

# Poly(ethylene-oxide)-*para*-Disubstituted Benzene Intercalates. Molecular Conformation of the Polymer Molecule From Far Infrared Spectra

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**Abstract.** The far infrared spectra of various poly(ethylene oxide)-*para*-disubstituted benzene intercalates are reported. From a detailed discussion, it is strongly suggested that the formula of these intercalates is either  $[(p\text{-C}_6\text{H}_4\text{XY})_3(\text{CH}_2\text{CH}_2\text{O})_{10}]_n$  (for  $\text{XY} = \text{ClCl}, \text{BrBr}, \text{BrCl}, \text{ICl}, \text{ClF}$  and  $\text{CH}_3\text{Br}$ ) or  $[(p\text{-C}_6\text{H}_4\text{XY})_2(\text{CH}_2\text{CH}_2\text{O})_7]_n$  (for  $\text{XY} = \text{BrF}$  and  $\text{IF}$ ). In both cases the conformation of the polymer molecule is nearly TTG. In addition the previously described relative disposition of the host and guest molecules is confirmed.

**Key words:** Poly(ethylene oxide) conformation; FTIR spectroscopy; *para*-disubstituted benzene poly(ethylene oxide) intercalates.

## 1. Introduction

Various *para*-disubstituted benzenes ( $p\text{-C}_6\text{H}_4\text{Cl}_2$ ,  $p\text{-C}_6\text{H}_4\text{Br}_2$ ,  $p\text{-C}_6\text{D}_4\text{Br}_2$ ,  $p\text{-C}_6\text{H}_4\text{FCl}$ ,  $p\text{-C}_6\text{H}_4\text{FBr}$ ,  $p\text{-C}_6\text{H}_4\text{FI}$ ,  $p\text{-C}_6\text{H}_4\text{ClBr}$ ,  $p\text{-C}_6\text{H}_4\text{CH}_3\text{Br}$ , etc.) are the guest compounds of intercalates in which poly(ethylene oxide) (PEO) is the host compound [1–5].

The present paper deals with a Fourier transform infrared (FTIR) study (in the range  $50\text{--}650\text{ cm}^{-1}$ ) of these compounds. The aims of the present study are the following.

- IR spectra (in the range  $500\text{--}3000\text{ cm}^{-1}$ ) [2], X-ray fiber diagrams [3], and measurement of optical properties [5] were previously used to determine the orientation of the *para*-disubstituted benzene guest molecule with respect to the helical axis of the PEO molecule. Confirmation of the results obtained from these studies is hoped for from the present study.
- A theoretical study [4] has shown that the far infrared part of the spectrum of an *isolated* PEO helix is the most sensitive to the actual conformation of the molecule. In fact previous studies [2–4] lead us to the conclusion that, in some of these intercalates, the conformation of the PEO molecule is a  $10/3$  (or possibly an  $11/3$ ) helix with nearly TTG configuration.

This seems well established for the  $p\text{-C}_6\text{H}_4\text{Cl}_2$ ,  $p\text{-C}_6\text{H}_4\text{Br}_2$ ,  $p\text{-C}_6\text{H}_4\text{BrCl}$ , and  $p\text{-C}_6\text{H}_4\text{ICl}$  PEO intercalates which give good X-ray fiber diagrams. Such a conformation differs from, but is very similar to, the  $7/2$  helix confirmation of the molecule in pure poly(ethylene oxide).

Definitive confirmation of these findings is hoped for from this study. But in the X-ray fiber diagrams of other intercalates (with  $p\text{-C}_6\text{H}_4\text{BrF}$ ,  $p\text{-C}_6\text{H}_4\text{ClF}$ ,  $p\text{-C}_6\text{H}_4\text{CH}_3\text{Br}$  as guest compounds) few layer lines are observed. For these compounds, the mid infrared spectra may equally well be explained on the basis of a  $7/2$  or of a

10/3 helical conformation. The expectation is that the far infrared spectra may allow a good choice between these two conformations.

- (c) This expectation relies on the assumption that in the intercalates the PEO IR spectrum is determined by intramolecular conformation and is not greatly affected by intermolecular interactions and that subtle details about the helical conformation of a polymer molecule in a crystal may be obtained by the sole examination of its infrared spectrum. That assumption itself is an interesting point.

## 2. Experimental

### 2.1. PREPARATION OF THE SAMPLES

The polymer used was an Aldrich PEO sample ( $\bar{M}_w = 5 \times 10^6$ ). Films were heated between two copper foils in a Carver press at 90°C and then quenched in liquid nitrogen. The films were cold-drawn to a draw ratio higher than 5 : 1. The measurement of the dichroic ratio [6] of the 840 cm<sup>-1</sup> band gave a value of 0.84 for the second order moment of the orientation function of the PEO chain axis. With a view to increasing the affinity of formation of the complex, the crystallinity of the PEO samples has been decreased by quenching the melted films. The characteristic band at 1349 cm<sup>-1</sup> [7] observed in the molten state (which corresponds to the solid bands at 1364 and 1345 cm<sup>-1</sup>) is the most convenient to estimate the amorphous content of the sample and is clearly observed in the spectra of the starting pure PEO samples. These films were swollen by the vapor of various *para*-disubstituted benzenes at 38°C for more than 250 h with formation of crystalline intercalates and subsequent reduction of the intensity of the 1349 cm<sup>-1</sup> band.

### 2.2. INFRARED SPECTROSCOPY

Infrared spectra were obtained on a Bruker IF 113V Fourier transform infrared spectrometer. Thirty two co-added interferograms were scanned (usually) at 2 cm<sup>-1</sup> (but sometimes 0.5 cm<sup>-1</sup>) resolution. The polarized spectra were obtained by using a Specac polarizer made of an aluminium wire grid deposited on KRS5 windows. Therefore no polarization measurements could be obtained below 200 cm<sup>-1</sup>. Polarized spectra were recorded with the electric vector either parallel (||) or perpendicular (⊥) to the fiber axis.

## 3. Results

Two intercalates were prepared from symmetrically *para*-disubstituted benzene derivatives. The symmetry species of the normal modes of these derivatives belong to the point group  $D_{2h}(V_h)$ . The infrared spectra of these compounds will be discussed first. The other intercalates were prepared from asymmetrically *para*-disubstituted benzene derivatives which belong to the point group  $C_{2v}$ . The infrared spectra of these compounds will be discussed separately.

### 3.1. SPECTRA OF SYMMETRICALLY *PARA*-DISUBSTITUTED BENZENE DERIVATIVES

The results for the absorption bands that are not badly overlapped by PEO bands are given in Table I. The assignments of the different vibrational modes of the molecules used are given according to Varsanyi [8].

Table I. Wavenumber values of the absorption bands of symmetrically *para*-disubstituted benzenes and of their intercalates in PEO.

Substituent	Assignment	Pure derivative <sup>a</sup>		Intercalates	Dichroic behaviour <sup>b</sup>
		Ref. [8]	This work		
Br	10b ( $b_{2g}$ )	282		282	
	20a ( $b_{1u}$ )	424	426.5	427.5	(2)
	16b ( $b_{3u}$ )	478	469.5(467.5)	487	⊥ (1)
Cl	16b ( $b_{3u}$ )	485	483(479, 474)	498,5	⊥ (1)
	20a ( $b_{1u}$ )	550	545.5; 542;	545; 541;	(2)
			538	537	
	?		558	556.5	(2)

<sup>a</sup> The numbers in brackets correspond to the wavenumber value of a shoulder or low intensity side bands.

<sup>b</sup> The numbers in brackets are estimations of the dichroic ratio (see text).

It is seen that the out-of-plane mode (16b) is strongly influenced in the intercalates. A frequency shift of 12–13.5  $\text{cm}^{-1}$  can be observed. The position of the  $\nu_{20a}$  CX stretching mode, which is partly a CH in-plane mode, is unchanged. The first results is not new [2] but it is recalled here because in other intercalates and for other out-of-plane modes such large shifts are not observed. Notice that in the *p*- $\text{C}_6\text{H}_4\text{Cl}_2$ -PEO intercalate the isotope splitting of the  $\nu_{20a}$  band appears clearly (see also Figure 1). Preliminary calculations show that the observed splitting has the right order of magnitude and that no noticeable isotope splitting is to be expected on observing other absorption bands.

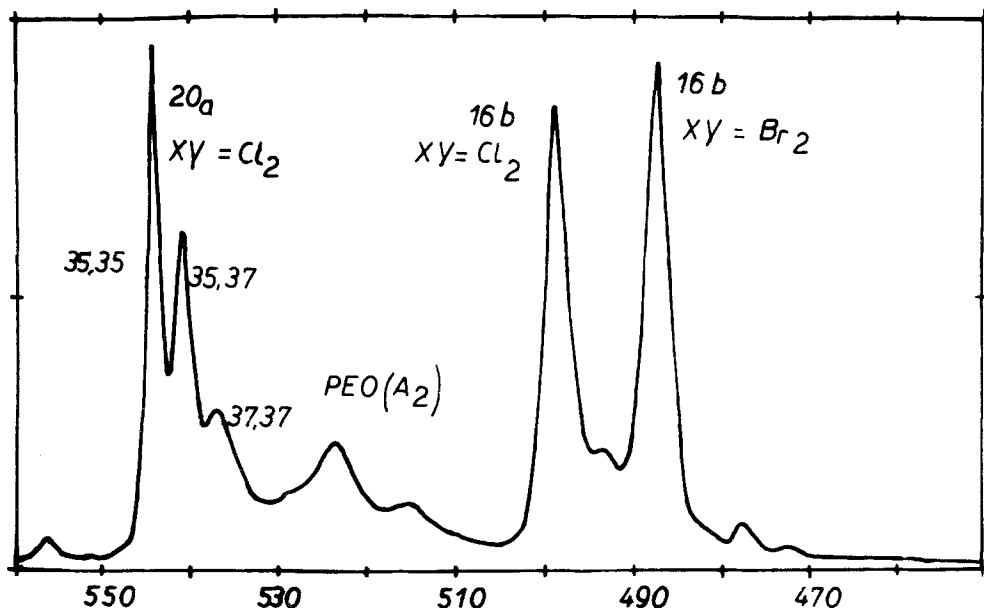


Fig. 1. Spectra of an oriented sample of an intercalate made of PEO with *p*- $\text{C}_6\text{H}_4\text{Cl}_2$  and *p*- $\text{C}_6\text{H}_4\text{Br}_2$ . Parallel polarization. The width of the  $A_2$  parallel band of PEO is reduced. The  $\nu_{20a}$  band of *p*- $\text{C}_6\text{H}_4\text{Cl}_2$  is isotopically split. The  $\nu_{16b}$  bands of *p*- $\text{C}_6\text{H}_4\text{Cl}_2$  and *p*- $\text{C}_6\text{H}_4\text{Br}_2$  are greatly shifted from the liquid phase values.

3.2. SPECTRA OF ASYMMETRICALLY *PARA*-DISUBSTITUTED BENZENES

The vibrational wavenumbers of the pure compound and for the compound as guest in the intercalates are given in Table II together with the estimation of the dichroic ratio ( $R = A_{\parallel}/A_{\perp}$  for  $A_{\parallel}$  and  $A_{\perp}$ , the peak optical density). In these  $C_6H_4XY$  derivatives the 16b out-of-plane mode of the ring is strongly influenced in the intercalates and frequency shifts of the order of 9–18  $cm^{-1}$  are observed. In  $p-C_6H_4ClBr$  it appears likely that due to the effect of the shift of the  $\nu_{16b}$  band, the  $\nu_{16b}$  and  $\nu_{20a}$  absorptions result in a single wide absorption band. By contrast such large shifts are not observed for the 10b out of plane mode (and perhaps neither for the  $\nu_{11}$  out of plane mode see Section 3.3). On the other hand no significant wavenumber shifts are observed for the in plane modes.

As expected [2] (and at the precision of the experiment) the dichroic ratio is zero for the  $b_2$  bands of all compounds with the exception of  $p-C_6H_4FI$ . As analysed below this anomaly is related to the low crystallinity of the  $p-C_6H_4FI$ -PEO intercalate sample used. On the other hand the  $a_1$  bands are slightly parallel and the  $b_1$  bands are slightly perpendicular as was found in the 500–3000  $cm^{-1}$  range of the spectra [2].

## 3.3. SPECTRA OF THE POLY(ETHYLENE OXIDE) COMPONENT

Because several absorption bands of PEO and the dihalogenobenzenes overlap, this section cannot be devoted exclusively to the discussion of the PEO spectrum. More specifically the question arises whether the bands at 130–135  $cm^{-1}$  are a PEO absorption band or result from a large displacement of the  $\nu_{11}$  bands of the *para*-dihalogenobenzenes.

The PEO spectra of the intercalates with  $p-C_6H_4BrF$  or  $p-C_6H_4IF$  as guests (and possibly  $p-C_6H_4ClF$ ) differ from those of the other intercalates which will be discussed first. For these other intercalates (with  $p-C_6H_4Cl_2$ ,  $p-C_6H_4Br_2$ ,  $p-C_6H_4ClBr$ ,  $p-C_6H_4ClI$  and  $p-C_6H_4CH_3Br$  and possibly  $p-C_6H_4ClF$  as guest component) the following common features are observed.

- (a) The 167  $cm^{-1}$   $E$  band of PEO which corresponds to a torsion around the CC and CO bonds is strongly influenced in the intercalates and frequency shifts to the high-frequency side of 7–14  $cm^{-1}$  can be observed.
- (b) The 217  $cm^{-1}$   $E$  band of PEO which corresponds to a skeleton mode involving COC and CCO bending presents a shift to the high-frequency side.
- (c) In Table III the band at 105–111  $cm^{-1}$  is compared to the 107  $cm^{-1}$   $A_2$  band which results from a torsion mode around the CO bonds. But it must be emphasized that the frequencies of this  $A_2$  mode of PEO and of the  $\nu_{11}$  out-of-plane mode of the benzene derivative are near one another and the corresponding vibrations results in a composite band. For instance, in pure  $p-C_6H_4Cl_2$ , the  $\nu_{11}$  band appears at 114  $cm^{-1}$  and the composite band at 110  $cm^{-1}$ . For  $p-C_6H_4Br$ ,  $p-C_6H_4ClBr$  and  $p-C_6H_4ClI$  these wavenumbers are somewhat lower. But we do not go further and we conclude solely that in *these intercalates* the shifts of the 107  $cm^{-1}$   $A_2$  band of PEO are rather low.
- (d) An additional band of low intensity (or a shoulder, see Table III) appears near 135  $cm^{-1}$  (131  $cm^{-1}$  in the  $p-C_6H_4ClI$  intercalate). The  $\nu_{11}$  modes of the *p*-dihalogenobenzenes are out-of-plane modes and it may be that the corresponding absorption bands are largely displaced to the high frequency side (as other out-of-plane bands, for instance  $\nu_{16b}$ ) from their various original positions (100–121  $cm^{-1}$ ). It

Table II. Vibrational wavenumbers of asymmetrically *para*-disubstituted benzenes compared pure vs. PEO intercalates and the dichroic ratios ( $R$ )<sup>a</sup>.

Substituents	FCI		FBr		FI		ClBr		ClI		BrCH <sub>3</sub>	
	Pure	Int.	Pure	Int.	Pure	Int.	Pure	Int.	Pure	Int.	Pure	Int.
15 ( $b_2$ )	266	269	223	ov.	197	196	194	196	174	ov.	216	ov.
10b ( $b_1$ )	337	340	322	327	311	288	284	288	275	276		
9b ( $b_2$ )	422	420	418	415	415	333	333	333	324	324	vl	361
16b ( $b_1$ )	497	515	597	513	509	494	479	494	471	488	(1)	490
6b ( $b_2$ )			628	627	626	623	623	623	624	621	626	632
12 ( $a_1$ )	636		596	596	576		575		596		597	2.3

<sup>a</sup> For the dichroic ratio  $R$ , the values given in brackets are estimates given despite the fact the absorbance is either too low or too high for precise values to be obtained; vl means very low; ov. means overlapped.

Table III. Vibrational Wavenumbers for poly(ethylene oxide) ( $\text{cm}^{-1}$ ).

Substituents	PEO			Intercalates					
	ClCl	BrBr	ClBr	ClI	BrCH <sub>3</sub>	ClF	BrF	IF	
Attributions									
$A_2$	107	111	107	107	105	105	115	116	110
Unknown <sup>d</sup>	(135) <sup>a</sup>	133	135	131 <sup>a</sup>	134	(134) <sup>b</sup>			134
$E$	167	181	174	179	177	176	171	174	170
$E$	217	226	224	221	219.5	219	220	223	221
$A_2$	509	516	514.5	515	514	515	ov.	ov.	510 <sup>c</sup>
	529	523	523	523	522.5	523	ov.	528	529
$E$	534	ov.	536	536	536	536	535	534	534
Wavenumber of $\nu_{11}$ band of $p\text{-C}_6\text{H}_4\text{XY}$									
	114	103	100	104	121	137	123	113	

<sup>a</sup> Shoulder; <sup>b</sup> Possibly a composite band because the frequency of the  $\nu_{11}$  band of pure  $p\text{-C}_6\text{H}_4\text{ClF}$  is  $137\text{ cm}^{-1}$ ; <sup>c</sup> Overlap of the displaced  $\nu_{16b}$  band of  $p\text{-C}_6\text{H}_4\text{FI}$ ; <sup>d</sup> See text.

appears however likely, having a practically well defined frequency, the observed vibration must be attributed to PEO.

- (e) The most striking feature of the spectra of these intercalates is the reduction of the separation of the peaks of the  $A_2$  doublet parallel band (at  $509\text{ cm}^{-1}$  and  $529\text{ cm}^{-1}$  in pure PEO). In all the intercalates of this group these bands are found at the same locations (within  $1\text{ cm}^{-1}$ ) viz.  $515\text{ cm}^{-1}$  and  $523\text{ cm}^{-1}$ .

It may be that the intercalate made from  $p\text{-C}_6\text{H}_4\text{ClF}$  falls in the same category. But the displaced  $\nu_{16b}$  band of this intercalate overlaps the  $A_2$  doublet band of PEO and prevents the estimation of the (very likely, see Figure 2) reduction of its width. Another reason why there is some doubt about the classification of this intercalate is the apparent displacement of the  $107\text{ cm}^{-1}$   $E$  band of PEO; but, again, overlap of that band and the  $\nu_{11}$  band of  $p\text{-C}_6\text{H}_4\text{ClF}$  ( $137\text{ cm}^{-1}$  in the pure compound) prevents a definitive conclusion being reached.

Let us now examine how the spectra of the  $p\text{-C}_6\text{H}_4\text{BrF}$  and  $p\text{-C}_6\text{H}_4\text{FI}$  intercalates differ from those just considered. The most striking difference concerns the  $A_2$  doublet band (at  $529\text{ cm}^{-1}$  and  $509\text{ cm}^{-1}$  in pure PEO) which remains unchanged on intercalation. In the case of the  $p\text{-C}_6\text{H}_4\text{BrF}$  intercalate only the  $528\text{ cm}^{-1}$  component of the doublet remains unmodified in position and intensity when  $p\text{-C}_6\text{H}_4\text{BrF}$  is poured in an initially pure PEO sample, until the intercalate is formed. A second characteristic of these two intercalates is the low value of the shift ( $4\text{ cm}^{-1}$ ) of the  $167\text{ cm}^{-1}$   $E$  band of PEO. Lastly in the  $110\text{ cm}^{-1}$  and  $130\text{ cm}^{-1}$  regions interference between the PEO and the  $p$ -dihalogenobenzene spectra

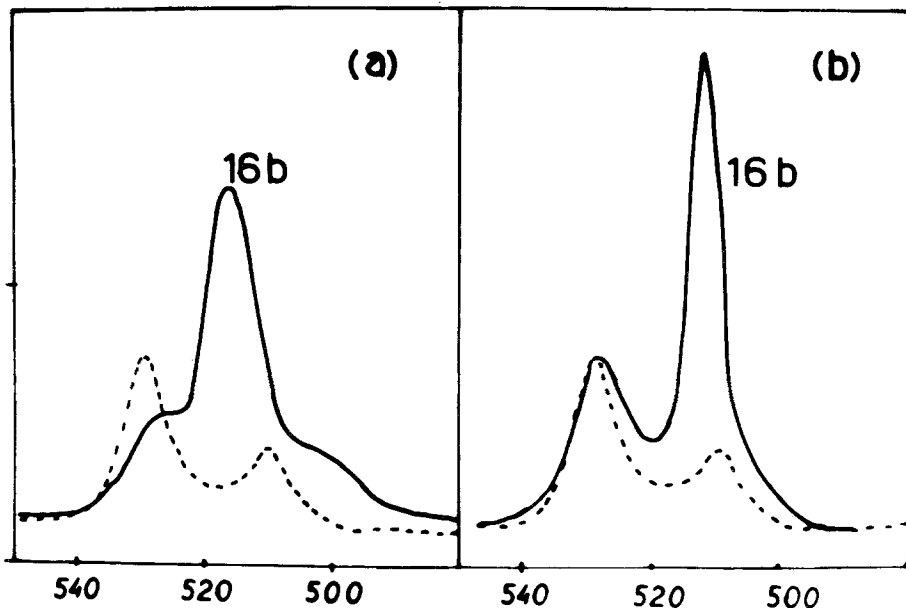


Fig. 2. Comparison of the parallel spectra of an oriented sample of PEO before and after intercalation by  $p$ -C<sub>6</sub>H<sub>4</sub>ClF (Fig. 2a) or by  $p$ -C<sub>6</sub>H<sub>4</sub>BrF (Fig. 2b).

(in which for the particular compounds considered here the  $\nu_{11}$  band is of fairly large intensity) discourage a further analysis of the spectra of these intercalates.

## 4. Discussion

### 4.1. ORIENTATION OF THE GUEST MOLECULES

Consider a rectangular Cartesian system of coordinate axes  $x$ ,  $y$  and  $z$  linked to the benzene ring, the twofold rotation axis containing the two substituents being defined as the  $z$  axis and the  $x$  axis being perpendicular to the plane of the benzene ring. Then  $b_2$  bands for asymmetrically disubstituted benzenes are polarized along  $y$ . From the values of the dichroic ratios quoted in Tables I and II we conclude that this axis is perpendicular to the fiber axis of the intercalate; this is a confirmation of a previously established result. Values of the other dichroic ratios for bands polarized along  $z$  (respectively  $b_{1u}$  and  $a_1$  for symmetrically and asymmetrically disubstituted compounds) and for bands polarized along  $x$  (respectively  $b_{3u}$  and  $b_1$ ) also confirm our previous conclusions [2, 3].

The dichroic ratio of the  $\nu_9(b_2)$  band of the  $p$ -C<sub>6</sub>H<sub>4</sub>FI PEO intercalate is rather high. However this does not invalidate the conclusion given above. In the same sample the  $\nu_{16b}$  band appears as a doublet, both components of which having nearly equal intensities. The undisplaced (with respect to the position of the  $\nu_{16b}$  band in pure C<sub>6</sub>H<sub>4</sub>FI) component corresponds to unoriented liquid  $p$ -C<sub>6</sub>H<sub>4</sub>FI very likely present in the amorphous part of the polymer. The other component of the doublet at 513 cm<sup>-1</sup> is given by the intercalated and thus oriented  $p$ -C<sub>6</sub>H<sub>4</sub>FI. It must also be noticed that observation in the spectra of this sample of the 1349 cm<sup>-1</sup> liquid PEO band [7] confirms that the crystallinity of the studied sample is lower than those of the other intercalates. It is thus quite normal to observe that the  $\nu_{9b}$  band has an apparent dichroic ratio as high as 0.4.

#### 4.2. SHIFTS OF IR ABSORPTION BANDS DUE TO INTERACTION BETWEEN HOST AND GUEST MOLECULES

It was previously stated [2] that in the range 500–3100  $\text{cm}^{-1}$ , the sole observed out-of-plane modes of the ring (16b and 17b) were shifted to the high frequency side by 15–27  $\text{cm}^{-1}$  and this is readily understood by considering that the rotation of the *p*-disubstituted benzenes around the I4 axis is severely impeded by the surrounding PEO molecules (see Figure 4 of ref. [3]). But it is now apparent that the shift of the  $\nu_{10b}$  band of unsymmetrically disubstituted benzenes (Table II) does not exceed a few  $\text{cm}^{-1}$ .

Thus, the large shift of the  $\nu_{16b}$  and  $\nu_{17b}$  bands cannot be simply related to the 'out-of-plane character' of the corresponding vibration. This requires a theoretical calculation of frequency shifts induced by encaging the guest molecules.

#### 4.3. CONFORMATION OF THE PEO HELICES IN THE VARIOUS INTERCALATES

A brief account of the previous work on this subject is necessary for a full discussion of this point. First, to a good approximation, the conformation of the molecule in pure PEO is a regular 7/2 nearly TTG helix [10]. Secondly, in a study of the IR spectra [2] of the PEO molecules in the *para*-dihalogenobenzenes/PEO we have shown, that (with an exception concerning the  $A_2$  parallel doublet near 520  $\text{cm}^{-1}$ , which will be again considered later) very small shifts, if any, of the PEO bands are observed with respect to the position observed in pure PEO. On this basis it was assumed that the conformation of the PEO molecules in the intercalates must be similar to that observed in the pure polymer. Thirdly, in the X-ray fiber diagrams of pure PEO and of the intercalates the position of the intense layer lines are very similar. That similarity shows solely that the axial length corresponding to one turn of the PEO helices are nearly equal. However, in the fiber diagrams of at least *p*- $\text{C}_6\text{H}_4\text{Br}_2$ , *p*- $\text{C}_6\text{H}_4\text{Cl}_2$ , *p*- $\text{C}_6\text{H}_4\text{ClBr}$  and *p*- $\text{C}_6\text{H}_4\text{ClI}$ , two layer lines of low intensity are observed between the equator and the first intense layer line, two further layer lines are observed between the first and second intense layer lines. From this and from the stoichiometry it was concluded that in *these* intercalates the PEO molecular conformation was very likely a 10/3 (or possibly a 11/3) conformation.

Fourthly, we have performed a normal mode analysis of the vibration of isolated PEO molecules of various conformations. The calculated spectra were found to be very sensitive in the low frequency range which is the subject of the present investigation [4]. Let us now pass to our conclusions.

- (1) From the values of the pitches of the PEO helices and for the known CC and CO bond lengths and CCC and COC bond angles two possible models were calculated [4] (for each helix type 7/2, 10/3 and 11/3). In one of these models (model I) the conformation is nearly TTG and in the other (model II) the torsion angles differ noticeably from 180 and  $\pm 60^\circ$ .

Normal mode analysis [4] leads to the prediction (Table IV) that if models II are adopted to describe the PEO molecule in the intercalates the 217  $\text{cm}^{-1}$  *E* band of pure PEO is shifted to the high frequency side by an amount of more than 60  $\text{cm}^{-1}$  and that the 167  $\text{cm}^{-1}$  *E* band is shifted to the low frequency side by an amount of about 50  $\text{cm}^{-1}$ . Such large shifts are not observed in the present experimental work and models II are definitively excluded. In all the intercalates the polymer molecule has a nearly TTG conformation.



- (2) The calculated shifts of the absorption bands when passing from the 7/2 nearly TTG conformation to the 10/3 and 11/3 nearly TTG models are given in Table IV. The 11/3 conformation cannot be retained because neither the predicted shifts of the 167 and 217  $\text{cm}^{-1}$   $E$  bands to the low frequency side are not observed nor the large displacement of the doublet parallel band (at 509  $\text{cm}^{-1}$  in pure PEO) to the high frequency side.

On the contrary, when the 10/3 model is used the predicted shifts for the 107  $\text{cm}^{-1}$  and 509/529  $\text{cm}^{-1}$   $A_2$  bands and for the 217 and 534  $\text{cm}^{-1}$   $E$  bands are compatible with the observed values. The calculated displacement of the 167  $\text{cm}^{-1}$   $E$  band is to the high frequency side, as observed, but its shift is predicted to be too low.

As a conclusion we adopt the nearly TTG 10/3 model for the conformation of the PEO molecule in all these intercalates (but also in the PEO  $p\text{-C}_6\text{H}_4\text{BrCH}_3$  intercalate which has a similar IR spectrum). A doublet parallel band at 513 and 520  $\text{cm}^{-1}$  appears as a signature of that conformation. Part of the shifts of the 167  $\text{cm}^{-1}$   $E$  band must be due to the interaction between host and guest molecules.

- (3) In the X-ray diagrams of the PEO- $\text{C}_6\text{H}_4\text{FI}$  and PEO  $p\text{-C}_6\text{H}_4\text{BrF}$  intercalates the position of the observed intense layer lines is nearly the same as in the X-ray fiber diagrams of the other intercalates (see 2 above) and of the pure polymer. But the paucity of the presently obtained X-ray data on these two compounds allows us solely to observe these intense layer lines but not to obtain the number of intermediate layer lines of low intensities.

For the intercalates, the models II, where the torsion angles greatly differ from 180 and  $\pm 60^\circ$ , were also rejected. The 11/3 model is also excluded from considerations similar to those given in the previous paragraph. From the two possible remaining conformations the nearly TTG 7/2 helix and the nearly TTG 10/3 helix, the first appears to be preferred because the width of the  $A_2$  doublet (509  $\text{cm}^{-1}$ , 529  $\text{cm}^{-1}$ ) is not reduced and because the shift of the 167  $\text{cm}^{-1}$  band is low.

We suggest that a doublet parallel band at 509  $\text{cm}^{-1}$  and 529  $\text{cm}^{-1}$  is the signature of the 7/2 conformation that is also observed in pure PEO. In this view the rather low shift ( $+4 \text{ cm}^{-1}$ ) of the 167  $\text{cm}^{-1}$  band on passing from pure PEO to the  $p\text{-C}_6\text{H}_4\text{FI}$ -PEO and  $p\text{-C}_6\text{H}_4\text{FCl}$ -PEO intercalates would be the consequence of intermolecular interaction.

- (4) The differences in the stoichiometry of the two classes of intercalates (7/2 or 10/3 conformation) cannot be confirmed by chemical analyses because, despite the high crystallinity of the samples, the presence of small amorphous parts, which contains an unknown amount of  $p\text{-C}_6\text{H}_4\text{XY}$  complicates the problem.

Table IV. Calculated shifts on passing from the 7/2 nearly TTG conformation to the other conformations [4].

Species	Wavenumber, $\text{cm}^{-1}$	Models I (nearly TTG)			Models II	
		10/3	11/3	7/2	10/3	11/3
$A_2$	107	+2	+3	+19	+23	+23
$E$	167	+7	-5	-43	+47	+23
$E$	217	+3	-18	+60	+63	+69
$A_2$	509-529	+3	+35	-132	-138	-125
$E$	534	+1	+1	-2	-7	+3

## 5. Summary and Conclusions

As previously established, measurement of the pitch of the polymer helices in *para*-dihalogeno benzene PEO intercalates, and stereochemical considerations leads to two possible models for each of the 7/2, 10/3 and 11/3 polymer helices, one model with nearly TTG conformation and the other in which the torsion angles differ noticeably from 180 and  $\pm 60^\circ$ . Moreover normal mode analysis [4] shows that the calculated far infrared spectra are very sensitive to the skeletal conformation. In the present work, the spectra of the intercalates were recorded in the 100–650  $\text{cm}^{-1}$  region and it is concluded that these compounds fall in two categories. For the *p*- $\text{C}_6\text{H}_4\text{Cl}_2$ , *p*- $\text{C}_6\text{H}_4\text{Br}_2$ , *p*- $\text{C}_6\text{H}_4\text{BrCl}$ , *p*- $\text{C}_6\text{H}_4\text{ICl}$ , *p*- $\text{C}_6\text{H}_4\text{ClF}$  and *p*- $\text{C}_6\text{H}_4\text{CH}_3\text{Br}$  PEO intercalates the idealized shape of the polymer molecule is a 10/3 nearly TTG helix. The signature of this conformation is the  $A_2$  doublet parallel band at 513  $\text{cm}^{-1}$  and 520  $\text{cm}^{-1}$ .

For the *p*- $\text{C}_6\text{H}_4\text{BrF}$  and *p*- $\text{C}_6\text{H}_4\text{IF}$  PEO intercalates the polymer has a 7/2 nearly TTG conformation the signature of which is the  $A_2$  doublet parallel band at 509  $\text{cm}^{-1}$  and 529  $\text{cm}^{-1}$ . The position of an *E* band at 171–181  $\text{cm}^{-1}$  is also sensitive to the change of conformation.

It is quite remarkable that IR spectroscopy allows us to distinguish between these two very similar conformations ( $\tau_{\text{CC}} = -66.3^\circ$ ,  $\tau_{\text{CO}} = 172.5^\circ$  in the 7/2 helices,  $\tau_{\text{CC}} = -64.6^\circ$ ,  $\tau_{\text{CO}} = 167.2^\circ$  in the 10/3 helices).

Incidentally the present work confirms the mutual orientation of the guest and host molecules. The  $y$  axis of the *para*-dihalogenobenzenes lying in the plane of the ring and perpendicular to the 1/4 axis, is perpendicular to the axis of the polymer molecule. It is also found that in this region of the spectrum, the  $\nu_{16b}$  band is the sole absorption band of the benzene derivatives to be noticeably shifted.

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