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The vibrational spectra of some dialkylamido derivatives of phosphorus and arsenic

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Abstract—Infrared and Raman spectra have been obtained and assigned for $X(NR_2)_3$, where X=P or As, R=Me or Et. The internal alkyl group modes could be analysed using a local symmetry of C_s for an isolated NR_2 unit. Skeletal modes were most consistent with an overall molecular symmetry of C_3.

INTRODUCTION

Compounds containing coordinated dialkylamide groups have not been studied very frequently by vibrational spectroscopists. A review by BRADLEY [1] summarised data available on the vibrational spectra of such compounds of metals up to 1971. Dimethylamidodichloro- and -difluorophosphines have been examined [2, 3], the data on the latter being much more complete [3]. A *trans*-geometry, of C_s symmetry, sufficed to explain the observed spectrum of $(Me_2N)PF_2$, and no evidence was found for the presence of rotational isomers. The arsenic-chloro analogue $(Me_2N)AsCl_2$, however, exists as a mixture of two isomers, *trans* (C_s symmetry) and *gauche* (C_1 symmetry), even at 80 K [4].

The only published work on $P(NMe_2)_3$ has been that of GOUBEAU *et al.* [5], who have also examined $XP(NMe_2)_2Cl$, $XP(NMe_2)Cl_2$ and $XP(NMe_2)_{3-n}Me_n$ (X=O or S; n=0, 1, 2 or 3) [6, 7]. For $P(NMe_2)_3$, it was suggested that the highest molecular symmetry compatible with the observations was C_s, although it is impossible to assess the validity of their conclusions, as complete spectral data were not listed and no Raman polarizations were reported.

A gas-phase electron diffraction study of $P(NMe_2)_3$, together with $P[N(CH_2)_2]_3$, on the other hand [8] indicates that the tris(dimethylamido)phosphine *does* possess three-fold symmetry.

In order to resolve this ambiguity, we have recorded the i.r. and Raman spectra of $P(NR_2)_3$ and $As(NR_2)_3$, where R=Me or Et, and assigned as many bands as possible to normal vibrational modes.

EXPERIMENTAL

All preparations were carried out under an atmosphere of pure, dry argon. Dimethylamine and diethylamine were dried by distillation from sodium wire, and the ether solvent was dried using $LiAlH_4$. The general method for preparing the four dialkylamide-compounds was based on those of BURG and SLOTA [9] and MOEDRITZER [10]. A six-fold molar excess of the appropriate amine was added to an ethereal solution of the metal trichloride, with stirring, at $-10^\circ C$. After warming to room temperature the precipitated amine hydrochloride was filtered off under vacuum. The ether was removed using a rotary evaporator, and the tris(dialkylamide) isolated by distillation *in vacuo*. Satisfactory C, H and N analyses were obtained in all cases.

Infrared spectra were obtained using a Perkin–Elmer 521 spectrometer (4000–250 cm^{-1}). Solid-, liquid- and vapour-phase samples were used (for dimethylamido compounds; liquid-phase only for those containing diethylamido groups). The spectra were calibrated using known wavenumbers of CH_4, HBr, CO, NH_3 and H_2O. All of the observed wavenumbers are accurate to ± 2 cm^{-1} (± 5 cm^{-1} for very weak or broad features.)

A Cary 81 spectrometer, modified by Anaspec Ltd., was used to record the Raman spectra, the excitation source being a Spectra-Physics 164 Argon ion laser (power output *ca.* 1W at both 488.0 and 514.5 nm). Liquid samples were distilled directly into glass capillaries (approx. 1 mm i.d.), and polarization measurements carried out by examining the spectrum with the incident light successively parallel and perpendicular to the axis of a polaroid analyser. The depolarization values so obtained were proportional to the true values.

RESULTS

The i.r. and Raman spectra of $P(NMe_2)_3$, $P(NEt_2)_3$, $As(NMe_2)_3$ and $As(NEt_2)_3$ are listed in Table 1–4. The proposed assignments are summarised below.

DISCUSSION

It will be convenient to divide this section as follows: (a) internal modes of the NMe_2 group, (b) internal modes of the NEt_2 group (c) skeletal modes of $P(NC_2)_3$ and (d) skeletal modes of $As(NC_2)_3$. In sections (a) and (b), data from both the P and As compound will be included.

(a) *Internal* NMe_2 *modes*

As assignment of the fundamental modes of dimethylamine is available [11, 12], which may be used as a basis for this assignment. The electron diffraction data of VILKOV *et al.* [8], suggest that the NMe_2 unit in $P(NMe_2)_3$ has a planar skeleton (local symmetry C_{2v}). It is known [13], however, that pyramidal NX_3 units have a very low barrier to inversion at the N atom (in the absence of restraining factors such as ring formation), and therefore it is likely that this apparent planarity is due to rapid inversion. We will assume $XNMe_2$ (X=P or As) to be pyramidal, of local symmetry C_s. The numbers and symmetry types of the

Table 1. The vibrational spectrum of tris(dimethylamido)-phosphine (all numbers in wavenumbers/cm^{-1})

Solid	Infrared liquid	Vapour	Raman liquid	Proposed assignment
2997 m	3000 sh′	3000 sh′		
2965 w		2974 ms	2974, sh′, dp	CH_3 stretch (A'')
2930 s	2940 vs	2940 vs	2931 ms dp	CH_3 stretch (A'')
2870 vs	2890 s	2888 s	2889 ms dp	CH_3 stretch (A'')
2785 s	2798 ms	2798 s	2797 s pol	CH_3 stretch (A')
2485 m	2470 m			
	2368 ms			
		2340 w		
	2150 w			
		2070 w		
1648 m	1658 w	1658 w	1630 w	
	1481 ms	1486 sh′	1481 s, dp	CH_3 deformation (A'')
1465 sh′	1463 ms	1465 ms	1465 ms	CH_3 deformation (A')
1454 s	1458 ms	1456 ms		CH_3 deformation (A')
		1444 sh′	1441 s, dp	CH_3 deformation (A'')
1419 w	1417 sh′		1417 m, dp	CH_3 deformation (A'')
1406 w		1404 w		
1364 w	1376 vw			
1356 w				
1322 m	1318 s			CH_3 deformation (A')
1295 sh′				
1278 s	1277 ms	1273 m	1280 mw, dp	CH_3 rock (A'')
1246 m		1248 w		
1204, 1190 } vs	1191 s	1204 ms	1195 vw, dp	CH_3 rock (A'')
	1178 sh′			
1164 s		1166 } s		
		1159 } s		
1150 s	1150 sh′	1148 } s	1147 w, pol	CH_3 rock (A')
	1123 vw			
1105 m	1104 sh′			
	1086 m			CH_3 rock (A')
1068 s	1069 m			NC_2 stretch (E)
1060 sh′		1062 mw		
1034 mw		1040 w		
	1016 sh′	1024 w		
988 vs	984 vs	978 sh′	981 ms, dp	NC_2 stretch (E)
958 vvs	962 vs	960 s	963 sh′, pol	NC_2 stretch (A)
946 s	947 sh′	945 sh′		NC_2 stretch (A)
	904 sh′			
895 m				
807 w				
		768 mw		
	738 w	745 m		
		720 m		
706 s	704 mw	705 sh′	697 sh′	PN_3 stretch (E)
675 s	680 s	675 s	676 vs, pol	PN_3 stretch (A)
654 s	659 m	652 sh′	647 sh′	
570 w	550 w			
506 w	510 w			
491 m	494 mw		499 w	PNC deformation (E)
417 s	420 m		416 w	PNC deformation (E)
	405 mw			NC_2 deformation (A or E)
389 s	392 mw		390 w	NC_2 deformation (A or E)
	384 w			
	360 vw			
340 mw	345 mw			
333 mw	332 ww		337 s, pol	PNC deformation (A)
	310 m			
			295 s, pol	CH_3 torsion (A')
			193 w, dp	NC_2 torsion (E)
			127 mw, dp	PN_3 deformation (E)

Table 2. The vibrational spectrum of tris(dimethylamido)-arsine (all numbers in wavenumbers/cm^{-1})

Solid	Infrared Liquid	Infrared Vapour	Raman liquid	Proposed assignment
	2993 sh′	2998 sh′		
2965 s	2963 sh′	2964 sh′	2965 ms, dp	CH_3 stretch (A'')
2955 s				
	2932 ms	2932 ms	2927 ms, dp	CH_3 stretch (A'')
2860 ms	2886 ms	2888 ms		CH_3 stretch (A'')
	2838 m	2840 sh′	2839 ms, pol	CH_3 stretch (A')
2785 s	2798 ms	2798 ms	2794 ms, pol	CH_3 stretch (A')
2450 s	2440 w	2450 w		
	1830 w			
1610 m				
1474 sh′	1474 ms		1473 ms, dp	CH_3 deformation (A'')
1465 s				
1455 sh′	1453 s	1453 ms		CH_3 deformation (A')
1440 sh′	1440 ms		1435 m, dp	CH_3 deformation (A'')
1410 mw	1414 w	1408 mw	1408 m, dp	CH_3 deformation (A'')
1360 w				
1310 w				
1254 mw	1254 m	1256 m	1257 ms, pol	CH_3 rock (A')
1231 w				
1182 m	1189 ms	1186 ms		CH_3 rock (A'')
1158 sh′	1164 m	1160 w		CH_3 rock (A'')
	1138 mw	1140 m	1139 vw	?CH_3 rock (A')
1115 w				
1090 mw	1098 w	1095 vw	1098 vw	?CH_3 rock (A'')
1050 vw	1065 ms	1063 m	1061 w	NC_2 stretch (E)
1019 ms	1024 w	1025 vw		
990 sh′				NC_2 stretch (E)
590 w	960 sh′		951 } broad	NC_2 stretch (A)
936 ms	939 s	940 vs	937 } ? pol	NC_2 stretch (A)
888 m				
840 sh′				
804 m				
	770 w			
740	735 w			
708				
666 w				
580 vvs	580 s	580 s	578 vvs, pol	AsN_3 stretch ($A+E$)
480 w				AsNC deformation (E).
	398 w		397 s, pol	NC_2 deformation (A)
385 sh′	378 w			NC_2 deformation (E)
			339 sh′, pol	AsNC deformation (E)
	310 w		308 vs, pol	AsNC deformation (A)
			273 s, pol	CH_3 torsion (A')
			153 w, dp	NC_2 torsion (E)
			109 w, dp	AsN_3 deformation (E)

Table 3. The vibrational spectrum of tris(diethylamido)-phosphine (all figures in wavenumbers/cm^{-1})

Infrared Liquid	Raman Liquid	Proposed Assignment
2960 s	2968 m	CH_3 stretch (A'')
2926 s	2930 s, pol	CH_2 i.p. stretch (A')
	2897 m, pol	CH_2 i.p. stretch (A')
	2891 ms, pol	CH_3 stretch (A')
2860 ms		CH_2 stretch (A'')
2820 s		CH_3 stretch (A')
2775 m		CH_3 stretch (A')
2745 sh′	2721 w, dp	
2475 w		
2380 w		
1460 s	1455 vs, dp	CH_3 deformation (A'')
1450 sh′		CH_3 deformation (A'')
1382 s	1377 mw, dp	CH_3 def. (A')+CH_2 o.o.p. scissors (A'')
1360 sh′	1369 mw? dp	CH_2 i.p. scissors (A')
1345 sh′	1344 mw	CH_3 deformation (A'')
	1335 sh′	CH_3 deformation (A')
1295 m	1291 mw, op	CH_3 rock (A'')
1208 s	1204 m, pol	CH_2 i.p. wag (A')
1170 s		CH_2 o.o.p. wag (A'')
1100 m	1101 sh′, dp	CH_3 rock (A'')
1080 m	1076 s, pol	CH_3 rock (A')
1063 m	1058 sh′, pol	CH_2 i.p. twist (A')
1018 s	1027 m, pol	C—C stretch (A')
	1009 mw, dp	C—C stretch (A'')
973 m		NC_2 stretch (A)
942 m		NC_2 stretch (E)
915 m	919 m, dp	NC_2 stretch (E)
887 w	887 m.w.? pol	NC_2 stretch (A)
800 m		CH_2 rock (A'')
792 sh′	793 m, pol	CH_2 rock (A')
695 w		PN_3 stretch (E)
674 sh′		
667 m		
	655 s, pol	PN_3 stretch (A)
643 w		
569 w		

522 w	525 vvw, dp	
	508 vvw, dp	
495 w	492 vw, pol	PNC deformation (A)
460 w	462 vw, pol	?PNC deformation
420 w		
392 w	387 m, pol	NC_2 deformation (A)
	311 s, pol	CH_3 torsion (A')

N.B. i.p. and o.o.p. are abbreviations for in-phase, out-of-phase respectively.

Table 4. The vibrational spectrum of tris(diethylamido)arsine (all figures in wavenumbers/cm^{-1})

Infrared liquid	Raman liquid	Proposed assignment
2973 s	2975 m	CH_3 stretch (A'')
2968 s	2965 m, dp	CH_3 stretch (A'')
2933 s	2931 s, pol	CH_2 stretch (i.p.) (A')
	2901 shr, dp	CH_2 stretch (o.o.p) (A'')
	2885 shr, dp	CH_3 stretch (A'')
2873 s	2871 s, pol	CH_2 stretch (i.p.) (A')
	2863 s	CH_2 stretch (o.o.p) (A'')
2843 s		CH_3 stretch (A')
2783 m	2781 w	CH_3 stretch (A')
2753 shr		?CH_3 stretch (A')
2728 shr		
2714 w	2719 vw	
2483 w		
2391 w		
1595 w		
1485 shr	1480 shr	CH_3 deformation (A'')
1462 m	1458 shr	CH_3 deformation (A')
1452 m	1452 s, dp	CH_3 deformation (A'')
1394 shr	1398 w	CH_3 deformation (A')
1373 m	1371 w, dp	CH_2 o.o.p. scissors (A'')
1362 shr	1364 w	CH_2 i.p. scissors (A')
1344 w	1343 dp	CH_3 deformation (A'')
	1323 m	CH_3 deformation (A'')
1292 m	1292 m, dp	CH_3 rock (A'')
1190 m	1194 w, pol	CH_2 i.p. wag (A')
1160 m	1161 w	CH_2 o.o.p. wag (A'')
1102 w	1099 w, dp	CH_3 rock (?A')
	1077 s, pol	CH_3 rock (A')
1067 w		CH_2 i.p. twist (A')
1052 m	1055 w, dp	CH_2 o.o.p. twist (A'')
	1048 w	CH_3 rock (A'')
1017 shr	1020 m, pol	C—C stretch (A')
1005 m	1007 w	C—C stretch (A'')
917 w	917 m, dp	NC_2 stretch (E)
	898 m, dp	NC_2 stretch (E)
877 m	875 w, dp	NC_2 stretch (?A)
808 shr	809 w	CH_2 o.o.p. rock (A'')
790 m	789 w	CH_2 i.p. rock (A')
777 shr		
723 w		
700 w	704 vw	
592 w	597 s, pol	AsN_3 stretch ($A+E$)
	501 w	
492 w		
477 w	479 w	AsNC deformation (E)
	433 w	?AsNC deformation (E)
	383 w	NC_2 deformation (E)
	374 w	NC_2 deformation (E)
	353 w	AsNC deformation (A)
	333 w, dp	?CH_3 torsion (A'')
	297 s, pol	CH_3 torsion (A')

N.B. i.p. o.o.p. are abbreviations for in-phase and out-of phase respectively.

NMe_2 normal modes are set out in Table 5. If significant coupling occurs between the NMe_2 units, then further bands would arise, and the problem would have to be treated under the overall symmetry of the molecule (C_3 or C_{3v}).

Finch *et al.* carried out an approximate normal coordinate analysis of an $XNMe_2$ group with X taken to be of variable mass (1–100 a.m.u.) [12] This showed that for larger X there is likely to be extensive mixing of modes, especially involving the methyl rocks and the N–X stretches.

Table 5. Vibrational modes of an isolated —NMe_2 ligand of C_s symmetry

CH_3 stretches	$3A'+3A''$
CH_3 deformations	$3A'+3A''$
CH_3 rocks	$2A''+2A''$
CH_3 torsion	$A'+A''$
NC_2 deformation	A'
(—NC_2 torsion	A'')

In describing the assignment of internal NMe_2 modes, figures quoted will refer to $P(NMe_2)_3$. The equivalent features in $As(NMe_2)_3$ almost always occur at very similar wavenumbers.

The highest-wavenumber fundamentals will, of course, be the C–H stretches. Table 6 shows that for an isolated -$N(CH_3)_2$ group we expect 6—three of which should be polarized in the Raman spectrum. The anti-

Table 6. Vibrational modes for an NEt_2 unit of C_s symmetry

CH_3 stretches	$3A'+3A''$
CH_2 stretches	$2A'+2A''$
CH_3 deformations	$3A'+3A''$
CH_2 scissors	$A'+A''$
CH_2 wags	$A'+A''$
CH_3 rocks	$2A'+2A''$
CH_2 twists	$A'+A''$
CH_2 rocks	$A'+A''$
CH_3 torsions	$A'+A''$
C—C stretches	$A'+A''$
NC_2 stretches	$A'+A''$
NC_2 deformation	A'
NCC deformations	$2A'+2A''$

symmetric CH_3 stretches generally occur at higher wavenumber than the symmetric, and can be assigned here to three medium-strong Raman bands, all depolarized at, 2974, 2931 and 2889 cm^{-1}; all have i.r. counterparts. Of the three predicted symmetric modes, however, only two give observable features—strong and polarized Raman bands at 2843 and 2797 cm^{-1} (with corresponding i.r. features). These are in the region expected for this type of mode in $N(CH_3)_2$ compounds [14], but no band due to the final symmetric mode could be detected.

The methyl deformations should also give six bands, three antisymmetric, predicted to fall within the range 1470–1410 cm^{-1}, and three symmetric, of much more variable wavenumber (dependent upon the electronegativity of the attached atom) [15]. Depolarized Raman bands at 1481, 1441 and 1417 cm^{-1} are definitely due to the three antisymmetric deformations, but no polarized Raman bands occur anywhere near these wavenumbers. Strong i.r. absorptions are, however, noted at 1463, 1458 and 1318 cm^{-1}, and these are assigned as the deformations of A' symmetry. This complete absence of symmetric modes from the Raman spectrum is most unusual.

The modes described so far are probably quite free from "mixing," but this is no longer true when discussing the CH_3 rocking and NC_2 stretching modes. Descriptions of modes appearing in the 900–1300 cm^{-1} region are likely to be approximate, as shown by the calculations of FINCH *et al.* [12], and assignments will be tentative. The following assignments are all quite reasonable, however. Four methyl rocking modes are expected, and can be assigned to four strong i.r. absorptions, at 1277, 1190, 1150 and 1086 cm^{-1}. A polarized Raman band at 1147 cm^{-1} shows that this corresponds to an A' mode, while depolarized bands at 1280 and 1195 cm^{-1} indicate that these are of A'' symmetry. The i.r. band at 1086 cm^{-1} has no Raman counterpart, but is necessarily the remaining A' mode.

For the modes which involve only the CH_3 groups, no evidence has been found for coupling between the NMe_2 groups. For the NC_2 stretches, however, it is possible that such coupling may be significant. As Table 5 shows, an isolated NMe_2 group would give only two such modes ($A'+A''$), but Table 7 (which will be discussed in detail for the skeletal modes of X-$(NMe_2)_3$) reveals that for the "whole molecule" model there would be 4 distinct NC_2 stretches, all i.r. and Raman active for C_3 symmetry ($2A+2E$), but only three active modes for C_{3v} symmetry (A_1+2E; A_2 totally inactive.)

Table 7. Skeletal vibrations of $X(NC_2)_3$ units

Mode type	Effective symmetry C_3	C_{3v}
X–N stretch	$A+E$	A_1+E
NC_2 stretch	$2A+2E$	A_1+A_2+2E
X–N–C deformation	$2A+2E$	A_1+A_2+2E
NC_2 deformation	$A+E$	A_1+E
NC_2 torsion	$A+E$	A_2+E

There is some uncertainty as to the position expected of the antisymmetric NC_2 stretch. Thus, DURIG and CASPER [4] favour a value of *ca.* 1250 cm^{-1}, while other workers [3, 6] favour a lower wavenumber. Since in $HNMe_2$ the NC_2 stretches are at 930 cm^{-1} (A') and 1024 cm^{-1} (A''), we follow the latter alternative. In the Raman spectrum of $P(NMe_2)_3$ we observe bands at 963 cm^{-1} (pol.) and 981 cm^{-1} (depol.), which are clearly due to symmetric and antisymmetric modes respectively. There are very strong i.r. absorptions corresponding to both of these and, in addition, absorptions at 1069 and 947 cm^{-1} which are of medium intensity in the liquid-phase, and strong in solid-phase spectra. These can also be assigned as NC_2 stretching fundamentals and we can therefore conclude (i) that there is sufficient vibrational coupling between the NMe_2 units to break down the "local symmetry" approximation for NC_2 stretches, and (ii) that the effective molecular symmetry must be C_3 rather than C_{3v}, since in the latter case only three stretches would be seen.

The X—N—C and NC_2 deformations are most conveniently discussed as molecular skeletal modes, leaving only the methyl torsions to be assigned in this section. In $HNMe_2$ these are at 290 cm^{-1} (A') and 250 cm^{-1} (A'') [11] in $P(NMe_2)_3$ a polarized Raman band is present at 295 cm^{-1}, while in $As(NMe_2)_3$ a very similar feature is seen at 273 cm^{-1}; these are assigned to the symmetric torsion, and no evidence was found for the antisymmetric mode.

(b) *Internal* NEt_2 *modes*

In this discussion data from $As(NEt_2)_3$ will generally be used for illustration, as the spectrum of $P(NEt_2)_3$ was less well resolved. In addition, the greater complexity of the data will lead to uncertainties in the assignments, and only very brief discussions will be given. The numbers and symmetry types of vibrations for an NEt_2 group of C_s symmetry are summarised in Table 6. Ten CH stretches should be present, and there are 10 observed wavenumbers, but assignment to specific modes is not easy. The assignments in Table 4 are, however, consistent with accepted characteristic wavenumbers in this region.

Methylene scissors deformation modes, when the CH_2 is adjacent to an amine residue, are generally within the range 1475–1445 cm^{-1} [16]. We have two candidates, at 1485 and 1462 cm^{-1}; the polarizations of neither could be detected in the Raman spectrum, so they are assigned arbitrarily as A'', A' respectively. Six bands can be assigned as CH_3 deformations, 1452–1323 cm^{-1} (Table 4).

All of the remaining CH_2 deformations (twist, wag, rock) and CH_3 rocking modes can be assigned similarly to features in the normally expected regions, and are summarised in Table 4.

C–C stretching modes in a number of diethylamido derivatives of boron are assigned[17] as 1008 cm^{-1} (symmetric) and 1080 cm^{-1} (antisymmetric). In As-$(NEt_2)_3$, a medium-intensity, polarized Raman band is seen at 1020 cm^{-1}, and is assigned as the A' mode (i.r. at 1017 cm^{-1}). The only band near this which could be due to the A'' mode is at 1007 cm^{-1} (of undetermined polarization).

As for the $X(NMe_2)_3$ compounds, more NC_2 stretches are seen than can be accounted for by a single, uncoupled NR_2 group. In $P(NEt_2)_3$, four bands are seen, as expected for a C_3 model, at 973, 887 cm^{-1} (A symmetry), 942, 917 cm^{-1} (E symmetry). $As(NEt_2)_3$

gives only three such bands, 876(A), 917, 898 cm^{-1} (E)—but the same symmetry is likely to apply here also. These wavenumbers are lower than for the NMe_2 compounds. This may be due to mass effects, or to coupling with νC–C or CH_3 rocks and CH_2 twists.

As for the NMe_2 groups, the X—N—C and NC_2 deformations are discussed as skeletal modes. This leaves only the CH_3 torsion—for which a Raman band (polarized) at 297 cm^{-1} is assigned as the A' mode, with a depolarized feature at 333 cm^{-1} possibly being the A'' mode (As compound); the former feature is at 311 cm^{-1} in $P(NEt_2)_3$.

(c) *Skeletal modes of* $P(NR_2)_3$

Detailed discussion will be given for R = Me, as assignments for the ethyl analogue are very similar. Predicted modes are summarised in Table 7. The NC_2 stretches have already been described, and the next-highest fundamentals will be the PN_3 antisymmetric stretches. GOUBEAU *et al.* showed [6] that for $OP(NMe_2)_3$ and $SP(NMe_2)_3$ these were at 752, 742 cm^{-1} respectively, with $\nu_s PN_3$ at 636, 722 cm^{-1} respectively. Exocyclic PN stretches in $P_3N_3F_{6-n}(NMe_2)_n$ gave bands at 680 cm^{-1} (symmetric) and 748 cm^{-1} (antisymmetric) [18]. $\nu_s PN_3$ in $P(NMe_2)_3$ is very easily assigned to a very strong, polarized Raman band at 671 cm^{-1}, while ν_{as} is apparently only slightly higher, at 700 cm^{-1}.

Both PN_3 modes are shifted to lower wavenumber in $P(NEt_2)_3$, probably due to simple mass effects (ν_s 655 cm^{-1}, ν_{as} 667 cm^{-1}).

PNC and NC_2 deformation modes will certainly be mixed extensively, and so assignments will be approximate. In $HNMe_2$, δNC_2 is at 397 cm^{-1} [12], and at 393 cm^{-1} in $MeNPF_2$[3]. Consequently, a tentative assignment of two NC_2 deformations in $P(NMe_2)_3$ is made to bands at 390 (i.r.), 392 cm^{-1} (Raman, unknown polarization) and 405 cm^{-1} (i.r. only) cm^{-1}. It is impossible to differentiate between that of A and that of E symmetry. This leaves candidates for δPNC as follows: (symmetric) 337 cm^{-1} (strong, polarized Raman band); (antisymmetric) 494 cm^{-1} (i.r.)/497 cm^{-1} (Raman), and 420 cm^{-1} (i.r.)/416 cm^{-1} (Raman). No evidence was found for the second symmetric deformation.

Two depolarized Raman bands are seen, at 197 and 127 cm^{-1}, due to the NC_2 torsion and $\delta_{as} PN_3$ respectively. The $\delta_s PN_3$ would be expected below 100 cm^{-1}, and was not detected, while the symmetric torsion mode is likely to only weakly allowed, since it is derived from an A_2 mode (forbidden) under C_{3v} symmetry.

(d) *Skeletal modes of* $As(NR_2)_3$

As in (c) above, the case with R = Me will be considered in greater detail. The NC_2 stretches, as for $P(NMe_2)_3$ are all above 900 cm^{-1}, the A modes giving a broad, polarized feature with maxima at 951 and 937 cm^{-1}, the E modes being at 1063 and (probably) 1024 cm^{-1}.

The next features to be considered at those due to ν_s and ν_{as} AsN_3. KOBER has reported [19] that νAsN in several Me_2AsNR_2 compounds is always close to 580 cm^{-1}, while DURIG showed that in Me_2NAsCl_2 it is at 585 cm^{-1} (*trans*) or 569 cm^{-1} (*gauche*) [4]. Thus, in $As(NMe_2)_3$ it is clear that $\nu_s AsN_3$ corresponds to the strong, polarized Raman band at 574 cm^{-1} (with an i.r. counterpart). In $P(NR_2)_3$, as seen above ν_s and $\nu_{as} PN_3$ are separated by *ca.* 20 cm^{-1}. It is a general rule that on increasing the mass of the central atom X, the separation between ν_s and ν_{as} for XY_n decreases. In fact no other band is seen between 580 and 600 cm^{-1} for $As(NMe_2)_3$ or $As(NEt_2)_3$, and thus ν_s and ν_{as} appear to be accidentally degenerate. Support for this view comes from the observation of only one νSN band in $S(NMe_2)_2$ [20], and only one νSbN in $Sb(NMe_2)_3$ (the only assignment given for this species) [21].

As in the phosphorus analogues, some mixing is expected between δAsNC and δNC_2 modes, so descriptions will be approximate. An i.r. band at 480 cm^{-1} in $As(NMe_2)_3$ (no Raman counterpart) is assigned as δ_{as}AsNC, while the equivalent symmetric mode is at 308 cm^{-1} (strong, polarized Raman band), and a second antisymmetric mode at 339 cm^{-1} (depolarized, Raman only). The symmetric NC_2 deformation is at 397 cm^{-1} (strong, polarized Raman band), with an antisymmetric deformation at 378 cm^{-1}.

An NC_2 torsional mode gives a depolarized Raman band at 153 cm^{-1}, with $\delta_{as} AsN_3$ at 109 cm^{-1}. The symmetric AsN_3 deformation (< 100 cm^{-1}) was not detected.

CONCLUSION

We have been able to assign satisfactorily the internal modes of the NR_2 units in $X(NR_2)_3$, where X = P or As; R = Me or Et. Except for NC_2 modes, a model involving non-interacting NR_2 units, of C_s symmetry, was sufficient. For skeletal modes (including NC_2) the possible symmetries were C_3 and C_{3v}. For νNC_2 there were definitely too many fundamental bands for the latter, and so C_3 appears to be the effective molecular symmetry.

REFERENCES

[1] D. C. BRADLEY, *Adv. Inorg. Radiochem.* **15**, 259 (1972).
[2] R. B. HARVEY and H. E. MAYHOOD, *Can. J. Chem.* **23**, 1552 (1955).
[3] M. A. FLEMING, R. J. WYMA and R. C. TAYLOR, *Spectrochim. Acta.* **21A**, 1189 (1965).
[4] J. R. DURIG and J. M. CASPER, *J. Mol. Struct.* **10**, 427 (1971).
[5] F. RAUCHLE, W. PÖHL, B. BLAICH and J. GOUBEAU, *Ber. Buns. Ges. Phys. Chem.* **75**, 66 (1971).
[6] D. KOTTGEN, H. STOLL, A. LENTZ, R. PANTZER and H. GOUBEAU, *Z. Anorg. Chem.* **385**, 56 (1971).
[7] R. PANTZER, W. D. BURKHARDT, E. WALTER and J. GOUBEAU, *Z. Anorg. Chem.* **416**, 297 (1975).
[8] A. VILKOV, L. S. KHAIKIN and V. V. EVDOKIMOV, *J. Struct. Chem. U.S.S.R.* **13**, 4 (1972).
[9] A. B. BURG and P. J. SLOTA, *J. Am. Chem. Soc.* **80**, 1107 (1958).
[10] K. MOEDRITZER, *Chem. Ber.* **92**, 2637 (1959).

[11] J. R. BARCELLO and H. BELLANATO, *Spectrochim Acta.* **8**, 27 (1956).
[12] A. FINCH, I. J. HYAMS and D. STEELE, *J. Mol. Spectrosc.* **16**, 103 (1965).
[13] F. C. KOHOUT and F. W. LAMPE, *J. Am. Chem. Soc.* **87**, 5796 (1965).
[14] N. B. COLTHUP, L. H. DALY and S. E. WIBERLEY, *Introduction to Infrared and Raman Spectroscopy*, 2nd edition, p. 222. Academic Press, New York (1975).
[15] *ibid*, pp. 226–227.
[16] *ibid*. p. 228.
[17] H. J. BECHER and H. T. BAECHLE, *Z. Phys. Chem.* **48**, 359 (1966).
[18] D. B. SOWERBY, *J. Chem. Soc.* A. 3487 (1971).
[19] F. KOBER, *Z. Anorg. Chem.* **400**, 285 (1973).
[20] R. PAETZOLD and E. RÖNSCH, *Spectrochim. Acta.* **26A**, 569 (1970).
[21] A. KIENNEMANN, G. LEVY, F. SCHUÉ and C. TANIÉLIAN, *J. Organomet. Chem.* **35**, 143 (1972).