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CHARGE TRANSFER COMPLEXES OF PHOSPHINE-NITROARYLS

M. Arshad Ali Beg and M. Siddique Siddiqui*

PCSIR Laboratories, Karachi-39

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Compounds of tertiary phosphines with nitroaryls like 1, 3, 5-trinitrobenzene, 2, 4-dinitrophenol and 2, 4, 6-trinitrophenol (picric acid) have been reported. Picrates of tertiary alkyl phosphines have been obtained in good yields from stoichiometric amounts of picric acid and tertiary phosphines, *viz,* trimethyl, phenyldimethyl, triphenyl and tri-*p*-tolylphosphines. Tertiary alkylphophines react instantaneously with the three nitroaryls at room temperature with the deposition of intensely coloured compounds. Tertiary arylphosphines react only with picric acid and their reaction is very slow; it needs long refluxing when dark crystalline solids are obtained.

Spectroscopic studies of phosphine nitroaryls suggest that they are charge transfer complexes. A band characteristic of charge transfer is found in the uv spectra of all complexes. This band shows a linear relationship with the ionization potential of tertiary phosphines. Charge transfer complex formation is further supported by ir study in which the ν_{as} (N-O) is shifted to higher frequency with the appearance of two bands and a red shift in γ (C-H) of the nitroaryl moiety on complexing with phosphines.

INTRODUCTION

Nitroaryls form crystalline complexes in 1:1, 1:2 and 2:3 molar ratios with donors like aromatic amines, phenols and hydrocarbons [1, 2]. Sometimes there is only an appearance of colour instead of crystal formation [3]. Complex formation has been detected by their vibrational spectra. The solid crystalline complexes obtained by the interaction of nitroaryls and amines are highly coloured with few exceptions. Such complexes exhibit properties characteristic of their components [4]. The stability of these compounds increases with increasing molecular complexity of hydrocarbons in respect of either alkyl group substitution in the ring or ring fusion. Electron attracting groups present in nitro components increases their stability.

The isolation of solid coloured crystalline compounds and formation of colour by the interaction of nitroaryls and amines has been related with the pKa values of both components [4]. The pKa values of amines and hydrocarbons are quite high since they are basic in nature as compared with those nitroaryls which show acidic behaviour. Inoue and Matsunaga [5] have prepared molecular complexes with anilines and 2, 4 dinitrophenol. They categorised them as proton transfer (P.T.) and charge transfer (C.T.) complexes. The formation of the two types of complexes has been found to depend on the difference between the pKa values of both the components. For example, anilines having pKa values above 4.02 form salts by proton transfer [4] with picric acid, while those having pKa values lower than this form charge transfer complexes. The proton transfer mechanism is supported by the presence of NH_3^+ absorption bands in the vibrational spectra of the compounds [6], which is absent in spectra of charge transfer complexes where a charge transfer band is obtained. The charge transfer band has been characterized by a linear graph plotted against the ionization potential of the donor molecules and $\lambda_{max.}$ of the picrates [7].

Nitroaryls also form charge proton transfer type complexes with amines, e.g. α-naphthylamine picrate having a 2:1 composition. In this case, proton transfer takes place from picric acid to α-naphthylamine and the interaction between picrate ion and the second molecule of α-naphthylamine produces a charge transfer band. It has generally been found [4, 5] that donor molecules having lower pKa values yield charge transfer type complexes while those having higher values produce proton transfer complexes [5].

Tertiary phosphines are basic in nature and form complexes with nitroaryls similar to amines. There is a brief mention [8-9] and no detailed study has been undertaken on the present complexes. The preparation, reactions and spectroscopic studies of some phosphine nitroaryls are being reported here.

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* From part of the Ph.D. thesis of M. Siddique Siddiqui.

EXPERIMENTAL

Preparation of phosphine-nitroaryl adducts. General Method. Phosphine-nitroaryl adducts were prepared by a simple admixture of reactants in a 1:1 molar ratio. Trialkylphosphines reacted with nitroaryls at low temperature but for arylphosphines refluxing of the reaction mixture was necessary. The preparation and characterization of the compounds are given in Table 1.

RESULTS

Addition compounds of tertiary phosphines with nitroaryls were prepared, using trimethyl, phenyldimethyl, triphenyl and tri-*p*-tolylphosphine on the one hand and 2, 4, 6-trinitrophenol (picric acid), 2, 4-dinitorphenol and 1, 3, 5-trinitrobenzene on the other.

Compounds of tertiary phosphines with 2, 4, 6-trinitrophenol. All four tertiary phosphines form compounds with 2, 4, 6-trinitrophenol. The reaction with tertiary alkylphosphines is faster than with tertiary arylphosphines. Tertiary alkylphosphines react at low temperatures but arylphosphines do not and for them refluxing of the reaction mixture is necessary. Tertiary alkylphosphines form yellow compounds below 0°C. These yellow compounds are unstable and difficult to isolate. They slowly turn red at room temperatue. The yellow and red compounds have different ir spectra but their elemental analyses are found to be the same. Tertiary arylphosphines form orange compounds with picric acid. The yield of these compounds with tertiary arylphosphines is always lower than with tertiary alkylphosphines.

These compounds are unstable towards air and water. They melt without decomposition, soluble in most of the polar organic solvents but insoluble in carbon tetrachloride and ether. They turn brown on treatment with warm water and eventually decompose into picric acid and the corresponding phosphines. The solution of the compounds in alcohol turns yellow on the addition of dilute hydrochloric acid but the original colour is restored on treatment with a base. Sodium picrate is obtained on warming the solution with sodium hydroxide.

Compounds of tertiary phosphines with 1, 3, 5-trinitrobenzene. Dark violet compounds are obtained on the treatment of tertiary alkylphosphines with 1, 3, 5-trinitrobenzene. Tertiary arylphosphines do not produce any addition compounds and also do not show any colour change in solution. The tertiary alkylphosphines-1, 3, 5-trinitrobenzene adducts are soluble in most of the polar organic solvents but insolube in ether and carbon tetrachloride. These solids decompose on standing in air but are stable on keeping under the solvents. The behaviour of these compounds with acids alkalis and water is similar to those of phosphine picrates.

Compounds of tertiary phosphines with 2, 4-dinitrophenol. Only alkylphosphines react with 2, 4-dinitrophenol. Their reaction is very slow and affords orange crystals only after refluxing for more than 5 hr. The crystals are unstable and decompose on standing in air and on reaction with water, acids and alkalis.

The ir spectra of phosphine-nitroaryls have been recorded in KBr pellets and nujol mulls. It has been observed that the spectra of the tertiary phosphine-nitroaryls are the summations of the absorption bands of the components in which the bands corresponding to nitroaryls are more marked than the phosphines. The ir absorption bands of the adducts with their tentative assignments are given in Tables 7-10.

Ultraviolet spectra of addition compounds have been recorded in methanol, acidic methanol and basic methanol. It has been found that the spectra are susceptible to change of pH as shown in Tabe 2 for trimethylphosphine picrate. The intensity of the bands increases with increase in the pH of the solution. The differnece is found at pH 8 where the

Table 1. Preparation and characterisation of phosphine-nitroaryls

No.	Reactants and quantities								Analysis					
	Phosphine		Nitroaryls			Yield	M.P.	Molecular	Calculated			Found		
	g,	mmoles	g,	mmoles	Colour	g (%)	°C	formula	C	H	N	C	H	N
1.	Me_3P-0.38	5	PA-1.14	5	Blood red	.92-60	118	$C_9H_{12}N_3O_7P$	35.4	3.93	13.7	35.3	3.95	13.5
2.	$PhMe_2P$-0.138	1.0	PA-1.229	1.0	Scarlet red	.22-60	77	$C_{14}H_{14}N_3O_7P$	45.7	3.8	11.4	46.04	4.08	11.5
3.	Ph_3P 2.62	1.0	PA-2.29	1.0	Orange red	1.78-40	145	$C_{24}H_{18}N_3O_7P$	52.8	4.4	8.5	53.08	3.57	8.5
4.	pT_3P 1.52	0.5	PA1.145	.5	Orange	0.8-30	112	$C_{27}H_{24}N_3O_7P$	50.7	4.5	7.8	60.45	4.51	7.9
5.	Me_3P-0.38	5	1, 3, 5 T.N.B. 1.06,	5	Dark violet	0.85-60	110	$C_9H_{12}N_3O_6P$	35.1	4.56	14.5	34.26	5.0	14.7
6.	$PhMe_2P$-0.69	5	1, 3, 5 T.N.B. 1.06,	5	Dark violet	1.48-60	80	$C_{14}H_{14}N_3O_6P$	47.8	3.6	12.0	47.47	3.96	12.2
7.	Me_3P-0.38	5	2, 4 D.N.P. 0.92,	5	Orange	0.52-40	95	$C_9H_{13}N_2O_5P$	41.5	5.0	10.8	40.78	4.75	11.4
8.	$PhMe_2P$-0.69	5	2.4 D.N.P. 0.92,	5	Orange red	0.58.30	120	$C_{14}H_{15}N_2O_5PH_2O$	49.4	5.0	8.8	49.81	4.82	9.1

[Me_3P = trimethyl phosphine, Ph Me_2P: Phenyl dimethylphosphine,
Ph_3P = triphenyl phosphine, pT_3P = p-tritolylphosphine,
P.A = Picric Acid, 1, 3, 5, T.N.B. = 1, 3, 5, trinitrobenzene,
2, 4 D.N.P. = 2, 4, dinitrophenol.

Table 2. Electronic spectra of trimethylphosphine picrate at different pH.

pH 2.5		pH 5.5		pH 6.0		pH 6.5		pH 8		pH 9		pH 11	
nm	log ϵ	nm	log ϵ	nm	log ϵ	nm	log ϵ	nm	log ϵ	nm	log ϵ	nm	log ϵ
400	3.95	400	4.14	400	4.04	400	4.04	400	4.04	400	4.06	400	4.06
360	4.11	360	4.24	360	4.20	360	4.2	360	4.2	360	4.21	360	4.21
275	3.66	275	3.72	280	4.2	275	3.54	x	x	x	x	x	x
230	4.15	240	4.2	232	4.38	230	4.11	230	4.1	230	4.13	240	4.18
212	4.15	220	4.28	212	4.4	212	4.2	212	4.2	210	4.22	210	4.33

Table 3. Absorption maxima of phospine nitroaryls adducts and ionization potential of phosphines.

		Absorption maxima					
Phosphines	I. P ^{o}F [19] phosphine	Phosphine picrate		Phosphine 2, 4 DNP		Phosphine sym TNB	
		nm	log ϵ	nm	log ϵ	nm	log ϵ
$PhMe_2P$	7.8	285	4.14	280	3.92	275	4.04
$PhMe_2P$	7.8	280	3.97	290	4.27	295	3.58
pT_3P	7.6	275	3.2				
Ph_3P	7.34	272	4.19				

Table 4. ν_{as} (N-O) of nitroaryls in phosphine nitroaryl complexes.

PA	$Me_3P.PA$ cm^{-1}	$PhMe_2P.PA$ cm^{-1}	$Ph_3P.PA$ cm^{-1}	$p\text{-}T_3P.PA$ cm^{-1}
1525	1550 m	1540 s	1540 s	1545 s
	1525 m	1520 w	1525 s	1520 ssh

2, 4-DNP cm^{-1}	Me_3P. 2, 4-DNP cm^{-1}	$PhMe_2P$.2, 4-DNP cm^{-1}
1525 s	1550 m	1555 m
1510 s	1520 w	1515 m

1, 3, 5-TNB cm^{-1}	Me_3P-1, 3, 5-TNB cm^{-1}	$PhMe_2P$-1, 3, 5-TNB cm^{-1}
1540 vs	1545 w	1550 w
	1550 s	1510 m

band at 280 ± 5 nm disappears. The solution of the compounds is acidic and the acidity of the solution increases with the addition of more acid, and therefore, the spectra of other phosphine nitroaryls are recorded only in methanol and alkaline media. The absorption and calculated log ϵ of the spectra are given in Table 5 and 6.

DISCUSSION

The formation of phosphine nitroaryl addition compounds depends on the nucleophilic behaviour of phosphines. Tertiary alkylphosphines readily form complexes with picric acid, 2, 4-dinitrophenol and 1, 3, 5-trinitrobenzene in high yields. On the other hand, arylphosphines form complexes with picric acid only; their reaction is slow and yield is poor. Their formation also seems to depend upon the accepting property of nitroaryls, among which picric acid having three strong electron withdrawing nitro groups, is the strongest to provide site for attack of electron rich phosphines to form the complex. Ability of complex formation decreases with decrease of the number of electron withdrawing groups as 2, 4-dinitrophenol and nitrobenzene do not form complexes with arylphosphines.

Conductivity measurements [10] of the phosphine-nitroaryl adducts show them to be weak electrolytes. Bonding with the nitroaryls seems to be weak as these compounds decompose on simple treatment with water and other polar solvents.

Spectroscopic studies suggest that they are charge transfer complexes. A band characteristic of charge transfer is found in the uv spectra of all compounds. The same band is also observed in the charge transfer complexes of amine nitroaryls [7, 11, 13]. They do not seem to be of proton transfer type since bands characteristic of proton transfer complexes such as P-H vibration and another band assigned to picrate salt [6] ν (C-O)$^-$ are not recorded in the ir region. They also do not seem to be charge-proton transfer type since the elemental analysis of phosphine nitroaryls indicates the formation of 1:1 complex, whereas a charge proton transfer complex demands a ratio of 1:2, 2:3 etc. [14].

The uv spectra of amine nitroaryls show [15-17] an absorption at 280 ± 5 nm. This band appears neither in amines nor in nitroaryls. Lawrey [16] suggests this absorption band to be an intermolecular charge transfer transition. Foster [7] noted a linear relationship between the

Table 5. Electronic spectra of phosphine-nitroaryls.

$Me_3P.PA$				$PhMe_2P.PA$				p-$T_3P.PA$				$Ph_3P.PA$			
Acid		Base		Acid		Base		Acid		Base		Acid		Base	
nm	log ϵ	nm	log ϵ	nm	log ϵ	nm	log ϵ	nm	log ϵ	nm	log ϵ	nm	log ϵ	nm	log ϵ
405	3.81	480	4.07	420	3.76	420	4.04	400	4.28	420	4.2	–	–	410	4.4
345	4.11	360	3.89	350	3.76	340	4.01	355	4.38	350	4.47	365	4.51	345	4.46
286	4.14			280	3.97			275	3.2	275	4.07	272	4.19	275	4.27
238	4.41	240	4.17	265	4.06	250	4.04	235	4.99	232	4.99	265	4.23	265	4.32
215	4.4	210	4.44	217	4.38	214	4.82	215	4.87	220	5.02	217	4.78	225	4.77
												212	4.79	217	4.9

Table 6.

$Me_3P.2, 4DNP$				$PhMe_2P.2, 4DNP$				$Me_3P.1, 3, 5TNB$				$PhMe_2P.1, 3, 5TNB$			
Acid		Base		Acid		Base		Acid		Base		Acid		Base	
nm	log ϵ	nm	log ϵ	nm	log ϵ	nm	log ϵ	nm	log ϵ	nm	log ϵ	nm	log ϵ	nm	log ϵ
405	3.74	480	4.07	410	3.83	400	4.36	410	3.24	470	3.97	405	3.5	450	3.15
355	3.77	360	3.89	350	4.11	355	4.49	360	3.24	425	4.13	360	4.1	350	4.22
280	3.92	–	–	290	4.27	–	–	275	4.04	340	3.35	270	4.02	290	3.91
										295	3.58	240	4.21	220	4.4
238	4.12	240	4.17	272	4.3	272	4.15	–	–	240	4.08				
												230	4.31	–	–
215	4.24	210	4.44	257	4.39	257	4.28	240	4.29	–	–				
										215	4.4	–	–	–	–
–	–	–	–	215	4.61	215	4.61	230	4.32						

charge transfer bands and the ionization potential of the donors for a particular acceptor. He used symmetric trinitrobenzene, symmetric trinitrotoluene and benzoquinone as acceptor and benzene, toluene, *m*-xylene, aniline, and *N, N*-dimethylaniline as donors and found a linear relationship between the charge transfer bands and the ionization potential of the donors for a particular acceptor.

Tertiary phosphine-nitroaryl adducts display new absorption maxima. Trimethyl, phenyldimethyl, tri-*p*-tolyl and triphenylphophine picrates show absorptions respectively at 285 nm (log ϵ 4.14), 280 nm (log ϵ 3.97), 275 nm (log ϵ 3.32) and 272 nm (log ϵ 4.19). These absorptions do not occur in alkylphosphines and picric acid but they do so in the spectra of tri-*p*-tolyl and triphenylphosphines at 280 nm. It appears that the absorption at 280 nm. in arylphosphines undergoes a blue shift on complex formation and appears at 275 and 272 nm. This is verified by running the uv spectra of tri-*p*-tolyl and triphenylphosphine complexes in ethanol at different pH. The absorption spectrum in ethanol and acidic ethanol has maxima at the same wavelength, but the one in the basic medium was completely different in that the band at 272 nm now appears at 280 nm. The shift is most likely due to the decomposition of the complexes into tertiary phosphine and sodium picrate in basic medium. Other complexes of phosphine-nitroaryls also behave in a similar manner indicating that the new band is a charge-transfer band.

A linear relationship exists between the ionization potential of tertiary phosphines and charge transfer bands of the tertiary phosphine-picrates (Fig. 1) indicating the absorption of phosphine-nitroaryls in the 280 nm region to be due to an intermolecular charge transfer transition similar to those found in amine-nitroaryls and other molecular complexes. The values of charge transfer bands and ionization potentials of the donor phosphines are shown in Table 3. This correlation thus supports the charge transfer nature of the complexes.

Certain characteristic vibrations are found in the ir spectra of the amine nitroaryl complexes with regard to the nitro asymmetric stretching vibration ν_{as} (N-O) and C-H out of plane bending vibration, γ (C-H). Kross and Fassel [1] studied the infrared spectra of forty picric acid molecular complexes and have classified them into three general

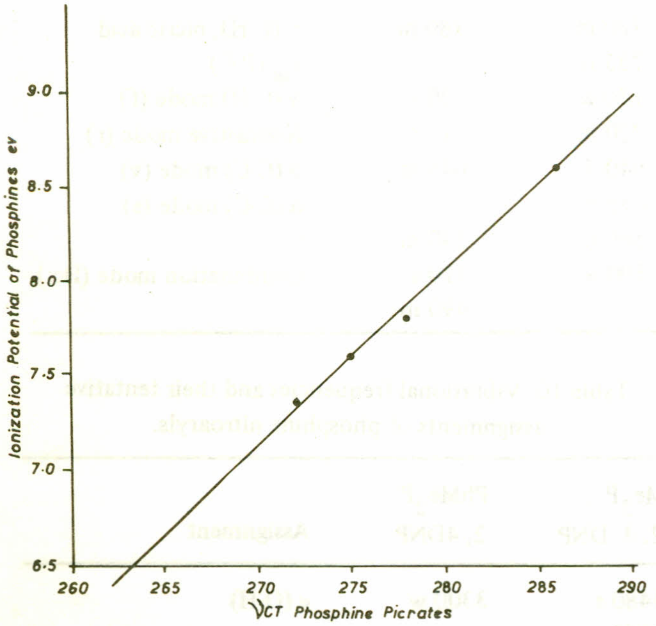

Fig. 1

Table 7. Vibrational frequencies and their tentative assignments of phosphine pictrates.

Me_3PPA	$PhMe_2PPA$	Assignment
3300 wbr	3350 whr	ν (O-H)
3150 wbr	3230 w	ν_{as} (C-H) aromatic
2920 s	2920 m	ν_{as} (C-H) aliphatic
2840 s	2670 m	ν_{Sym} (C-H)
1625 m	1625 m	
	1615 w	ν (C-C) mode (k)
1550 m	1540 st	
1525 m	1520 w	ν_{as} (N-O) + mode (1)
1450 m	1490 m	ν (C-C) mode (m)
1440 sh	1435 m	ν (C-C) mode (n)
1370 s	1365 m	
1360 m	1345 w	ν_{Sym} (N-O) + ν (C-C) mode (o)
	1310 m	
1290 w	1290 w	δ_{Sym} (C-H)
1250 mbr	1270 w	ν (P-C) or ν (O-H)
	1260 m	
1200 mbr	1190 w	β (C-H) mode (e)
1180 mbr	1180 w	β (C-H) mode (a)
	1160 m	
	1110 m	X-sensitive mode (q)
1040 mbr	1030 w	β (C-H) mode (b)
1015 m	1020 w	
	1000 m	Ring breathing mode (p)
950 m	935 m	
900 mbr	905 m	Methyl rock
810 m	790 m	γ (C-H) Picric acid.
780	770 w	ν_{as} (P-C)
760 m	745 m	γ (C-H) mode (f)
710 m	710 m	ϕ (C-C) mode (v)
	695 m	
625 m	620 m	α (C-C) mode (s)
580 m	595 w	
510 m	490 wbr	Combination (t + x)
400 m	435 wbr	ϕ (C-C) mode (w)
360 w		

(continued on column 2)

Table 8. Vibrational frequencies and their tentative assignments of phosphine picrates.

Ph_3PPA	p-T_3PPA	Assignment
3180 mbr	3480 br	ν (O-H)
2890 wbr	2920 sbr	ν_{as} (C-H)
1610 m	1630 m	ν (C-C) mode (k)
	1610 m	
1585 s	1595 m	ν (C-C) mode (1)
1570 m	1550 s	ν (C-C) mode (m)
1540 s	1545 s	
1525 s	1520 s sh	ν (N-O)
	1495 m	
1470 m	1465 w	δ_{as} (C-H)
1465 m		
1420 s	1430 m	ν (C-C) mode (n)
1415 s		
1345 s	1400 m	δ_{Sym} (C-H)
	1360 m	
1325 s	1340 s	ν_{Sym} (N-O)
	1310 s	
1295 s	—	δ_{Sym} (C-H)
1250 s	1265 mbr	ν (P-C) or β (O-H)
	1190 m	β (C-H) mode (e)
1165 w	1160 m	β (C-H) mode (a)
1140 m		β (C-H) mode (c)
1130 m		
1100 s	1110 s	X-sensitive mode (q)
	1105 sh	
1065 sh	1075 m	β (C-H) mode (d)
1060 s	1035 m	β (O-H)
1015 w	1025 m	β (C-H) mode (b)
1005 w		ring breathing mode (p)
950 m	960 w	γ (C-H) mode (j)
925 w	940 w	γ (C-H) mode (h)

(continued. . . . .)

(Table 8, continue)

895 m	890 w	γ (C-H) mode (i)
870 m	880 w	(C-H) isolated hydrogen
820 w	845 w	γ (C-H) mode (g)
	805 s	
785 m	790 m	γ (C-H) pionic acid
760 m	750 m	γ (C-H) mode (f)
735 s	740 m	
705 s	710 s	X-sensitive mode (r)
695 s	665 s	φ (C-C) mode (v)
670 s	630 m	
595 w	525 s	combination mode (t + x)
540 w		
480 s	460 s	X-sensitive mode (t)
425 m		
385 m	350 w	φ (C-C) mode (w)
360 w		

Table 9. Vibrational frequencies and their tentative assignments of phosphine nitroaryls.

Me$_3$P , 1, 3, 5TNB.	PhMe$_2$P , 1, 3, 5TNB.	Assignment
2900 s	3100 mbr	ν_{as} (C-H) aromatic
	2990 mbr	
2850 s	2900 mbr	ν_{as} (C-H) aliphatic
2700 w		
1605 s	1620 m	ν_{as} (C-C) mode (k)
	1600 s	
1545 w	1550 w	ν (N-O) + mode (1)
1500 s	1510 m	
1490 w	1490 m	ν (C-C) mode (m)
	1470 m	
1450 s	1450 s	ν (C-C) mode (n)
1370 m	1380 m	ν_{Sym} (N-O) + mode (o)
1340 w	1340 s	
1290 w	1290 m	δ_{Sym} (C-H)
1210 w	1210 w	β (C-H) mode (e)
1200 mbr	1190 w	
1140 m	1150 br	β (C-H) mode (a)
	1110 w	X-Sensitive mode (q)
1040 m	1045 s	β (C-H) mode (b)
	1000 m	ring breathing mode (p)
950 m	975 m	
940 m	930 msh	methyl rock.
910 m	920 s	
850 w	860 m	
780 m	780 m	γ (C-H); picric acid
755 m		ν_{as} (P-C)
730 w	730 s	γ (C-H) mode (f)
720 m	710 s	X-sensitive mode (r)
640 m	645 m	φ (C-C) mode (v)
635 m		α (C-C) mode (s)
560 m	540 m	
500 w	510 s	Combination mode (l+x)
	490 m	

(continued on column 2)

Table 10. Vibrational frequencies and their tentative assignments of phosphine nitroaryls.

Me$_3$P , 2, 4, DNP.	PhMe$_2$P , 2, 4DNP.	Assignment
3480 s	3300 w	ν (O-H)
3360 vs		
3120 w	3080	ν_{as} (C-H)
2920 m	2920 vs	ν_{Sym} (C-H)
	2740 vs	
1600 s	1600 s	ν (C-C) mode (k)
1570 m		ν (C-C) mode (l)
1550 m	1555 m	
1520 w	1515 m	ν_{as} (N-O) + mode (m)
1480 m	1450 s	δ_{as} (C-H)
1440 sh	1535 sh	ν (C-C) mode (n)
	1440 m	
1370 sh	1370 m	δ_{Sym} (C-H)
1340 sh	1340 vs	ν_{Sym} (N-O) + mode (o)
	1330 vs	
1300 mbr	1300 W	δ (C-H)
	1290 m	
1175 m		
1160 w	1160 w	β (C-H) mode (a)
1135 m	1125 vs	β (C-H) mode (c)
1100 m	1110 w	X-sensitive mode (q)
1060 m	1060 m	β (O-H)
	1020 w	ring breathing mode (p)
990 w	990 w	
950 m	950 m	
930 m	930 m	methyl rock.
880 w	920 m	
	900 m	
860 w	860 s	γ (C-H) isolated hydrogen of nitroaryl
850 m	840 m	γ (C-H) of two hydrogens
	825 m	

(continued. . . . .)

(Table 10, continue)

790 s		
750 m	735 s	γ (C-H) mode (f)
730 w	730 w	
720 w	700 ms	X-sensitive mode (r)
700 w	690 s	ϕ (C-C) mode (v)
640 m	630 m	
615 s		α (C-C) mode (s)
535 s	550 w	Combination mode (t+x)
500 w	500 w	
	480 s	
	450 m	X-sensitive mode (t)
	425 s	
370 w	370 w	ϕ (C-C) mode (w)
350 w	350 w	

groups on the basis of the appearance of nitro asymmetric stretching ν_{as} (N-0) vibration.

Changes in ν_{as} (N-0) frequency have analogously been observed in phosphine-nitroaryl complexes. Since the donor molecules (tertiaryphosphines) contain an atom which permits them to act as n-base the charge transfer takes place between the non-bonding orbital of the phosphorus atom and the vacant orbital of one of the nitro groups of the nitroaryls. Thus there should be a gain in the bond order of the nitro group due to transfer of charge and there should be a gain in the ν_{as} (N-0) frequency. The ν_{as} (N-0) shifts to higher freqency in phosphine-nitroaryls. The ν_{as} (N-0) is found in picric acid [19] at 1525 cm^{-1}, in 2, 4-dinitrophenol at 1525 cm^{-1} and 1510 cm^{-1} and in 1, 3, 5-trinitrobenzene at 1540 cm^{-1}. In phosphine-nitroaryls, two bands corresponding to ν_{as} (N-0) are found in which one band is located at the same position at which the nitroaryls absorb and the other at higher frequency as shown in Table 4.

The frequency of γ (C-H) of the nitroaryls in the amine nitroaryl complexes also shows significant changes. In the nitroaryl complexes of naphthalene, aniline, β-naphthylamine which have been characterized as π-π complexes, the γ (C-H) is shifted to lower frequency. In the n-π type complexes such as pyridine or atropine nitroaryls, it is shifted to higher frequencies. The γ (C-H) of the nitroaryls, in the phosphine-nitroaryls shows variations similar to those shown by n-π type nitroaryl complexes of pyridine, atropine etc. For example, the γ (C-H) of picric acid, 2, 4-dinitrophenol and 1, 3, 5-trinitrobenzene are found respectively at 783 cm^{-1}, 775 cm^{-1}, and 770 cm^{-1}. On complexing with phosphines these absorptions are found respectively at 785-810 cm^{-1} 790-860 cm^{-1} and 780 cm^{-1} regions.

Proton transfer and proton-charge transfer mechanisms for the formation of phosphine-nitroaryl complexes have already been found to receive no support from experimental findings. The shifting of the ν_{as} (N-0) to higher frequency with the appearance of two bands, red shift of γ (C-H) of the nitroaryls on complexing with phosphines and the appearance of intermolecular charge transfer band in the ultraviolet region, all suggest that the phosphine-nitroaryls are charge transfer complexes.

REFERENCES

1. R.D. Kross and V.A. Fassel, J. Am. Chem. Soc., **79**, 38 (1957).
2. W.R. Burton and R.E. Richards, J. Chem. Soc., 1361 (1950).
3. N.V. Sidgwick, *Organic Chemistry of Nitrogen:* (Clarendon Press, Oxford, 1966), p. 396.
4. G. Saito and Y. Matsunaga, Bull Chem. Soc. Japan, **46**, 714 (1973).
5. N. Inove and Y. Matsunaga, *Ibid.,* **45**, 3478 (1972).
6. R.P. Mariella, M.J. Gruber and J.W. Elder, J. Org. Chem, **26**, 3217 (1961).
7. R. Foster, Nature, **176**, 746 (1955).
8. J.H. Boyer and S.E. Ellzey, J. Org. Chem, **26**, 4648 (1961).
9. L. Horner and K. Klupfel, Ann. Chem, **591**, 69 (1955).
10. M. Siddique Siddiqui, Molecular Addition Compounds of Phosphines, Ph.D thesis, University of Karachi (1981).
11. G. Saito and Y. Matsunaga, Bull. Chem. Soc. Japan, **45**, 963 (1972).
12. C.E. Moore and R. Peck, J. Org. Chem, **20**, 673 (1955).
13. R.S. Mulliken, J. Am. Chem Soc, **72**, 600 (1950), **79**, 4839 (1957); J. Phys. Chem, **56**, 801 (1952).
14. Y. Matsunaga and G. Saito, Bull. Chem. Soc. Japan, **45**, 963 (1972).
15. J. Landaver and H.Mc. Connel, J. Am. Chem. Soc, **74**, 1221 (1952).
16. D.M.G. Lawrey and H.Mc. Connel, *Ibid*, **74**, 6175 (1952).
17. C.G. Le, Fevre and R.J.W. Le Fevre, J. Chem. Soc, 1829 (1950).
18. S.C. Abrahams, J. Am. Chem. Soc, **2693**, 74 (1952).
19. Yosuo Wada and Robert W. Kiser, J. Phys. Chem, 68, 2290 (1964).