

Ultraviolet Absorption Spectra of *ortho*- and *para*-Linked Polyphenyls

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The electronic absorption spectra of biphenyl, *o*- and *p*-terphenyl, *o,o'*-, *o,p'*- and *p,p'*-quaterphenyl have been measured in solution down to 195 $m\mu$. By adapting the pressed disk technique, good solid state spectra could be obtained with KCl down to 210 $m\mu$. They are very similar to the solution spectra; the bands are broad and without structure. In oriented samples of the linear polyphenyls the "conjugation band" in the region 250—300 $m\mu$ is so reduced that a weak hidden transition at 275 $m\mu$ is revealed; this band does not move with chain length and shows vibrational structure. The strongest band in all spectra is found at about 205 $m\mu$.

The observed bands have been tentatively interpreted, and factors of importance for the development of vibrational structure briefly discussed.

Interplanar angles in the solid state have been considered in relation to intermolecular forces which seem to favour mutually perpendicular orientation of ring planes in adjacent molecules.

An earlier study of the electronic absorption spectra of polyenes¹ led to the conclusion that all minor bands had to be interpreted as overtone transitions of the total chromophore and could hardly be due to independent partial chromophores, as had been suggested in some cases. It could also be shown that the minor bands correspond in wave length location with the main band of shorter chromophores of lengths equal to integral fractions of the chromophore considered, and that stereochemical factors determine the distribution of extinction value among the bands.

The principle was found to be valid even in more complicated systems. However, in the series of "through-conjugated" polyphenyls, which consist of chains of *ortho*- or *para*-linked benzene nuclei, the experimental material was rather meagre, since only the spectrum of biphenyl² was known below 210 $m\mu$. For the terphenyls the spectra were complete above 210 $m\mu$ ³⁻⁵, but for *o,o'*- and *p,p'*-quaterphenyl only incomplete spectra have been reported^{6,7}. For all these compounds, as well as for *o,p'*-quaterphenyl, the preparation of which

has been described in the preceding paper ⁸, the spectra have now been extended down to 195 $m\mu$ in solution and have been given as full curves in Fig. 1.

Since biphenyl and the *p*-polyphenyl molecules have been shown to be planar in the solid, crystalline state ⁹⁻¹², and infrared spectroscopic evidence has been given in the preceding paper indicating that they are non-planar in solution ⁸, it was of interest to record also the spectra of the solids, as it would be expected that the degree of interaction between the π -electron systems of

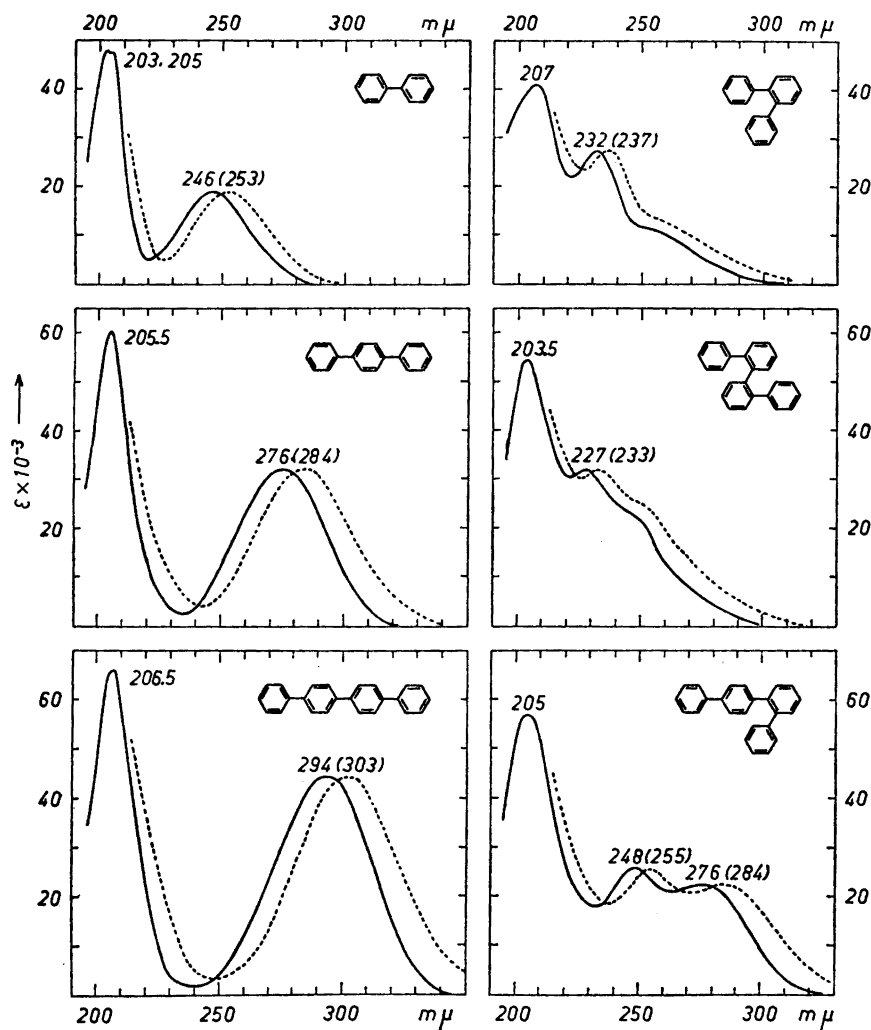


Fig. 1. Ultraviolet spectra of polyphenyls in hexane solution (full lines) and as pressed KCl-disks (dashed lines). The extinction scale of the latter curves is arbitrary.

the rings might be different and manifest itself as a spectral change. By adapting the well known KBr pressed disk technique developed for infrared spectroscopy¹³, but using KCl instead of KBr, good qualitative spectra could be obtained down to 210 $m\mu$, and have been given as dashed curves in Fig. 1. Unfortunately, reliable absolute extinction values could not be obtained, and the extinction of the main band has been arbitrarily set equal to its extinction in solution.

The most surprising feature of Fig. 1 is that there are no significant differences between solution and solid state spectra; just a normal, or slightly larger than normal, red-shift which increases with wave length in the same way as the red-shift observed with compounds like naphthalene and anthracene (see Experimental part), which obviously cannot assume other conformations in solution than in the crystal lattice.

VIBRATIONAL STRUCTURE

Another interesting result is that there is no indication of vibrational structure in the solid state spectra of the linear polyphenyls. It has been suggested by Merkel and Wiegand¹⁴ that the lack of structure in the solution spectrum of biphenyl etc. is due to the non-planarity of the molecules, which would imply that vibrational structure should appear in the solid state if the molecules are then planar. The presence of vibrational structure is, however, a very doubtful criterion of coplanarity, as it is well recognized that when voluminous substituents occupy all four *ortho*-positions of biphenyl, the pronounced structure of the low intensity band of the unconjugated benzenoid chromophore is rather an indication that the rings are not coplanar^{3,15}, although each isolated chromophore is of course strictly planar. Since the broad, structureless appearance of the conjugation bands of the linear polyphenyls persists in the planar molecules of the crystal, whereas condensed aromatics show sharp structure both in solution and in the crystal, the explanation proposed by Kortüm and Dreesen¹⁶ receives considerable support; these authors have emphasized that the appearance of vibrational structure is more a question of rigidity than of coplanarity of the molecules. In biphenyl the lack of structure was assumed to be connected with the possibility of low-frequency torsional oscillations of the rings against each other. This possibility is still present when the interplanar equilibrium angle is zero, since the double bond character of the "pivot bond" is rather small ($\sim 10\%$), and this bond is therefore not very stiff even when the rings are coplanar. In polyenes the "single" bonds are much stiffer; hence, structure develops.

On the other hand, the great increase in vibrational structure of the main absorption band through the series *p*-polyphenyls \rightarrow polyenes \rightarrow polyynes might be explained alternatively by the rapidly decreasing number of normal vibrations of the right symmetry type that according to the Franck-Condon principle can be coupled with the electronic transition. For instance, quinoid polarization of a benzene ring would already be expected to excite three E_{2g} vibrations, which all involve appreciable percentages of CC-stretching¹⁷ but have so different frequencies (1 595, 1 178, and 606 cm^{-1} in the ground state, and somewhat lower in the excited state) that the peaks may overlap each other

and the structure become blurred. In the transition responsible for the conjugation band of biphenyl and the *p*-polyphenyls the situation will of course be very much more complicated, since the electronic transition depends on the symmetry of the chromophore, that is, the whole molecule, whereas most of the vibrations are related to the symmetry of the separated ring in which they occur⁸. A very large number of different vibrations will therefore be coexcited.

The strongest transition of a polyene should mainly arouse one or several symmetrical C=C stretching modes, with frequencies just above 1 600 cm⁻¹ in the ground state, since calculations by Kynch and Penney¹⁸ show that the length of the "single bonds" remains almost unchanged during the transition, whereas the "double bonds" increase in length, especially the central ones. But also other modes of the same symmetry, classified as mainly CH-in-plane-deformations and with frequencies in the region 1 300—1 400 cm⁻¹¹⁹, will probably involve much CC-stretching. The spacings 1 570 cm⁻¹ and 1 230 cm⁻¹ observed at low temperatures²⁰ agree well with these expectations, and are so close that peaks spaced at the average value of about 1 400 cm⁻¹ are quite distinct under ordinary conditions.

In polyynes one or several symmetrical C≡C stretching frequencies at about 2 000 cm⁻¹ will be the only ones that can be excited in an electronic transition which preserves the linear shape of the molecule. This explains the enormously sharp peaks in these spectra²¹.

The above statements are not contradicted by the very sharp structure of the well known and weak 260 mμ band of benzene, because this forbidden transition, ¹A_{1g} → ¹B_{2u}, is of a symmetry type²² which will arouse strongly only the breathing frequency at 923 cm⁻¹ in the excited state, neglecting the single quantum of the E_{2g} vibration at 520 cm⁻¹ which is necessary to deform the skeleton and make the transition possible.

However, it is most likely that for the development of structure both these factors must be considered of importance: a rigid structure; and relatively few vibrations, or several with close-lying frequencies, that can couple with the electronic transition. This is equivalent to saying that the normal vibrations should depend on the symmetry of the whole chromophore.

REVELATION OF HIDDEN TRANSITIONS

The lack of structure in the spectrum of solid biphenyl as pressed KCl-disk would seem to be in conflict with the qualitative statement by Merkel and Wiegand¹⁴ that sharp peaks appear in the spectrum of biphenyl crystals*. However, in view of the marked orientation effects observed with the linear polyphenyls in the infrared (*cf.* preceding paper⁸), one should expect that, also in the ultraviolet, bands that are due to transitions with dipole moment along the long molecular axis, such as the strong conjugation band, would disappear in the spectra of thin layers of solidified melts or sublimed crystals, so that weak bands which are transversely polarized, and normally hidden

* The banded absorption at 300—330 mμ, observed in thin crystal plates of biphenyl²³, is so extremely weak that it must be due to some singlet-triplet transition, and is of little interest in this connection.

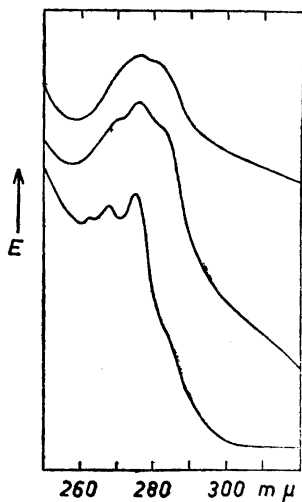


Fig. 2. Ultraviolet spectra of oriented solid samples of linear polyphenyls; bottom, biphenyl; middle, *p*-terphenyl; and top, *p,p'*-quaterphenyl. Incident radiation is parallel to the long axis of the molecules.

by the stronger band, may be detected. This could be confirmed experimentally, either by letting an extremely thin film of melted substance ($< 1 \mu$) solidify between silica plates; by evaporation of a thin layer of solution; or by sublimation on to a silica window. The absorption curves of oriented samples of biphenyl and the linear polyphenyls are shown in Fig. 2 and reveal that there is a band showing structure with a maximum at about $275 m\mu$ for all compounds. Although the extinction coefficients could not be determined exactly, they may be very roughly estimated to about 1 000—2 000. These values are reasonable, since appreciably lower values would not be sufficient to let this band protrude from the rudiments of the strong band, which, at least for longitudinally polarized bands in the infrared, amounts to about 5 % of the full value⁸. The extinction coefficient, which for biphenyl is 19 000, would thus be reduced to about 1 000.

The $275 m\mu$ band can scarcely be due to the forbidden transition, discussed by Platt², between a localized π -orbital with a longitudinal node and a polyene-like orbital (see below). This transition has been assumed by Platt to be hidden by the conjugation band and predicted to move towards the red about half as fast upon lengthening of the system, whereas the $275 m\mu$ band remains stationary throughout the series. Rather, it may be related to the forbidden $260 m\mu$ transition in benzene, as already suggested by Wenzel²⁴ for the hidden transition in biphenyl, and for which she deduced, from a comparison with substituted biphenyls, position and intensity in good agreement with the present findings. Correcting for the "normal red-shift", the location of the peaks of biphenyl corresponds very well with the peaks of a mono-substituted benzene ring like toluene⁵. The less resolved structure and very slight red-shift in *p*-terphenyl and *p,p'*-quaterphenyl is presumably due to overlapping of similar bands arising from *p*-disubstituted rings, since the peaks in the *p*-xylene spectrum⁵ are shifted to the red as compared with toluene. According to the ideas outlined above, the presence of structure in

this band can also be taken as an indication that the transitions occur within each isolated rigid ring, rather than as an indication of coplanarity of the rings.

The conjugation band can also be weakened, and shifted to shorter wave lengths, by providing large deviations from coplanarity, so that the weak hidden transition in each ring may be revealed. The well-known effect of large alkyl-substituents in the *ortho*-positions of biphenyl is an example of this³. Furthermore, in the vapour phase²⁵ the angle of twist is as large as 45°, and the hidden transition is probably identical with the structureless absorption tail that appears in the gas spectrum²⁶ at around 270 m μ . The lack of structure, the broadening towards the red, and the increase in intensity with temperature (170—520° C), may be explained by the increased population of vibrational levels in the ground state. Some of the vibrations destroy the hexagonal symmetry of each ring so that the electronic transition becomes allowed.

INTERPLANAR ANGLES

The displacement towards the ultraviolet and the weakening of the conjugation band must be related to the reduced electronic interaction when the interplanar angle is increased. According to calculations by Guy²⁷ this angle of twist may become as large as 22° before the resonance energy is appreciably reduced, and somewhere between 45 and 68° before it reaches zero. Since the spectra of solids and solutions are so similar, one should therefore expect that the interplanar angle of biphenyl in solution would not exceed much the value of 22°. The values of +34°, -27° and +24° reported for solid 1,3,5-triphenylbenzene²⁸ are surprisingly large, since the steric repulsion between *ortho*-hydrogen atoms should be the same as in biphenyl. Moreover, both molecules have angles of twist near 45° in the vapour phase^{25,29}. The planar structure of solid biphenyl and the *p*-polyphenyls is not immediately understandable as being necessary to obtain the most favourable packing, because the molecules are in fact rather loosely packed, having their planes not parallel, which would give the densest packing, but mutually inclined at an angle of approximately 66°^{9,11}. On the other hand, the molecules of solid 1,3,5-triphenylbenzene form an approximately layer arrangement²⁸, and in this case planar molecules would obviously have been able to pack more densely.

A simple explanation can be arrived at by assuming that intermolecular forces operate in such a way that aromatic hydrocarbon molecules tend to avoid being stacked with their planes parallel, and instead prefer mutually perpendicular orientation. Whether these forces are simply repulsive forces between filled π -orbitals, or some sort of bonding forces between hydrogen atoms and π -electrons, is irrelevant for the present discussion. The crystal structure of benzene³⁰ most strikingly demonstrates this feature; adjacent molecules have their planes mutually perpendicular and form a loosely knit structure. More elongated molecules like naphthalene and anthracene also have their planes tilted away from each other, but at somewhat smaller angles³¹. It will now be easily realized that the planar conformation of *p*-polyphenyl molecules is best suited to obtain a relatively large inclination angle between the ring planes of adjacent molecules with a minimum of empty space between the molecules.

The larger disk-like molecules, like coronene and ovalene³¹, cannot be packed in this manner, because too large voids would result. Instead, they are stacked in columns, but the molecules of adjacent columns still have their planes perpendicular to each other. In 1,3,5-triphenylbenzene, packing of mutually perpendicular molecules would be very awkward and lead to an excessively loose structure. The molecules therefore have to form roughly planar layers²⁸, but phenyl groups of each layer can be twisted about the pivot bond to make fairly large angles with the planes of phenyl groups in the next molecular layer twisted in the opposite sense. In this way the curious crystal structure, the large and dissimilar angles of twist, and the lack of perfect cleavage parallel to the molecular layer planes can be understood. The apparent strength of the intermolecular forces in the crystal suggests that the angles of twist may even be smaller in solution than in the solid for this compound.

In *o*-terphenyl the angle between adjacent ring-planes is 45–50° in the solid³², and increases to very roughly 90° in the vapour phase³³. Considering the spectral similarity, the angle at *ortho*-links in solution most likely is not much larger than in the solid. However, this conclusion concerning one state, the ground state, based entirely on the ultraviolet spectrum, which involves two states, is presented with much reserve.

EMPIRICAL CLASSIFICATION OF THE BANDS

Several authors have calculated the energy levels of biphenyl and the *p*-polyphenyls^{34–38}, but their results will not be discussed here. The present approach will instead be limited to correlations of a more qualitative nature.

The strongest band in the spectra of all the polyphenyls investigated appears at around 205 $m\mu$. According to Platt², transitions between localized π -orbitals within each mono- and *p*-disubstituted benzene ring, that is, orbitals which have a longitudinal node and thus cannot conjugate with adjacent rings to form polyene-like whole-molecular orbitals, would be expected to give rise to intense absorption in this region. This is then a band for which the term "partial" is certainly justified.

The long-wave absorption bands, except weak bands like the hidden transition in biphenyl, which will not be further considered, should originate from transitions between whole-molecular, polyenelike π -orbitals made up from ring orbitals with no longitudinal node², and are the bands to be considered when testing the validity of the empirical rule established for polyene spectra¹. At *ortho*-links the molecular orbital picture will not be so simple, and, of course, there will be a great steric hindrance preventing coplanarity, so that the electronic interaction will be reduced, and a blue shift of all bands might be expected.

When trying to correlate the bands, the wave length position of the main band of the linear polyphenyls must be plotted against number of linked chain nuclei. The question then arises which value should be used for benzene. The strongest band of benzene is at 185 $m\mu$ ⁵, but there are reasons for using a value of about 205 $m\mu$; on the one hand, because this medium intensity band in benzene fits best with the value obtained from extrapolation of wave length

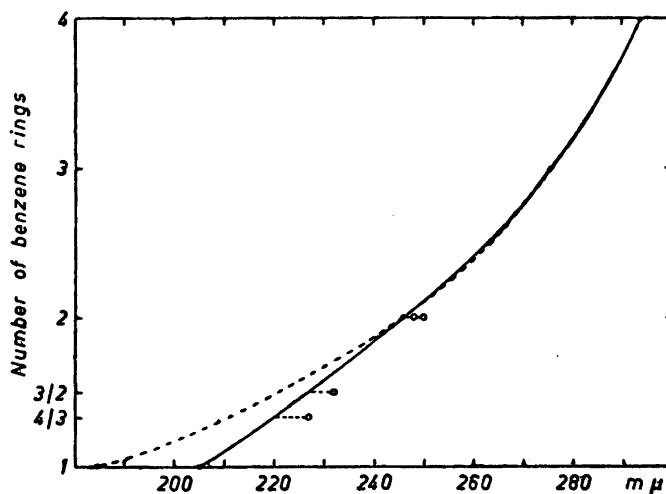


Fig. 3. Wave length position of the "conjugation band" of linear polyphenyls plotted against number of benzene rings. Dashed curve is obtained by using an alternative value for benzene. Positions of assumed overtone bands of non-linear polyphenyls have been indicated as circles; horizontal lines give the deviation from estimated values.

position and intensity of the conjugation band of *p*-polyphenyls²⁴; on the other hand, because it happens to be the center of gravity of the four one-quantum transitions which are assumed to arise from strong splitting due to the high symmetry of benzene³⁹. In Fig. 3 both values have been used in drawing the lines used for calculation. Experimentally observed wave lengths for assumed overtone bands have been given as circles, and are seen to come closest to the 205 $m\mu$ curve.

Considering the linear polyphenyls first, it is seen that there are here no overtones, and none would be expected either in such a strictly linear chain, except possibly a weak λ_3 -band in *p,p'*-quaterphenyl. The band at 205 $m\mu$ may in part be due to the overtone transition corresponding to one benzene ring in all compounds, that is, λ_2 for biphenyl, λ_3 for terphenyl, and λ_4 for quaterphenyl; it may be of special preference, since there would be no displacement of electron density from one ring to the other during excitation^{1,40}.

In *o*-terphenyl the step-out at around 260 $m\mu$ may be regarded as a λ_1 -band which is reduced in intensity and shifted to shorter wave lengths because of the bent shape and steric hindrance. The λ_2 -band at 232 $m\mu$ is correspondingly stronger since it is allowed in this bent molecule and takes over much of the intensity.

In *o,p'*-quaterphenyl the bands at 276 and 248 $m\mu$ are similarly interpreted as λ_1 - and λ_2 -bands, respectively. A λ_3 -band should be of no special preference, and is not observed.

In *o,o'*-quaterphenyl it is necessary to assume that the λ_1 -band is so degraded because of the many sterically hindered links and the kinked shape, that it is represented by the absorption tail in the 270—290 $m\mu$ region. In a hypo-

thetical coplanar *trans*-conformation the λ_2 -band would be forbidden, but as the molecule cannot become planar, it will be weakly allowed. The observed shoulder at 250 $m\mu$ is in good agreement with this expectation. A *cis*-like conformation would require a strong λ_2 -band, so it is believed that the molecule has a *trans*-conformation both in solution and in the solid phase. This conclusion is supported by the lack of significant differences between the two states both in the ultraviolet and the infrared⁸ absorption spectra. The λ_3 -band would be strongly allowed, and would also have to take over intensity from the hindered transitions; it fits well with the strong band at 227 $m\mu$.

Also for the non-linear polyphenyls one would expect an overtone band to coincide with the partial band at 205 $m\mu$.

Admittedly, the agreement between the graphically estimated and the observed wavelength maxima is only qualitative, but certainly better than might be expected considering the complexity of these branched π -electron systems. However, one should be cautious and not attach too much theoretical significance to this result, but consider it only as an empirical classification. It is noteworthy that the spectra might in this way be interpreted in a more satisfactory manner than by postulating partial chromophores consisting of 1, 2 or 3 benzene rings. Much more convincing material, illustrating the success of the "overtone" interpretation and the failure of the "partial chromophore" concept, will be presented in a later paper on the spectra of conjugated chains consisting of alternating ethylenic bonds and benzene nuclei (stilbene homologs).

EXPERIMENTAL

The preparation or origin of the compounds studied has been given in the preceding paper⁸.

The *solution spectra* were recorded in a Beckman DK-1 instrument using hexane as a solvent. In the lowest wave length region 2 mm silica cells were used.

The *solid state spectra* were measured in a Beckman DU instrument. The disks were pressed under vacuum in the usual manner, but were of only half the ordinary thickness. Since KBr starts to absorb appreciably below 240 $m\mu$, KCl was tried and found useful throughout the whole range of the instrument. Disks of 0.55 mm thickness made from 150 mg KCl (Merck, *p. a.*), which had been precipitated from water solution with hydrochloric acid to obtain small particle size⁴¹, showed a transmission of around 75 % at 400 $m\mu$, 65 % at 300 $m\mu$, 55 % at 250 $m\mu$, 40 % at 220 $m\mu$, and 25 % at 205 $m\mu$. Using KCl which had been melted and rapidly cooled⁴², the transmission was still better, namely 80 %, 75 %, 65 %, 55 %, and 40 %, respectively, at the corresponding wave lengths (*cf.* Ford and Wilkinson⁴³). However, it was easier to get the organic substance evenly dispersed in the precipitated salt, so that the loss by scattering was much smaller, and this grade was used throughout. Usually, about 1 mg of the substance was thoroughly ground in a mortar with 200 mg KCl, preferably with a small amount of a volatile solvent. 1 mg of the dry mixture was then ground with 150 mg of new KCl, and pressed into a disk. Unfortunately, the extinction values were not reproducible. The loss of the more volatile compounds like biphenyl, and even the terphenyls, during grinding and evacuation of the press, was so great that a considerable excess of substance had to be weighed in. However, the wave length position of the extinction maxima could be reproduced as long as the disks looked clear to the eye. The spectra of disks which became slightly milky because of imperfect dispersion of the substance, showed distortion of the bands with a slight shift of the maxima (Christiansen effect) like what is very often observed in the infrared with non-transparent disks and, particularly, with mineral oil mulls^{43,44}.

The *normal red-shift* of rigid molecules, from hexane solution to the solid state, was determined by measuring the solid state spectra of naphthalene and anthracene (wave lengths are in $m\mu$; values in parentheses refer to hexane solutions):

Naphthalene: 292(285), 281(275), 272(267), 223(221).

Anthracene: 394(376), 373(357), 353(339), 336(324), 318(309), 256(252), 249(246).

When the differences are plotted against wave length, the red-shift is seen to increase regularly from about 2 $m\mu$ at 220 $m\mu$ to 8 $m\mu$ at 300 $m\mu$, and to 19 $m\mu$ at 400 $m\mu$.

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Received January 12, 1957.