Conformation and Stereodynamics of 2-Dialkylamino-1,3-dimethyl-2,3-dihydro-1*H*-1,3,2-benzodiazaphospholes. An Experimental Nuclear Magnetic Resonance, Ultraviolet Photoelectron, and Theoretical MNDO Investigation

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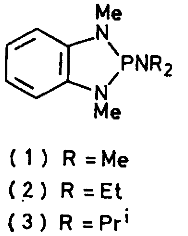
Conformational information on the title compounds obtained from low temperature ^{13}C and ^{1}H n.m.r. studies is in agreement with the geometry calculated by the MNDO SCF molecular orbital procedure. The barriers to rotation about the exocyclic P–N bond have been measured and the rotational transition state has been investigated by MNDO. Some u.v. photoelectron and ^{15}N n.m.r. data are reported and the possibility of enhanced π-bonding in the exocyclic PN bond is discussed.

THERE is considerable current interest in the molecular and electronic structure of hexamethylphosphorus triamide, $P(NMe_2)_3$, and its cyclic analogues.[1-12] We now report on an n.m.r. and SCF molecular orbital study of the conformation and stereodynamics of the 2-dialkylamino-1,3-dimethyl-2,3-dihydro-1*H*-1,3,2-benzodiazaphospholes (1)—(3) and give some ^{15}N n.m.r. and u.v. photoelectron (u.p.s.) data for (3).



(1) R = Me
(2) R = Et
(3) R = Pr^i

Compounds (1)—(3) were prepared from *NN'*-dimethyl-1,2-diaminobenzene *via* 2-chloro-1,3-dimethyl-2,3-dihydro-1*H*-1,3,2-benzodiazaphosphole. The *NN*-dimethyl and *NN*-diethyl compounds (1) and (2) were found to be unstable and decomposed during attempted isolation. However, ^{1}H and ^{13}C n.m.r. spectra obtained on freshly prepared solutions were fully consistent with the structures. The more hindered *NN*-di-isopropyl derivative (3) proved to be sufficiently stable for isolation and characterization. Mass spectral data for (2) and (3) gave a molecular ion at the expected *m/e* value together with an intense peak at *m/e* 165 characteristic of the relatively stable aminophosphorus cation (4).[13,14]

The ^{13}C n.m.r. spectra recorded at ambient temperature showed doublet signals for all nitrogen-bonded carbons due to phosphorus coupling, though the magnitude (and sign) of $^{2}J_{PNC}$ differed markedly for each type of carbon (Table 1). Coupling to phosphorus *via* three bonds was observed for the terminal carbons in the diethyl- and di-isopropyl-amino groups of (2) and (3), but not for the aryl carbons α to the diazaphosphole ring.

On lowering the probe temperature the *NN*-dialkyl signals broadened and finally split into two sets with approximately equal intensities (see Figure 1). The non-equivalence of the *N*-alkyl groups at low temperature together with the absence of any further splitting of the ring *N*-methyl or -aryl signals indicates a preferred ground-state conformation around the exocyclic P–N bond approximating to (5). This is confirmed by the difference in the sign and magnitude of the PNC coupling constants for the non-equivalent *N*-alkyl groups (Table 1). The large positive $^{2}J_{PNC}$ values observed for the more deshielded NMe or NCH_2 signal in (1) and (2), and for

TABLE 1

^{13}C N.m.r. data

			exo-NC		Ring NMe		C-4, -5		Aryl CH	*exo*-NCMe	
Compound	Solvent	t/°C	δ (p.p.m.)	$^{2}J_{PC}$ Hz[a]	δ (p.p.m.)	$^{2}J_{PC}$ Hz[a]	δ (p.p.m.)	$^{2}J_{PC}$ Hz	δ (p.p.m.)	δ (p.p.m.)	$^{3}J_{PC}$ Hz
(1)	$CDCl_3$	30	36.0	+17.1	28.8	+22.6	139.2	9.2	105.3, 117.8		
	$CHFCl_2$	−110	33.6 38.0	−9.2 +43.3	28.7	+20.8	139.1	9.2	105.1, 117.4		
(2)	$CDCl_3$	30	38.5	+18.3	28.7	+22.6	139.4	8.8	104.9, 117.4	15.2	2.4
	$CHFCl_2$	−80	35.8 39.8	−9.2 +46.3	28.8	+21.4	139.1	9.2	104.9, 117.3	13.3	<3
(3)	$CDCl_3$	53	44.4	+10.4	28.8	+23.8	139.1	8.8	104.9, 117.2	24.6	7.3
	$CHFCl_2$	−50	42.9 44.9	+26.9 −8.6	28.7	+22.6	138.8	8.6	104.5, 116.7	21.4 27.6	<2 13.4

[a] The signs of $^{2}J_{PNC}$ (relative to $^{3}J_{PNCH}$ which was assumed to be positive) were determined by off-resonance ^{1}H irradiation of (2) and inferred by analogy for (1) and (3).

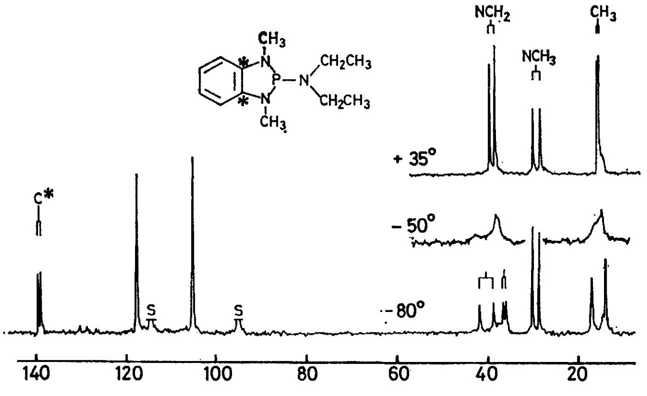
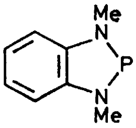


FIGURE 1 ^{13}C N.m.r. spectra of (2) at various temperatures in $CHCl_2F$ solution (spectrum at 35° in $CDCl_3$); s = truncated solvent signals

the more shielded NCH signal in (3), are typical of a group *syn* to a phosphorus lone pair.[15-17] Similarly the smaller negative PNC couplings observed for the other *N*-alkyl group are characteristic of a group *anti* to a phosphorus lone pair.[15-17] The phosphorus–carbon coupling constants in (1)—(3) are very close to those reported previously[9] for 2-dialkylamino-1,3-dimethyl-1,3,2-diazaphospholans (6) which adopt a similar conformation about the P–NR_2 bond. Conformation (5) probably minimises the repulsion between the vicinal lone pair orbitals on phosphorus and the exocyclic nitrogen (*i.e.* ϕ_{PN} 90°).



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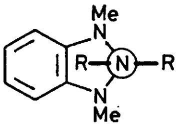

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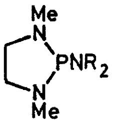


(6)

The non-equivalence of the NR_2 groups in (1)—(3) can also be seen in the ^{1}H n.m.r. at low temperatures, and the $^3J_{PNCH}$ couplings of 12 and <5 Hz in (1) (Table 2) are again typical of *N*-methyl groups *syn* and *anti*, respectively, to a phosphorus lone pair. The *anti* *N*-methyl protons resonate at δ 1.93 which is at abnormally high field for an aminophosphorus(III) compound (usually δ PNMe lies in the range 2.5—2.9). This would be consistent with this methyl group experiencing shielding by the proximate aryl ring in conformation (5).

Analysis of the ^{1}H and ^{13}C n.m.r. bandshapes of appropriate *N*-alkyl signals in the temperature region of maximum exchange broadening enabled the rate constants and free energy barriers for exocyclic PN bond rotation to be evaluated. The barriers determined from the ^{1}H and ^{13}C spectra are given in Table 2 and are identical within experimental error. The observed marked increase in $\Delta G^\ddagger$ along the series R = Me, Et, Pr^i suggests that the transition state for PN bond rotation is more hindered than the ground state, though n–σ^* π-bonding[18] from nitrogen to phosphorus could also be facilitated by electron release by the more substituted *N*-alkyl groups. Molecular models show a steric interaction between the ring *N*-methyl groups and the exocyclic NR_2 group in the 90° twisted transition state for PN rotation when the ring nitrogens are coplanar. This interaction can be minimised by deforming the ring *N*-methyl groups out of the ring plane in the direction *anti* to the P-NR_2 moiety, but this would presumably involve some sacrifice in the conjugation energy of the nitrogen lone pairs with the aryl ring and with the phosphorus atom.

The PN torsional barriers in (2) and (3) are *ca.* 3 kcal mol^{-1} higher than those reported in the analogous diazaphospholans (6).[9] Possibly the ring *N*-methyl groups in (6) can more readily adopt a nonplanar configuration in the transition state for PN bond rotation since the cyclic nitrogens in (6) are not in conjugation with an aryl ring. Although this steric factor might conceivably raise the barriers in the present series, an alternative electronic factor can be advanced. Hence, if π-bonding between the nitrogen lone pairs and appropriate receptor orbitals on phosphorus (σ^* or *d*-type) contributes to the PN rotational barrier, all three nitrogens in the diazaphospholans (6) will be competing for the phosphorus receptor orbitals. In (1)—(3), however, the ring nitrogen lone pairs interact strongly with the aryl ring and may not compete effectively with the exocyclic nitrogen for the available phosphorus orbitals. The MNDO cal-

TABLE 2

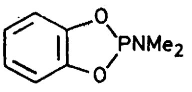
Dynamic ^{13}C and ^{1}H n.m.r. data for exocyclic P–N bond rotation

Compound	Observed nucleus	Observed signals	t/°C [a]	δ	t_C/°C [b]	k/s^{-1}	$\Delta G^\ddagger$/ kcal mol^{-1}
(1)	^{13}C	NMe [c]	−110	33.6 (d, $^2J_{PC}$ −9.2 Hz) 38.0 (d, $^2J_{PC}$ +43.3 Hz)	−83.5	205	8.9
	^{1}H	NMe [c]	−118	1.93 (s, $^3J_{PH}$ <5 Hz) 2.73 (d, $^3J_{PH}$ 12 Hz)	−76.5	318	9.1
(2)	^{13}C	NCH_2 [c]	−80	35.8 (d, $^2J_{PC}$ −9.2 Hz) 39.8 (d, $^2J_{PC}$ +46.3 Hz)	−54.0	71	10.8
	^{1}H	NCMe [c]	−76	0.70 (t, $^3J_{HH}$ 6.7 Hz) 1.02 (t, $^3J_{HH}$ 6.9 Hz)	−56.1	60	10.8
(3)	^{13}C	$NCMe_2$ [d]	−50	21.4 (s, $^3J_{PC}$ <2 Hz) 27.6 (d, $^3J_{PC}$ 13.4 Hz)	0.0	166	13.2
	^{1}H	$NCMe_2$ [d]	−50	0.81 (d, $^3J_{HH}$ 6.6 Hz) 1.41 (d, $^3J_{HH}$ 6.6 Hz)	−7.7	102	13.0

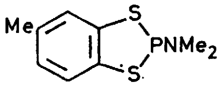
[a] Temperature in the slow region at which the limiting signal positions (δ) were determined. [b] Temperature in the region of maximum exchange broadening at which the rate constant (k) was determined by bandshape fitting. [c] Solvent $CHFCl_2$. [d] Solvent $CDCl_3$.

culations and ^{15}N chemical shifts (see below) provide some support for this suggestion.

Reported PN rotational barriers in the benzodioxaphosphole (7), $\Delta G^{\ddagger}$ 7.8 kcal mol^{-1}, and the benzodithiaphosphole (8), $\Delta G^{\ddagger}$ 8.9 kcal mol^{-1}, are also higher than those in (9) and (10) where $\Delta G^{\ddagger} < 6.5$ and 7.6 kcal mol^{-1}, respectively.[19]



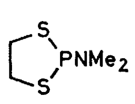
(7)



(8)

$(MeO)_2PNMe_2$

(9)



(10)

In order to obtain further information on the conformation and stereodynamics of these compounds, molecular orbital calculations were performed on (1) using the MNDO [20] SCF method. We have previously shown that MNDO gives a remarkably good account of the structure of several aminophosphorus(III) compounds.[21] The completely optimized geometry of (1) is depicted in Figure 2, and the principal bond angles and bond lengths are given in Table 3. It can be seen that the conformation about the exocyclic PN bond is precisely that inferred from the low temperature n.m.r. studies, *i.e.* one *N*-methyl group lies across the face of the ring and the other is *syn* to the phosphorus lone pair. The calculated exocyclic PN bond length (1.661 Å) is appreciably shorter than the ring PN bonds (1.673 Å), whereas the calculated *exo* and ring PN bond lengths in the diazaphospholan (6; R = Me), are almost equal (1.666 and 1.664 Å, respectively [22]) and intermediate between the values for (1). This would be consistent with the suggestion (see above) that stronger π-bonding occurs in the exocyclic PN bond of (1).

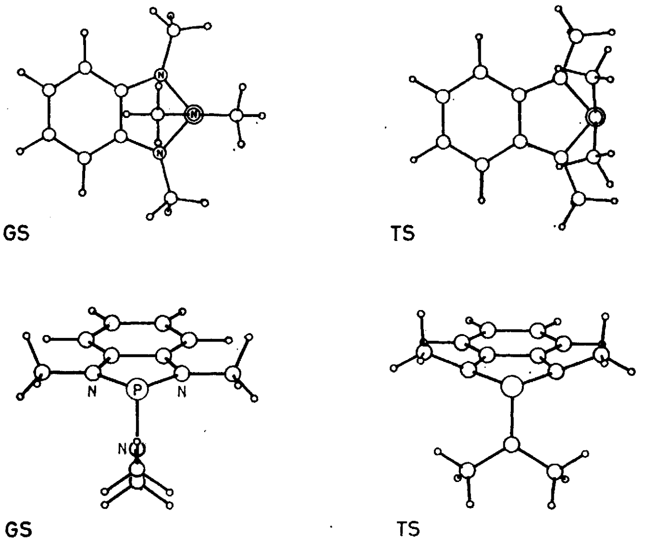


FIGURE 2 Optimized MNDO geometry for the ground state (GS) and twisted PN torsional transition state (TS) of (1), depicted as projections down the exocyclic N–P bond (upper) and perpendicular to this bond (lower)

TABLE 3

Optimized MNDO geometry for (1)

Bond lengths (Å)			Bond angles (°)		
exo	P–N	1.661	*exo*	NPN	105.5, 105.5
Cyclic	P–N	1.674, 1.673	Cyclic	NPN	94.1
exo	N–CH$_3$	1.454, 1.454	*exo*	PNC	113.8, 129.8
Ring	N–CH$_3$	1.449, 1.449	Ring	PNC	123.2, 123.3
Cyclic	N–C	1.408, 1.408	Cyclic	PNC	111.9, 111.8
Aryl	C–C	1.401—1.410	*exo*	CNC	116.4
Aryl	C–H	1.090	Ring	CNC	124.6, 124.6
Methyl	C–H	1.115	Cyclic	NCC	111.0, 111.1
			Aryl	CCC	120.0 ±1.0
			Methyl	NCH	111.5
			Dihedral	ϕ_{PN} [a]	90.0

Heat of formation −22.52 kcal mol^{-1}
Dipole moment 1.18 D

[a] ϕ_{PN} is the dihedral angle between the axes of the phosphorus and nitrogen lone pairs (defined using the 'dummy atom' facility in MNDO).

The *exo* and ring nitrogens in (1) are both calculated to be planar (sum of the bond angles at nitrogen are: *exo* 360.0°, ring 359.7°). It is interesting that the PNC coupling constants for the ring NMe in (1)—(3) (Table 1) are almost identical to the corresponding $^2J_{PNC}$ values in the diazaphospholans (6).[9] Since $^2J_{PNC}$ is known to be highly dependent on conformation, it can be inferred that compounds (1)—(3) and series (6) have similar geometry at the ring nitrogens (probably planar).* Furthermore, $^2J_{PNC}$ for the ring carbons (C-4 and -5) in (1)—(3) has the same absolute value as $^2J_{PNC}$ for the ring carbons in the diazaphospholan series (6),[9] though the sign of this coupling was not determined in the present series due to the absence of protons on these carbons. Assuming that $^2J_{PNC}$ in (1)—(3) is indeed negative as in (6), it follows that these carbons must be directed *anti* to the phosphorus lone pair since $^2J_{PNC}$ for the *anti*-exocyclic NMe group is −9 Hz (Table 1). The approximately coplanar ring geometry for (1) indicated by the MNDO calculations (Figure 2) corresponds to a dihedral angle of *ca.* 125° between the ring C–N bonds and the axis of the phosphorus lone pair. This dihedral angle could move closer to 180° if the ring were distorted into a *P*-flap envelope conformation with the NR_2 group pseudo-axial and the phosphorus lone pair pseudo-equatorial. However the precise behaviour of $^2J_{PNC}$ in the region 90—180° is not sufficiently well documented for a coplanar ring conformation to be excluded, though it seems likely from the n.m.r. data that any distortion

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* MNDO calculations on (6; R = Me), give essentially planar geometry at all nitrogens.[22]

must be in the direction which places the exocyclic NR_2 group predominantly pseudoaxial.*

Calculations were also performed on the transition state for exocyclic PN bond rotation in (1) by enforcing a 90° twist about this bond, relative to the ground state conformation (all other geometrical variables were optimized). The large amount of computer time required for MNDO calculations on (1) precluded the calculation of a complete rotational co-ordinate, but the 90° twist form clearly corresponds with the transition state since the 80° twisted form was found to have lower energy. The 90° twisted conformation was found to lie 5.8 kcal mol^{-1} above the ground state, compared with the experimental PN barrier of 9.0 kcal mol^{-1} (Table 2). Calculations on other compounds also indicate that the MNDO method tends to underestimate the PN rotational barriers.[21] The geometries of the rotational transition state and the ground state are depicted in Figure 2. The exocyclic PN bond length increases to 1.673 Å in the twisted state. The exocyclic nitrogen remains essentially planar, but there is a very marked secondary perturbation in that the *ring* *N*-methyl groups move 30° out of the ring plane. This deformation is in the direction opposite to the NMe_2 group and relieves steric interactions between the ring and exocyclic *N*-methyl groups in the transition state for PN bond rotation. The diazaphospholan ring conformation remains essentially planar as in the ground state.

The ^{15}N n.m.r. spectra of (3) showed the expected two doublet signals (Table 4). The marked difference in $^1J_{PN}$ for the *exo* and ring nitrogens closely parallels the situation in the diazaphospholans (6) [9] and enables the signals to be assigned. The fact that both $^1J_{PN}$ values in (3) are similar (within 5 Hz) to those in the analogous diazaphospholan (6; R = Pr^i) further indicates that both series have approximately the same geometry about both the ring and the *exo*-nitrogens (see above). The difference in the endo- and exo-cyclic PN couplings probably arises from the differing ground state torsional conformation about these bonds, though other factors [9] cannot be excluded.

TABLE 4

^{15}N N.m.r. data for (3) [a]

δ_N (p.p.m.) [b]	$^1J_{PN}$/Hz [c]	Relative intensity
−316.8	55.6	1.0
−267.9	98.9	0.7

[a] Determined in CD_2Cl_2 solution. [b] Chemical shifts are relative to external neat $Me^{15}NO_2$. [c] Digital resolution 0.6 Hz.

The 37 p.p.m. deshielding of the ring nitrogens in (3) relative to (6; R = Pr^i) is consistent with the known α-effect of aryl substituents on ^{15}N shifts,[23] but the 18 p.p.m. relative deshielding of the exocyclic nitrogen in (3) relative to (6; R = Pr^i) is surprising since the aryl ring is three bonds removed from this nitrogen. This deshielding effect would be consistent with a higher degree of π-bonding in the exocyclic PN bond of (3). Thus it has been shown that the ^{15}N resonance in aminoboranes and amides moves downfield with increasing π-bonding in the BN or CN bond.[24,25]

The photoelectron spectrum of (3) shown in Figure 3 is quite informative in that seven ionization processes are detected in the low ionization energy region (<12 eV).

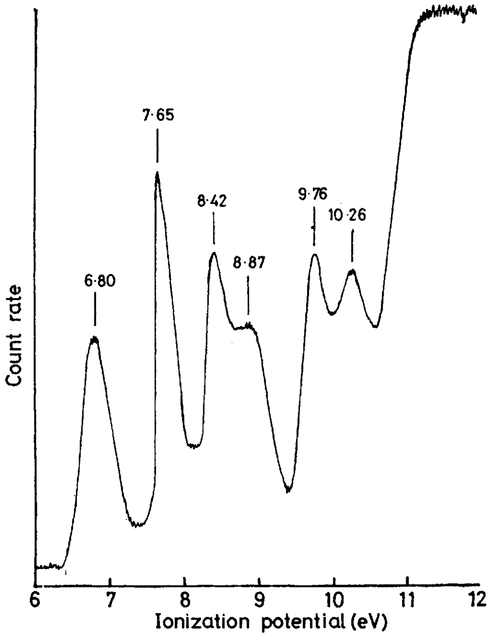

FIGURE 3 U.v. photoelectron spectrum of (3). The excitation source was the He^I resonance line

This is precisely the number of processes expected in this region given that the highest occupied molecular orbitals should have predominant contribution from the four heteroatom 'lone-pair' and three aromatic π basis orbitals. Assignment of the seven bands to ionization of specific orbitals, however, represents a major challenge. The MNDO SCF MO method and previous u.p.s. work in these laboratories on the diazaphospholans (6) will be employed here in proposing tentative assignments.

The band assignments predicted by MNDO (Koopmans' theorem) for (3; R = Me) are presented in Table 5. There is a fairly decent correlation between u.p.s. ionization energies and MNDO orbital energies if a 1.4 ± 0.2

TABLE 5

Experimental and calculated ionisation energies for (3) and (1) respectively

U.p.s. (eV) [a]	MNDO (eV) [b]	Principal localisation
6.80	8.01	*endo* N–aromatic ring
7.65	8.88	*endo* N–aromatic ring
8.42	9.73	*exo* N
8.87	10.53	P, but heavily mixed [c]
9.76	11.15	*endo* N
10.26	11.79	P–*endo* N
Unresolved	12.37	Aromatic ring

[a] Experimental values for (3); derivative (1) could not be studied because of its low stability. [b] Koopmans' theorem values for (1). [c] Heavily mixed with the nitrogens and the aromatic ring.

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* The presence of the fused aryl ring in (1)—(3) should constrain N-1 and -3 and C-4 and -5 to be approximately coplanar, thereby excluding other ring conformations (*e.g.* the *N*-flap envelope) from consideration.

eV correction is applied to the latter. Although the MNDO calculation was for the methyl derivative rather than the isopropyl one (for which the u.p.s. data was accumulated), the orbital ordering scheme should not change in the series for (3).

The natures of the MNDO eigenvectors for the upper seven molecular orbitals may be suspect. For example, it has been concluded earlier in these laboratories that the u.p.s. assignments for the diazaphospholan (6; R = Pr^i) should be (ionization energy in eV, orbital assignment): 7.40, anti-symmetric combination of the P and the two *endo* N lone-pair basis orbitals; 7.65, anti-symmetric combination of the two *endo* N lone-pair basis orbitals; 8.37, *exo* N lone-pair basis orbital which is orthogonal to the other lone-pair basis orbitals; 9.75, symmetric combination of the P and the two *endo* N lone-pair basis orbitals.[8] The MNDO method does predict that the third u.p.s. band at 8.42 eV for (3) should correspond to ionization of the *exo* N lone-pair orbital, which agrees well with our assignment for the 8.37 eV band for (6). However, MNDO predicts that the highest two molecular orbitals for (3) are quite delocalized and comprised primarily of a combination of basis orbitals involving the two *endo* N atoms and the aromatic ring with very little P contribution. In fact, MNDO predicts that the first molecular orbitals having appreciable P lone-pair character are 2.5—3.0 eV more stable than the HOMO (Table 5). Although frontier MO arguments are certainly tenuous at best, electrophilic attack would likely occur at the P lone-pair for (3) and (6). It is difficult to rationalize an attack of an orbital which is >50 kcal mol^{-1} more stable than the HOMO. We have noted previously the tendency of MNDO to stabilize P lone-pair orbitals relative to N lone-pair orbitals to seemingly too great an extent.[12,26] The MNDO assignment of the seventh u.p.s. band above 11 eV to ionization of a molecular orbital which is predominantly confined to the aromatic ring is undoubtedly correct, as a similar band is observed in the u.p.s. of benzene. However, we believe that either the HOMO at −6.80 eV or the second highest orbital at −7.65 eV for (3) should in fact have a substantial ' phosphorus lone-pair ' contribution which is not in accord with the prediction provided by MNDO. It should be stressed, however, that the possible failure of MNDO to compute the correct orbital-ordering scheme for (3) by no means detracts from its worth in predicting geometric structures and rotational barriers for diazaphospholes, as has been demonstrated earlier in this paper.

EXPERIMENTAL

Materials.—*NN'*-Dimethyl-1,2-diaminobenzene, b.p. 61—64° at 0.5 mmHg, was prepared from 1,2-diaminobenzene by the route described by Cheeseman.[27] However, considerable difficulty was encountered in dimethylating the intermediate bis-*p*-tolylsulphonyl derivative, and it was necessary to repeat the alkaline dimethyl sulphate treatment *ca.* three times until an ^{1}H n.m.r. assay indicated complete dimethylation, δ_H ([$^2H_6$]dimethyl sulphoxide) 2.43 (6 H, s, Me), 3.13 (6 H, s, NMe), 7.03 (4 H, AA'BB', aromatic), 7.52 (8 H, AA'BB', tosyl).

2-*Chloro*-1,3-*dimethyl*-2,3-*dihydro*-1H-1,3,2-*benzodiazaphosphole*.—Phosphorus trichloride (0.64 cm^3, 7.3 × 10^{-3} mol) in dry ether (2.5 cm^3) was added to a mixture of *NN'*-dimethyl-1,2-diaminobenzene (1.0 g, 7.3 × 10^{-3} mol) and dry triethylamine (2.05 cm^3, 1.46 × 10^{-2} mol) in ether (7 cm^3) at 0° under nitrogen. After 1 h the precipitated triethylamine was removed by filtration to afford an ether solution of the product. Removal of the solvent afforded a waxy solid which decomposed on exposure to air or during attempted sublimation or recrystallisation. The ^{1}H and ^{13}C n.m.r. spectra obtained on freshly prepared material were consistent with the structure, δ_H (CDCl$_3$) 3.33 (6 H, d, $^3J_{PNCH}$ 16.0 Hz, NMe), 7.06 (4 H, AA'BB', aromatic); δ_C (CDCl$_3$) 29.4 (d, $^2J_{PNC}$ 18.6 Hz, NMe), 110.1 (s, aromatic), 121.4 (s, aromatic), and 137.2 (d, $^2J_{PNC}$ 9.8 Hz, aromatic C-4, -5).

Caution. Exposure to traces of the vapour of this material may be associated with stomach cramp and nausea (see also ref. 28), therefore these compounds should be handled particularly carefully in a good fume hood.

2-*Dialkylamino*-1,3-*dimethyl*-2,3-*dihydro*-1H-1,3,2-*benzodiazaphospholes* (1)—(3).—The appropriate dialkylamine (1.46 × 10^{-2} mol) was added dropwise at 0° under nitrogen to the above ether solution containing *ca.* 7.3 × 10^{-3} mol of the crude 2-chloro-compound. The reaction was monitored using ^{1}H n.m.r. to follow the disappearance of the 2-chloro-compound and was complete after 1 h for compounds (1) and (2) or after 18 h for the more hindered di-isopropyl analogue (3). The precipitated amine hydrochloride was removed by filtration under nitrogen and concentration of the ether solution at, or below, ambient temperature afforded the product as a *waxy solid* which was very unstable in the case of the dimethyl and diethyl derivatives (1) and (2). The di-isopropyl compound (3) survived sublimation *in vacuo* to afford a colourless waxy *solid*, m.p. 60° (Found: C, 62.9; H, 9.3; N, 15.7%; M^+, 215.172. $C_{14}H_{24}N_3P$ requires C, 63.4; H, 9.1; N, 15.8%; *M*, 265.171); *m/e* 166 (48%), 165 (100), 150 (45), 86 (46), 44 (53), 43 (22), 42 (25), 41 (24), and 27 (26); δ_H (CDCl$_3$) 1.1br (12 H, CMe$_2$), 2.95 (2 H, m, NCH), 2.95 (6 H, d, $^3J_{PNCH}$ 10.0 Hz, NMe), and 6.51 (4 H, AA'BB' m, aromatic). Compound (1) had δ_H (CDCl$_3$) 2.35 (6 H, d, $^3J_{PNCH}$ 8.3 Hz, *exo*-NMe), 2.96 (6 H, d, $^3J_{PNCH}$ 10.0 Hz, cyclic NMe), 6.55 (4 H, AA'BB' m, aromatic). Compound (2) had δ_H (CDCl$_3$) 0.90 (6 H, t, CMe), 2.78 (4 H, q, NCH$_2$), 2.97 (6 H, d, $^3J_{PNCH}$ 10.0 Hz, NMe), and 6.56 (4 H, AA'BB' m, aromatic). ^{13}C Data for (1)—(3) are given in Table 1.

Spectroscopic Studies.—^{13}C N.m.r. spectra were recorded at 15 MHz on a JEOL FX-60 Fourier-transform instrument, ^{1}H spectra at 100 MHz on a Varian Associates XL-100 continuous wave instrument, and ^{15}N spectra at 18 MHz on a Bruker WB-180 Fourier-transform spectrometer. Probe temperature was measured as described previously,[9,18] and exchange-broadened band shapes were analysed using the multi-site INMR program.[18] Components of spin-coupled multiplets were treated as separate sites with the appropriate relative intensity (all ^{13}C spectra were first order and the ^{1}H multiplets analysed were close to first order).

Photoelectron spectra were obtained on a Perkin-Elmer PS-18 spectrometer using the He^I resonance line as the excitation source.

MNDO Calculations.—The molecular orbital calculations were performed on the CDC 7600 computer at the Manchester University Regional Centre *via* the link to Birmingham University. The MNDO program (QCPE no. 353) was modified to include the phosphorus parameters recently proposed by Dewar *et al.*[29]

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