Solution and Single-crystal Raman Study and Revised Assignment for Hexachlorocyclotriphosphazene

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The long-sought $\nu_4(a_1')$ mode of $(PNCl_2)_3$ has been located at 172 cm^{-1} in solution and its symmetry species confirmed by a Raman study of an oriented single crystal. Experimental evidence from the crystal spectra also allowed distinction between e' and e'' species. A reassignment of the spectrum is offered.

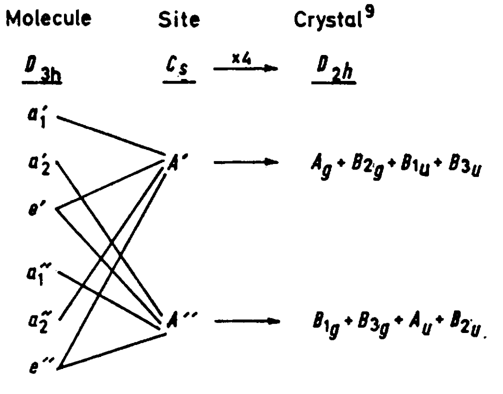
HEXACHLOROCYCLOTRIPHOSPHAZENE (I), executes four totally symmetric modes of vibration. Two of these were observed as strongly polarised bands by Ficquelmont, Magat, and Ochs [1] (672 and 366 cm^{-1}), who were the first to study the Raman spectrum of this molecule. Later Daasch [2] reported, in addition, a weak band, probably polarised (at 785 cm^{-1}), and all subsequent Raman studies have confirmed the identification of these three a_1' modes.[3-6] The location of the fourth totally symmetric mode has proved difficult: we present evidence that it is at 172 cm^{-1} and not at either 304 or *ca.* 100 cm^{-1} as has been claimed.[2,3,5]

TABLE 1

Unit cell analysis and correlation scheme for phosphonitrilic chloride trimer

D_{2h}^{16}	A_{1g}	B_{1g}	B_{2g}	B_{3g}	A_u	B_{1u}	B_{2u}	B_{3u}
N_T	20	16	20	16	16	20	16	20
T_A						1	1	1
T	2	1	2	1	1	1	0	1
R	1	2	1	2	2	1	2	1
N_i	17	13	17	13	13	17	13	17

N_T = Total number of modes; T_A = acoustic modes; T = translatory modes, optical branch; R = rotatory modes; N_i = internal molecular modes.



In principle, it should be simple to deduce an assignment for compound (I) based upon the particularly helpful D_{3h} selection rules, but in practice we come unstuck at one of the key steps—identification of i.r.–Raman coincidences (e' modes) due to the disparity of i.r. and Raman intensities. Further complications arise in deciding which of the observed bands are due to fundamentals. The Raman spectrum of compound (I) has not been studied using an oriented single crystal; in view of this and of the unsatisfactory basis of part of the current assignment we thought it worthwhile to perform these experiments and to re-examine the solution spectrum.

Selection rules have been published previously and are summarised here for convenience (i.r. and R in paren-

$$\Gamma = 4a_1'(\mathrm{R}) + 2a_2' + 6e'(\mathrm{i.r.} + \mathrm{R}) + a_1'' + 3a_2''\ (\mathrm{i.r.}) + 4e''(\mathrm{R})$$

theses indicate activities). For the crystal spectra the unit cell analysis and correlation scheme of Table 1 are applicable. It is also valuable when making the assignment to bear in mind the approximate mode

TABLE 2

Assignment for hexachlorocyclotriphosphazene

a_1'	ν_1	Ring breathing	669
	ν_2	Ring in-plane deformation	786
	ν_3	$\nu(PCl_2)_s$	364
	ν_4	$\delta(PCl_2)_s$	172
a_2''	ν_5	Ring out-of-plane deformation	619
	ν_6	$\nu(PCl_2)_a$	552
	ν_7	$\rho_r PCl_2$	(188) [a]
a_1''	ν_8	$\rho_r PCl_2$	
a_2'	ν_9	Ring stretch	
	ν_{10}	$\rho_w PCl_2$	
e'	ν_{11}	Ring stretch	1226
	ν_{12}	Ring stretch	1202 or 875
	ν_{13}	Ring in-plane deformation	529
	ν_{14}	$\nu(PCl_2)_s$	334
	ν_{15}	$\rho_w PCl_2$	157
	ν_{16}	$\delta(PCl_2)$	218
e''	ν_{17}	$\nu(PCl_2)_a$	584
	ν_{18}	Ring out-of-plane deformation	202 [c]
	ν_{19}	$\rho_T PCl_2$	(132) [a]
	ν_{20}	$\rho_r PCl_2$	( ) [b]

[a] Speculative assignment, see text. [b] Missing from Raman spectrum. [c] The order of these modes is unknown.

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[1] A. Ficquelmont, M. Magat, and L. Ochs, *Compt. rend.*, 1939, **208**, 1900.

[2] L. W. Daasch, *J. Amer. Chem. Soc.*, 1954, **76**, 3403.

[3] A. C. Chapman and N. L. Paddock, *J. Chem. Soc.*, 1962, 635.

[4] E. Steger and R. Stahlberg, *Z. anorg. Chem.*, 1964, **326**, 243.

[5] I. C. Hisatsune, *Spectrochim. Acta*, 1965, **21**, 1899.

[6] J. Emsley, *J. Chem. Soc.* (*A*), 1970, 109.

descriptions, Table 2, in which we follow Califano's numbering scheme.[7,8]

RESULTS AND DISCUSSION

Our new data are in Tables 3 and 4.

TABLE 3

Raman frequencies/cm^{-1} for solutions [a] of $(PNCl_2)_3$

786m	P	298vw	P
669s	P	202m	dP
584w	dP	172m	P
529vw	dP	157m	dP
364vs	P	*ca.* 97m	dP [b]
334w	dP		

[a] Only very approximate relative intensities are given as several different solvents were used. [b] The frequency of this band varies slightly from solvent to solvent.

a_1' Modes.—Two of these modes (ν_1 and ν_2) are essentially motions of the P_3N_3 ring, the others being reasonably described as P–Cl stretching (ν_3) and PCl_2 deformation (ν_4). Phosphorus pentachloride has stretching frequencies at 594 and 394 cm^{-1}; frequencies of P–Cl bonds in compound (I) are expected to be fairly near these values. Accordingly we assign the 364 cm^{-1} line as ν_3. Some qualitative support for this view comes from a recent discussion of the optical properties of crystals of (I) in which it was concluded that the refractive indices are determined primarily by the polarisability of the chlorine atoms:[9] the 364 cm^{-1} band is by far the most intense in the whole Raman spectrum. The totally symmetric ring breathing mode, ν_1, is most probably associated with the intense 669 cm^{-1} band; it is reasonable that ν_2 (which is essentially an antiphase stretch) should come at higher frequency, *viz.* 786 cm^{-1}. If $\nu(P–Cl)_s$ is at 364 cm^{-1}, ν_4 will not be above 200 cm^{-1} and a somewhat lower value is probable.

A weak polarised band at 304 cm^{-1} has been reported earlier and assigned as ν_4. We confirm the observation but reject the assignment on the above grounds. We also confirm the observations of others [1-3] that a broad feature is present *ca.* 100 cm^{-1}, probably polarised, but we consider this to be associated with the structure of the solution rather than that of the solute because (*i*) there is no equivalent band in the crystal spectra and (*ii*) low-frequency Raman emission is now known to be a feature of liquids and is associated with their quasi-lattice modes.

In dichloromethane solution we find that the 172 cm^{-1} band is significantly polarised, see Figure 1. We do not understand why this has not been detected previously but we do find that the depolarisation ratio varies slightly with solvent. In the crystal the corresponding band is at 178 cm^{-1} and shows both A_{1g} and B_{2g} components as required for an a_1' molecular mode. In contrast, the neighbouring solution bands at 165 and 202 cm^{-1} both yield crystal bands with all four components present ($A_g + B_{1g} + B_{2g} + B_{3g}$), which they must do as they are *e* modes by elimination as well as by observation. It is true that the 178 cm^{-1} band shows very weak B_{1g} and

TABLE 4

Raman bands and intensities (arbitrary units) for single crystal $(PNCl_2)_3$

		Set 1 [a]				Set 2 [a]				Set 3 [a]				Assignment	
	ν/cm^{-1}	$z(yy)x$	$z(xy)x$	$z(xz)x$	$z(yz)x$	$z(xx)y$	$z(yx)y$	$z(xz)y$	$z(yz)y$	$y(zz)x$	$y(xy)x$	$y(xz)x$	$y(zy)x$	Crystal	Molecular
c	23						8	12	90	25	28	5	75	$A_g + B_{1g} + B_{3g}$	Translatory lattice modes
	28					173	42	45		10	28	50		$A_g + B_{1g} + B_{2g}$	
b c	42							45		35		45		B_{2g}	Rotatory lattice modes
	46								65				55	B_{3g}	
	49					100								A_g	
	53						125				100			B_{1g}	
	57							73	60			92	58	$B_{2g} + B_{3g}$	
	59					87				85				A_g	Overtone
	132				<1									B_{3g}	e''?
	163	130	78	33	44	62	53	25	36	33				$A_g + B_{1g} + B_{2g} + B_{3g}$	e'
	178	140	8	100	10	67	12	65	15	90				$A_g + B_{2g}$	a_1'
	205	14	40	60	65	48	32	45	45	98				$A_g + B_{1g} + B_{2g} + B_{3g}$	e''
	218			15		9		5		*ca.* 10				$A_g + B_{2g}$	e'
	338	70	34	25	20	40	22	20	16	27				$A_g + B_{1g} + B_{2g} + B_{3g}$	e''
	365	155	10	67	8	135	20	97	23	*ca.* 300				$A_g + B_{2g}$	a_1'
	521	<1				<1								A_g	e'
b	568	<1	3		3									$A_g + B_{1g} + B_{2g} + B_{3g}$	e''
	573	2		3		10				10					
	576			4	5										
	667	100	5	15		50	8	21	8	52				$A_g + B_{2g}$	a_1'
	676	~30				*ca.* 18		*ca.* 8		*ca.* 20				A_g	
	783	78		22		23	5	14	5	15				$A_g + B_{2g}$	a_1'
c	812	7												A_g	
	1250		10		3									$B_{1g} + B_{3g}$	e'

[a] Intensities are not strictly comparable between the three sets. [b] Intensities in this region are approximate due to overlapping of bands. [c] These intensities should be divided by about 3 to make them comparable with other regions.

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[7] S. Califano, *J. Inorg. Nuclear Chem.*, 1962, **24**, 483.

[8] S. Califano and A. Ripamonti, *J. Inorg. Nuclear Chem.*, 1962, **24**, 491.

[9] G. J. Bullen, *J. Chem. Soc.* (*A*), 1971, 1450.

B_{3g} components, but these we regard as residuals; the intensely polarised 364 cm^{-1} line, which is undoubtedly due to an a_1' mode, shows similar residuals in the crystal. Indeed, we note that all four frequencies which we now assign to the a_1' class show identical behaviour in the oriented crystal spectra, and that this behaviour is exactly that required by theory. We also recall that Chapman and Carroll in their force field study[10] of compound (I) found that ν_4 is to a large extent dependent upon the other three 'diagonal' force constants in the a_1' block and is necessarily not much lower than 200 cm^{-1}.

The solution depolarisation ratios are in excellent agreement with the values calculated from individual derived scattering tensor components shown by the oriented crystal. Thus:

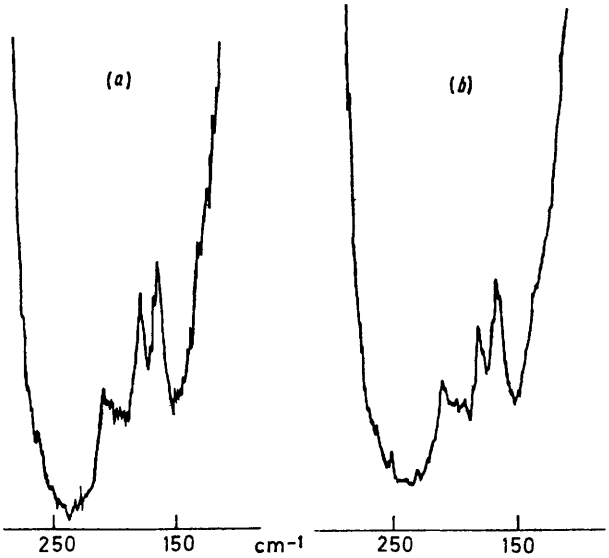

FIGURE 1 Raman spectrum of $(PNCl_2)_3$ in CH_2Cl_2 solution showing polarisation behaviour of the bands at 157dP, 172P, and 202dP cm^{-1}. Spectral slit width 1 cm^{-1}, 632·8 nm excitation, 30 mW at the sample; (a) ∥, (b) ⊥

Band/cm^{-1}	364	172
ρ observed	0·03	0·65
ρ calculated	0·02	0·68

The ρ values for e' and e'' bands were all near the depolarised value 0·86.

a_2'' *Modes.*—These are unique to the i.r. spectrum. One a_2'' mode, ν_7, is a PCl_2 rock and will be below 250 cm^{-1}. There is no clear-cut evidence for its assignment, see below.

Two reports of i.r. studies on oriented samples of compound (I) are broadly in agreement[8,11] that the two higher frequency a_2'' modes are at *ca.* 544 and 610 cm^{-1} (average values), corresponding to vapour frequencies 552 and 619 cm^{-1}. Califano assigned these as ν_6, ν(P–Cl) and ν_5, ring out-of-plane bend, respectively.

e' and e'' *Modes.*—These ten modes are Raman-active with the six e' modes also i.r.-active. Four of these ($2e' + 2e''$) will be below 250 cm^{-1} as they are deformational motions of the PCl_2 groups, whilst two more are ν(P–Cl) modes and must therefore be between 300 and 600 cm^{-1}.

In the Raman spectrum of the oriented crystal e' can be distinguished from e'' modes because the latter give rise to crystal A_g modes which lack a (yy) component. Thus, reorientation of the D_{3h} Raman tensor components for a_1', e', and e'' species using the transformation matrix (**1**) yields the following results.

$$\begin{pmatrix} 0\cdot9205 & 0 & 0\cdot3907 \\ 0 & 1 & 0 \\ -0\cdot3907 & 0 & 0\cdot9205 \end{pmatrix} \qquad (\mathbf{1})$$

$$a_1'\begin{pmatrix} a & & \\ & a & \\ & & b \end{pmatrix} \longrightarrow \begin{pmatrix} 0\cdot8472a + 0\cdot1527b & 0 & -0\cdot3596a + 0\cdot3596b \\ 0 & a & 0 \\ -0\cdot3596a + 0\cdot3596b & 0 & 0\cdot1527a + 0\cdot8472b \end{pmatrix}$$

$$e'\begin{pmatrix} c & d & \\ d & -c & \\ & & 0 \end{pmatrix} \longrightarrow \begin{pmatrix} 0\cdot8472c & 0\cdot9205d & -0\cdot3596c \\ 0\cdot9205d & -c & -0\cdot3907d \\ 0\cdot3596c & -0\cdot3907d & 0\cdot1527c \end{pmatrix}$$

$$e''\begin{pmatrix} & & f \\ & & g \\ f & g & 0 \end{pmatrix} \longrightarrow \begin{pmatrix} 0\cdot7192f & 0\cdot3907g & 0\cdot6945f \\ 0\cdot3907g & 0 & 0\cdot9205g \\ 0\cdot6945f & 0\cdot9205g & -0\cdot7192f \end{pmatrix}$$

In solution we find the following depolarised bands: 157, 202, 334, 529, and 584 cm^{-1}. Most previous investigations failed to reveal any Raman solution bands above 800 cm^{-1} but Emsley[6] has recently reported feeble emission at 901 and 1212 cm^{-1}, and it is sobering to note that a very weak 1230 cm^{-1} band was detected in 1939.[1] Certainly, all of the bands of any intensity have been located: further studies may yet show up more feeble features, and possibly confirm the very weak bands above 800 cm^{-1}, but even if they do the question still arises as to whether they are fundamentals.

In the oriented crystal spectra all of these bands show the $A_g + B_{1g} + B_{2g} + B_{3g}$ components expected for e-type modes, apart from the 528 cm^{-1} band. Hisatsune[5] failed to find an equivalent of this solution band in the solid: we find exceedingly weak emission at 521 cm^{-1} in three crystal orientations. As there is a strong band in the i.r. spectrum of the solution at 527 cm^{-1} we conclude that this is an e' fundamental but the low Raman intensity in the solid does not inspire confidence.

The Raman-active e modes can now be assigned using the relative intensity predictions of the oriented tensor components. The 205 cm^{-1} band has a very weak (yy) component whereas that at 163 cm^{-1} is particularly strong in this spectrum as predicted for e'' and e' species respectively. An e'' mode should also have equally intense (xx) and (zz) spectra whilst for e' modes the (zz) intensity should be about one sixth of that in (yy). Although the observed intensity ratios are not in exact agreement, they are sufficiently close to these predictions to lend strong support to the assignment 163, e'; 205 e''. A rather weak feature at 218 cm^{-1} has a very weak (yy) component and an intense i.r. counterpart: it is therefore of e' symmetry.

From its i.r. coincidence the 338 cm^{-1} band must be of e' symmetry; this is confirmed by its strong (yy) component. It is assigned to the ν(P–Cl) mode, ν_{14}. The

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[10] A. C. Chapman and D. F. Carroll, *J. Chem. Soc.*, 1963, 5005.

[11] U. Stahlberg and E. Steger, *Spectrochim. Acta*, 1967, **23A**, 627.

complex band at *ca.* 570 cm^{-1} is extremely weak in (yy) but clearly present in all other orientations: we conclude that it is of e'' symmetry.

By elimination of the a_2'' modes the remaining i.r. bands must correspond to e' modes and should all have Raman counterparts. In the vapour Califano[7] found bands at: 336m, 533vs, 552s, 584vw, 619vs, 636m, 1202s, 1226vs together with others above 1000 cm^{-1} not due to fundamentals. The extremely weak 584 cm^{-1} band was attributed to the Raman-active ν_{17}, e'' made i.r.-active by Coriolis coupling with the intense e' mode at 533 cm^{-1}. The 636 cm^{-1} band has no Raman counterpart in any state and is therefore unlikely to be a fundamental. (The 669 cm^{-1} line does show a slight 'tail' on the low frequency side in some orientations; this might be associated with a counterpart to the 636 cm^{-1} line but we are inclined to doubt it.) Whether the 1202, 1226 cm^{-1} vapour bands and their complex i.r. solid state equivalents are to be considered as one or two e' fundamentals is uncertain. Califano considered the alternative possibility that the 875 cm^{-1} band (i.r., solid), which shows classic e' behaviour in oriented samples, is a fundamental but was unable to decide. More recently, Stahlberg and Steger have more definitely assigned it as a fundamental.[11]

Thus far the evidence upon which we have based assignments has been strong. We have located all four a_1' modes; two of the three a_2'' (552, 619 cm^{-1}); five of the six e' (157, 218, 334, 529, 1226 cm^{-1}); two of the four e'' modes (202, 584 cm^{-1}). In addition the remaining e', which is a ring stretch and expected at least above 800 cm^{-1}, is catered for by two possibilities (875, 1202 cm^{-1}).

Speculative Assignments.—We have yet to locate: a_2'' (PCl$_2$ rock, below 250 cm^{-1}), and two e''. One of the e'' modes will certainly be below 250 cm^{-1} as it is a PCl$_2$ 'external' vibration. The band already assigned to e'' (205 cm^{-1}) may be either the other PCl$_2$ external mode or the ring out-of-plane deformation; accordingly the second of the missing e'' modes may or may not be above 250 cm^{-1}.

Hisatsune reported weak i.r. bands, present in both solid and solution, at 140 and 188 cm^{-1}. We tentatively assign the higher of these as ν_7, a_2''. The missing e'' modes can only be Raman-active. An exceedingly weak feature was found at 132 cm^{-1} in the (yz) orientation; in the absence of any other candidates we label it as of e'' symmetry.

Lattice Modes.—There are two groups of lattice modes *ca.* 25 and 50 cm^{-1}. The lower pair bear multiple symmetry labels, but there is sufficient intermolecular interaction in the modes generating the higher group to split out the various contributions. Three A_g modes are predicted but four were found. It is probable that one of these is an overtone which has gained intensity by Fermi resonance: it is logical to assume then that two of the A_g fundamentals are in the lower group, thereby requiring these to be primarily translatory in nature. This conjecture is supported by the frequency spread

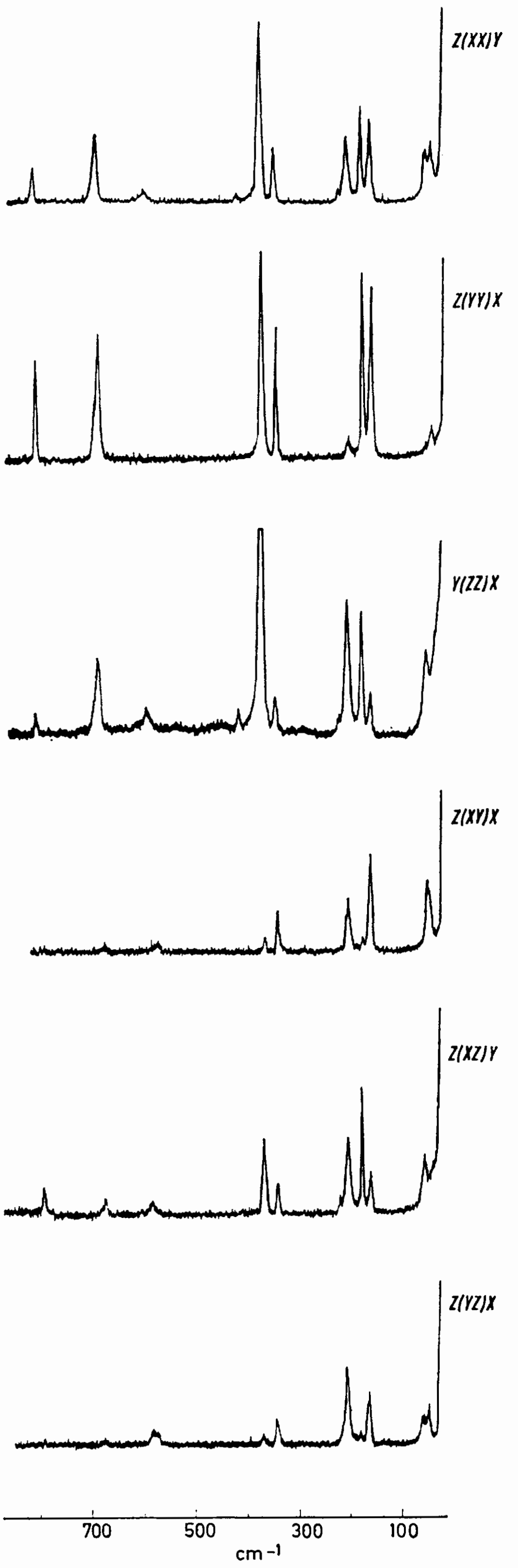

FIGURE 2 Raman spectra of a (PNCl$_2$)$_3$ crystal, orientations described in the Porto nomenclature. Spectral slit width 2 cm^{-1}, 632·8 nm excitation, 30 mW at the sample

of the bands attributed to rotational motion, as this is principally dependent upon the three moments of inertia. In contrast, the translational modes will be roughly proportional to $\sqrt{M}$ and will therefore occupy a narrower range, as is found.

CONCLUSIONS

The use of oriented single crystal Raman measurements has provided firm evidence for assignment of most of the Raman-active modes of $(PNCl_2)_3$ to their symmetry species. The most important outstanding experiment is a far-i.r. study of an oriented single crystal: we hope to do this shortly.

EXPERIMENTAL

A commercial sample was recrystallised several times from n-hexane and its purity checked by mass-spectrometric analysis. Large single crystals were grown from the same solvent and had the form of thick tabular plates with well developed (010) faces. (100) and (001) faces were also present and were developed further by grinding.

Raman spectra were obtained using Coderg PH0 and PH1 instruments with 632·8 and 488·0 nm excitation. All solvents were of spectroscopic grade.

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