

Interpretation of UV Spectra of Isomeric Terphenyls and Triphenylbenzenes

by

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To obtain information concerning the possibility of conjugation between four nuclei in the 1,2,3-triphenylbenzene molecule, UV spectra of three isomeric triphenylbenzenes and of the linear quaterphenyl have been compared with those of terphenyls and polyphenyls.

The molecules of the above hydrocarbons consist of diphenyl units. The diphenyl spectrum shows one absorption maximum ($\lambda_{\text{max}} = 250 \text{ m}\mu$, $\epsilon = 18,300$ [1]), which points to the possibility of conjugation between the nuclei.

Investigations of absorption spectra in the *m*- and *p*- series of polyphenyls [1] yielded valuable information supporting the assumption as to the existence of conjugation in those systems.

With the increasing number of benzene nuclei ("semidiphenyl" units [1]) in the series of *p*-polyphenyls a gradual bathochromic displacement of the absorption band could be observed along with an increase of the extinction coefficient, due to conjugation throughout the whole molecule (Fig. 1).

Absorption maxima of the *m*-polyphenyls are about $250 \text{ m}\mu$ (like diphenyl), whereas the intensity of absorption gradually increases with the increasing number of benzene nuclei ("semidiphenyl" units, Fig. 1).

Conjugation throughout the whole molecule in the *m*-polyphenyl series is impossible, hence the spectra of these compounds seem to be due to superposition of the spectra of a certain number of isolated chromophoric units ("semidiphenyls").

Although the spectra of *o*-, *m*-, and *p*-terphenyls have long been known, they have not been analysed in detail. Recently, they have been measured by Derkosch and Langer [2], Fig. 2. As could be expected, the spectrum of *p*-terphenyl has an intense absorption band at $\lambda = 279 \text{ m}\mu$ ($\epsilon = 29,000$), thus showing in comparison with the diphenyl spectrum a strong bathochromic shift along with the increased intensity of absorption. These results indicate the possibility of conjugation throughout the whole molecule and what follows — a flat conformation of the three nuclei.

The spectrum of *o*-terphenyl has a fairly strong band at $\lambda = 233 \text{ m}\mu$ ($\epsilon = 26,500$) and a weak inflection at $\lambda = 250 \text{ m}\mu$ ($\epsilon = 11,500$). In comparison with the spectra

of *p*-terphenyl and diphenyl, the spectrum of *o*-terphenyl shows a distinct hypsochromic effect for the main absorption band, which suggests an inhibition of the conjugation throughout the whole molecule. This inhibition of resonance must be ascribed to a considerable deflexion of the nuclei off the molecule plane, which

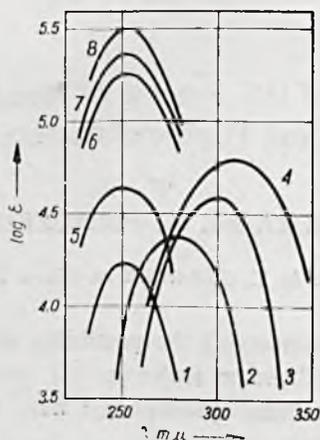


Fig. 1. UV absorption spectra of *p*- and *m*-polyphenyls (in CHCl_3) [1]

1. diphenyl; 2. *p*-terphenyl; 3. *p*-quaterphenyl; 4. *p*-quinquephenyl; 5. *m*-terphenyl; 6. *m*-noviphenyl; 7. *m*-duodeciphenyl; 8. *m*-quindeciphenyl

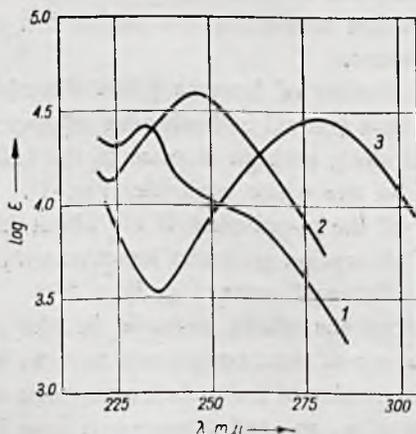


Fig. 2. UV absorption spectra of *o*-, *m*-, and *p*-terphenyls (in $\text{C}_2\text{H}_5\text{OH}$) [2] λ_{max} λ inf.

1. *o*-terphenyl; 2. *m*-terphenyl; 3. *p*-terphenyl

is typical of *o*-derivatives of diphenyl. The inflection at $\lambda = 250 \text{ m}\mu$ might be ascribed to a small probability of conjugation within two nuclei.

For illustration the spectrum of triphenylene [3] is given (Fig. 3). This compound contains an *o*-terphenyl unit along with an additional ring closed by a bond between position *o'* and *o''*, thus having a flat conformation.

The *m*-terphenyl spectrum has a maximum very close to that of diphenyl ($\lambda = 247 \text{ m}\mu$) with the extinction coefficient twice as high as that of diphenyl, thus suggesting the superposition of the spectra of two diphenyl units.

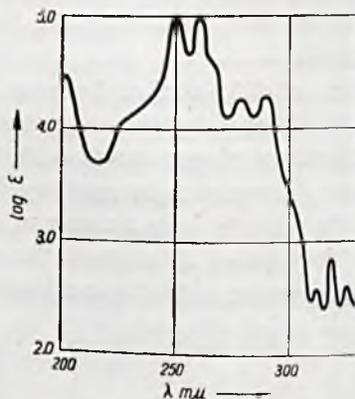


Fig. 3. UV absorption spectrum of triphenylene [3]

Spectra of 1,3,5- and 1,2,4-triphenylbenzenes are known, but they have not been discussed as yet.

Absorption measurements for three isomers of triphenylbenzene, as well as for linear quaterphenyl were performed in their alcohol and chloroform solutions.

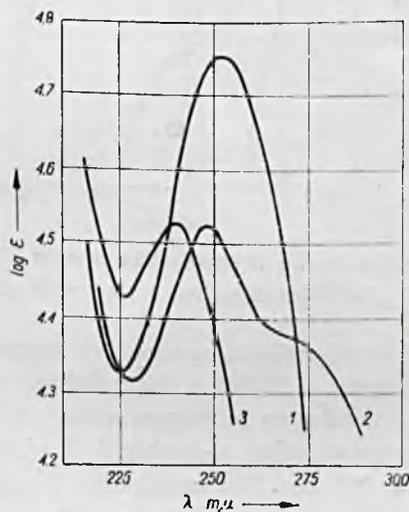


Fig. 4. UV absorption spectra of triphenylbenzenes (in $\text{C}_2\text{H}_5\text{OH}$) λ_{max} , λ_{infl} .
1. 1,3,5-triphenylbenzene; 2. 1,2,4-triphenylbenzene; 3. 1,2,3-triphenylbenzene

This choice of solvents enabled to compare the results with those for the terphenyl and polyphenyl spectra obtained in alcohol and chloroform solutions, respectively. The differences in absorption, resulting from the use of various solvents proved small.

The spectrum of linear quaterphenyl isomeric with triphenylbenzene, shows one maximum at $\lambda = 298 \text{ m}\mu$ ($\epsilon = 44,000$), which is fairly consistent with values given in the literature [1]. In comparison with the diphenyl spectrum, a strong bathochromic effect can be observed here, indicating the possibility of conjugation throughout the whole molecule.

The absorption spectrum of 1,3,5-triphenylbenzene shows a maximum at $\lambda = 260 \text{ m}\mu$, similar to that of diphenyl, but the corresponding extinction coefficient is three times as high as for the diphenyl spectrum ($\epsilon = 58,000$). Hence, the spectrum of 1,3,5-triphenylbenzene can be regarded as resulting from a superposition of spectra of three diphenyl units similarly as in the case of *m*-terphenyl and *m*-polyphenyls. Thus, there is no conjugation throughout the whole molecule of *sym*-triphenylbenzene, while the conjugation within three diphenyl units is quite probable.

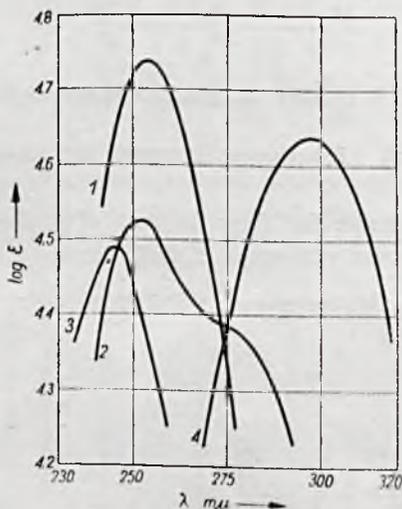


Fig. 5. UV absorption spectra of triphenylbenzenes (in CHCl_3) λ_{max} λ infl.

1. 1,3,5-triphenylbenzene; 2. 1,2,4-triphenylbenzene; 3. 1,2,3-triphenylbenzene; 4. *p*-quaterphenyl

The spectrum of 1,2,4-triphenylbenzene shows an intense band at $\lambda = 249 \text{ m}\mu$ with the extinction coefficient $\epsilon = 33,700$. A fairly distinct inflection at $\lambda = 270 \text{ m}\mu$ could also be observed. According to the present authors, the system shows features characteristic of two terphenyl units: *m*-terphenyl ($\lambda = 248 \text{ m}\mu$) and to a lesser extent — *p*-terphenyl ($\lambda = 279 \text{ m}\mu$). The conjugation throughout the whole molecule does not seem probable, because of steric hindrances due to two adjacent benzene nuclei. The predominance of absorption characteristics of *m*-terphenyl is due to the superposition of the conjugation of two diphenyl units. The probability of conjugation in the linear terphenyl system is negligible.

The spectrum of 1,2,3-triphenylbenzene shows an absorption band at $\lambda = 239 \text{ m}\mu$ with the extinction coefficient $\epsilon = 33,600$. (The values of extinction coefficients of all triphenylbenzenes are always higher than those of corresponding terphenyls). Similarly as in the case of *o*-terphenyl, a distinct hypsochromic effect can be observed

here, which is typical of *o*-substituted diphenyl derivatives. This suggests an inhibition of the conjugation throughout the whole molecule, which is to be ascribed to steric hindrances caused by benzene nuclei in positions 1,2 and 3. In contrast with the *o*-terphenyl spectrum the inflection at $\lambda = 250 \text{ m}\mu$, characteristic of diphenyl absorption, was not observed here.

The spectrum of 1,2,3-triphenylbenzene shows neither features of a non-disturbed diphenyl system, nor those of an *m*-polyphenyl system (a *p*-polyphenyl system does not exist in the molecule). On the other hand it is very similar to the spectra of *o*-terphenyl and other *o*-substituted derivatives of diphenyl. This indicates the existence of some hindrances in the conjugation even between two nuclei of the system: the central one and one of the peripheral ones. A simultaneous conjugation of three, the more so of four, nuclei is impossible.

The comparison of the spectra of isomeric triphenylbenzenes gives an idea of the steric structure of the 1,2,3-triphenylbenzene molecule and suggests a non-planar conformation of the latter.

Materials and methods

1,2,3-Triphenylbenzene has been known since 1893; it was obtained by Smith [8] and by Knoevenagel [9] by distillation of 3,4,5-triphenylphenol with zinc dust, as well as by distillation of 3,4,5-triphenylcyclohexene-2-one-1 with zinc chloride. Only analytical amounts were obtained.

We have found that by reduction of the above ketone by the Wolf-Kishner method 1,2,3-triphenylbenzene can be obtained with a 50% yield. The schemes of the reactions involved are presented in Fig. 6.

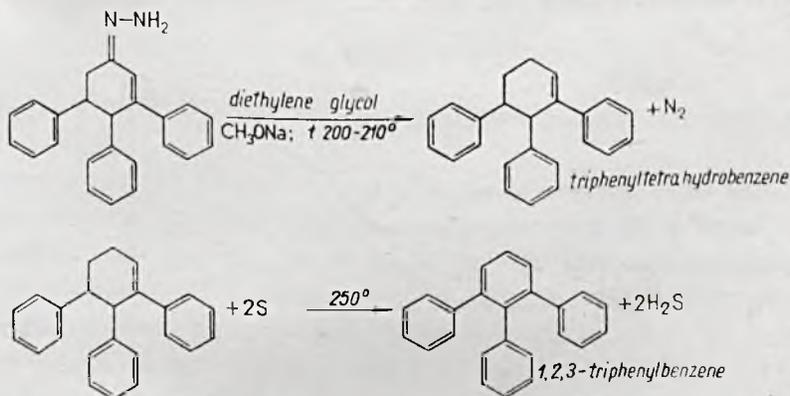


Fig. 6. Preparation of 1,2,3-triphenylbenzene. Reaction scheme

3,4,5-Triphenylcyclohexene-2-one-1 hydrazone (m.p. 162–164°) when heated in a diethylene glycol solution in the presence of sodium methylate until nitrogen evolution stops, yields triphenyltetrahydrobenzene, which is then dehydrogenated by heating with sulphur to give 1,2,3-triphenylbenzene. For absorption measurements the obtained product was purified by superheated steam distillation, followed by repeated crystallization from petroleum ether (b.p. 70–80°), m.p. 159–160°.

1,2,4-Triphenylbenzene [10] was purified by vacuum sublimation (80–90°; 1 mm Hg), followed by repeated crystallization from acetic acid, benzene and petroleum ether (b.p. 70–80°), m.p. 121.5–122°.

1,3,5-Triphenylbenzene [11], [12] was purified by repeated crystallization from acetic acid and then from benzene, m.p. 171—172°.

p-Quaterphenyl [13] was purified by vacuum sublimation (290°; 1 mm Hg), followed by repeated crystallization from benzene, m.p. 316—318°.

Absorption measurements were carried out using a Unicam type apparatus.

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