Infrared Absorption Spectra of ortho- and para-Linked Polyphenyls

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The absorption spectra of biphenyl, o- and p-terphenyl, o,o'-, o,p'- and p,p'-quaterphenyl have been recorded from 2 to 25 μ both in solution and in the solid state. Oriented crystallization takes place when melts of the linear compounds solidify between salt plates. Some of the bands observed in the spectra obtained by the KBr technique are lacking in the oriented crystal spectra; they must be due to vibrations polarized parallel to the long molecular axis. Most of the vibrations seem to occur independently within each ring of the chain, and assignments can be made on the basis of the assignments for methylbenzenes given by Pitzer and Scott. For the linear compounds the intensity variation of the bands classified as due to in-plane skeletal deformation modes suggests that these vibrations are coupled together, the selection rules being determined by the symmetry of the whole molecule, and that the molecules are planar in the crystalline state, but non-planar in solution.

The synthesis of o,p'-quaterphenyl is described.

In connection with a study of the ultraviolet spectra of through-conjugated polyphenyls in the solid state and in solution (cf. the following paper), it was of great interest to know whether any change of conformation would occur in going from one state to the other, since such changes would be expected to affect the degree of interaction between the π-electron systems of the linked benzene nuclei. In particular it was of importance to ascertain whether the p-polyphenyl molecules are planar in solution as they are known to be in the crystal2-5, or non-planar, as has been established for biphenyl in the gaseous state6. For one of the non-linear compounds, o,o'-quaterphenyl, one might even anticipate, as a result of the tendency towards coplanarity, the existence of cis- and trans-like conformations, for which the electronic absorption spectra would be expected to differ.

Biphenyl and all the possible o- and p-linked terphenyls and quaterphenyls were studied. Of these, o,p'-quaterphenyl has not been described before, and a method for its synthesis is given in the experimental part.

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I.R. SPECTRA OF POLYPHENYLS

Fig. 1. Infrared spectra of linear polyphenyls in solution (1 % or saturated, 1 mm cell thickness) and in the solid, crystalline state. The dotted curves represent spectra of melts solidified between salt plates (0.01 mm layer thickness) in regions where these differ from the spectra of pressed KBr disks (full line). The solvents used in the various regions have been indicated in the lower part of the figure.

Infrared spectra of some of these compounds have been reported earlier \(^7-^{11}\), but these spectra are partly of poor quality, especially for solids prepared as mineral oil mulls \(^{10}\); they are mostly not available for both solid state and solution; and they cover only the NaCl-region, or part of it \(^7\). Since the skeletal deformation vibrations would be expected to be most sensitive to changes of molecular shape, it was considered especially important for the present purpose to include the long-wave region from 15 to 25 \(\mu\) (KBr-prism).

The infrared spectra are given in Figs. 1 and 2. Below 5 \(\mu\) they are very similar, the absorption due to the various CH-stretching modes appearing as an unresolved band at 3 040—3 060 cm\(^{-1}\) for all members. This region has not therefore been reproduced in the figures and will not be further discussed. The solid state spectra were taken both of solidified melts and of pressed KBr-
Fig. 2. Infrared spectra of non-linear polyphenyls in solution (1 %, 1 mm cell thickness) and in the solid, crystalline state. Pressed KBr disks and solidified melts give indistinguishable spectra. The solvents used in the various regions have been indicated in Fig. 1.

disks. While these were identical for the non-linear compounds, it was observed that for the linear compounds some of the bands present in the KBr-disk spectra were missing or of very low intensity in the spectra of the solidified melts. Evidently, oriented crystallization between the salt plates must be responsible for this effect *, since just these compounds tend to crystallize in very thin leaflets. It was also observed that if the linear polyphenyls are sublimed on to a salt plate, the same bands are absent in the spectra. It is easy to understand that in this case the leaflets that are oriented parallel to the salt plate must make by far the largest contribution to the absorbing area. Now it is known from X-ray diffraction that these molecules have their long axis perpendicular to the main plane of the crystal leaflets 2-5. The bands that are

* From a spectrum of biphenyl, published by Richards and Thompson 6, it may be seen that they have also had a strongly oriented sample, apparently without being aware of it.

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absent in the oriented samples must therefore be due to those vibrations which are polarized parallel to the long axis, and we have thus a means of sorting out vibrations of this symmetry type.

It was further found that when the solution spectra were compared with the solid state spectra, there are practically no differences in the non-linear compounds (Fig. 2), whereas for the linear compounds (Fig. 1) some bands present in the solution spectra disappear completely in the spectra of the solid, crystalline state *. For this latter case one is thus at once forced to conclude that the molecules, which are planar in the solid state, become non-planar in solution, since by such a change the symmetry of the molecule will be altered (loss of symmetry center) and the selection rules will change. However, this concerns only a few bands below 800 cm⁻¹; the remaining bands seem to behave as if they belonged to separate rings with the same substitution, as has already been noted by Cannon and Sutherland 19.

BANDS CHARACTERISTIC OF MONO-SUBSTITUTED BENZENES.

A complete assignment of the main bands below 1 600 cm⁻¹ in the biphenyl spectrum, and most of the bands in the other spectra, could be made on the basis of the assignment given by Pitzer and Scott for methylbenzenes 15, because of the fortunate circumstance that most of the vibrations seem to occur independently within each nucleus. Since there are no disturbing bands due to methyl groups, and the vibrations of symmetry class A₁ can be identified with certainty, as shown above, it is believed that the present assignments for biphenyl (Table 1) are quite reliable, and may be of value in the revision of Pitzer and Scott’s data which Plyler considers necessary 13. To be specific, vibrations 6a and 6b (using Wilson’s numbering scheme 14) had to be interchanged, although good arguments have been advanced for their classification in monosubstituted benzenes based on the mass sensitivity of the lower frequency band and constancy of the higher one 13. Furthermore, vibrations 19b, 3 and 5 had to be shifted to much higher frequencies; for vibration 5 the new position is in good agreement with calculations by Cole and Thompson 15.

By comparing the classification according to main vibrational type in Table 1 with the spectrum of biphenyl in Fig. 1 it is seen that the bands due to CC-stretching modes (ν CC in Table 1) are rather similar in solution and in the solid state, except that for the pair just below 1 600 cm⁻¹, 8a is more intense than 8b in solution, while 8b is the stronger band in the solid. Their assignment is strongly supported by the appearance of intense Raman lines 16 at 1 600 and 1 584 cm⁻¹. The bands attributed to CH-in-plane-deformation modes (δ CH) are characterized by being sharp in the solid, but broad and diffuse, even weak, in solution. This broadening may perhaps be due to interaction between the hydrogen atoms and the solvent, or to oscillations of the rings about some interplanar equilibrium angle. The bands which represent CH-

* The spectrum of biphenyl as mineral oil mull, given by Burton and Richards *, reveals that it is actually a mixture of solid and solution; the substance must have been partly dissolved by the oil.

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Table 1. Tentative assignments of the main absorption bands of monosubstituted benzene rings in polyphenyl chains.

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<th>Biphenyl soln.</th>
<th>p-Terphenyl cryst.</th>
<th>p-Terphenyl soln.</th>
<th>p,p′-Quaterphenyl cryst.</th>
<th>p,p′-Quaterphenyl soln.</th>
<th>o-Terphenyl cryst.</th>
<th>o-Terphenyl soln.</th>
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Symmetry type" refers to the symmetry of the separate ring, not of the whole molecule. An asterisk denotes that the vibration is strictly infrared inactive, but occurs in violation of the selection rules.

and CC-out-of-plane-deformation modes (γ CH and γ CC) are very similar in both states, except that the 16b vibration is displaced to higher frequency in solution.

The remaining three bands due to the CC-in-plane-deformation modes (β CC), illustrated for benzene in Fig. 3, are the most important ones, since two of these bands, 12 ** and 6b, are just those which do not appear in the solid; the third one, 6a, disappears on lengthening the chain (p-terphenyl) and reappears on further lengthening (p,p′-quaterphenyl). It would seem reason-

* It should be emphasized at this point that of the two bands 10b and 4, which are very strong and characteristic in monosubstituted benzenes, 10b is chiefly a γ CH-vibration, while 4 is chiefly a γ CC-vibration. They are both commonly and confusingly referred to in the literature as γ CH-vibrations, 11, 17.

** This vibration has been assigned by Frühling 14 to a strong Raman line at 1 028 cm⁻¹, close to its frequency in benzene, but this line is rather due to the 18a vibration which in the infrared gives rise to a band at 1 042 cm⁻¹.

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Fig. 3. The three normal modes of in-plane-deformation vibration of benzene according to Pitzer and Scott.

Fig. 4. "Whole-molecular" vibrations obtained by coupling in-plane-deformation modes of the rings in the manner suggested by the intensity variations of the corresponding bands; a) vibration 6a; b) vibration 6b.

able to expect that skeletal deformation vibrations in the plane should be coupled most strongly through the whole molecule, more so than skeletal deformation vibrations perpendicular to the molecular plane. But although the selection rules seem to be determined by the symmetry of the whole molecule, the frequencies are apparently not much affected; thus, Raman lines are observed in solid biphenyl at the same frequencies as for the infrared bands 12 and 6b in solution.

Let us now consider the 6a vibration. If it is coupled together as shown in Fig. 4a (the other possible manner would lead to stretching of the bond connecting the rings), it is easy to see that this will explain why the vibration should be allowed in the infrared for biphenyl, \( p,p' \)-quaterphenyl, etc., but forbidden for \( p \)-terphenyl, \( p \)-quinquiphenyl, etc., and why it is unaffected by rotation of the rings relative to each other about the connecting bonds or "pivot bonds" upon dissolution.

The 6b vibration can be coupled together in the manner shown in Fig. 4b. This coupled vibration would give rise to no absorption in planar molecules irrespective of the length, in agreement with the spectral evidence (Fig. 1). In non-planar molecules of any length it will become allowed, and the intensity

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will depend on the interplanar angle. The forbidden 6b vibration of the 
$p$-disubstituted ring (Table 2) which "transmits" the coupled vibration through 
the longer chains, is apparently so mixed with the 6b vibration of the mono-
substituted rings that two bands appear, subject to the same "molecular" 
selection rules (cf. the terphenyl spectrum). Their classification is obviously 
only tentative.

The 12 vibration is more difficult to interpret. If it is coupled together in 
a manner analogous to the coupling of 6a above, one should expect absorption 
both for planar and non-planar molecules irrespective of the number of nuclei 
in the chain. Instead, a band appears only in the solution spectra. There are 
other ways in which this vibration may be coupled to fit the observations, 
but since additional assumptions are needed, further discussion does not seem 
justified.

However, the important fact is that the three vibrations which do not 
obey the selection rules of separated rings, all belong to the skeletal in-plane-
deformation modes. The only obvious conclusion from the behaviour of these 
bands is that the linear polyphenyl molecules are planar in the solid crystalline 
state, and non-planar in solution. Nothing definite can be said about the 
magnitude of the interplanar angle, but since Frühling 16 has concluded from 
polarization measurements of the Raman lines of liquid biphenyl, that the 
molecules have a center of symmetry, the interplanar angle may be quite 
small.

It remains to be mentioned that a band corresponding to the 7a vibration, 
which in toluene represents stretching of the CC-bond between the methyl 
group and the ring 18, is not found in the biphenyl spectrum, since it would 
here correspond to the pivot-bond stretching, which, even with less symmetric 
substitution than in biphenyl, would be expected to be inactive in the infrared, 
but give a very strong, polarized Raman line. In fact, the strongest line observed 
in the Raman spectrum of biphenyl 16, 18 as well as the terphenyls 18, 19, 
is at around 1 280 cm$^{-1}$ and has been attributed to this stretching mode 18. 
The absence of this band in the infrared spectrum strongly confirms this assignment. A very weak band at 1 275 cm$^{-1}$ in the infrared spectrum of 
$p,p'$-quaterphenyl might be due to stretching of the two unsymmetrically substituted 
pivot bonds, since it is polarized parallel to the long axis of the molecule.

A strong band is present at 1 089 cm$^{-1}$ in solid biphenyl but absent in solution 
and in all the other compounds. Its origin is uncertain. On the other hand, 
a few of the weak bands can be interpreted. Thus, the inactive 10a vibration 
can be detected at 840 cm$^{-1}$ in biphenyl. It may be significant that it belongs 
to the $y$ CH-vibrations which are generally the strongest bands of aromatics. 
The weak band at 1 377 cm$^{-1}$ is probably the first overtone of vibration 4 at 
696 cm$^{-1}$.

Of the normal vibrations still not accounted for, there are five CH-stretching modes: 
2, 7b, 13, 20a, and 20b; and one CC-stretching mode: 14. Then there is one CH-out-of-plane 
deformation mode, 17a, which is only Raman active, and one CC-out-of-plane 
derformation, 16a, active in the Raman 18 at 402 cm$^{-1}$. Vibrations 18b and 11, which are 
CH-in-plane and out-of-plane deformations respectively in benzene, would in biphenyl 
correspond to bending vibrations of the rings against each other and should occur below 
400 cm$^{-1}$.

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In the spectra of the remaining polyphenyls it is possible to trace most of the bands due to vibrations in monosubstituted rings through the whole series (Table 1). The very constant frequency of many of them is noteworthy. In o-terphenyl a few bands split in the solid, possibly because of non-equivalence of the two mono-substituted rings caused by packing effects in the crystal lattice. In o,p'-quaterphenyl doubling of some bands persists even in solution, since the two rings are unequally substituted.

BANDS CHARACTERISTIC OF DISUBSTITUTED BENZENE RINGS

The bands that are left over must then be due to vibrations within para- and ortho-disubstituted benzene rings, respectively. The most characteristic of these bands have been tentatively classified on the basis of Pitzer and Scott's work 12, and are given in Tables 2 and 3. Of course, other bands due to the disubstituted rings may be hidden by bands already assigned to mono-substituted rings. In particular, the bands are so numerous below 800 cm⁻¹ for the more complex molecules, that their classification is rather uncertain.

For p-disubstituted rings (Table 2) the most characteristic bands are the CC-stretching 19b at 1400 cm⁻¹ and the CH-out-of-plane-deformation 17b at 830—840 cm⁻¹. It should be noted that a few vibrations give infrared bands in violation of the selection rules.

Table 2. Tentative assignments of some characteristic absorption bands of para-disubstituted benzene rings in polyphenyl chains (see Footnote to Table 1).

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<th>Numbering acc. to Wilson</th>
<th>Symmetry type</th>
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<th>p,p'-Quaterphenyl</th>
<th>o,p'-Quaterphenyl</th>
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For o-disubstituted rings (Table 3) the bands are more numerous, but less characteristic. In o,o'-quaterphenyl there is a doubling of the CC-stretching 19b, but since the two rings are identical, the reason may be strong coupling between them for this stretching mode. It will be noticed that the γ CH-vibration 10a has been correlated with a band at 750 cm⁻¹. This is in agreement with calculations by Cole and Thompson 15, although Pitzer and Scott did not assign the strong band at 740 cm⁻¹ of o-xylene to this mode 12. Two other γ CH-vibrations, 3 and 17a, give rise to bands in violation of the selection rules.

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Table 3. Tentative assignments of some characteristic absorption bands of ortho-di-
substituted benzene rings in polyphenyl chains (see Footnote to Table 1).

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<td>867</td>
<td>873</td>
<td>874</td>
</tr>
<tr>
<td></td>
<td>17a</td>
<td>A₅₃</td>
<td>849</td>
<td>842</td>
<td>843</td>
</tr>
<tr>
<td></td>
<td>10a</td>
<td>B₁</td>
<td>749</td>
<td>(748)</td>
<td>756</td>
</tr>
<tr>
<td>δ CC</td>
<td>12</td>
<td>B₁</td>
<td>781</td>
<td>776</td>
<td>780</td>
</tr>
<tr>
<td></td>
<td>6a</td>
<td>A₁</td>
<td>558</td>
<td>558</td>
<td>570</td>
</tr>
</tbody>
</table>

They are weak in o-terphenyl, but stronger in o,o'-quaterphenyl where the
selection rules are not strictly valid because the two substituents on each ring
are unequal.

The great similarity between the solid state and the solution spectra of the
non-linear polyphenyls even below 800 cm⁻¹ would indicate that there are no
great conformational differences between these two states. However, a small
increase in interplanar angles upon dissolution would not lead to a change in
symmetry and selection rules as it does in the linear series, and such widening
of interplanar angles might well take place. Whether a mixture of cis- and
trans-like conformations of o,o'-quaterphenyl exists in solution, or the trans-
like conformation is alone present in both solution and solid, cannot be decided
with certainty, but the spectra are so similar that the latter alternative appears
most likely.

EXPERIMENTAL

The spectra were recorded in a Perkin-Elmer double-beam instrument, Model 21,
using a NaCl prism from 2 to 15 μ and a KBr-prism from 15 to 25 μ. 1 % solutions in a
1 mm cell were used, except for p-terphenyl and p,p'-quaterphenyl which were measured
as saturated solutions. In addition to CCl₄ and CS₄ it was found necessary with this cell
thickness to use ethyldiene chloride to get reliable readings in a few wavelength regions
(Fig. 1).

Biphenyl and p-terphenyl (1,4-diphenylbenzene) were commercial samples purified by
sublimation.

p,p'-Quaterphenyl (4,4'-diphenylbibiphenyl) was prepared according to Bowden,²⁰
recrystallized from benzene, and sublimed in vacuo.

o-Terphenyl (1,2-diphenylbenzene) and o,o'-quaterphenyl (2,2'-diphenylbibiphenyl) were
prepared as described by Bachmann and Clarke.³¹ o-Terphenyl was recrystallized from
methanol; o,o'-quaterphenyl first from ethanol, and then several times from acetone.

o,p'-Quaterphenyl (2,4'-diphenylbibiphenyl) was prepared in the following manner:
A mixture of o-iodobiphenyl (4 g), p-iodobiphenyl (4 g), and 10 g of finely ground copper
powder (commercially available as "copper bronze" pigment) was heated to 260° C for
30 min, then cooled and extracted with benzene. The extract was purified by running it

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through an alumina column. Some of the \( p,p' \)-quaterphenyl that is formed in the reaction had entered the extract, but separated out on evaporation. Formed biphenyl could be removed either by distillation or by chromatography from petrol ether on alumina, but it was not possible to separate \( o,p' \)-quaterphenyl from formed \( o,o' \)-quaterphenyl by either method, nor by fractional crystallization. However, when the mixture was very slowly crystallized from ethanol, the \( o,o' \)-compound formed large bipyramids, while the \( o,p' \)-compound crystallized as long, thin needles. By decanting off the stirred mixture, only the fine needles followed the liquid. The needles were allowed to settle, and the mother liquor decanted back. By repeating this procedure about 20 times, a quantitative separation could be effected. Yield: 0.9 g \( o,p' \)-quaterphenyl or 20 \% of the theoretically possible total yield of quaterphenyls. Since the yield of \( o,p' \)-quaterphenyl is 1.1 g or 25 \%, it is probable that the yield of \( o,p' \)-quaterphenyl may be increased by using more \( p \)-iodobiphenyl than \( o \)-iodobiphenyl.

The needles were recrystallized several times from acetone, giving large beautiful monoclinic crystals melting at 117.5—118 °C (as compared with 118.5 °C for the \( o,o' \)-compound). C and H content, as well as molecular weight, were in good agreement with calculated values.

REFERENCES

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