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Vibrational study of diphenylphosphorus halides Ph_2PX (X = Cl, Br, I)

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Abstract—The Raman and i.r. spectra of diphenylphosphorus halides, Ph_2PX (X = Cl, Br, I), have been measured and concerted assignments have been made confirmed by an approximate normal coordinate analysis for the skeletal vibrations of Ph_2PCl using a three mass model for the phenyl group.

INTRODUCTION

Serious disagreement exists in the interpretation of the vibrational spectra of diphenylphosphorus chloride [1, 2]. The assignments are tentative in both studies as they were not confirmed by a normal coordinate analysis. Recently, in a vibrational study [3] of various pentadeuterophenylphosphorus compounds, a restricted number of frequencies of Ph_2PCl are assigned based on approximate calculations using a three mass model [4] for the phenyl ring.

We wish to report on the i.r. and Raman spectra of the diphenylphosphorus halides, Ph_2PX (X = Cl, Br, I). Assignments are proposed confirmed by an approximate normal coordinate analysis of the C_2PCl skeletal vibrations.

EXPERIMENTAL

Synthesis. Commercial diphenylphosphorus chloride was used after appropriate purification. $(C_6H_5)_2PBr$ [5–9] (b.p. 146°C/2 mm Hg) was prepared by a halogen exchange reaction between $(C_6H_5)_2PCl$ and PBr_3. By cleaving the P–P bond in $(C_6H_5)_4P_2$ with I_2, $(C_6H_5)_2PI$ (b.p. 181°C/5 mm Hg) has been synthesized [10].

Spectroscopy. The i.r. spectra of the liquids were recorded on a Perkin–Elmer 580 double-beam spectrometer. A Coderg Raman spectrometer equipped with a He–Ne gas laser, OIP model 181 E, has been used for the Raman study.

RESULTS AND DISCUSSION

The analysis of the vibrational spectra of the Ph_2PX derivatives can be approached by the concept of isolated group vibrations. In a first approximation the phenyl ring vibrations are treated on the base of a Ph_nY (Y = rest of the molecule) system whereas the vibrations involving the phosphorus atom are considered in a C_2PX skeleton.

Vibrational spectra of Ph_nY systems with weak interacting benzene rings are treated in terms of monosubstituted benzene rings belonging to the point group C_{2v}. For the substituent-insensitive vibrations an accidental degeneracy is observed. However the substituent sensitive vibrations give rise to multiple components which are attributed either to nonequivalence of the benzene rings [11] or to in-phase and out-of-phase vibrations of the various benzene rings [12]. This leads to symmetrical and asymmetrical normal vibrations. Only the ring vibrations in the frequency region of interest (below 650 cm^{-1}) are considered. The normal vibrations of the pyramidal C_2PCl skeleton (point group C_s) are collected in Table 1. However, in order to avoid double assignment one has to realise that the C_6H_5–X (heavy) stretching vibration (7*a*) [13] corresponds essentially to the PC_2 stretching vibrations ν_2 and ν_5 of the C_2PCl skeleton. Furthermore the C_6H_5–X in-plane bending (9*b*) is clearly associated with the PC_2 bending vibration ν_4. The assignments for the vibrational frequencies below 650 cm^{-1} are collected in Table 2. Several assignments are straightforward and need no discussion. The absorption bands for ν_2 and ν_5 are expected in the frequency interval 400–500 cm^{-2}. The strong, polarized Raman bands at 458 (Cl), 481 (Br) and 476 (I) are assigned to ν_2, the weak depolarized Raman bands at 427 (Cl), 429 (Br) and ~ 430 (I) to ν_5.

In the Raman spectra of Ph_2PCl and Ph_2PBr four bands are observed in the region 300–200 cm^{-1}. The very strong, polarized, *X*-sensitive bands at 284 (Cl) and 235 (Br) are ascribed to ν_3; the *X*-insensitive bands at 263 (Cl) and 261 (Br) to 10*b*. The depolarized, *X*-sensitive bands at 232 (Cl) and 221 (Br) are assigned to ν_6; the *X*-insensitive bands at 205 (Cl) and 203 (Br) to ν_4.

For Ph_2PI, ν_3 is observed at 193 and ν_4 is masked by this very strong ν_3 band. A shoulder band at 210 cm^{-1} is assigned to ν_6. In order to confirm the band assignments an approximate normal coordinate analy-

Table 1. Normal vibrations of the C_2PCl skeleton (point group C_s)

Designation	Description	Symmetry type
ν_1	νPCl	A'
ν_2	$\nu_s PC_2$	A'
ν_3	$\delta_s C_2PCl$	A'
ν_4	δPCl_2	A'
ν_5	$\nu_{as} PC_2$	A''
ν_6	$\delta_{as} C_2PCl$	A''

Table 2. Vibrational frequencies (cm^{-1}) and assignments for the Ph_2PX derivatives

Ph_2PCl		Ph_2PBr		Ph_2PI		Assignment	
I.r.	Raman	I.r.	Raman	I.r.	Raman		
617 m	620	618 vw	617 dp	618 vw	617 dp	6*b**	
553 w		544 m	~550	548 m	~550	16*b*	
500 vs	500 p	508 s	~500	505 s	~500		
500 vs	500 p	394 vs	394 p	365 vs	365 p	ν_1	
458 m	458 p	481 s	481 p	476 m	476 p	ν_2	7a
427 m	427 dp	430 s	429 dp	428 m	~430 dp	ν_5	
402 w	401	405 sh	404 dp	404 vw	402 dp	16*a*	
	284 p		235 p		193 p	ν_3	
	263 p		261 sh		260 p	10*b*	
	232 dp		221 sh		210 dp	ν_6	
	205 dp		203 sh			ν_4	

* Wilson notation see Ref. [13].

sis is carried out for the skeletal vibrations of Ph_2PCl using a three mass model [4] as an approximation for the phenyl group. Indeed a rigorous treatment is not possible since the structural data are not available and estimated bond and angle data are used in the calculations. The estimated structural data are: $d_{P\text{-}Cl} = 2.04$ Å, P–C = 1.82 Å, C–Y = 1.40 Å, $\alpha_{C\text{-}P\text{-}C} = 103°$, $\alpha_{C\text{-}P\text{-}Cl} = 100°$ and $\alpha_{P\text{-}C\text{-}Y} = 120°$.

General vibrational analysis programs [14] utilizing the Wilson *GF* matrix method for a "general unsymmetrized molecule" are used.

The relevant internal coordinates of the $(Y_2C)_2PCl$ skeleton and the optimized set of force constants are summarized in Table 3. Observed and calculated frequencies and the potential energy distribution (PED) for Ph_2PCl are collected in Table 4. Despite the crudeness of the model a fairly good agreement is obtained between the observed and calculated frequencies using a reasonable set of force constants. The PED shows intensive coupling especially between the phenyl ring stretching (breathing), approximated as a Y–C–Y three mass vibration, and the phenyl-P-stretching. This marked mixing of normal vibrations is responsible for the low frequencies of ν_{P-C} with respect to the alkylphosphorus compounds ($\nu_{C-P} = 620$–$720\,cm^{-1}$).

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Table 3. Relevant internal coordinates of $(Y_2C)_2PCl$ skeleton

Designation	Description	Valence force constants in mdynes/Å	
r_1	P – Cl stretch	$fr_1 = 1.99$	$fr_2r_3 = 0.45$
$r_2 = r_3$	P – C stretch	$fr_2 = 3.23$	$f\alpha_{12}\alpha_{13} = 0.05$
α_{23}	C – P – C bend	$f\alpha_{23} = 0.14$	$fr_2\beta_{45} = 0.30$
$\alpha_{12} = \alpha_{13}$	Cl – P – C bend	$f\alpha_{12} = 0.28$	
$\beta_{45} = \beta_{67}$	Y–C–Y bend		

Table 4. Observed and calculated frequencies and potential energy distribution (PED) for Ph_2PCl

Designation	Observed	Calculated	PED (> 10%)
ν_1	503	503	$\Delta r_1(70)$, $\Delta\alpha_{12}(18)$
ν_2	458	457.9	$\Delta r_2(42)$, $\Delta\beta_{45}(26)$, $\Delta\alpha_{12}(18)$
ν_5	427	427	$\Delta r_2(47)$, $\Delta\beta_{45}(36)$, $\Delta\alpha_{12}(14)$
ν_3	284	283.9	$\Delta\alpha_{12}(63)$, $\Delta r_1(28)$
ν_6	232	232.2	$\Delta\alpha_{12}(80)$,$\Delta r_1(13)$
ν_4	205	204.8	$\Delta\alpha_{23}(89)$

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