Determination of the Molecular Structures of Tri(t-butyl)phosphine Oxide and Tri(t-butyl)phosphine Imide in the Gas Phase by Electron Diffraction

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The molecular structures of the oxide and imide of tri(t-butyl)phosphine in the gas phase have been determined by electron diffraction. For PBu^t_3O important parameters (r_a) are: r(P=O) 159.0(12), r(P–C) 188.8(6), r(C–C) 151.9(3) pm, OPC 106.1(5), and CCC 109.1(4)°. The butyl groups are tilted 3.1(8)° away from each other, and twisted 15.8(7)° away from the positions in a structure with C_{3v} symmetry, thus minimising steric interactions between the groups. For PBu^t_3NH important parameters are: r(P=N) 165.2(11), r(P–C) 191.3(6), r(C–C) 153.2(2) pm, NPC 109.6(7), and CCC 107.8(5)°, the tilt and twist angles of the butyl groups are −2.3(11) and 18.5(14)° respectively. The structures are such that the oxygen and imide group are sterically well protected from attack, thus accounting for the remarkable chemical and thermal stability of the compounds.

It has been widely observed that compounds featuring bulky substituents have unusual chemical properties. Often it has been found that large groups can be used to confer thermal or chemical stability on otherwise extremely reactive species. Thus, for example, the first stable disilene,[1] sila-alkene,[2] and dialkylphosphido-radical[3] all had substituents such as bis(trimethylsilyl)methyl, mesityl, or adamantyl. In the same way, the oxide, imide, and other derivatives of tri(t-butyl)phosphine are all unusually inert.[4] The imide is resistant to hydrolysis, and undergoes thermal decomposition only at 470 K, to give the free phosphine, while the oxide is stable to above 520 K. We have therefore studied these two compounds in the gas phase, to see how their remarkable chemical properties relate to their structures, and to compare their geometrical parameters with those of the unoxidised tri(t-butyl)phosphine.[5]

Experimental

A sample of tri(t-butyl)phosphine oxide was prepared by oxidation of the parent phosphine with hydrogen peroxide in the presence of an iodine catalyst, in diethyl ether solution.[4] Tri(t-butyl)phosphine imide was prepared by hydrolysis of $PBu^t_3(NSiMe_3)$ by sulphuric acid in methanol solution.[4] After purification by vacuum sublimation the purities of both samples were checked by i.r. and n.m.r. spectroscopy.

Electron-diffraction scattering intensities were recorded photographically in Oslo on Kodak Electron Image plates using a Balzers' KD.G2 apparatus,[6] with an accelerating voltage of 42 kV. The nozzle temperature was *ca.* 420 K for PBu^t_3O and *ca.* 415 K for PBu^t_3NH. In general, three plates at each camera distance were used, but only two good long-distance plates for PBu^t_3NH were available. Data were obtained in digital form using a Joyce-Loebl MDM6 computer-controlled densitometer at the S.E.R.C. Laboratory, Daresbury.[7] Calculations were carried out using standard least-squares refinement[8] and data-reduction[7] programs, modified to take into account the experimental details relating to the Balzers' apparatus. In Table 1 some experimental data are listed, including weighting points used in setting up the off-diagonal weight matrices, correlation parameters, scale factors, and electron wavelengths [determined from the scattering patterns of gaseous benzene and based on a C–C bond length of 139.75 pm (r_a)]. In all calculations the scattering factors of Schäfer *et al.*[9] were used.

Molecular Model.—For both molecules, it was assumed that there was three-fold symmetry for each C–CH_3 group, for each $C(CH_3)_3$ group, and for the PBu^t_3O or PBu^t_3N group. The structure of the oxide was then defined by the four different bonded distances, the valence angles OPC, CCC, and CCH, by twist angles for methyl and butyl groups, with zero twist representing a staggered conformation, and a tilt angle for the butyl groups. This last angle was defined as the angle between the local C_3 axis of the butyl group and the P–C bond, with a positive angle representing a tilt of the group towards the molecular C_3 axis. The observed negative tilt is therefore as expected, with the butyl groups tilted away from each other. For the imine three more parameters were required, to define the position of the extra hydrogen atom. These were the N–H bond length, PNH angle, and a CPNH dihedral angle.

Table 1. Weighting functions, correlation parameters, scale factors, and wavelengths

Compound	Camera height/mm	Δs	$s_{min.}$	sw_1	sw_2	$s_{max.}$	Correlation parameter	Scale factor	Wavelength/pm
		nm^{-1}							
PBu^t_3O	247.8	4	40	50	250	296	0.150	0.684(23)	5.871
	497.8	2	20	50	120	144	−0.240	0.625(19)	5.871
PBu^t_3NH	247.8	4	40	50	240	296	−0.194	0.808(25)	5.871
	497.8	2	20	50	120	148	−0.016	0.714(20)	5.871

Table 2. Portion of the least-squares correlation matrix for PBu^t_3O showing all elements ⩾ 50% (k_1 and k_2 are scale factors)

		Angle										
r_1	r_3	1	2	3	4	u_{29}	u_{30}	u_{31}	k_1	k_2		
	−66	−64							71	59	r_1	
			52	67							r_2	
					−83				−56	−55	1	Angle
								−82	−52	−74	3	
			−50				57				5	
56				−56				59	66	69	u_4	
50		−64			59	−52					u_6	
									60	79	u_{31}	
										71	k_1	

Table 3. Portion of the least-squares correlation matrix for PBu^t_3NH showing all elements ⩾50% (k_1 and k_2 are scale factors)

Angle											
2	3	4	u_4	u_6	u_{19}	u_{29}	u_{30}	k_1	k_2		
			53					68	55	r_1	
56	56									r_2	
		−61		−50						1	Angle
	83								−54	2	
				55					−54	3	
					65		55			6	
						50				u_2	
								67	59	u_4	
									63	k_1	

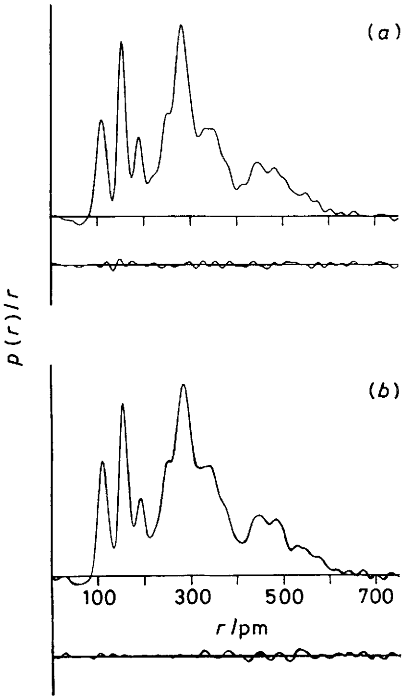

Figure 1. Observed and final difference radial distribution curves, $P(r)/r$, for (*a*) PBu^t_3O and (*b*) PBu^t_3NH. Before Fourier transformation the data were multiplied by $s \cdot \exp[-0.00002s^2/(Z_P - f_P)(Z_C - f_C)]$

Structure Refinement.—The radial distribution curves for the two compounds (Figure 1) are extremely similar, and the courses of the two refinements were therefore closely parallel. The four types of bonds give rise to three peaks, at *ca.* 110 (C–H), 155 (C–C and P=O or P=N, overlapping), and 190 pm (P–C), while the pairs of atoms separated by two bonds gave a shoulder at 215 pm (CCH) and peaks at 250(CCC), 280 (PCC and CPO or CPN, overlapping), and 310 pm (CPC). This clear separation of most of the peaks meant that it was a straightforward matter to refine the four main bond lengths and three valence angles for each molecule, and correlations between these parameters were not severe, despite the similarity of the C–C and P=O or P=N distances. Correlation matrices are given in Tables 2 and 3.

Although the geometrical parameters refined easily, it was necessary to fix some amplitudes of vibration, particularly those relating to the C–C and P=O or P=N bonds. Without these constraints, the bond distances and amplitudes would not refine satisfactorily. The amplitudes chosen are typical values for C–C and P=O bonds, but as in this case the P=O and P=N distances are exceptionally long it may be that the associated vibrational amplitudes should also be larger. Unfortunately, the vibrational spectra of these compounds are so complicated that they are of little help in giving reliable estimates of the amplitudes. However, even in refinements in which the fixed values were substantially increased, the refined P=O and P=N distances were always greater than C–C distances, and varied little. Thus, although there must always be some measure of doubt about such unexpected results, we are satisfied that they represent the best fit to the available data.

The outer parts of the radial distribution curves are complex, and include contributions from many atom pairs, particularly C • • • C and C • • • O or C • • • N, as listed in Table 4, and a great many distances involving hydrogen, which are not all listed. It is by fitting this pattern that the remaining parameters, relating to the conformations of the methyl and butyl groups and the tilt of the butyl groups, can be determined. As expected, these angles are correlated with each other, and with other geometrical parameters (Tables 2 and 3), but nevertheless they could all be refined easily and with reasonable precision. Final parameters are given in Table 5. This just leaves the three parameters relating to the odd hydrogen atom in PBu^t_3NH. Each of these was varied stepwise over a range of values, and the value giving

Table 4. Interatomic distances[a] and amplitudes (pm)

	PBu^t_3O		PBu^t_3NH	
	Distance	Amplitude	Distance	Amplitude
d_1 P=O/N	159.0(12)	4.2^b	165.2(11)	4.2^b
d_2 P–C	188.8(6)	5.5(7)	191.3(6)	7.0(7)
d_3 C–C	151.9(3)	4.5^b	153.2(2)	4.5^b
d_4 C–H	109.0(3)	7.2(6)	110.7(3)	7.1(6)
d_5 C(P)N/O	278.6(11)	7.6(7)	291.8(15)	7.8(8)
d_6 P(C)C	284.6(15)	9.8(7)	288.7(19)	12.2(7)
d_7 P(C)C	275.9(10)		282.1(17)	
d_8 P(C)C	278.4(6)		284.2(8)	
d_9 C(P)C	314.0(10)	8.5^b	312.1(14)	8.5^b
d_{10} C(C)C	247.4(6)	7.6(7)	247.5(7)	7.8(8)
d_{11} C(PC)C	346.4(12)	7.9^b	336.9(22)	15.3^b
d_{12} C(PC)C	361.2(10)		370.3(25)	
d_{13} C(PC)C	443.8(8)	8.8^b	444.7(14)	12.5^b
d_{14} C(PC)C	380.1(12)	7.9^b	376.7(30)	15.3^b
d_{15} C(PC)C	439.3(11)	8.8^b	442.9(17)	12.5^b
d_{16} C(PC)C	331.6(11)	7.9^b	332.1(17)	15.3^b
d_{17} C(CPC)C	354.1(25)	11.7^b	343.0(55)	19.5^b
d_{18} C(CPC)C	457.0(20)	8.8^b	465.4(50)	12.5^b
d_{19} C(CPC)C	503.6(12)	11.3(17)	497.5(25)	17.3(20)
d_{20} C(CPC)C	493.7(12)		487.9(21)	
d_{21} C(CPC)C	473.9(19)		487.1(30)	
d_{22} C(CPC)C	552.8(14)		563.2(23)	
d_{23} C(CPC)C	479.4(11)		483.5(17)	
d_{24} C(CPC)C	353.6(28)	11.7^b	340.6(52)	19.5^b
d_{25} C(CPC)C	317.2(16)	11.7^b	331.0(38)	19.5^b
d_{26} C(CP)N/O	411.5(13)	8.8^b	424.3(18)	12.5^b
d_{27} C(CP)N/O	300.2(13)	7.9^b	315.8(23)	15.3^b
d_{28} C(CP)N/O	335.2(10)		354.7(28)	
d_{29} C(C)H	215.5(20)	11.8(14)	219.0(16)	12.0(16)
d_{30} P(CC)H	284—381	11.3(28)	291—387	15.4(30)
d_{31} C(CC)H	265—343	19.6(60)	267—346	8.1(26)

Values in parentheses are estimated standard deviations, increased to allow for systematic errors.

[a] Other non-bonded C ··· H, P ··· H, N ··· H, O ··· H, and H ··· H distances were included in refinements, but are not listed here. [b] Fixed.

Table 5. Molecular parameters for PBu^t_3O and PBu^t_3NH

(*a*) Independent distances (pm)

	PBu^t_3O	PBu^t_3NH *
r_1(P=O/N)	159.0(12)	165.2(11)
r_2(P–C)	188.8(6)	191.3(6)
r_3(C–C)	151.9(3)	153.2(2)
r_4(C–H)	109.0(3)	110.7(3)
(*b*) Independent angles(°)		
Angle 1 (OPC)/(NPC)	106.1(5)	109.6(7)
Angle 2 (CCC)	109.1(4)	107.8(5)
Angle 3 (CCH)	110.3(16)	111.1(14)
Angle 4 (Butyl tilt)	−3.1(8)	−2.3(11)
Angle 5 (Methyl twist)	−7.3(34)	−8.9(25)
Angle 6 (Butyl twist)	15.8(7)	18.5(14)

Values in parentheses are estimated standard deviations, increased to allow for systematic errors.

* r(N–H) = 102.0 pm (fixed). Angle PNH = 114.0 (fixed), Dihedral angle CPNH = 160.0° (fixed).

the lowest R factor in each case was used in all subsequent refinements. Parameters obtained by this means are given in Table 5, and are all reasonable, but as the changes in R were extremely small the values are not very significant. Final R factors (R_G) were 0.097 for PBu^t_3O and 0.120 for PBu^t_3NH.

The final parameter sets for both compounds are given in Table 5, and full lists of interatomic distances and amplitudes of vibrations in Table 4. Combined molecular scattering curves are

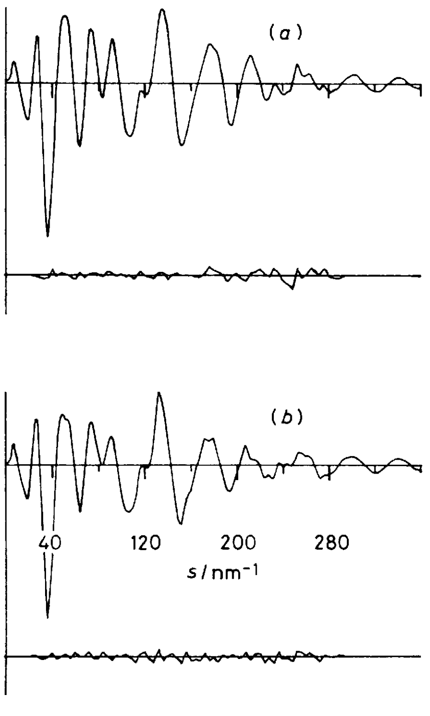

Figure 2. Experimental and final weighted difference molecular scattering intensity curves for (*a*) PBu^t_3O and (*b*) PBu^t_3NH

Table 6. Structural parameters for some t-butylphosphines

Compound	r(P–C)/pm	CPC/°	r(C–C)/pm	CCC/°	Bu twist/°	Ref.
PBu^t_3	191.9(5)	109.9(7)	153.4(3)	107.8(4)	14.0(13)	5
PBu^t_3O	188.8(6)	112.9(5)	151.9(3)	109.1(4)	15.8(7)	This work
PBu^t_3NH	191.3(6)	109.4(7)	153.2(2)	107.8(5)	18.5(14)	This work
$PBu^t_4{}^+$	192.4(4)	109.5	153.1(7)	106.5(4)	14	10
PBu^t_2F	185.9(6)	113.8(19)	153.0(4)	109.6(13)	7.8(31)	5
PBu^tF_2	182.2(12)	—	151.7(10)	109.2(13)	0	5

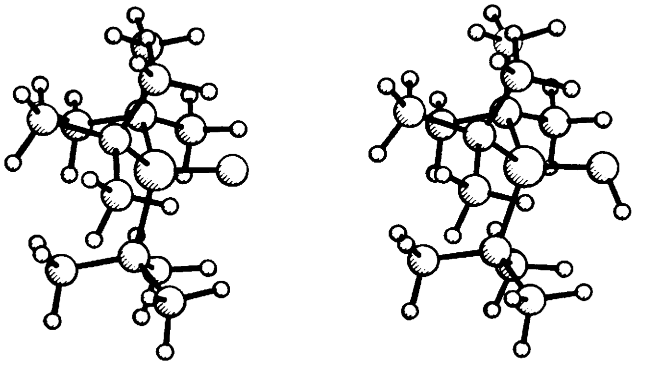
(a) (b)

Figure 3. Perspective views of (*a*) PBu^t_3O and (*b*) PBu^t_3NH

shown in Figure 2, and perspective views of the molecules in Figure 3.

Discussion

Some important parameters for PBu^t_3,[5] the oxide and imide of the present study, and the phosphonium ion, $PBu^t_4{}^+$,[10] are given in Table 6. The most striking feature is the extreme similarity of the parameters of PBu^t_3, PBu^t_3NH, and $PBu^t_4{}^+$. Thus although steric strain is manifested in the phosphine in widening of the CPC angles from around 100° in simple trialkylphosphines to 110°, and lengthening of the P–C bonds from *ca.* 183 to 192 pm, there is nevertheless room to incorporate a fourth t-butyl group, giving $PBu^t_4{}^+$, without any further distortion of the butyl groups. It is not surprising, therefore, that the imido-group can be accommodated without difficulty. However, the structure of the oxide is slightly, but significantly, different. The angles between the P–C bonds have increased from 110 to 113°, and this has reduced the steric interactions between the butyl groups, so that the P–C and C–C bonds are somewhat shortened, and the CCC angles are increased. The pattern of relaxation of strain is very much the same as is seen in PBu^t_2F,[5] parameters for which are also included in Table 6. The structure of an unstrained butylphosphine is illustrated by the P–C and C–C distances [182.2(12) and 151.7(10) pm] and CCC angle [109.2(13)°] in PBu^tF_2.[5]

The other remarkable feature of the two structures is the extreme lengths of the P=O and P=N bonds. These repeatedly refined to 159.0(12) and 165.2(11) pm respectively, even when refinements were started with them set at short distances. Typical P=O distances are 146(1) pm in PPh_3O[11] and 147.4(4) pm in $P(C_6H_4Me\text{-}o)_3O$,[12] with P=N distances about 7 pm longer, whereas the values we find are in the ranges usually found for P–O and P–N single bonds. We therefore suggest that these compounds should be regarded as $PBu_3{}^+\text{–}O^-$ and $PBu_3{}^+\text{–}NH^-$, rather than $PBu_3\text{=}O$ and $PBu_3\text{=}NH$. Such a formulation is consistent with the near-tetrahedral angles at phosphorus, and can be attributed to the electron-releasing properties of the butyl groups. There is no steric requirement for these bonds to be long. The oxygen and nitrogen atoms are well separated both from their neighbouring carbon atoms and from the methyl-group atoms.

Finally, we note that if the P–O and P–N bonds are long, they should also be weak. The inertness of the compounds must therefore indicate kinetic, and not thermodynamic, stability. The drawings of the molecules (Figure 3) show that the oxygen and nitrogen atoms are sheltered by hydrogen atoms, and this probably makes close approach of reactive molecules difficult.

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