Restricted Rotation in Methyl- and Cyanomethyl-tris-(2,4,6-trimethylphenyl)phosphonium Compounds. A ^1H Nuclear Magnetic Resonance Spectroscopic Study. The Crystal Structure of Cyanomethyltris-(2,4,6-trimethylphenyl)phosphonium Tetraiodomercurate(II)

By **Anthony J. Bellamy,*** **Robert O. Gould,** and **Malcolm D. Walkinshaw,** Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ

The crystal structure of cyanomethyltris-(2,4,6-trimethylphenyl)phosphonium tetraiodomercurate(II), $[\mathrm{Mes_3\overset{+}{P}CH_2CN}]_2\cdot\mathrm{HgI_4}^{2-}$, is reported, and the bonding and conformational characteristics of the cation are compared with those related structures which also exist in a propeller conformation. The dynamic stereochemistry of $\mathrm{Mes_3\overset{+}{P}CH_2CN}$, $\mathrm{Mes_3\overset{+}{P}CH_3}$, and $\mathrm{Mes_3P}$, as studied by ^1H n.m.r. spectroscopy, is described. The calculated $\Delta G^‡$ values for enantiomerisation of the propeller configuration, assumed to occur *via* the two-ring flip mechanism, are discussed in the context of related studies. For $\mathrm{Mes_3\overset{+}{P}CH_2CN}$, the enantiomerisation mechanism is related to the conformation in the crystalline state.

In the last 10 years there has been considerable interest in the dynamic stereochemistry of propeller-shaped molecules,[1] the work of Mislow and his group [1,2] on systems of the types Ar_3Z and Ar_3ZX, *e.g.* $\mathrm{Mes_3CH}$ (Mes = 2,4,6-trimethylphenyl),[3] being particularly prominent. Since we had already prepared cyanomethyltris-(2,4,6-trimethylphenyl)phosphonium iodide ($\mathrm{Mes_3\overset{+}{P}CH_2CN\ I^-}$) for use as a precursor for the electrogeneration of $\mathrm{^-CH_2CN}$,[4] we decided that a study of its dynamic stereochemical behaviour, and that of the related methyl-tris-(2,4,6-trimethylphenyl)phosphonium salt ($\mathrm{Mes_3\overset{+}{P}CH_3\ X^-}$), would be of interest for comparison with the behaviour of $\mathrm{Mes_3P}$ [5] and $\mathrm{Mes_3CH}$.[3] We report here the *X*-ray crystal structure determination of $[\mathrm{Mes_3\overset{+}{P}CH_2CN}]_2\cdot\mathrm{HgI_4}^{2-}$, and the variable-temperature ^1H n.m.r. spectroscopic study of $\mathrm{Mes_3\overset{+}{P}CH_2CN}$, $\mathrm{Mes_3\overset{+}{P}CH_3}$, and $\mathrm{Mes_3P}$ (and $\mathrm{Mes_3\overset{+}{As}CH_3}$ [6]), together with a full characterisation of the $\mathrm{Mes_3\overset{+}{P}CH_2CN}$ salts (see Experimental section).

Crystal Structure of $[\mathrm{Mes_3\overset{+}{P}CH_2CN}]_2\cdot\mathrm{HgI_4}^{2-}$.—*Crystal data.* $[\mathrm{C_{29}H_{35}NP^+}]_2\cdot\mathrm{HgI_4}^{2-}$, $M = 1\,565$, pale yellow monoclinic crystals, $a = 24.383(6)$, $b = 12.999(3)$, $c = 23.192(4)$ Å, $\beta = 126.184(18)°$, $U = 5\,933$ Å^3, $D_o = 1.77$, $D_c = 1.75$ g cm^{-3}, $Z = 4$. Space group $C2/c$ (No. 15), Mo-K_α radiation, $\lambda = 0.710\,69$ Å, $\mu = 48.5$ cm^{-1}.

Structure determination. Unit-cell dimensions and intensity data were measured on a Nonius CAD 4 diffractometer. A crystal of dimensions 0.5 × 0.5 × 0.7 mm was used with zirconium-filtered Mo-K_α radiation. Of 2 957 unique reflections measured to $2\theta_{max.} = 50°$, 2 506 had $I > 3\sigma(I)$ where σ is the standard deviation of the background corrected count. An empirical absorption correction was applied.

The MULTAN-77 [7] system was used to locate the mercury atom and the two crystallographically independent iodine atoms.

All other non-hydrogen atoms were located from subsequent difference-Fourier maps. After full least-squares refinement using SHELX [8] with mercury, iodine, and phosphorus atoms anisotropic and all carbon atoms included in the structure, all hydrogen atoms could be located with reasonable certainty in Fourier-difference maps. Methyl group hydrogens were included and refined in the structure as rigid groups; all phenyl

TABLE 1

Fractional co-ordinates of atoms * with standard deviations

	x	*y*	*z*
Hg	0.5000	0.221 99(4)	0.2500
I(1)	0.512 03(3)	0.074 95(5)	0.168 66(3)
I(2)	0.396 34(3)	0.359 62(5)	0.157 98(3)
P(1)	0.119 6(1)	0.232 2(2)	0.070 8(1)
C(1)	0.062 7(4)	0.234 7(7)	−0.028 4(4)
H(2)	0.061 4(48)	0.308 3(59)	−0.042 2(49)
H(1)	0.088 2(45)	0.201 6(71)	−0.043 1(49)
C(2)	−0.006 0(5)	0.196 3(7)	−0.063 1(5)
N(1)	−0.060 5(4)	0.170 4(7)	−0.091 4(4)
C(11)	0.064 4(4)	0.211 7(6)	0.098 5(4)
C(12)	0.009 4(4)	0.279 6(6)	0.071 8(4)
C(13)	−0.035 8(4)	0.263 9(7)	0.088 4(4)
C(14)	−0.027 2(4)	0.183 7(7)	0.132 9(5)
C(15)	0.028 3(4)	0.120 3(7)	0.160 9(4)
C(16)	0.075 6(4)	0.132 3(6)	0.146 0(4)
C(19)	0.136 2(4)	0.061 1(7)	0.185 5(4)
C(17)	−0.004 7(4)	0.375 1(7)	0.025 8(5)
C(18)	−0.078 6(5)	0.166 3(9)	0.148 7(6)
C(21)	0.158 3(4)	0.359 1(6)	0.094 9(4)
C(22)	0.181 3(4)	0.400 6(6)	0.056 0(4)
C(23)	0.200 0(4)	0.503 0(7)	0.066 0(5)
C(24)	0.198 6(5)	0.565 4(7)	0.113 7(5)
C(25)	0.181 4(4)	0.522 0(7)	0.155 3(5)
C(26)	0.162 8(4)	0.420 1(6)	0.148 2(4)
C(29)	0.154 0(5)	0.380 3(7)	0.204 0(5)
C(27)	0.189 5(4)	0.340 0(7)	0.006 1(4)
C(28)	0.216 5(6)	0.679 3(9)	0.119 8(6)
C(31)	0.182 5(4)	0.133 8(6)	0.095 0(4)
C(36)	0.252 3(4)	0.151 9(6)	0.148 1(4)
C(35)	0.298 5(5)	0.081 7(7)	0.153 8(5)
C(34)	0.278 5(4)	−0.006 3(7)	0.111 3(5)
C(33)	0.210 2(4)	−0.025 0(7)	0.063 4(5)
C(32)	0.161 9(4)	0.041 8(6)	0.055 4(4)
C(37)	0.088 5(4)	0.008 0(7)	0.004 3(5)
C(39)	0.282 3(4)	0.236 7(7)	0.202 7(4)
C(38)	0.330 4(5)	−0.079 7(8)	0.119 0(6)

* The $\mathrm{PCH_2CN}$ unit is numbered P(1), C(1), H(1), H(2), C(2), and N(1), respectively. Carbon atoms in the trimethylphenyl groups are numbered C(ab), where a denotes the ring number (1—3) and b the position in the ring (1—6). The proximal *ortho*-methyl carbons are C(a7), the distal *ortho*-methyl carbons are C(a9), and the *para*-methyl carbons are C(a8). Hydrogen atoms in the trimethylphenyl groups are numbered H(abc), where ab refers to the numbering of the carbon atom to which the hydrogen atom is bonded, and c the number of the hydrogen atom on that carbon (1—3).

TABLE 2

Bond lengths (Å)					
Hg(1)–I(1)	2.819 3(8)				
Hg(1)–I(2)	2.788 5(6)				
C(1)–C(2)	1.453(14)				
C(2)–N(1)	1.131(14)				
P(1)–C(1)	1.857(8)				
P(1)–C(11)	1.821(12)	P(1)–C(21)	1.817(8)	P(1)–C(31)	1.813(9)
C(11)–C(12)	1.407(12)	C(21)–C(22)	1.420(16)	C(31)–C(32)	1.408(11)
C(12)–C(13)	1.380(18)	C(22)–C(23)	1.382(12)	C(32)–C(33)	1.385(15)
C(13)–C(14)	1.393(14)	C(23)–C(24)	1.388(17)	C(33)–C(34)	1.372(12)
C(14)–C(15)	1.376(13)	C(24)–C(25)	1.379(19)	C(34)–C(35)	1.397(13)
C(15)–C(16)	1.394(17)	C(25)–C(26)	1.378(12)	C(35)–C(36)	1.394(15)
C(11)–C(16)	1.414(12)	C(21)–C(26)	1.417(14)	C(31)–C(36)	1.412(10)
C(17)–C(12)	1.538(13)	C(27)–C(22)	1.508(16)	C(37)–C(32)	1.515(11)
C(18)–C(14)	1.516(21)	C(28)–C(24)	1.526(15)	C(38)–C(34)	1.509(17)
C(19)–C(16)	1.510(11)	C(29)–C(26)	1.522(17)	C(39)–C(36)	1.503(12)
Bond angles (°)					
I(1)–Hg(1)–I(2)	109.18(2)				
I(1)–Hg(1)–I(1′)	94.59(3)				
I(1)–Hg(1)–I(2′)	122.79(2)				
I(2)–Hg(1)–I(2′)	100.20(2)				
C(1)–C(2)–N(1)	177.1(10)				
P(1)–C(1)–C(2)	117.0(10)				
C(1)–P(1)–C(11)	105.8(4)	C(1)–P(1)–C(21)	103.7(4)	C(1)–P(1)–C(31)	105.8(4)
C(11)–P(1)–C(21)	112.5(4)	C(11)–P(1)–C(31)	117.0(4)	C(21)–P(1)–C(31)	110.8(4)
P(1)–C(11)–C(12)	117.6(7)	P(1)–C(21)–C(22)	118.5(7)	P(1)–C(31)–C(32)	119.1(5)
P(1)–C(11)–C(16)	122.6(7)	P(1)–C(21)–C(26)	122.3(8)	P(1)–C(31)–C(36)	121.1(6)
C(11)–C(12)–C(17)	125.2(10)	C(21)–C(22)–C(27)	124.8(7)	C(31)–C(32)–C(37)	123.9(9)
C(13)–C(12)–C(17)	115.1(8)	C(23)–C(22)–C(27)	116.9(11)	C(33)–C(32)–C(37)	116.2(7)
C(13)–C(14)–C(18)	120.4(9)	C(23)–C(24)–C(28)	120.0(12)	C(33)–C(34)–C(38)	121.1(9)
C(15)–C(14)–C(18)	121.3(10)	C(25)–C(24)–C(28)	121.4(11)	C(35)–C(34)–C(38)	121.0(7)
C(11)–C(16)–C(19)	126.1(10)	C(21)–C(26)–C(29)	125.0(7)	C(31)–C(36)–C(39)	126.4(9)
C(15)–C(16)–C(19)	115.9(8)	C(25)–C(26)–C(29)	115.3(9)	C(35)–C(36)–C(39)	115.8(7)
Torsion angles (°)					
		C(2)–C(1)–P(1)–C(11)	−14.8		
		C(2)–C(1)–P(1)–C(21)	−133.3		
		C(2)–C(1)–P(1)–C(31)	110.0		
Non-bonded distances (Å)					
P(1)–C(17)	3.16	P(1)–C(27)	3.18	P(1)–C(37)	3.17
C(1)–C(17)	3.17	C(1)–C(27)	3.03	C(1)–C(37)	3.02
C(2)–C(17)	3.09	C(2)–C(27)	4.45	C(2)–C(37)	3.08
N(1)–C(17)	3.46	N(1)–C(27)	5.56	N(1)–C(37)	3.61
C(2)–C(11)	3.07	C(2)–C(21)	4.08	C(2)–C(31)	3.92
N(1)–C(11)	3.62	N(1)–C(21)	5.09	N(1)–C(31)	4.88
C(17)–C(21)	3.30	C(27)–C(31)	3.45	C(37)–C(11)	3.69
C(19)–C(31)	3.06	C(29)–C(11)	3.04	C(39)–C(21)	3.00
C(19)–C(29)	4.17	C(19)–C(39)	4.05	C(29)–C(39)	3.66
Intermolecular non-bonded distances (Å)					
I(1)–C(1)	3.61	I(1)–H(351)	2.97		
I(1)–H(2)	2.81	I(2)–H(1)	3.01		
I(1)–H(172)	3.06	I(2)–H(183)	2.98		
I(1)–H(273)	3.31	I(2)–H(272)	3.32		
I(1)–H(292)	3.04	I(2)–H(392)	3.09		

hydrogen atoms were included in the structure assuming idealised positions; H(1) and H(2) were refined independently with the C–H bond length constrained to 1.08 Å.

The weighting scheme applied in the last few cycles was: $F_o < 90$, $\omega^{-1} = 1 + 0.000\,013(90 - F_o)^2$; and $F > 90$, $\omega^{-1} = 1 + 0.000\,025(F_o - 90)^2$. The final R factor was 0.031 ($R_\omega = 0.033$).

Positional parameters of atoms are given in Table 1, and pertinent bond length, bond angles, torsion angles, non-bonded distances, and intermolecular non-bonded distances are given in Table 2. Tables of positional parameters of hydrogen atoms, vibrational parameters and calculated structure amplitudes have been deposited as Supplementary Publication No. SUP 23067 (17 pp.).*

Views of the cation are shown in the Figure. All P–C bonds are of normal length, *viz.* 1.86 Å for P(1)–C(1) *versus* 1.88 Å for $Ph_3\overset{+}{P}CH_2CH_3$ [9] and 1.84 Å for $Ph_3\overset{+}{P}CH_2Ph$,[10] and 1.83 Å for P(1)–C_{aryl} *versus* 1.78 Å for $Ph_3\overset{+}{P}CH_2CH_3$,[9] 1.82 Å for $Ph_3\overset{+}{P}CH_2Ph$,[10] and 1.78—1.80 Å for $Ph_3\overset{+}{P}CH_3$.[11] The P(1)–C_{aryl} bond lengths are also similar to those reported for Ph_3P (1.83 Å),[12] and Mes_3P (1.84 Å).[13] The average C–Me bond length (1.52 Å) is not significantly different from those reported for Mes_3P [13] and Mes_3CH.[14]

The geometry at P is slightly distorted from a regular tetrahedral shape, C(1)–P(1)–C_{aryl} being slightly reduced (105°) and C_{aryl}–P(1)–C_{aryl} being slightly enlarged (113°); compare with $Ph_3\overset{+}{P}CH_3$,[11] $Ph_3\overset{+}{P}CH_2CH_3$,[9] and $Ph_3\overset{+}{P}CH_2Ph$ [10] which have a regular tetrahedral shape, Mes_3P has C_{aryl}–P–C_{aryl} 109.5°,[13] while Mes_3CH is slightly more flattened (C_{aryl}–C–C_{aryl} 116°).[14] All C_{aryl}–C_{aryl}–Me_{ortho} angles are distorted, and the *ortho*-methyl carbon atoms are significantly displaced from the mean planes of the phenyl rings to which they are

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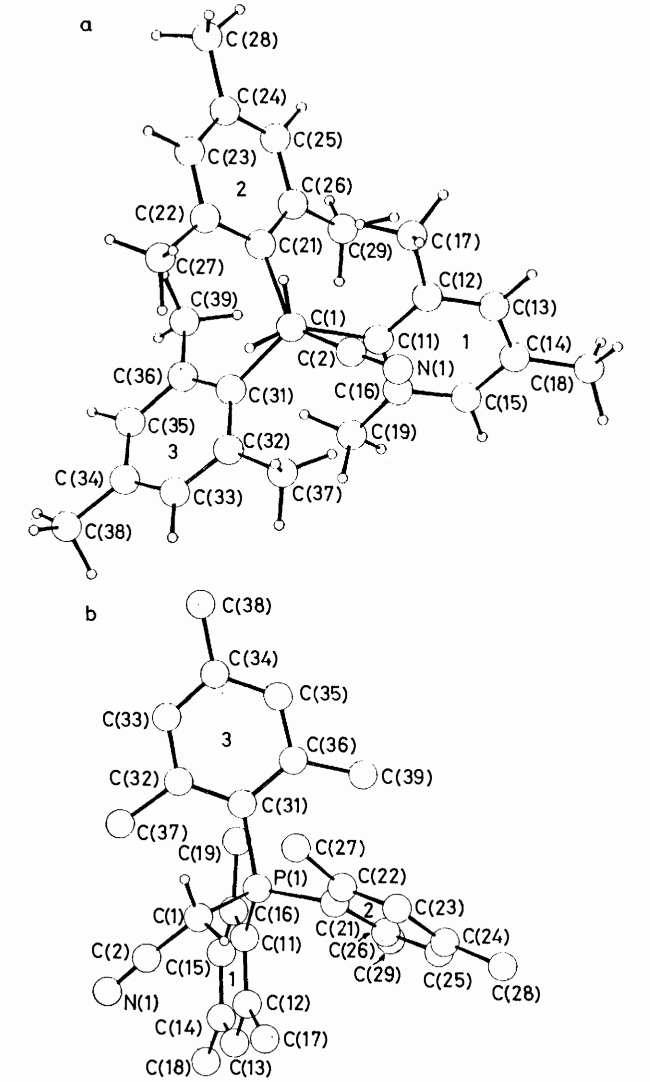
* For details of Supplementary Publications see Notice to Authors No. 7 in *J. Chem. Soc., Perkin Trans. 2*, 1980, Index issue.

bonded: C(17) 0.116, C(19) 0.135, C(27) 0.165, C(29) 0.251, C(37) 0.150, and C(39) 0.188 Å.

The cation adopts a distorted propeller shape, with ring 1 being more twisted (53.2°) than rings 2 and 3 (45.7 and 43.8°, respectively).* A survey of related structures suggests that the degree of twist is very dependent upon crystal packing forces. Mes_3CH has C_3 symmetry with a twist angle of 38°.[14] Mes_3P has two symmetry unrelated molecules per unit cell; one has approximate C_3 symmetry and a twist angle of *ca.* 45°, the other deviates significantly from C_3 symmetry with twist angles of 50, 43, and 38°.[13] $Ph_3\overset{+}{P}CH_3$ exists as a distorted propeller with the P–CH_3 bond being almost coplanar with one of the rings;[11b] however the shape adopted by $Ph_3\overset{+}{P}CH_3$ probably depends upon the nature of the counter ion. Ph_3P also deviates significantly from C_3 symmetry with twist angles of 60, 27, and 24° (calculated from data in ref. 12). $(o\text{-}MeC_6H_4)_3P$ also has two symmetry unrelated molecules per unit cell, one being closer to C_3 symmetry than the other (twist angles 47, 46, and 41° *versus* 49, 43, and 37°); in both molecules all methyl groups are proximal to the orbital of the lone-pair electrons.[15]



a, View of $Mes_3\overset{+}{P}CH_2CN$ looking along C(1)–P(1) bond. b, View of $Mes_3\overset{+}{P}CH_2CN$ looking perpendicular to ring 3 [hydrogen atoms except H(1) and H(2) omitted]

Although C(2) lies closer to C(11) than to C(21) and C(31) [the torsion angle C(2)–C(1)–P(1)–C(11) is −14.8°], due to the lower twist of ring 3 there are significant non-bonded interactions between the CN group and both rings 1 and 3, the most severe being those involving the proximal † methyl groups, C(17) and C(37), and C(2). Other severe interactions involve all three proximal methyl groups C(17), C(27), C(37) with C(1) and P(1) and all three distal † methyl groups, C(19), C(29), and C(39) with C(31), C(11), and C(21), respectively. The mean distance between C(19) and C(31), C(29) and C(11), and C(39) and C(21) (3.03 Å) is comparable with that for Mes_3CH (3.00 Å),[14] and Mes_3P (3.02 and 3.06 Å).[13] The mean distance between C(17) and C(21), C(27) and C(31), and C(37) and C(11) (3.48 Å) is larger than that for Mes_3CH (3.27 Å),[14] but comparable to that for Mes_3P (3.46 and 3.47 Å).[13]

Dynamic Stereochemistry.—Stereoisomerisation. The temperatures at which coalescence of the two singlets for the diastereotopic *ortho*-methyl groups, and for the diastereotopic *meta*-hydrogen atoms occurs were measured for Mes_3P, $Mes_3\overset{+}{P}CH_3$ BF_4^-, $Mes_3\overset{+}{P}CH_2CN$ I^-, and $Mes_3\overset{+}{As}CH_3$ I^-. In order to calculate the rate constant for enantiomerisation (k_{en}) it was assumed that all four systems produce signal averaging by three consecutive two-ring flip processes,[1,2] as shown by Mislow *et al.* to occur for Mes_3CH.[3] The coalescence temperature gives $k_{coalescence}$ (k_c), which is the overall rate constant for three consecutive steps. Since only one two-ring flip is required to enantiomerise the helicity of the molecular propeller (the threshhold mechanism), $k_{en} = 3k_c$. The activation energy for enantiomerisation, $\Delta G_{T_c}^{\ddagger}$, (the threshhold barrier) at the coalescence temperature was calculated from k_{en}. The relevant data are given in Table 3. There is good agreement between the $\Delta G_{T_c}^{\ddagger}$ values calculated from both the *ortho*-methyl signals and the *meta*-hydrogen signals, although the former are considered to be more accurate due to the larger $\Delta\nu$ involved. For completeness, the results of other workers for Mes_3CH,[3a] Mes_3P,[5] and Mes_3As[5] are included in Table 3. Our value of $\Delta G_{T_c}^{\ddagger}$ for Mes_3P is lower than that reported (12.4 kcal mol^{-1});[5] however the reported value was calculated using $k_c/3$, not k_{en}.[16,17] A recalculation of the reported data *via* k_{en} gives 11.4 kcal mol^{-1}. A similar correction for Mes_3As gives 8.0 kcal mol^{-1}.

Empirical force-field calculations on Mes_3CH have revealed[3b] that in the transition state for the two-ring

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* The twist angle is defined as the angle between the mean plane of a phenyl ring and the plane defined by the central atom, the carbon atom of the phenyl group attached to the central atom, and C(1) (H in the case of Mes_3CH; the centre of gravity of the plane of the three carbon atoms attached to the central atom in the case of Ar_3P).

† Relative to CH_2CN.

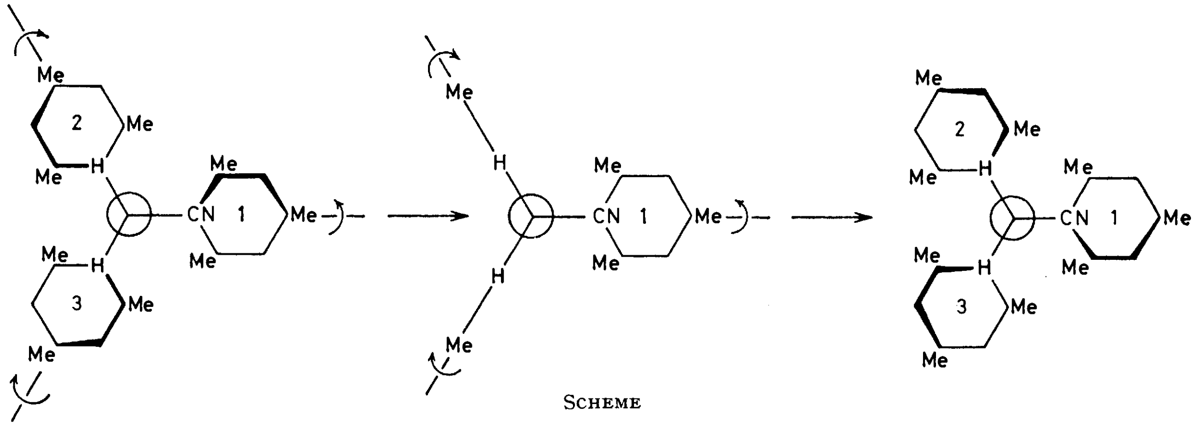
TABLE 3

Coalescence temperatures and $\Delta G^{\ddagger}$ values for some $\mathrm{Mes_3ZX}$ systems

Compound (solvent)	$\Delta\nu_{o\text{-Me}}$/ Hz	$T_c(o\text{-Me})$/ °C	k_{en} [a]/ s^{-1}	$\Delta G_{T_c}^{\ddagger}$ [b]/ kcal mol^{-1}	$\Delta\nu_{m\text{-H}}$/ Hz	$T_c(m\text{-H})$/ °C	k_{en} [a]/ s^{-1}	$\Delta G_{T_c}^{\ddagger}$ [b]/ kcal mol^{-1}
$\mathrm{Mes_3CH}$ ($\mathrm{C_4Cl_6}$) [c]	17	167	113	21.9				
$\mathrm{Mes_3P}$ ($\mathrm{CDCl_3}$) [d, e]	44	−38	293	11.0	13	−53	87	10.8
$\mathrm{Mes_3\overset{+}{P}CH_3\ BF_4^-}$ ([$^2H_6$]DMSO) [d, f]	40	91	266	17.4	18	78	120	17.3
$\mathrm{Mes_3\overset{+}{P}CH_2CN\ I^-}$ ([$^2H_6$]DMSO) [d]	46	113	306	18.4	17	97	113	18.3
$\mathrm{Mes_3As}$ ($\mathrm{CS_2}$) [g]		−101		8.8				
$\mathrm{Mes_3\overset{+}{As}CH_3\ I^-}$ ($\mathrm{CDCl_3}$) [h]	37	25	246	14.2	13	10	87	14.0

[a] $k_{en} = k_{\text{enantiomerisation}} = 3k_{\text{coalescence}}$ (assumes two-ring flip mechanism, see ref. 3*a*); $k_{\text{coalescence}} = \pi\Delta\nu/\sqrt{2}$. [b] $\Delta G^{\ddagger}$ for enantiomerisation $= -RT_c \ln(k_{en}h/T_ck)$. [c] Ref. 3*a*. [d] With ^{31}P decoupling. [e] lit.,[5] T_c (*o*-Me) −35 °C, $\Delta G^{\ddagger}_{-35}$ 12.4 kcal mol^{-1} (in $\mathrm{CDCl_3}$) (see Discussion section). [f] For the corresponding iodide, $\Delta G^{\ddagger}_{74}$ 17.1 kcal mol^{-1}. [g] Ref. 5 (see Discussion section). [h] Ref. 6.

flip mechanism, the most severe non-bonded interactions are between the pairs of proximal and distal *ortho*-methyl groups of the flipping rings, and their associated ring carbon atoms, and between the *ortho*-methyl groups of the non-flipping ring and the region around the carbon atoms attached to the central atom in the flipping rings (see Figures 9—11 of ref. 3*b*). Any lengthening of the bonds between the rings and the central atom should relieve these interactions and thus lower the energy of the transition state.* (The ground-state energy will probably also be lowered, but less so.) The general trend observed for $\Delta G_{T_c}^{\ddagger}$, $\mathrm{Mes_3CH} > \mathrm{Mes_3\overset{+}{P}CH_2CN}$, $\mathrm{Mes_3\overset{+}{P}CH_3} > \mathrm{Mes_3\overset{+}{As}CH_3} > \mathrm{Mes_3P} > \mathrm{Mes_3As}$, can be largely attributed to such a lengthening of the central bonds. The central bonds in representative members of the series are 1.54 for $\mathrm{Mes_3CH}$,[14] 1.83 for $\mathrm{Mes_3\overset{+}{P}CH_2CN}$, 1.84 for $\mathrm{Mes_3P}$,[13] and 1.99 Å for $\mathrm{(2,5\text{-}Me_2C_6H_3)_3As}$.[19] The differences between the phosphine and the phosphonium cations, and between the arsine and the arsonium cation, can be attributed to the extra non-bonded interactions between the proximal *ortho*-methyl groups in the two flipping rings and the introduced group, with the introduction of a fourth group ($\mathrm{CH_3}$) having a larger effect ($\Delta\Delta G_{T_c}^{\ddagger}$ 6.4 for $\mathrm{Mes_3P \longrightarrow Mes_3\overset{+}{P}CH_3}$, and 5.4 kcal mol^{-1} for $\mathrm{Mes_3As \longrightarrow Mes_3\overset{+}{As}CH_3}$) than changing the central atom, and hence the central bond length ($\Delta\Delta G_{T_c}^{\ddagger}$ 2.2 for $\mathrm{Mes_3As \longrightarrow Mes_3P}$, and 3.2 kcal mol^{-1} for $\mathrm{Mes_3\overset{+}{As}CH_3 \longrightarrow Mes_3\overset{+}{P}CH_3}$).



SCHEME

The slightly larger $\Delta G_{T_c}^{\ddagger}$ value for $\mathrm{Mes_3\overset{+}{P}CH_2CN}$ *versus* $\mathrm{Mes_3\overset{+}{P}CH_3}$ no doubt arises because of the extra non-bond intereactions created by replacing H by CN. However, examination of the conformation adopted by $\mathrm{Mes_3\overset{+}{P}CH_2CN}$ in the crystalline state, with the CN group closer to ring 1 than rings 2 and 3, and ring 1 more twisted than the other two (see Figure), suggests that the $\mathrm{Mes_3\overset{+}{P}CH_2CN}$ may enantiomerise by a two-ring flip mechanism in which CN is positioned over ring 1, while rings 2 and 3 flip. The enantionerisation is completed by simultaneous rotation of ring 1 (see Scheme). Such a mechanism allows the CN group to avoid severe non-bond interactions with the proximal *ortho*-methyl groups of rings 2 and 3 in the transition state. In fact the transition state in this case would not be greatly different from that for $\mathrm{Mes_3\overset{+}{P}CH_3}$, any differences arising from a restriction of the free rotation about P(1)–C(1) and small non-bonded interactions with ring 1. We hope to explore this situation further using molecular mechanics calculations. The mechanism as shown in the Scheme, while effecting enantiomerisation of the propeller, only interchanges the magnetic environment of the *ortho*-methyl groups and the *meta*-hydrogen atoms on ring 1. To achieve site exchange of all *ortho*-methyl groups and *meta*-hydrogen atoms, there have to be two more two-ring flip processes, the second with CN over ring 2 (or 3) with flipping of rings 1 and 3 (or 2), the third with CN over ring 3 (or 2) with flipping of rings 1 and 2 (or 3).

In the context of mechanisms of enantiomerisation of

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* This argument is supported by empirical force-field calculations on model systems.[18] Using $\mathrm{Mes_3CH}$ as a base, the length of the central bond was increased in stages from 1.43 to 2.11 Å. As the bond length increased, so the $\Delta G^{\ddagger}$ for the two-ring flip process decreased, and for each stage the two-ring flip process remained the threshold mechanism for enantiomerisation.

molecular propellers, an interesting situation is reported [11f] for methyltriphenylphosphonium bis-7,7,8,8-tetracyanoquinodimethide $[Ph_3PCH_3]^+[TCNQ]_2^{\cdot-}$. In the crystalline state, the cation exists as a distorted propeller with the P–CH$_3$ bond almost coplanar with one of the phenyl rings. The other two rings are inclined to the P–CH$_3$ bond, the angle of twist being dependent upon temperature. Below 42.7 °C, the angles of twist are −19 and −67°, respectively. At 42.7 °C there is a phase transition, and above this temperature the cation exists in two configurations, one (10%) with the same configuration as in the low-temperature phase (twist angles −20 and −49°) and the other (90%) with the opposite configuration, with twist angles 37 and 68°. The mechanism by which the configuration in the low-temperature phase converts to the major configuration in the high-temperature phase is not clear, but it is tempting to suggest that with one phenyl ring coplanar with the P–CH$_3$ bond, the other, least twisted ring moves towards coplanarity also, and the most twisted ring moves towards a twist angle of 90°, *i.e.* towards the transition state for the two-ring flip mechanism. Subsequently one of the coplanar rings and the perpendicular ring rotate to produce the inverted propeller.

EXPERIMENTAL

Tris-(2,4,6-*trimethylphenyl*)*phosphine*.—The phosphine was prepared from bromomesitylene and phosphorus trichloride by the method of Stepanov *et al.*[20] It had m.p. 195—199 °C (lit.,[20] 192—193 °C), and its i.r. spectrum was identical to that reported;[20] δ ($CDCl_3$; 30 °C) 2.0 (s, 2 *ortho*-Me), 2.20 (s, *para*-Me), 6.74 (2 H, unsym. d, $J_{H,P}$ 4 Hz, *meta*-H); irradiation of the ^{31}P absorption caused the doublet at δ 6.74 to collapse to a singlet, and the singlet at 2.02 to sharpen; δ (−66 °C; ^{31}P decoupled) 1.78 (s, *ortho*-Me), 2.22 (s, *ortho*-Me + *para*-Me), 6.72 (s, *meta*-H), and 6.85 (s, *meta*-H) [lit.,[1] δ ($CDCl_3$) 2.15 (*ortho*-Me), 2.31 (*para*-Me), and 7.15]; for ^{13}C and ^{31}P n.m.r. spectra see Table 4; *m/e* 388 (*P*), 373 ($P - CH_3$), 253 (Mes_2Me), and 238 (Mes_2).

Methyltris-(2,4,6-*trimethylphenyl*)*phosphonium Iodide and Fluoroborate*.—Tris-(2,4,6-trimethylphenyl)phosphine (0.5 g) in methyl iodide (5.0 ml) was heated under reflux during 6 h. Methyl iodide was evaporated to give a light yellow solid (0.63 g), which was purified by dissolving in ethanol and adding ether, m.p. 315—317 °C (lit.,[20] 314—317 °C) (Found: C, 63.25; H, 7.0. Calc. for $C_{28}H_{36}IP$: C, 63.4; H, 6.85%), δ ($CDCl_3$; 30 °C) 1.92 (s, *ortho*-Me), 2.34 (s, *ortho*-Me + *para*-Me), 2.90 (d, $J_{H,P}$ 11 Hz, P-CH$_3$), and 6.94br and 7.14br (2 d, *J* 4 Hz, 2 *meta*-H); irradiation of the ^{31}P absorption caused the doublets at δ 2.90, 6.94, and 7.14 to collapse to singlets; δ ([$^2H_6$]DMSO; ^{31}P decoupling; 30 °C) 1.90 (s, *ortho*-Me), 2.30 (s, *ortho*-Me), 2.36 (s, *para*-Me), 2.95br (s, P-CH$_3$), 7.12br and 7.30br (s, *meta*-Hs); at 114 °C, the singlets at δ 1.90 and 2.30, and at 7.12 and 7.30, had collapsed to singlets at δ 2.12 and 7.18 respectively; for ^{13}C and ^{31}P n.m.r. spectra see Table 4; *m/e* 389 (Mes_3PH, $P - CH_2I$) was the only significant peak.

The iodide (0.2 g) was dissolved in a minimum amount of ethanol and 40% aqueous fluoroboric acid (0.35 ml; 4 equiv.) was added. Ether was added to precipitate the salt, which was isolated, washed with ether, and purified by disolving in hot ethanol and adding ether. The fluoroborate (0.114 g), m.p. 320—323 °C, was a white powder, mixed m.p. with the iodide, 313—320 °C. Tests for iodide were negative. The ^1H n.m.r. spectrum ([$^2H_6$]DMSO; ^{31}P decoupling) was identical to that of the iodide, δ_F ([$^2H_6$]-DMSO; $CFCl_3$ reference) −148.100 (septet, $J_{F,^{10}B}$ 0.37 Hz, ^{10}B *ca.* 20%), and −148.154 (q, $J_{F,^{11}B}$ 1.15 Hz, ^{11}B *ca.* 80%), $\nu_{max.}$ (Nujol) 1 095 and 1 055 cm^{-1} (BF_4^-).

Cyanomethyltris-(2,4,6-*trimethylphenyl*)*phosphonium Iodide*.—The phosphine (0.5 g) and iodoacetonitrile (2.5 ml; Aldrich Chemical Co.) were heated at 110 °C during 4.5 h. The excess of iodoacetonitrile was evaporated under high vacuum at 100 °C to give a dark residue which was dissolved

TABLE 4

^{13}C and ^{31}P chemical shifts for Ar_3P, $Ar_3\overset{+}{P}CH_3$, and $Ar_3\overset{+}{P}CH_2CN$ (Ar = Ph, Mes)

	^{13}C, δ (p.p.m. from Me_4Si) ($J_{C,P}$/Hz)									^{31}P, δ (p.p.m. from 80% aqueous H_3PO_4)
Compound (solvent)	C(1)	C(2)	C(3)	C(4)	*o*-Me	*p*-Me	CH_3	CH_2	CN	
Ph_3P ($CDCl_3$) [a]	137.03	133.49	128.25	128.44						−4.98
	(11.0)	(18.9)	(6.7)							
Mes_3P ($CDCl_3$)	131.52	142.56	129.65	137.41	22.68	20.86				−35.61
	(18.3)	(18.4)			(16.6)					
$Ph_3\overset{+}{P}CH_3$ Br^- ($CDCl_3$) [b]	118.21	132.88	129.70	134.38			10.04			21.41
	(88.6)	(10.7)	(12.9)	(2.9)			(56.8)			
$Mes_3\overset{+}{P}CH_3$ I^- ($CDCl_3$) [c, d]	119.33	143.10	132.60	144.52	23.67	20.58	26.21			7.75
	(79.4)	(11.3)	(11.3)	(3.5)	(5.2)		(62.8)			
		142.63	132.38		23.27					
		(10.5)	(11.3)		(6.1)					
$Ph_3\overset{+}{P}CH_2CN$ Br^- ([$^2H_6$]DMSO)	116.27	133.80	130.54	135.98				14.73	112.83	21.12
	(88.7)	(10.9)	(13.1)	(2.5)				(55.1)	(9.4)	
$Mes_3\overset{+}{P}CH_2CN$ I^- ([$^2H_6$]DMSO) [c, e]	116.95	144.32	132.92	145.37	23.60	20.62		25.38	115.09	10.56
	(78.5)	(10.5)	(12.2)	(2.6)	(4.4)			(62.8)	(8.7)	
		144.15	132.68		23.25					
		(11.3)	(11.3)		(5.2)					

[a] In agreement with reported spectra.[21,22] [b] In agreement with reported spectra.[21,23] [c] Spectrum recorded at $T \ll T_c$. Therefore, diastereotopic carbon atoms C(2),C(6), C(3),C(5), and *o*-Me groups exhibit separate absorptions. Multiple absorptions arising from restricted rotation (chemical shift differences) and from coupling to phosphorus were differentiated by running the spectra at 20 and 360 MHz. [d] Assignment of C(2) and C(3), based on relative intensities. [e] Assignment of C(2) and C(3), same relative intensity, but as for $Mes_3\overset{+}{P}CH_3$ I^-, one group of signals is in approximately the same position as C(2) in Mes_3P, and other group is in approximately the same position as C(3) in Mes_3P; the C(2) and C(3) absorptions in Ph_3P, $Ph_3\overset{+}{P}CH_3$ Br^-, and $Ph_3\overset{+}{P}CH_2CN$ Br^- also remain approximately constant *viz.* 132—134 and 128—131, respectively.

in nitromethane (5 ml) and precipitated with ether. The solid was isolated, washed with acetone (5 ml), filtered off, and washed with more acetone (2—3 ml). The light coloured residue was dissolved in hot nitromethane, the solution was filtered, and ether was added to precipitate cyanomethyltris-(2,4,6-trimethylphenyl)phosphonium iodide (0.5 g), as an off-white powder, m.p. 253.5—254.5 °C (Found: C, 59.45, 59.55; H, 5.95, 6.15; N, 2.5, 2.55. Calc. for $C_{29}H_{35}INP$: C, 62.7, H, 6.35; N, 2.5%). Due to the poor agreement between the observed analytical data and those expected the product was recrystallised slowly (4 weeks) from nitromethane to give yellow crystals, m.p. 267—268.5 °C (Found: C, 44.3, 44.3; H, 4.55, 4.59; N, 2.05, 2.1%). An *X*-ray structure determination on the yellow crystals indicated they had the molecular formula $[Mes_3\overset{+}{P}CH_2CN]_2{\cdot}HgI_4^{2-}$ ($C_{58}H_{70}HgI_4N_2P_2$ requires C, 44.5; H, 4.51; N, 1.8%). *X*-Ray fluorescence spectroscopy confirmed the presence of mercury. Analysis of the iodoacetonitrile used in the preparation by atomic absorption spectroscopy gave 0.20% mercury (see below). Assuming that the phosphonium salt initially isolated contained only I^- and HgI_4^{2-} as the counter ions, the average analytical data indicate that these were present in the ratio 82.5% I^-, 17.5% HgI_4^{2-}. Recrystallisation from nitromethane had given the HgI_4^{2-} salt selectively.

The ' iodide ' was converted to the corresponding *fluoroborate* as described above for $Mes_3\overset{+}{P}CH_3\ I^-$. The product had m.p. 284—286.5 °C (crystals from nitromethane) (Found: C, 67.85; H, 6.9; N, 2.65. $C_{29}H_{35}BF_4NP$ requires C, 67.6; H, 6.85; N, 2.7%).

The ' iodide ' had the following spectroscopic properties: δ ([$^2H_6$]DMSO; 30 °C) 1.92 (s, *ortho*-Me), 2.38 (s, *ortho*-Me + *para*-Me), 5.30 (d, $J_{H,P}$ 12 Hz, CH_2), 7.19 and 7.36 (2 d, *J* 4 Hz, 2 *meta*-H); irradiation of the ^{31}P absorption caused the doublets at δ 5.30, 7.19, and 7.36 to collapse to singlets; at 135 °C (with ^{31}P irradiation) the singlets at δ 1.92 and 2.38, and at 7.19 and 7.36, collapsed to singlets at δ 2.16 and 7.27, respectively (the *para*-Me singlet remained at 2.38); for ^{13}C and ^{31}P n.m.r. spectra see Table 4; *m/e* 388 (Mes_3P) and 373 ($Mes_3P - CH_3$).

Cyanomethyltris(2,4,6-*trimethylphenyl*)*phosphonium Tetraiodomercurate*(II) $[Mes_3\overset{+}{P}CH_2CN]_2{\cdot}HgI_4^{2-}$.—The ' iodide ' (56 mg) in hot ethanol was treated with mercury(II) iodide (23 mg, 0.5 equiv.) in hot ethanol. On cooling a solid, probably the iodide, separated. The ethanol was evaporated and the residue was dissolved in a small quantity of hot nitromethane. On cooling, yellow crystals were isolated. After recrystallisation from nitromethane they had m.p. 266—268 °C (Found: C, 44.6; H, 4.55; N, 2.05. $C_{58}H_{70}HgI_4N_2P_2$ requires C, 44.5; H, 4.5; N, 1.8%).

Analysis of Iodoacetonitrile.—The source of the mercury found in the preparation of $Mes_3\overset{+}{P}CH_2CN\ I^-$ was shown to be the iodoacetonitrile (Aldrich Chemical Co.) * as follows. (i) Analysis for mercury in the ICH_2CN by atomic absorption spectroscopy showed (after acid digestion) 0.20% (0.11% without acid digestion). (ii) Mass spectrometry of ICH_2CN (at 130 °C) showed characteristic groups of peaks (Hg isotopes) around *m/e* 456 ($^{202}HgI_2$), 329 (^{202}HgI), 228 ($^{202}HgI_2^{2+}$), and 202 (^{202}Hg). The combined intensity of peaks around 456 was greater than that of the peak at 167 (ICH_2CN). (iii) One of four samples of ICH_2CN deposited a few red crystals of HgI_2 (identified by m.p., chemical tests, and *X*-ray powder diffraction).

When a 1.0 g sample of ICH_2CN was evaporated under high vacuum at 100 °C, the residue was < 1 mg (HgI_2 readily sublimes and would probably distil with the ICH_2CN).

Having established the presence of HgI_2 in the iodoacetonitrile, the formation of the HgI_4^{2-} salt can be rationalised as: $2\ Mes_3\overset{+}{P}CH_2CN\ I^- + HgI_2 \longrightarrow [Mes_3\overset{+}{P}CH_2CN]_2{\cdot}HgI_4^{2-}$.

We also examined each of the four samples of ICH_2CN by i.r. spectroscopy. All the spectra (liquid film) were similar and exhibited the expected characteristic bands, but only one had the bands at 1 730 and 1 270 cm^{-1} (both medium strong) which are present in the reported [24] spectrum of ICH_2CN. The band at 1 730 cm^{-1} has been assigned [24b] as an overtone of bands at 944 and 802 cm^{-1}. This assignment must be incorrect if it is absent from the spectra of three of our samples. We conclude that the sample which does contain these two bands, and the samples used for the reported spectra, are impure; the bands at 1 730 and 1 270 cm^{-1} are due to an impurity.

We thank Drs. B. M. Lowe and J. L. Casci for the *X*-ray powder diffraction measurements, and Professor J. Sandström for helpful discussions.

[1/134 *Received*, 29*th January*, 1981]

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* Iodoacetonitrile currently sold by Aldrich Chemical Co. does not contain mercury, personal communication.

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