCl_3$. Presumably, DMSO-d_6 forms a hydrogen bond with the NH proton, thus facilitating an even stronger interaction between the nitrogen lone pair and the *d* orbitals of phosphorus:



$^2J_{PH}$ also shows temperature dependence, giving higher values at −50° vs. 30°C. This is probably due to the relative inversion at the α nitrogen affecting the lone pair interaction with the *d* orbitals of phosphorus. The inversion barrier for acyclic amines are 6 to 7 kcal.[30] The conformational stereochemistry of acyclic hydrazines and the barriers to inversion at their nitrogens have been studied quite extensively.[31–33] Their inversion barriers are much larger than those of the corresponding amines because of the lone pair interactions on the adjacent nitrogen atoms. The preferred conformation is that in which the dihedral angles containing the lone pairs are near perpendicular to each other. As a result, the nitrogens prefer to be

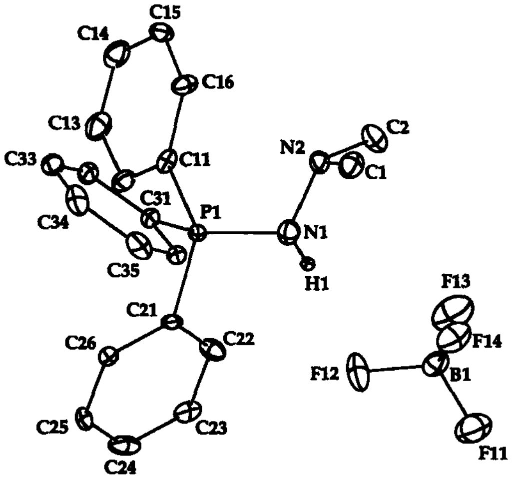


FIGURE 5 ORTEP drawing of $(C_6H_5)_3\overset{+}{P}$—$NHN(CH_3)_2$ BF_4^- with numbering of atoms.

TABLE V

Selected bond distances and bond angles for **10**[a]

	Bond Distance, Å		
C(1) - C(2)	1.571 (15)	C(6) - C(7)	1.566 (18)
P(1) - C(1)	1.822 (13)	P(2) - C(6)	1.787 (11)
P(1) - C(11)	1.793 (11)	P(2) - C(41)	1.798 (14)
P(1) - C(21)	1.768 (13)	P(2) - C(51)	1.800 (12)
P(1) - C(31)	1.808 (11)	P(2) - C(61)	1.785 (13)
	Bond Angles, deg		
P(1) - C(1) - C(2)	120.3 (8)	P(2) - C(6) - C(7)	124.0 (1)
C(1) - P(1) - C(11)	111.5 (5)	C(6) - P(2) - C(41)	114.3 (5)
C(1) - P(1) - C(21)	112.6 (6)	C(6) - P(2) - C(51)	105.9 (6)
C(1) - P(1) - C(31)	107.1 (6)	C(6) - P(2) - C(61)	110.5 (6)
C(11) - P(1) - C(21)	109.5 (5)	C(41) - P(2) - C(51)	107.2 (5)
C(11) - P(1) - C(31)	108.9 (5)	C(41) - P(2) - C(61)	109.5 (5)
C(21) - P(1) - C(31)	107.0 (5)	C(51) - P(2) - C(61)	109.2 (5)

[a] Esd's in units of the least significant figure are in parentheses.

TABLE VI

Selected bond distances and bond angles for **22**[a]

		Bond Distance, Å	
P(1)-N(1)	1.621 (5)	N(1)-N(2)	1.418 (7)
P(1)-C(11)	1.793 (6)	N(1)-H(1)	0.660 (46)
P(1)-C(21)	1.788 (5)	N(2)-C(1)	1.464 (8)
P(1)-C(31)	1.796 (5)	N(2)-C(2)	1.457 (9)
		Bond Angles, deg	
P(1)-N(1)-N(2)	114.5 (4)	N(1)-P(1)-C(11)	110.3 (3)
P(1)-N(1)-H(1)	120 (5)	N(1)-P(1)-C(21)	106.9 (3)
N(2)-N(1)-H(1)	121 (5)	N(1)-P(1)-C(31)	112.7 (3)
C(11)-P(1)-C(21)	108.9 (3)	N(1)-N(2)-C(1)	111.3 (5)
C(11)-P(1)-C(31)	108.6 (3)	N(1)-N(2)-C(2)	109.4 (5)
C(21)-P(1)-C(31)	109.4 (3)	C(1)-N(2)-C(2)	111.8 (5)
		Intermolecular Distances, Å	
F(12) · · · N(1)	3.049 (14)		
F(13) · · · N(1)	3.237 (12)		

[a] Esd's in units of the least significant figure are in parentheses.

pyramidal, which would account for much larger $^2J_{PH}$ for the hydrazinophosphonium salts (**21** and **22**) vs. the aminophosphonium salts (**18**, **19**, and **20**).

From the NMR data, the α nitrogen of 2,2-dimethylhydrazinotriphenylphosphonium tetrafluoroborate (**22**) appears to be more pyramidal than that of the other salts in Table IV. Its X-ray structure is shown in Figure 5. The pertinent bond distances and bond angles are listed in Table VI. The bond angles, however, show its α nitrogen to be nearly planar. Nevertheless, in solution, the lone pair interactions combined with rotation around the N—N bond would render the α nitrogen more pyramidal.

CONCLUSIONS

The ^1H, ^{13}C, and ^{31}P NMR data of alkyltriarylphosphonium salts have been rationalized in terms of hyperconjugative π bonding between the α C—H bonds and 3*d* orbitals of phosphorus. The NMR data of mono-N-substituted aminotriphenylphosphonium salts are consistent with the nitrogen lone pair interaction with the *d* orbitals of phosphorus. The trends of their data are similar to those of the alkylphosphonium salts. This is taken as a strong support for the hyperconjugative π bonding in the alkylphosphonium salts.

EXPERIMENTAL

NMR Spectra

^1H, ^{13}C (75.46 Mz), and ^{31}P (121.47 MHz) NMR spectra of alkyltriarylphosphonium salts were recorded on ~0.5 M solutions in $CDCl_3$ using a Nicolet NT-300 spectrometer. A broad-based noise decoupler was used to eliminate $^{31}P—^{1}H$, $^{13}C—^{1}H$, and $^{29}Si—^{1}H$ couplings. The ^{1}H, ^{13}C, and ^{29}Si chemical shifts are downfield from internal Me_4Si; and the ^{31}P chemical shifts are downfield from external reference of 85% H_3PO_4.

^{1}H, ^{13}C (100.577 MHz), and ^{31}P (161.903 MHz) NMR spectra of mono-N-substituted aminotriphenylphosphonium salts were recorded on Varian 400 MHz spectrometer using 0.05 M solutions in $CDCl_3$, unless mentioned otherwise. Their ^{15}N (30.484 MHz) NMR spectra were recorded on a GE omega 300WB spectrometer. The ^{15}N DEPT experiments were run using the standard DEPT sequence[34] assuming $J_{HN} \approx 82-92$ Hz for directly bonded protons on nitrogen and $J_{HN} \approx 7$ Hz for nitrogen with the methyl groups with a θ pulse of 45°.

Preparation of Methyltriarylphosphonium Iodides (**6–9**)

Methyltriphenylphosphonium iodide (**6**) was purchased from Aldrich Chemical Co., Inc. Other methylphosphonium salts were prepared by the following procedure: To 0.01 mol of triarylphosphine was added 10 mL of freshly distilled CH_3I and the mixture was refluxed under N_2 for 5 min. About 50 mL of ethyl acetate was added to complete the precipitation of the phosphonium salts, which were then collected by filtration; >90% yield. Analytical samples were prepared by recrystallization from chloroform/ethyl acetate.

Methyl-tris(p-toluylphenyl)phosphonium iodide (**7**): mp 187–8°C (dec). Its ^{1}H NMR: δ 7.65–7.36 (m, 12H), 3.01 (d, $^{2}J_{PH}$ = 13.2 Hz, 3H), 2.49 (s, 9H). Anal. Calcd for $C_{22}H_{24}IP$: C, 59.19; H, 5.38. Found: C, 59.25; H, 5.18.

Methyl-tris(p-methoxyphenyl)phosphonium iodide (**8**): mp 219–20°C (dec). Its ^{1}H NMR: δ 7.65–7.08 (m, 12H), 2.92 (d, $^{2}J_{PH}$ = 13.1 Hz, 3H), 3.92 (s, 9H). Anal. Calcd for $C_{22}H_{24}IO_3P$: C, 53.44; H, 4.86. Found: C, 53.19; H, 4.61.

Methyl-tris(p-dimethylaminophenyl)phosphonium iodide (**9**): mp 289–90°C (dec). Its ^{1}H NMR: δ 7.40–6.75 (m, 12H), 2.54 (d, $^{2}J_{PH}$ = 13.0 Hz, 3H), 3.07 (s, 18H), Anal. Calcd for $C_{25}H_{33}IN_3P$: C, 56.28; H, 6.19. Found: C, 56.23; H, 6.29.

Ethyl-, n-Propyl, and Isobutyltriphenylphosphonium Iodides

Ethyltriphenylphosphonium was purchased from Alpha®. *n*-Propyl- and isobutyltriphenylphosphonium iodides were prepared as follows: A mixture of 26.2 g (0.1 mol) of triphenylphosphine and 40 mL of freshly distilled *n*-propyl iodide or isobutyl iodide was refluxed under N_2 for 2 h. The phosphonium salts separated as solids. The excess iodide was bulb-to-bulb distilled in vacuo, and the remaining solid washed with ethyl acetate to remove any unreacted triphenylphosphine. The phosphonium salts, isolated in 85–90% yield, were recrystallized from chloroform/ethyl acetate. *n*-Propyltriphenylphosphonium iodide: mp 203–4°C (lit.[36] 204°C). Its ^{1}H NMR: δ 7.90–7.75 (m, 15H), 3.59 (dt, $^{2}J_{PH}$ = 12.5 Hz, $^{3}J_{HH}$ = 8.2 Hz, 2H), ~1.74 (complex pattern, 2H), 1.26 (t, $^{3}J_{HH}$ = 7.3 Hz, 3H). Isobutyltriphenylphosphonium iodide: mp 180–181°C (lit.[2] 186–8°C). Its ^{1}H NMR: δ 7.96–7.70 (m, 15H), 3.56 (dd, $^{2}J_{PH}$ = 12.8 Hz, $^{3}J_{HH}$ = 6.3 Hz, 2H), ~2.15 (complex pattern, 1H), 1.08 (d, $^{3}J_{HH}$ = 6.6 Hz, 6H). Anal. Calcd for $C_{22}H_{24}IP$: C, 59.19; H, 5.38. Found: C, 59.19; H, 5.32.

Preparation of Neopentyltriarylphosphonium Iodides (**10–13**)

Neopentyltriphenylphosphonium iodide (**10**) is a known compound.[26] Other neopentylphosphonium salts were prepared as follows: A mixture of 0.01 mol of a triarylphosphine and 3.96 g (0.02 mol) of freshly distilled neopentyl iodide was heated under N_2 in a Wood's metal bath at 150°C for 6 h. The reaction mixture was then cooled to room temperature, and ca. 100 mL of ethyl acetate was added. On standing, phosphonium salts separated as white solids, which were collected by filtration. Analytical samples were prepared by recrystallization from chloroform/ethyl acetate.

Neopentyl-tris(p-toluyl)phosphonium iodide (**11**): yield 1.7 g (34%); mp. 201°C. Its ^{1}H NMR: δ 8.10–7.31 (m, 12H), 3.63 (d, $^{2}J_{PH}$ = 12.9 Hz, 2H), 2.47 (s, 9H), 1.03 (s, 9H). Anal. Calcd for $C_{27}H_{32}IP$: C, 61.15; H, 6.37. Found: C, 61.54; H, 6.41.

Neopentyl-tris(p-methoxyphenylphosphonium iodide (**12**): The reaction was actually run for 18 h. Addition of 100 mL of ethyl acetate and 100 mL of anhydrous ether precipitated a mixture (4.3 g) of eight phosphonium salts.[35] No effort was made to isolate the above phosphonium salt in pure form; rather its spectral data (listed in Tables II and III) was obtained from the mixture itself.

Neopentyl-tris-p-dimethylaminophenyl)phosphonium iodide (**13**): yield 2.6 g (44%); mp 284°C. Its ^{1}H NMR: δ 7.78–6.56 (m, 12H), 3.05 (s, 18H), 3.02 (d, $^2J_{PH}$ = 12.8 Hz, 2H), 1.01 (s, 9H). Anal. Calcd for $C_{29}H_{41}IN_3P$: C, 59.08; H, 6.96. Found: C, 58.99; H, 6.88.

Preparation of (Trimethylsilyl)methyltriarylphosphonium Salts (**14–17**)

A mixture of 0.005 mol of a triarylphosphine and 4.28 g (0.02 mol) of (trimethyl)silylmethyl iodide was refluxed in 20 mL of dry benzene under N_2 for 16 h. The reaction was then cooled to room temperature, and a mixture of 50 mL of ethyl acetate and 50 mL of anhydrous ether was added. Phosphonium salts separated as white solids (60–80%) which were collected by filtration and handled under N_2 to minimize hydrolysis to the corresponding methyltriphenylphosphonium salts. Their spectra, run on samples as isolated, showed the presence of small amounts of the methyltriarylphosphonium salts as the hydrolysis by-products. Efforts to prepare pure samples of (trimethylsilyl)methyltriarylphosphonium salts by recrystallization from chloroform/ethyl acetate or chloroform/ether were unsuccessful. The samples still contained the methyltriarylphosphonium salts impurities, and sometimes more hydrolysis of (trimethylsilyl)methyltriarylphosphonium salts occurred during recrystallization.

Preparation of Mono-N-Substituted Aminotriphenylphosphonium Tetrafluoroborates (**18–22**)

These salts were prepared from the corresponding phosphonium bromides[37] by metathesis reaction with lithium tetrafluoroborate. Solutions of 0.02 mol of the respective phosphonium bromide and of 2.0 g (0.021 mol) of lithium tetrafluoroborate in minimum amounts of MeOH were mixed and stirred for 15 min. Methanol was then bulb-to-bulb distilled, and the remaining solid washed with water to remove LiBr. The phosphonium salts, after drying in a vacuum oven at 70°C, were isolated as white solid in essentially quantitative yield. Recrystallization from chloroform/ethyl acetate gave shiny crystals.

Aminotriphenylphosphonium tetrafluoroborate (**18**): mp 185–7°C (lit.[38] 178°C). Its ^{1}H NMR: δ 7.76–7.53 (m, 15H), 5.61 (d, $^2J_{PH}$ = 3.5 Hz, 2H). Anal. Calcd for $C_{18}H_{17}BF_4NP$: C, 59.21; H, 4.66; N, 3.84. Found: C, 58.90; H, 4.58; N, 3.77.

Methylaminotriphenylphosphonium tetrafluoroborate (**19**): mp 125–6°C (same as lit.[39]). Its ^{1}H NMR: δ 7.80–7.60 (m, 15H), 5.49 (dq, $^2J_{PH}$ = 8.6 Hz, $^3J_{HH}$ = 5.5 Hz, 1H), 2.77 (dd, $^3J_{PH}$ = 13.2 Hz, $^3J_{HH}$ = 5.5 Hz, 3H).

t-Butylaminotriphenylphosphonium tetrafluoroborate (**20**): mp 155–6°C (lit.[39] 169°C). Its ^{1}H NMR: δ 7.89–7.59 (m, 15H), 5.41 (d, $^2J_{PH}$ = 7.2 Hz, 1H), 1.25 (s, 9H). Anal. Calcd for $C_{22}H_{25}BF_4NP$: C, 62.74; H, 5.95; N, 3.33. Found: C, 61.95; H, 5.95; N, 3.19.

Hydrazinotriphenylphosphonium tetrafluoroboroate (**21**): mp 188–9°C. Its ^{1}H NMR: δ 7.79–7.60 (m, 15H), 7.09 (d, $^2J_{PH}$ = 25.8 Hz, 1H), 2.54 (s, 2H). Anal. Calcd for $C_{18}H_{18}BF_4NP$: C, 56.87; H, 4.74; N, 7.37. Found: C, 56.32; H, 4.56; N, 7.34.

2,2-Dimethylhydrazinotriphenylphosphonium tetrafluoroborate (**22**): mp 155–6°C. Its ^{1}H NMR: δ 7.80–7.60 (m, 15H), 6.94 (d, $^2J_{PH}$ = 35.0 Hz, 1H), 2.51 (s, 6H). Anal. Calcd for $C_{20}H_{22}BF_4N_2P$: C, 58.85; H, 5.39; N, 6.87. Found: C, 58.17; H, 5.47; N, 6.72.

X-ray Structure of **10**

A colorless block with dimensions of 0.15 × 0.16 × 0.40 mm obtained by recrystallization from chloroform/ethyl acetate was mounted on a glass fiber and placed on an Enraf-Nonius CAD4 diffractometer equipped with a Mo Kα source, graphite monochromator, and an FTS low-temperature refrigeration unit operating at −70°C. The CAD4 routines indicated a monoclinic unit cell space group with dimensions a = 10.578(9) Å, b = 12.998(3) Å, c = 16.269(10) Å, β = 106.44(6)°. With Z = 4 the calculated density of $C_{23}H_{26}IP$ is 1.408 g/cc. A total of 2457 independent reflections with $I \geq 3\sigma(I)$ were obtained from $7.7° \leq 2\theta \leq 54.7°$ using the ω-scan mode with $\omega = 0.8 \pm 0.35 (\tan \theta)$. The structure was solved via the heavy atom Method and refined by using full matrix anisotropic least squares with 220 variables to a conventional R = 4.7% and R_w = 4.2%. The solution required two independent ion pairs in the asymmetric unit. The enantiomorph chosen was that corresponding to the minimum R for the two possibilities. The largest peak on the final different map, 0.47 e/Å^3 was general background.

X-ray Structure of **22**

A colorless plate with dimensions of −0.29 × 0.09 × 0.40 mm obtained by recrystallization from chloroform/ethyl acetate was mounted on a glass fiber and placed on a Syntex R3 diffractometer equipped with a Mo Kα source, graphite monochromator, and an LT1 low-temperature refrigeration unit operating at −90°C. The Syntex routine indicated a monoclinic unit cell space group $P2_1/n$ with dimensions a = 10.256(3) Å, b = 13.710(4) Å, c = 14.389(5) Å, β = 98.14(2)°. With Z = 4 the calculated density of $C_{20}H_{22}N_2PBF_4$ is 1.354/cc. A total of 4296 independent reflections with $I \geq 3\sigma(I)$ were obtained from $4.0° \leq 2\theta \leq 52.0°$ using the ω-scan mode. The structure was solved by direct methods (MULTAN)[40] and refined by full-matrix anisotropic least squares with 368 parameters to a conventional R = 5.7% and R_w = 5.1%. The solution required one ion pair in a general position. The largest peak on a final difference map 0.36e/Å^3 near N1.

Supplemental Material Available

Tables of X-ray data containing fractional coordinates, anisotropic thermal parameters, interatomic distances, and intramolecular angles for **10** (4 pages) and **22** (5 pages). Ordering information is given on any current masthead page.

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