Study of the influence of pressure on the p-terphenyl phase transition by Raman Scattering

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Résumé. — L’influence de la pression sur la transition de phase du p-terphényle est analysée par diffusion Raman. Cette étude améliore la compréhension du mécanisme de cette instabilité structurale reliée aux forces antagonistes inter et intramoléculaires. Aussi, comme prévu, le diagramme de phase montre que la température de transition décroît quand la pression augmente. L’observation d’un mode mou, à haute pression dans la phase basse température, indiquant que la transition passe d’un régime ordre-désordre à un régime displacif, est aussi en accord avec le mécanisme de transition proposé. Par ailleurs, notre étude montre que la transition devient clairement discontinue à haute pression.

Abstract. — The influence of pressure on the p-terphenyl phase transition is analysed by Raman Scattering. This study improves the understanding of the mechanism of this structural instability which is related to competing intramolecular and intermolecular forces. So, as expected, the phase diagram shows that the transition temperature decreases with increasing pressure. The observation of a soft mode, at high pressure in the low temperature phase, showing a change-over from an order-disorder regime to a displacive one, also agrees with the transition mechanism. Furthermore, our study indicates that the transition becomes clearly discontinuous at high pressure.

1. Introduction.

Crystalline p-polyphenyls undergo unusual structural phase transitions associated with a change of the mean molecular conformation [1]. These structural instabilities are directly related to a delicate balance between competing intramolecular and intermolecular forces. Therefore, a study of the influence of hydrostatic pressure may be very fruitful.

The p-polyphenyls are non-polar aromatic molecular compounds which consist of phenyl rings connected by single C-C bonds in para position: biphenyl (C$_{12}$H$_{10}$), p-terphenyl (C$_{18}$H$_{14}$), ... The ortho hydrogen repulsion induces a non-planar conformation for the isolated molecule, since a torsional angle exists between the planes of phenyl rings (about 40°) [2-3]. In the crystalline state, the crystal packing forces counterbalance these steric hindrance effects and the room temperature structures are constructed from molecules with a mean planar conformation. The space group is P 2$_1$/a (Z = 2) [4-8], a very common one for planar aromatic molecules. While the molecules of biphenyl present a large classical torsional thermal motion [9-10], those of p-terphenyl are disordered between two equivalent non-planar conformations. This means that, contrary to biphenyl, the mean torsional motion is governed by a local double-well potential [11]. The structural phase transitions which occur at low temperatures correspond to a stabilization of the molecules in non-planar conformations [12-14].

This type of structural instabilities is unusual in molecular crystals since it is related to an internal degree of freedom (torsion) and not to an external one (translation or rotation). Their mechanism has been discussed in relation with the competition between intramolecular and intermolecular forces [1, 15-22]. In particular, this has allowed us to understand the difference of the dynamical nature of these phase transitions for the different p-polyphenyls : displacive in biphenyl, it becomes order-disorder in p-terphenyl due to the increase of the repulsive intramolecular interactions with the number of interphenyl bonds. The best understanding of
the mechanism of these conformational instabilities can be given by the study of pressure effects, since pressure changes the balance between intramolecular and intermolecular forces. Pressure increases the relative strength of intermolecular interactions which favour planar conformations and, therefore, the transition temperatures are expected to decrease with increasing pressure. Furthermore, an interesting feature is that the dynamical nature of the transitions can be modified and especially in the case of p-terphenyl, the local double-well potential governing the single molecular motions at atmospheric pressure can be changed at sufficiently high-pressure into a single well (order-disorder → displacive).

A series of experiments by Raman and neutron scattering has been undertaken on both biphenyl and p-terphenyl in order to investigate the effects of hydrostatic pressure. Short communications of the different results have been presented at the Fifth European Meeting on Ferroelectricity (Benalmadena 1983) and at the Meeting of Dynamics of Molecular Crystals (Grenoble 1986). In this paper we report the complete results of the Raman study on hydrogenated and deuterated p-terphenyl crystals.

This compound has earlier been extensively investigated at atmospheric pressure by means of different techniques: X.R. diffraction [7, 11, 12, 25]; neutron diffraction [11, 26, 27]; electronic diffraction [28]; inelastic [29] and quasi-elastic [30-32] incoherent neutron scattering; inelastic coherent neutron scattering [33, 34]; Raman scattering [35-37]; Brillouin scattering [38, 39]; infrared absorption [40]; N.M.R. [41-44]; E.P.R. [45]; calorimetry [46, 47]. These studies have shown that the most characteristic features of the transition temperatures are expected to decrease with increasing pressure. During these experiments we have observed that, under high pressure, in the low temperature phase, the broadenings of all the modes were much smaller than those observed at atmospheric pressure. Figure 1 shows for the hydrogenated compound at 84 K the low frequency Raman spectra on both sides of the pressure transition $P_0 = 3 750$ bar.

2. Experimental procedure, results and data analysis.

Single crystals were grown by the Bridgman technique after several zone melting refinements. The samples chosen have a right angled parallelepiped shape and their approximate dimensions are $2 \times 3 \times 5$ mm. Their edges are parallel to the principal axes of the index ellipsoid which have been found to be nearly in the directions of the crystallographic axes [35]. The grating spectrometer was a LRDH 800 Coderg Raman Spectrometer and the exciting light was a He-Ne 6 328 Å line. The high pressure hydrostatic cell was designed and built at the « Laboratoire de Chimie Physique des Matériaux Amorphes, Université de Paris XI, Orsay ». It can be used up to 4 kbar and from room temperature down to liquid nitrogen temperature [48]. The pressure transducer was a XR17 intersonde while temperature was measured with a chromel-alumel thermocouple. The pressure and temperature stabilities are better than 20 bar and 0.25 K, respectively.

In our Raman studies at atmospheric pressure [35, 37], we have shown that the most characteristic phenomenon allowing the transition temperature to be determined is the evolution of the width of the lowest frequency mode. We have assigned to this mode a preponderant libration of molecules around the principal axis of inertia perpendicular to the mean molecular plane. To draw the $(P, T)$ phase diagram we have therefore observed the linewidth behaviour of this mode on one hand under constant pressure and variable temperature, on the other hand under constant temperature and variable pressure. During these experiments we have observed that, under high pressure, in the low temperature phase, the broadenings of all the modes were much smaller than those observed at atmospheric pressure. Figure 1 shows for the hydrogenated compound at 84 K the low frequency Raman spectra on both sides of the pressure transition $P_0 = 3 750$ bar.

Fig. 1. — Evolution of the low frequency spectrum of the hydrogenated p-terphenyl at different pressures and at constant temperature $T = 84$ K. $(P_0 = 3 750$ bar). The arrows indicate the soft mode.
It is obvious that the modes remain well resolved in the ordered phase, i.e. on the spectra at 2 000, 2 500, 3 000, 3 510 bar whereas in the disordered phase at \( P = 3 980 \) bar the lines are very broad and unresolved. A similar evolution is observed for the deuterated compound (\( P_0 = 3 255 \) bar at 84 K). In the constant pressure and variable temperature experiments performed in the low temperature phase we have observed that the mode overlappings become more weak as the pressure increases. So, for these experiments under pressure, it has been possible, in the spectral range around the lowest frequency mode, to deconvolute the experimental lines from the resolution function and to refine them. The intensity profile is fitted by the following convolution formula:

\[
I(v') = \int_0^\infty A(v' - v) \cdot \sum \frac{L_i(v)}{d
\]

where \( A(v' - v) \) is a triangular resolution function

\[
A(v' - v) = \begin{cases} 0 & \text{if } |v' - v| \geq \Delta A \\ KA(\Delta A - |v' - v|) & \text{if } |v' - v| < \Delta A \\ \end{cases}
\]

(\( \Delta A \) is the width of the triangular function taken equal to 0.8 cm\(^{-1} \) in all our calculations, \( K_A \) is a constant and \( v' \) is the frequency of the triangular function centre) and where \( L_i(v) \) is the Lorentzian function

\[
L_i(v) = \frac{A_i \cdot (\Gamma_i/2)}{(v - v_i)^2 + \Gamma_i^2/4}
\]

\( A_i \) is the integrated intensity, \( \Gamma_i \) the linewidth and \( v_i \) the frequency of each Lorentzian function. The \( i \) index refers to the number of modes lying in the studied spectral interval (\( i = 1 \) refers to the lowest frequency mode and so on).

The subsequent refinement program uses a least squares method. For each analysis, the fitted spectral range is defined so that the flat basic line is equal in each extremity. We have fitted, for both deuterated and hydrogenated samples, four sets of experiments at variable temperature and constant pressure (\( P = 3 500, 3 000, 2 000 \) and 1 000 bar for \( H_{10} \) p-terphenyl, \( P = 3 000, 2 500, 1 800 \) and 1 000 bar for \( D_{10} \) p-terphenyl) and one set of experiments at variable pressure and constant temperature (\( T = 84 \) K for both samples). For each set of experiments the background is considered as constant and taken equal to the flat basic line value measured on the spectrum recorded at the lowest temperature. Consequently, we suppose that the flat basic line modifications between different experiments proceeded solely from lines observed in the studied spectral range. From fitting, we obtain for each mode \( i \) the three parameters \( v_i, \Gamma_i \) and \( A_i \). Note that we have tried to improve the results by introducing in the convolution formula the Bose factor and by assimilating the experimental curves to damped oscillator response functions. The results are not significantly different from the previous ones as the values of \( \Gamma_i \) remain smaller than those of \( v_i \). So all the refined values presented in this paper have been obtained from fits using Lorentzian functions. Figure 2 shows the refinement results in two limit cases: in the considered spectral interval, firstly the two modes are completely separated, secondly the two modes overlap. We can observe the good agreement between experimental and fitted curves.
As examples, figures 3 and 4 show for the hydrogenated sample the $\Gamma_1$, $\Gamma_2$, $\nu_1$ and $\nu_2$ behaviours respectively versus pressure at constant temperature ($T = 84$ K) and versus temperature at constant pressure ($P = 3\,000$ bar). For the set of experiments at constant temperature (Fig. 3) we can emphasize the principal features: the $\nu_1$ frequency increases with pressure according to the usual behaviour. The $\Gamma_1$ linewidth is constant for the low values of pressure, increases from $P_0 - 400$ bar and undergoes a large discontinuity at the pressure transition $P_0$. This linewidth behaviour is to compare with that observed in the experiments at atmospheric pressure [35, 37] where no such discontinuity has been found. The $\nu_2$ frequency has an unusual behaviour versus pressure, it decreases and vanishes at $P_0$ whereas the $\Gamma_2$ linewidth increases more and more when approaching $P_0$. A very similar behaviour is observed for the deuterated p-terphenyl. Nevertheless the $(\nu_1 - \nu_2)$ deviation at $P_0$ is more important for the deuterated compound than for the hydrogenated one. For the set of experiments at constant pressure ($P = 3\,000$ bar for H$_{10}$ p-terphenyl) the parameters behaviour (see Fig. 4) is nearly analogous to that described above: the mode 1 broadens when the transition is approached below, its linewidth $\Gamma_1$ undergoes a discontinuity at the transition temperature $T_0$ larger than that observed at constant temperature. The $\nu_1$ frequency decreases weakly when temperature arises. $\nu_2$ has, also, a normal behaviour with temperature up to $T_0$ where the mode 2 disappears. For the other sets of experiments at constant pressure and variable temperature the same general features can be carried out.

In addition to the spectra obtained under pressure, we have also fitted, for the two compounds, the spectra recorded at atmospheric pressure but the results are not very satisfactory. For these two sets of experiments we think that, because of lines broadenings larger than those observed under pressure, the flat basic line modifications proceed from bands of the whole Raman spectra and not solely from bands observed in the studied spectral interval. Then our previous hypothesis is no more valid and this could explain the discrepancy
between experimental spectra and fitted spectra. So we will not take account of the fitted spectra of experiments at atmospheric pressure.

3. Phase diagrams.

From the transition points easily determined on the $\Gamma_1 = f(T)$ and $\Gamma_1 = f(P)$ curves we have drawn the $(T, P)$ phase diagrams of the hydrogenated and deuterated p-terphenyl (Fig. 5). The corresponding values $(T_0, P_0)$ are summarized in Table I. Note that the curve for the deuterated compound is very close (±1 K) to that obtained by neutron diffraction [1].

The transition temperature decreases strongly when increasing pressure with a non linear behaviour: $T_0$ slows down to 84 K for $P_0 = 3 255$ bar (C$_{18}$D$_{14}$) and $P_0 = 3 750$ bar (C$_{18}$H$_{14}$).

The main feature of these phase diagrams is that of their planar conformation, i.e., for the double-well potential, the barrier height decreases and the two positions of the minima become closer to each other. This shifts the transition temperature towards the low temperatur-es. Such a behaviour can be nicely understood in the two limit cases. For an order-disorder regime, this lowering of the transition temperature results, within a pseudo-spin modelling, from a decrease of the inter-spin interaction energies. For a displacive re-gime, this results from a smaller thermal energy needed for oscillating above the barrier height.

At all pressures, the deuteration reduces the transition temperature. This effect is opposite to that observed for KDP compound [49], but similar to that observed for naphthalene-TCNB [50] and for anthracene-TCNB [51] phase transitions. It could be explained by the slight difference of length between C-H and C-D bonds. Indeed, due to zero-point vibration, the average C-D distance is shorter than the average C-H distance and so, the steric hindrance effect is weaker in the deuterated compound. In their modelling calculations, Raich and Bernstein [20] estimate that a change of less than one per cent would be sufficient to explain such an effect.

4. Behaviour of line broadenings at the transition.

At atmospheric pressure the different curves $I = f(T)$ do not show the existence of a discontinui-ty at the transition [35, 37]. This is to be compared to the behaviour of the superstructure intensity $I = f(T)$ [27]. However, a fit of the temperature evolution of this intensity with a power law $I \sim (T - T_c)^{2\beta}$ has given a very low apparent critical exponent: $\beta = 0.15$. This indicates that the phase transition has probably a weak first order character. Therefore, we could expect to observe under pressure an evolution of the transition character towards a second order one as for ND$_4$Cl [52] or KDP [53] where tricritical points occur at moderate pressure.

Actually, the behaviour of p-terphenyl under pressure is different. In figures 6 and 7, the different curves $\Gamma_1 = f(T)$ obtained for both compounds at different constant high pressures exhibit clearly a large discontinuity at the transition temperature. This shows that the transition becomes clearly first order at high pressure. Moreover, this first order

Table I. — Transition temperature at five constant pressures and transition pressure at constant temperature $T = 84$ K for the hydrogenated and deuterated p-terphenyl.

<table>
<thead>
<tr>
<th>Compound</th>
<th>P (bar)</th>
<th>1</th>
<th>1 000</th>
<th>2 000</th>
<th>3 000</th>
<th>3 500</th>
<th>3 750 ± 10</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$<em>{18}$H$</em>{14}$</td>
<td>T(K)</td>
<td>193.3</td>
<td>175.5 ± 0.5</td>
<td>149.9 ± 0.4</td>
<td>116.3 ± 0.3</td>
<td>95.3 ± 0.2</td>
<td>84</td>
</tr>
<tr>
<td>C$<em>{18}$D$</em>{14}$</td>
<td>P (bar)</td>
<td>1</td>
<td>1 000</td>
<td>1 800</td>
<td>2 500</td>
<td>3 000</td>
<td>3 255 ± 15</td>
</tr>
<tr>
<td>T(K)</td>
<td>178</td>
<td>158.9 ± 0.4</td>
<td>137.7 ± 0.3</td>
<td>115.2 ± 0.3</td>
<td>95.5 ± 0.3</td>
<td>84</td>
<td></td>
</tr>
</tbody>
</table>
character increases with pressure. The transition being quasi-continuous at atmospheric pressure, it appears that the tricritical point corresponds probably to a negative pressure and cannot be physically reached.

This strengthening of the first order character of the transition with pressure, which agrees with the neutron diffraction results [1], can be also observed on the whole low frequency spectra. Figure 1 shows, for the H_{10} p-terphenyl crystal, a very slow evolution of spectra between 2 000 and 3 500 bar (the same evolution is observed between atmospheric pressure and 2 000 bar): the only modification is a shift of the lines frequencies under pressure. On the other hand, through the transition (P_0 = 3 750 bar), the spectra are greatly modified: the lines broaden and overlap. This evolution is very different from that observed at atmospheric pressure and variable temperature where the spectra modifications occur on a large temperature range in the low temperature phase [35, 37].

Examination of the \( \Gamma_1 = f(T) \) curves (Figs. 6 and 7) shows another interesting phenomenon. In the high temperature phase a slight increase of the \( \Gamma_1 \) linewidths is observed near the transition. This phenomenon which has not been displayed at atmospheric pressure [35, 37] is obvious for all the experiments at constant pressure or at constant temperature for both hydrogenated and deuterated compounds. A similar behaviour seems to appear on the curve \( \Gamma = f(T) \) of a mode of squaric acid [54]. At the present time we have no explanation for this phenomenon.

5. Change-over from order-disorder to displacive regime.

In our study at atmospheric pressure [37] we have rejected for p-terphenyl the hypothesis [55-57] connecting the modes broadening to the relaxation time between the two wells. This is confirmed by the study under pressure. Indeed in this hypothesis the mode linewidths \( \Gamma \) are related to their frequencies \( \omega \) and to the relaxation time \( \tau \) by the following law:

\[
\Gamma = (a + b\tau) + c \frac{\tau}{1 + \omega^2 \tau^2}
\]

where the first part corresponds to a classical anharmonic broadening and the second part to a broadening due to a jump of the particle from one well to the other one (relaxation). We have calculated the second part contribution for each set of experiments by removing the classical anharmonic broadening which is illustrated in figure 6, by the dashed line for \( P = 1 000 \) bar. So the vertical line shows the contribution \( \Delta \Gamma_1 \) due to the relaxation. For both compounds \( \Delta \Gamma_1 \) decreases with increasing pressure: from 1.3 cm\(^{-1}\) at 1 000 bar to 0.8 cm\(^{-1}\) at 3 500 bar in the H_{10} p-terphenyl and from 1.4 cm\(^{-1}\) at 1 000 bar to 1.0 cm\(^{-1}\) at 3 000 bar in the D_{10} p-terphenyl. According to the \( \Gamma = f(\tau) \) law, it would mean an increase of the relaxation time \( \tau \) and consequently of the potential barrier height with pressure. This assertion is inconsistent with the transition mechanism previously described. Therefore, we retain the other hypothesis which relates the linewidth broadening in the low temperature phase to the progressive setting of disorder when the temperature increases [58]. Indeed, when disorder exists, the crystal is spatially inhomogeneous, i.e. the configuration of neighbouring molecules differs from one place to another place. This induces a dispersion of vibrational frequencies and we observe a mode broadening which increases with the amount of disorder. Notice the behaviour of the lowest frequency mode which broadens less than the other ones. This is consistent with the fact that the motion assigned to this mode is not very sensitive to the
disorder. Indeed, this motion corresponds to a preponderant libration of molecules around the axis perpendicular to the mean molecular plane \[37\] and it is clear that this libration is not strongly affected by the perturbations due to the distribution of phenyl rings between the two equivalent conformations. Moreover, we can understand the decrease of \(\Delta I_1\) under pressure. In fact in the displacive transitions the high temperature phases are considered as ordered phases and no mode broadening is expected for these transitions. So for p-terphenyl crystal, the barrier height would decrease with pressure and the mechanism of transition would modify towards a displacive regime. Then the mode broadening would reduce gradually with increasing pressure. The \(\Delta I_1\) evolution is in agreement with this description and we can expect the mode broadening to vanish for pressures higher than 4 000 bar. (Maximum pressure imposed by the experimental conditions.)

Moreover a similar evolution under increasing pressure is observed if we compare the \(I_1\) linewith for different pressures in the high temperature phase, at constant temperature. Table II gives the \(I_1\) linewith \(versus\) pressure at \(T = 200\) K for \(H_{10}\) p-terphenyl and \(D_{10}\) p-terphenyl. The decrease of \(I_1\) with increasing pressure is in agreement with the transition evolution previously described.

Table II. — Pressure dependence at constant temperature of the \(\Gamma_1\) linewith in the high temperature phase of hydrogenated and deuterated p-terphenyl.

<table>
<thead>
<tr>
<th>(P (\text{bar}))</th>
<th>(\Gamma_1 (\text{cm}^{-1}))</th>
<th>(P (\text{bar}))</th>
<th>(\Gamma_1 (\text{cm}^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 000</td>
<td>2.6</td>
<td>1 000</td>
<td>2.7</td>
</tr>
<tr>
<td>2 000</td>
<td>2.6</td>
<td>1 800</td>
<td>2.6</td>
</tr>
<tr>
<td>3 000</td>
<td>2.3</td>
<td>2 500</td>
<td>2.4</td>
</tr>
<tr>
<td>3 500</td>
<td>2.1</td>
<td>3 000</td>
<td>2.1</td>
</tr>
</tbody>
</table>

\(C_{18}H_{14}\) \(T = 200\) K \quad \(C_{18}D_{14}\) \(T = 185\) K

A stronger argument for an evolution towards a displacive regime is given by a soft mode observation at high pressure. In the high temperature phase, the soft mode located at the zone boundary point \(C (1/2, 1/2, 0)\), is two fold degenerated. So in the low temperature phase two active Raman soft modes are expected. Figure 1 shows the low frequency spectra of the hydrogenated p-terphenyl at different pressures and constant temperature. We can note that most of the modes have a normal behaviour \(versus\) pressure, i.e. their frequencies increase with pressure. Only one mode presents a contrary behaviour: the mode whose frequency is equal to 42 cm\(^{-1}\) at \(P = 2 000\) bar (indexed 2 in Figs. 3, 4 and 8). Figure 8 shows for both hydrogenated and deuterated compounds its frequency evolution \(versus\) pressure. Its frequency decreases with pressure, the slope of the \(\nu = f(P)\) curve becomes greater and greater when approaching transition pressure and this mode is not observed above the transition pressure as we expect for a soft mode located at zone boundary. This experimental observation confirms that the transition moves towards a displacive regime with pressure. At this time, no clear assignment has been made for the second soft mode.

Note that this evolution is not so evident from the \(\nu_2 = f(T)\) curves (an example is given in Fig. 4).

Two main reasons can explain this:

— Pressure and temperature have contrary effects on the Raman lines: under pressure the « normal » Raman lines and the soft modes shift in opposite ways whereas, under temperature, they shift in the same one.

— The second reason is connected to the feature of the phase diagram \(\frac{dT_0}{dP} < 0\) and to our experimental conditions. It is obvious that, as pressure increases, the displacive nature of the transition will become clearer. Unfortunately large values of pressure correspond to small values of \(T_0\). Then, owing to our high pressure cell and to our cryostat which does not allow experiments at temperature lower than 84 K, the number of experimental data becomes insufficient. Under these conditions no obvious conclusion can be given from the constant pressure and variable temperature studies. Then it is important to notice the great interest of the constant...
temperature and variable pressure experiments which have greatly favoured the observation of a soft mode in p-terphenyl crystals.

In figure 3, the $v_1 = f(P)$ and $v_2 = f(P)$ curves show that modes 1 and 2 seem to cross. This phenomenon has been also observed for both crystals and for several experiments at constant pressure and variable temperature. In the low temperature phase, the Raman active modes, belonging to the Ag representation, cannot cross. A coupling of these modes would be observed with respective character exchange. From our experiments, such a coupling is certainly very weak in p-terphenyl. We can only note that the slight decrease of the mode 1 intensity, which has been observed when the two modes seem to cross, could be connected to this very weak coupling.

6. Conclusion.

In this paper we have reported the pressure dependence of the p-terphenyl phase transition. We have drawn the phase diagrams of both hydrogenated and deuterated compounds. The feature of these curves ($\frac{dT_0}{dP} < 0$) agrees with a description of this structural instability as a delicate balance between competing intramolecular and intermolecular forces. This study also shows that the character of this phase transition becomes clearly first order under pressure. Especially interesting is the observation of a mode softening which indicates unambiguously the evolution of the p-terphenyl transition from an order-disorder mechanism to a displacive one. This soft mode being located at the zone boundary in the high temperature phase, neutron scattering experiments are in progress in this phase in order to get a better understanding of this evolution.

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References