Infrared and Raman Spectroscopic Studies of Conformations in Liquid and Solid Triethyl-, Diethyl(methyl)- and Ethyldimethyl-amines, -phosphines, and -arsines

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Infrared and Raman spectra of YMe_3, YEt_3, $YMeEt_2$, and YMe_2Et (Y = N, P, or As) have been recorded for the liquids and the solids. Study of the YC_3 stretching bands indicates that the liquids (except YMe_3) contain a mixture of conformational isomers. The solids are simpler. All the YEt_3 compounds on crystallization adopt a C_3 configuration, and YMe_2Et also crystallize to a single form. The compounds $YMeEt_2$ solidify to glasses containing one or two conformers, depending on the conditions. The vapour-phase i.r. spectrum of NMe_2Et has been analyzed to ascertain its structure. It is suggested that the preferred conformations in the solids have all the C–Me groups *gauche* to the lone pair of the central atom.

MICROWAVE studies of trimethylamine indicate that the molecule adopts a C_{3v} equilibrium configuration in the vapour state,[1] in which one C–H bond of each methyl group is *trans* to the nitrogen lone pair. Kamur[2] used this model in considering triethylamine, and from vibrational spectra obtained evidence for at least two conformations differing in their relative proportions between the solid, liquid, and vapour states. Green[3] concluded from vibrational spectra that at least three forms of triethylphosphine are present in the liquid.

Here, we have used i.r. and Raman spectroscopy in a more extensive analysis of the conformations occurring in this type of system. Trialkyl-amines, -phosphines, and -arsines of the type YMe_3, YMe_2Et, $YMeEt_2$, and YEt_3 have been investigated in the liquid and solid states, and in the case of NMe_2Et in the vapour state as well. We intend to investigate subsequently the configurations which these molecules adopt when complexed to a metal.

RESULTS AND DISCUSSION

On the basis of the trimethylamine model,[1] replacement of H by Me can be *trans* (*t*) or *gauche* (*g*) to the lone pair on Y. Thus there are, in principle, two vibrationally differentiable conformations for YMe_2Et, six for $YMeEt_2$, and seven for YEt_3. Molecular models suggest that configurations which have two *gauche*-methyl groups inclined towards each other, or two or more *trans*-methyl groups, will be particularly unfavourable as a result of steric crowding. The remaining configurations are depicted in Figure 1.

It is to be expected that Y–C stretching vibrations will be sensitive to the configuration of the alkyl groups and that their spectroscopic behaviour will be simpler to rationalize than that of other types of vibration. In the arsines these modes occur in the range 500—600 cm^{-1}, free from interference from other vibrations. The corresponding range in phosphines, 600—720 cm^{-1}, appears to be just below a group of C–H rocking modes in ethyl groups which are intense in the i.r. but very weak in the Raman spectra. For amines the position is much less straightforward. The similarity of masses of carbon and nitrogen will blur the individuality of central atom–carbon stretching character in any band and there are further complications due to other ethyl-group vibrations in the same wavenumber region.

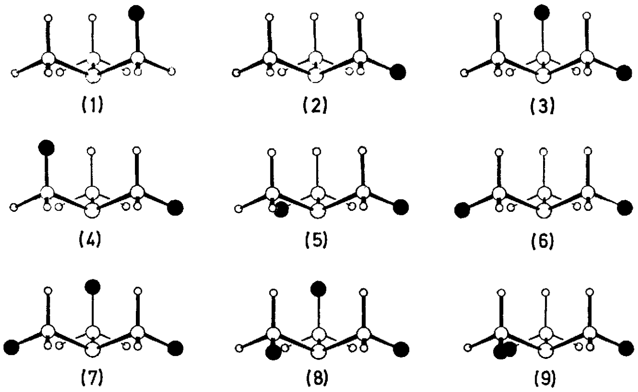

FIGURE 1 Schematic representation of likely configurations for YMe_2Et (1) and (2), $YMeEt_2$ (3)—(6), and YEt_3 (7)—(9). ● = CH_3, o = H

The lattice vibrations of crystalline materials give sharp bands below *ca.* 100 cm^{-1} in their Raman spectra, especially at low temperatures. Two types of spectra were observed for the solidified compounds, sharp and broad (Figure 2), which we assume to indicate crystalline and glassy materials respectively. In some instances the

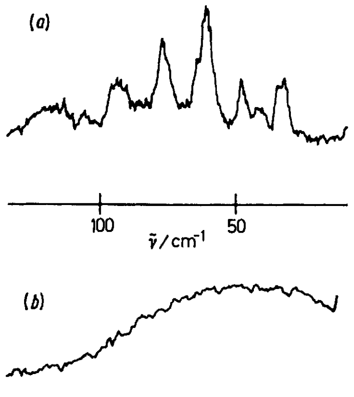

FIGURE 2 Raman spectra of (*a*) $AsEt_3$ and (*b*) $NMeEt_2$ in the lattice region

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[1] J. E. Wollrab and V. W. Laurie, *J. Chem. Phys.*, 1969, **51**, 1580.

[2] K. Kamur, *Chem. Phys. Letters*, 1971, **9**, 504.

[3] J. H. S. Green, *Spectrochim. Acta*, 1968, **A24**, 137.

degree of crystallinity, as judged from the lattice vibrations, could be improved by temperature cycling near the melting point.

Tables 1—4 give only the details relevant to the structural diagnosis. The full lists of wavenumbers for the solid triethyl compounds, which were isolated as single structures, are given in Table 5.

TABLE 1

YC_3 Stretching wavenumbers (cm^{-1}) in solid and liquid YMe_3 (Y = N, P, or As) from Raman spectra

Compound		T/K	YC_3 str.	
			A_1	E
NMe_3	liquid	253	828vs	1 041m
	solid	95	828vs	1 039s
PMe_3	liquid	293	654vs	708m
	solid	106	658vs	708vs, 710s, 711vs
$AsMe_3$	liquid	293	570vs	585m
	solid	107	573vs	584m, 586vs, 589w(sh)

Trimethyl Systems.—Recently, Raman spectra of solid PMe_3[4] and $AsMe_3$[5] at 14 K have been reported in detail. Our own observations on these systems are in good agreement with these reports except that we observed fine solid-state splittings on the asymmetric YC_3 stretching bands at high spectrometer resolution (Table 1). The importance of this for the present work is that it indicates the likely magnitude of splittings which may be due to crystal-state effects (up to 3 cm^{-1}) when a single conformer is present.

TABLE 2

YC_3 Stretching wavenumbers (cm^{-1}) of YEt_3 (Y = N, P, or As)

Compound	Conditions	T/K	YC_3		Suggested structure [a]
			sym	asym	
NEt_3	I.r.(l)	298	736ms		(7) or (8)
			745m		(9)
	Raman(l)	293	737s,p		(7) or (8)
			746wm(sh),p		(9)
	I.r.(s)	100 [b]	736vw(sh)		(7) or (8)
			745ms		(9)
	Raman(s)	103	746s		(9)
PEt_3	I.r.(l)	298	607w	658m, 690s [c]	(7) or (8)
			618w	669s	(9)
			624w	690s,[c] 717m	(8) or (7)
	Raman(l)	293	607s,p	660m,dp, 691m, dp [c]	(7) or (8)
			618ms,p	669m, dp	(9)
			624w(sh),p	691m,dp,[c] 716vw	(8) or (7)
	I.r.(s)	150 [d]	622wm	672s	(9)
			640wm	689s, 711s	(8) or (7)
	I.r.(s)	150 [b]	623wm	672s	(9)
	Raman(s)	95	623vs	672vs, 675vs	(9)
$AsEt_3$	I.r.(l)	298	535w	556s, 565s	(7) or (8)
			ca. 548(sh)	571(sh)	(9)
	Raman(l)	293	536vs,p	559s(sh),dp, 570s,dp	(7) or (8)
			549vs,p	570s,dp	(9)
	I.r.(s)	150 [b]	550s	572vs	(9)
	Raman(s)	100	550vs	571vs, 573vs	(9)

[a] As in Figure 1. [b] Annealed. [c] Band coincidence invoked (see text). [d] Unannealed.

The Raman spectrum of solid NMe_3 did not show splitting of the NC_3 asymmetric stretch. Incidentally, the E and A_2 methyl torsions were observed at 307m and 280vw cm^{-1}, just slightly higher than the values deduced by Lide and Mann.[6]

Triethyl Systems.—The PC_3 stretching features of liquid triethylphosphine can be clearly grouped into two sets, those below 640 cm^{-1} being more intense in the Raman spectra than those above (Table 2). Being highly polarized these bands must relate to symmetric modes. The relative intensities of the two sets are reversed in the i.r.

On cooling the sample to 100 K, a crystalline solid was obtained which gave a very simple Raman spectrum (Figure 3). Assuming that the fine splitting at *ca.* 673 cm^{-1} is due to crystal-state effects, the species present must have three-fold rotational symmetry [(9) of Figure 1]. Low-temperature deposition from the vapour phase gave, initially, five i.r. bands in this region, two of which correspond to the Raman bands of the crystalline solid. The other three disappear in unison when the sample is warmed to near its melting point and recooled, and must therefore arise from a second conformation of lower symmetry. The band in the symmetric PC_3 stretching region of this species is at higher wavenumber than any such band in the liquid, but rather than accept that it is a form absent from the liquid we suggest that it is related to the weak feature at 624 cm^{-1} of the latter. In conjunction with this we suggest that the peak at 623 cm^{-1} in the solid is related to the band at 618 cm^{-1} of the liquid.

The liquid has an additional conformer giving rise to bands at 607 and 660 cm^{-1}. Furthermore, the band at *ca.* 690 cm^{-1}, which is somewhat asymmetric in the i.r. spectrum, is more prominent and broader relative to

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[4] H. Rojhantalab, J. W. Nibler, and C. J. Wilkins, *Spectrochim. Acta*, 1976, **A32**, 519.

[5] H. Rojhantalab and J. W. Nibler, *Spectrochim. Acta*, 1976, **A32**, 947.

[6] D. R. Lide and D. E. Mann, *J. Chem. Phys.*, 1958, **28**, 572.

715 cm^{-1} in the liquid than in the metastable species obtained in the solid; this strongly suggests that part of its intensity is associated with the extra species in the liquid. On the basis of intensities it appears to be at least as abundant as either of the other two forms in the liquid, although totally absent from any of the solid-state spectra. This and the metastable solid form presumably relate to types (7) and (8) but the spectra do not differentiate between them. Points relevant to any speculation on these two structures are: (*i*) there are twice as many close *trans-gauche* methyl–methyl interactions in (7) as there are in (8), favouring the latter at low temperatures; (*ii*) (8) more closely resembles the form adopted in the stable crystal; (*iii*) if there were no

TABLE 3

YC_3 Stretching wavenumbers (cm^{-1}) of $YMeEt_2$ (Y = N, P, or As)

Compound	Conditions	T/K	YC_3 sym	YC_3 asym	Suggested structure [a]
$NMeEt_2$	I.r.(l)	298	750vw(sh)		(3) or (4)
			760m		(5) or (6)
			775wm		(6) or (5)
	Raman(l)	293	750wm(sh),p		(3) or (4)
			761s,p		(5) or (6)
			777m,p		(6) or (5)
	I.r.(s)	100	762s		(5) or (6)
			776s		(6) or (5)
	Raman(s)	110	763ms		(5) or (6)
			778ms		(6) or (5)
$PMeEt_2$	I.r.(l)	298	610vw(sh)	686w 661(sh)	(3) or (4)
			615w	698s [b]	(4) or (3)
			627m	670s, 698s [b]	(5) or (6)
			645w(sh)	666s(sh), 710s	(6) or (5)
	Raman(l)	293	610m,p	687w,p 661w(sh)dp	(3) or (4)
			616m,p	698m,p [b]	(4) or (3)
			628s,p	670m, dp, 700m,p [b]	(5) or (6)
			645m,p	666w(sh),dp, 709w,p	(6) or (5)
	I.r.(s)	150	613vvw		(3) or (4)
			629m	672s, 700s	(5) or (6)
	Raman(s)	108	612w		(3) or (4)
			633s	676m, 703m	(5) or (6)
			649m	667w(sh), 715m	(6) or (5)
$AsMeEt_2$	I.r.(l)	180	541w	561m(sh), 571s [b]	(3) or (4)
			554m	571s,[b] 583s	(5) or (6)
	Raman(l)	293	537vs,p	561(sh),[b] 570s [b]	(3) or (4)
			550vs,p	567s,[b] 577s	(5) or (6)
	I.r.(s)	150	553ms	571s, 581s	(5) or (6)
	Raman(s)	100	542ms		(3) or (4)
			555vs	570vs, 584vs	(5) or (6)

[a] As in Figure 1. [b] Composite band (see text).

TABLE 4

YC_3 Stretching wavenumbers (cm^{-1}) of YMe_2Et, (Y = N, P, or As)

Compound	Conditions	T/K	YC_3 sym	YC_3 asym	Suggested structure *
NMe_2Et	I.r.(l)	298	786s		(2)
	Raman(l)	293	777wm(sh),p		(1)
			787vs,p		(2)
	I.r.(s)	100	785s		(2)
	Raman(s)	105	791s		(2)
	Raman(g)	310	788s		(2)
PMe_2Et	I.r.(l)	298	616w	719w(sh)?	(1)
			638m	687vs, 709vs	(2)
	Raman(l)	293	617m,p		(1)
			638vs,p	687m,p, 709wm,dp	(2)
	I.r.(s)	77	641m	687vs, 711vs	(2)
	Raman(s)	95	642vs	690s, 712s	(2)
$AsMe_2Et$	I.r.(l)	180	541vw		(1)
			558m	576s, 582s	(2)
	Raman(l)	293	543m,p		(1)
			559vs,p	577s,p, 581m(sh),dp	(2)
	Raman(l)	170	545wm,p		(1)
			561vs,p	579s,p, 585m,dp	(2)
	I.r.(s)	150	558s	577s, 584m(sh)	(2)
	Raman(s)	100	562vs	581vs, 588vs	(2)

* As in Figure 1.

energy difference between the two, (8) would be statistically preferred in the liquid state; (*iv*) (7) requires a two-step reorganization through (8) in converting it into (9).

Identification of all the species in liquid triethylarsine is more difficult because the wavenumber range is more compressed. The crystalline solid clearly also has C_3 symmetry [(9)]. The liquid certainly contains a second species whose bands are at lower wavenumber, but the features are not well resolved. We cannot rule out the possibility of a third form being present but obscured by band overlap. The spectra are shown in Figure 4.

TABLE 5

Infrared and Raman spectra (below 1 500 cm^{-1}) [a] of solid YEt_3 (Y = N, P, or As)

NEt_3 [b]	PEt_3		$AsEt_3$	
Raman, 103 K	Raman, 95 K	I.r., 150 K [c]	Raman, 100 K	I.r., 150 K [c]
14vw	36ms		33m	
31w	48w(sh)		42w	
42w	55m		48m	
44w	64s		61s	
57vw	81ms		77ms	
71wm	92wm		93m	
103vw,br(sh)	94wm		116m,br	
130w,br	108m		146wm	
237w,br	126vw		155m	
255vw,br(sh)	135m,br		170m	
299w	165w		226m	
332w	174w		248m	
439w(sh)	193m		302ms	
441s	237m		312s	
483w(sh)	260m		318m	
490ms	338s		545w	
746s	365s		550vvs	550s
795w	370w		565w	
800w	554vw		571vvs	572vs
916s	574w		573vvs	
1 021m	623vvs	623m		720ms
1 065ms	672vvs	672s	726w	726m
1 071ms	675vs			734s
1 088s	715w	711vw		745w
1 090m(sh)	748ms	747m		763m
1 155wm	752vw(sh)	752m		784w
1 201m	761w			910m
1 296ms	766w	767vs		919w
1 300(sh)	970ms	969wm	960w,br	956m
1 379w	973w(sh)	973wm		964m
1 446(sh)	981ms	982vw	975ms	
1 453(sh)	990s	990w	1 038m	1 038s
1 459s	1 045ms	1 043s		1 047m
1 474m	1 233m,br	1 234w		1 051w(sh)
	1 242m	1 242wm	1 214m,br	1 216s
	1 247m	1 246(sh)	1 223m	
	1 258ms	1 258wm	1 229vw	1 230m
	1 377wm	1 377m,br	1 235ms	1 237m
	1 408vw(sh)	1 409wm		1 373m
	1 416m,br		1 376w	1 377m
	1 423m,br	1 428m		1 379w(sh)
	1 434w		1 410vw	1 411m
	1 449m	1 451(sh)	1 419m	1 421wm
	1 459s	1 457s	1 445w	1 452s
		1 461(sh)	1 461m	1 461w
	1 466w(sh)	1 465s	1 466m,br	
	1 468s	1 468(sh)		

[a] The low-frequency limit was *ca.* 10 cm^{-1} for Raman spectra, 400 cm^{-1} for i.r. (owing to masking by water vapour bands). [b] Infrared sample not obtained entirely in one configuration, even after annealment. [c] Annealed.

In his studies of triethylamine, Kamur [2] deduced that (7) was the favoured conformation in the vapour state and that both it and (9) were present in the liquid. On solidification the relative abundances of the two reversed. The polarized Raman bands near 740 cm^{-1} should certainly reflect NC_3 stretching behaviour. There are two such bands in the liquid and we found that the lower disappeared on crystallization. We have not given details of NC_3 asymmetric stretching in Tables 2—4 because of confusion with other vibrations of ethyl groups occurring in the same wavenumber region.

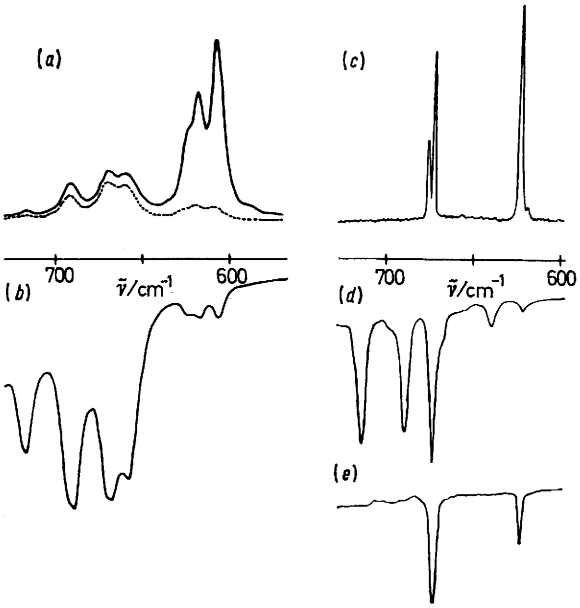

FIGURE 3 Spectra of PEt_3: (*a*) Raman, 293 K; (*b*) i.r., 298 K; (*c*) Raman, 100 K; (*d*) i.r. (unannealed), 150 K; (*e*) i.r. (annealed), 150 K

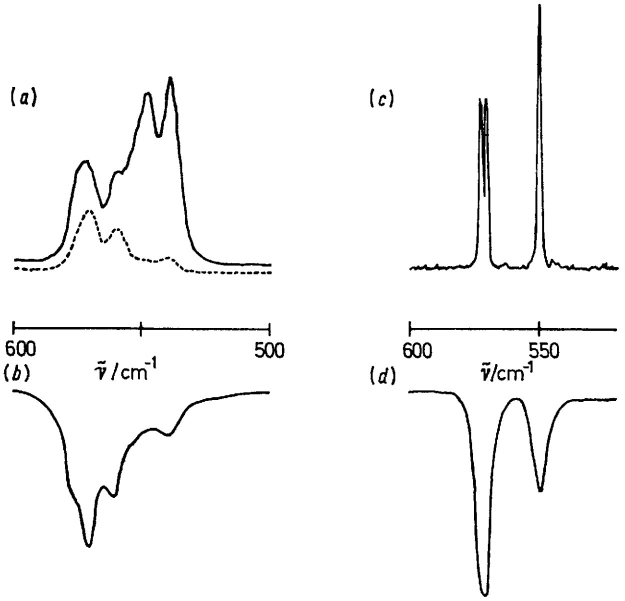

FIGURE 4 Spectra of $AsEt_3$; (*a*) Raman, 192 K; (*b*) i.r., 198 K; (*c*) Raman, 100 K; (*d*) i.r. (annealed), 150 K

(The bands of this region which disappeared on crystallization were at 903, 999, 1 047, and 1 095 cm^{-1}; those remaining are listed in Table 5.) The behaviour parallels our observations on $AsEt_3$ and the lowest two bands of PEt_3, suggesting that here again (9) is the preferred configuration in the solid state.

Diethyl(methyl) Systems.—At room temperature, liquid diethyl(methyl)phosphine shows 10 Raman bands (seven polarized) between 600 and 720 cm^{-1} and corresponding features in the i.r. (Table 3). The clearly polarized bands relate to the low-wavenumber set (below 650 cm^{-1}, ρ *ca.* 0) and the high-wavenumber set (above 680 cm^{-1}, ρ *ca.* 0.5). Since the corresponding modes of trimethylphosphine are higher than those of C_3 triethylphosphine it is tempting to suggest that the highest group are more indicative of P–Me stretching and the lower sets P–Et stretching, although the similarity of energies must mean that there is a very high degree of mixed character in the motions.

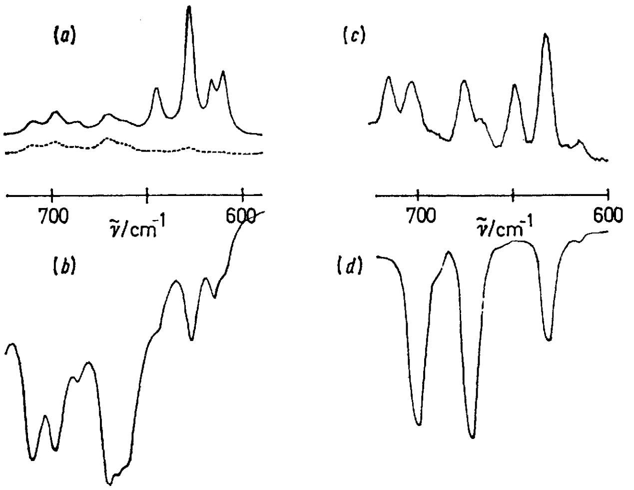

FIGURE 5 Spectra of $PMeEt_2$: (*a*) Raman, 293 K; (*b*) i.r., 298 K; (*c*) Raman, 108 K; (*d*) i.r., 150 K

The i.r. spectrum of the sample deposited at low temperature must relate to a single form, showing only one band in each of the three regions (Figure 5). The liquid sample used for Raman measurements froze to a glass containing largely two isomers, one corresponding to that obtained in the i.r. We presume that these two forms are (5) and (6) of Figure 1. The four bands which have almost disappeared are likely to relate to (3) and (4), and on cooling the liquid to near its freezing point the Raman bands at 616 and 610 cm^{-1} progressively diminish relative to 628 and 645 cm^{-1} (the higher one more rapidly). This change is accompanied by some reduction in the prominence of the band at 698 cm^{-1} and a shift of its maximum to higher wavenumber suggesting that it has a contribution from one of these species.

Diethyl(methyl)arsine was also obtained in a single conformation on deposition from the gas phase. All four Raman bands of the liquid at room temperature have substantial polarized character, the lower two being practically eliminated under the crossed-polarization condition. To judge from the depolarization ratios for the corresponding phosphine, the higher two bands must be composite, and indeed the maximum of the feature at 567 cm^{-1} shifts to 570 cm^{-1} under crossed polarization and there is a shoulder at 561 cm^{-1} (both corresponding to band maxima in the i.r.). On cooling to near the melting point the intensity of the band at 537 cm^{-1} decreases relative to that at 550 cm^{-1} and is considerably further reduced on freezing to a glass. From the wavenumber relation with $PMeEt_2$ and the triethyl systems we suggest that this band belongs to configuration (3) or (4) and that the single species observed in the low-temperature i.r. experiment is (5) or (6). The problems of spectral band overlap preclude comment on whether the other species of the latter pair is present in the liquid or not.

The 760 cm^{-1} region of diethyl(methyl)amine shows three polarized Raman bands for the liquid at room temperature with corresponding i.r. bands. On freezing to a glass the highest-wavenumber component grows relative to the middle one and the lowest disappears. The relative intensities of the two remaining bands did not change after temperature cycling. The solid deposited in the i.r. experiment gave the same two bands, of about equal intensity. After warming to the melting point and recooling over a period of 3 h the ratio of intensities altered slightly in favour of the higher-wavenumber component (*ca.* 15%). The bands in the i.r. spectrum of the vapour did not have a clearly resolved *PQR* structure, precluding analysis, and the complexity of the spectrum suggests that two (or more) species are present in the gas phase also.

The results are summarized in Table 3.

Ethyldimethyl Systems.—Four bands occur in the relevant region of the Raman spectrum of liquid ethyldimethylphosphine (Table 4). The lowest pair are much more strongly polarized (ρ *ca.* 0) than the band at 687 cm^{-1} (ρ *ca.* 0.3) and presumably relate to PC_3 symmetric stretching in the two possible conformers. The band at 617 cm^{-1} becomes weaker on cooling the liquid and is completely absent from the crystalline solid. If our interpretation of the behaviour of the other systems is correct then the preferred configuration is *gauche* [(2) of Figure 1].

The results for ethyldimethylarsine are virtually the same. The highest two features of the dominant conformer are part of a composite band with the lower-wavenumber component moderately polarized. The two contributions separate in the liquid on cooling and are quite distinct in the crystalline state. Ethyldimethylamine behaved similarly. As well as the feature at 777 cm^{-1} (Table 4), weak bands at 925 and 1 030 cm^{-1} in both i.r. and Raman disappeared on crystallization (other weak bands also disappeared in the case of PMe_2Et).

The i.r. spectrum of NMe_2Et in the vapour phase showed no evidence of a second conformer and the wavenumbers are close to those of the dominant form in the liquid. We have made calculations (*cf.* Kumar [2]) to determine whether the two possible configurations can be distinguished by the gas-phase spectrum. The moments of inertia were calculated assuming r(C–N) 1.455, r(C–C) 1.54, and r(C–H) 1.09 Å and all angles tetrahedral, giving values of 77.44, 114.51, and 139.97 a.m.u. * Å^2 for the *trans* isomer and 60.64, 134.18, and 175.82 a.m.u. Å^2 for the *gauche* isomer.

For the *trans* configuration, the Badger and Zumwalt parameters [7] are $\kappa = -0.45$ and ρ^* 0.66 and hence the i.r. spectrum of the vapour should show three types of band contour: type A having a medium strong Q branch with a PR separation [7,8] of *ca.* 20 cm^{-1}; type B having a $PQQR$ structure with prominent Q branches and a PR separation of *ca.* 22 cm^{-1}; and type C having a medium strong Q branch with PR spacing of *ca.* 27 cm^{-1}. Calculation of the Badger and Zumwalt parameters for the *gauche* form gives $\kappa = -0.67$ and ρ^* 1.45 and hence three types of band contour are expected: type A with a medium Q branch and a PR separation of *ca.* 17 cm^{-1}; type B having a PR structure with separation of *ca.* 13 cm^{-1}; and type C having a strong Q branch and a PR spacing of *ca.* 26 cm^{-1}.

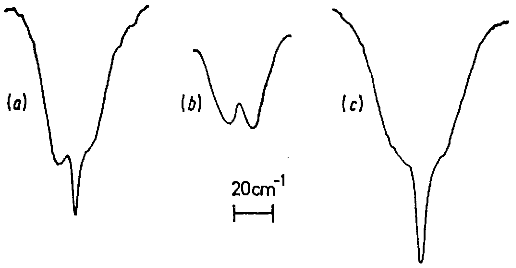

FIGURE 6 Typical i.r. band contours of gaseous NMe$_2$Et: (*a*) type A, 954 cm^{-1}; (*b*) type B, 1 224 cm^{-1}; (*c*) type C, 788 cm^{-1}

The band contours observed in the i.r. spectrum of gaseous NMe$_2$Et (Table 6) agree with those expected for the *gauche* form. Representative type A, B, and C bands are shown in Figure 6. The structure of the type B band is typical of a molecule having a large value of ρ^*.[7]

Conclusions.—The molecules YEt$_3$ exist as mixtures of two or three conformational isomers in the liquid state but crystallize in a single structure having C_3 symmetry. This high-symmetry form is not predominant in the liquid state. Diethyl(methyl)arsine appears to exist in four conformations in the liquid state. Two of these persist on cooling to a glass whereas only one is present when the sample is deposited at low temperature from the vapour phase. Diethyl(methyl)phosphine behaves similarly except that only two species could be identified in the liquid with certainty owing to band overlap. Diethyl(methyl)amine exhibits three forms in the liquid, the most minor of which is absent from the solid. The relative abundances of the two major species is altered on change of state. In all the above cases, the predominant conformer at room temperature has a lower YC$_3$ symmetric stretching frequency than that of the structure preferred in the solid.

Ethyldimethylamine adopts the *gauche* structure in the gas phase. The same configuration is likely to be present in the liquid (dominant form) and crystalline states; if so, the minor species in the liquid is likely to be the *trans* isomer. The behaviour of PMe$_2$Et and AsMe$_2$Et is similar, in each case the YC$_3$ symmetric stretching frequency being higher for the preferred configuration.

TABLE 6

Infrared spectrum (700—1 500 cm^{-1}) of NMe$_2$Et vapour (310 K)

Band centre	Band structure	PR separation (cm^{-1})
788s	PQR	26
954ms	PQR	18
1 050vs,br	composite	
1 089w	PQR	*ca.* 18
1 104m	PQR	18
1 169s,br	PQR	*ca.* 27
1 224m	PR	12
1 280s,br	composite	
1 361vw	PQR	*ca.* 18?
1 363w	PQR	17
1 387s,br	PQR	*ca.* 18?
1 419w	PQR	26
1 437w(sh)	PQR	*ca.* 19
1 457s,br	composite	

In view of the spectra of the crystalline triethyl compounds, the vapour-phase spectrum of NMe$_2$Et, and the correlations of 'YC$_3$ symmetric stretching' wavenumbers, it is probable that the preferred forms of the solids have all C–Me groups *gauche* to the lone pair on the central atom rather than *trans* to it.

EXPERIMENTAL

Raman spectra were measured with a Coderg model T800 triple monochromator using photon-counting detection. Excitation at 647.1 or 514.5 nm was provided by Coherent Radiation Laboratories model 52G krypton- and argon-ion lasers respectively. A prism pre-monochromator was employed to eliminate extraneous plasma emissions from the incident light. For low-temperature studies a Coderg Cryocirc cryostat with liquid-nitrogen cooling was used, temperatures down to 95 K being obtained and stabilized (±5 K) by adjustment of the liquid-nitrogen uptake rate in the cryostat head. Wavenumbers quoted are accurate to ±2 cm^{-1}, but within a given spectrum errors are predominantly systematic.

Room-temperature i.r. spectra were recorded with a Perkin-Elmer model 225 spectrophotometer (±1 cm^{-1}). The low-temperature spectra were obtained with a Perkin-Elmer model 457 spectrophotometer (±2 cm^{-1}). The samples were deposited on to a CsI window, maintained at the required temperature by a Displex model DE 202 helium refrigerator in a system similar to that previously described,[9] by slow bleeding of the vapour into the cryostat cuvette *in vacuo*.

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* 1 a.m.u. = 1.660 × 10^{-27} kg.

[7] R. M. Badger and L. R. Zumwalt, *J. Chem. Phys.*, 1938, **6**, 711.

[8] W. A. Seth Paul and G. Dijkstra, *Spectrochim. Acta*, 1967, **A23**, 2861.

[9] 'Cryochemistry,' eds. M. Moskovits and G. A. Ozin, Wiley, New York, 1976, p. 9.

Preparation of the Compounds.—The phosphines and arsines were prepared by standard Grignard techniques. For the mixed-alkyl systems the pure methylphosphorus (arsenic) chlorides were used as starting materials. The products were purified by distillation under nitrogen and the fractions collected had boiling points in agreement with the literature values.[10,11] Their ^1H n.m.r. spectra were consistent with the absence of any hydrogen-containing impurities. Trimethylphosphine was obtained by thermal decomposition of pure $[AgI(PMe_3)]$ as described previously.[12]

Trimethylamine was used directly from a lecture bottle (B.D.H.). Triethylamine (B.D.H.) was redistilled before use. The compounds $NMeEt_2$ and NMe_2Et (ICN; K and K Laboratories Inc.) were dried over CaH_2 and redistilled. Carbon-13 n.m.r. spectra showed no carbon-containing impurities above *ca.* 2% noise limitation.

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[10] E. Krause and A. von Grosse, 'Die Chemie der metallorganischen Verbindungen,' Dr. Martin Sändig oHG, Wiesbaden, 1965.

[11] 'Organo Phosphorus Compounds,' eds. G. M. Kosolapoff and L. Maier, Wiley, New York, 1972.

[12] P. L. Goggin and J. R. Knight, *J.C.S. Dalton*, 1973, 1489.