

SUBSTITUTED p-OLIGOPHENYLENES

PART I:

Syntheses and Properties of Substituted p-Oligophenylenes

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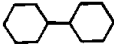

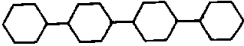
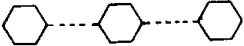
I. INTRODUCTION

p-Oligophenylenes are defined as initial members of the homologous p-polyphenylene series. A special criterion of this class of material is the inflexible rod-shaped molecular form. In this regard, these substances are very different from all common organic compounds. This fact made them very interesting, especially in the field of polymer chemistry (1). Thus, the investigations to be reported were not begun with the aim to develop organic radiation detectors.

The rapid decline of the solubility (Fig. 1) with increasing degree of condensation, made doubtful the usefulness of these oligophenylenes as model substances with definite molecular form. It was found, however, that their solubility can be strongly increased by substituting methyl or methoxyl groups (2-5).

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FIGURE 1

Structure	S [g/l]
	440
	8
	0,2
	

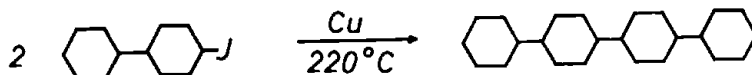
s = solubility in toluene at 20°C

Chiefly two reaction procedures were chosen for the synthesis of substituted *p*-oligophenylenes: the Ullmann reaction and the organometallic carbonyl reaction according to Mayer and Schiffner (6).

II. SYNTHETIC PROCESSES

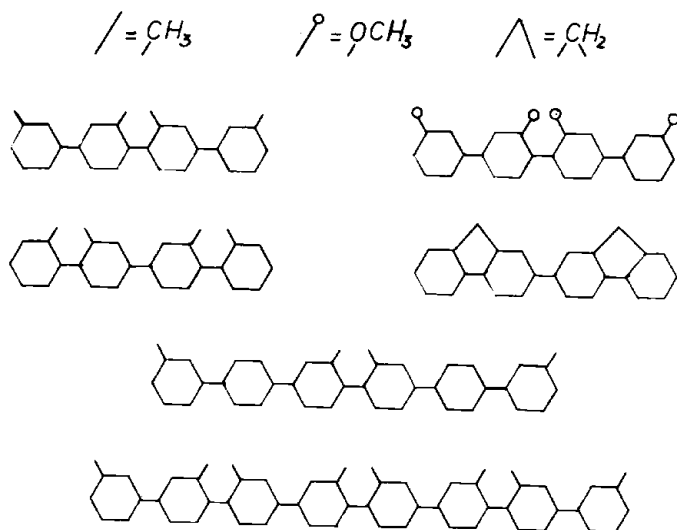
1. The Ullmann reaction

(a) Ullmann himself had already applied this reaction to the synthesis of the unsubstituted *p*-quaterphenyl (Fig. 2) (7).



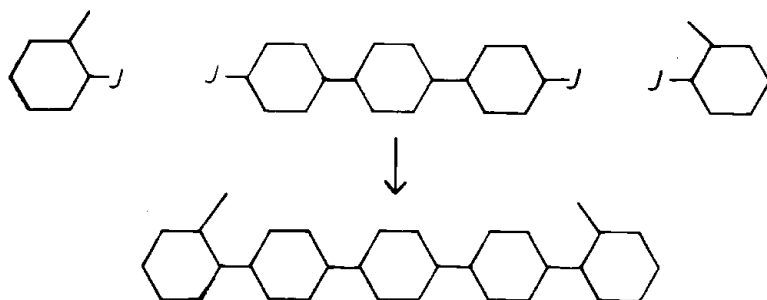
The simplicity of this procedure made this reaction quite useful. In the course of the investigations we acquired much experience in governing the reaction as well as in working up the reaction mixtures, so that we hope to enlarge the number of compounds sketched on Fig. 3 (8-10).

FIGURE 3



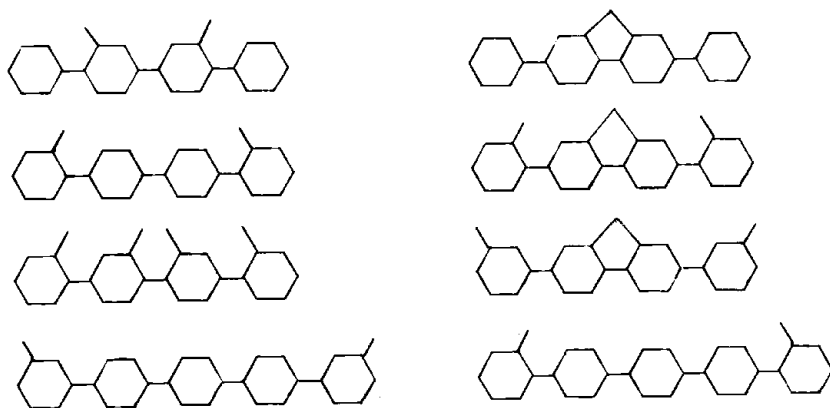
(b) Using our knowledge of Kern's duplication process (12), we could also successfully apply the Ullmann reaction in the sense of a co-condensation (Figure 4). The monoiodo

FIGURE 4



compounds, as here the *o*-iodotoluene, were applied in greater excess, in order to restrain the polycondensation of the bifunctional reaction components. All oligophenylenes, which were prepared according to this principle of synthesis are shown in Fig. 5 (11, 13).

FIGURE 5

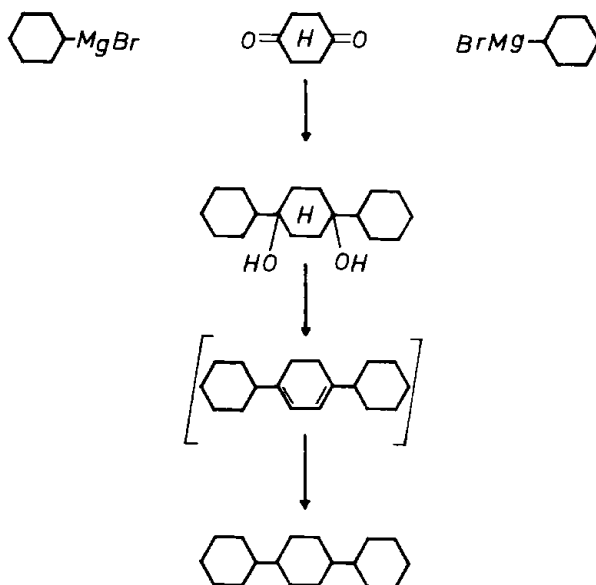


(c) To sum it up, the Ullmann reaction presents an efficient method of synthesis for substituted oligophenylenes. The simplicity of the method has already been mentioned. In addition the iodine compounds which are necessary starting materials are very accessible.

2. The organometallic carbonyl reaction

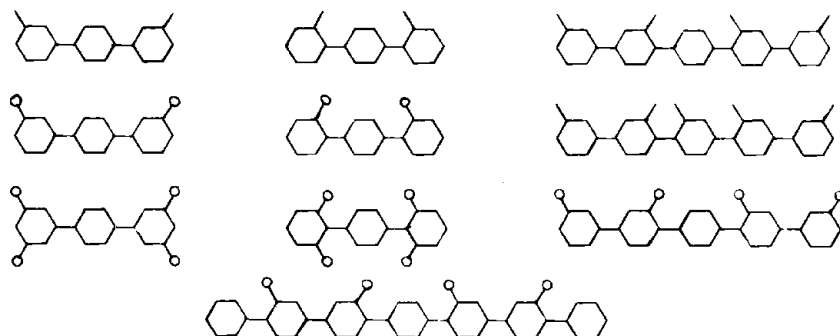
This principle of synthesis was first applied by Mayer and Schiffner for the preparation of *p*-terphenyl (Fig. 6) (6). We have greatly extended this synthetic process, and by variation of the aromatic organometallic compounds, as well as the ring ketones, have prepared 15 methyl substituted and 16 methoxyl substituted *p*-oligophenylenes up to a degree of condensation of 8.

FIGURE 6



(a) The compounds which were prepared by use of monocyclic diketones are grouped in Fig. 7 (10, 13-16). In this

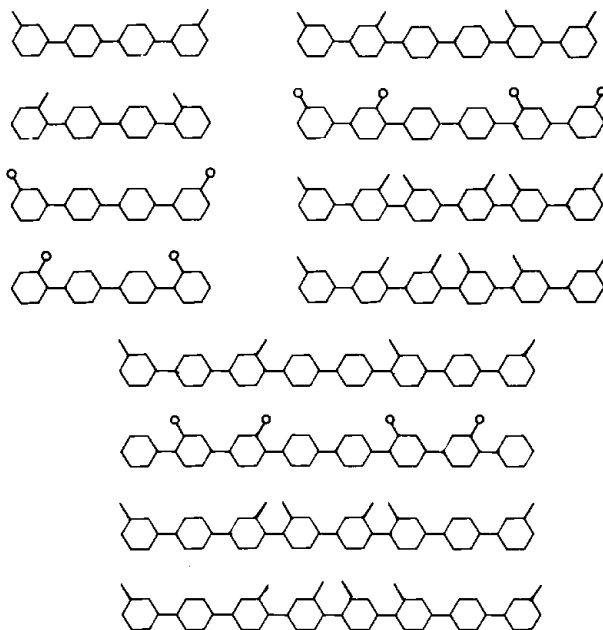
FIGURE 7



case, the middle benzene ring is derived from the appropriate diketones.

(b) By application of bicyclic diketones, we formed the compounds shown in Fig. 8 (9, 10, 16, 17). In this case the

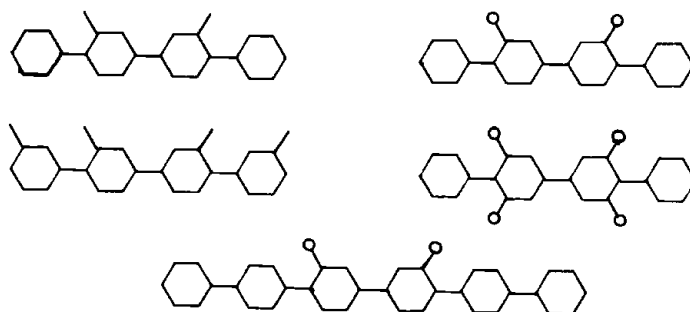
FIGURE 8



two middle rings are produced from the appropriate carbonyl compounds.

(c) We obtained other oligophenylenes inversely through the action of bifunctional organometallic compounds on monofunctional ring ketones, in other words, through exchange of functionality (11, 13, 16, 17). Figure 9 indicates the structure of these compounds. Here, the two middle rings

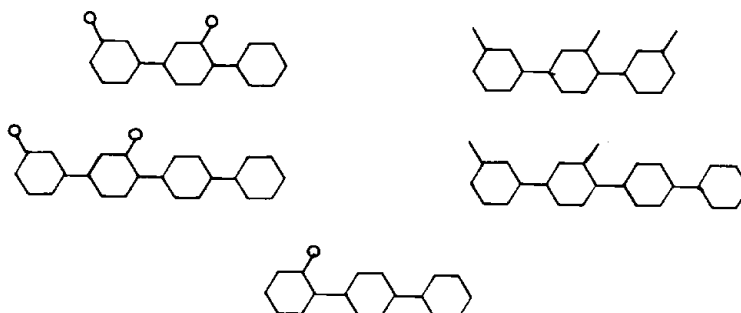
FIGURE 9



are produced from the organometallic derivatives.

(d) Finally, you can see in Figure 10 (10, 16, 18) all of the compounds by the synthesis of which, monofunctional reaction components were applied.

FIGURE 10



(e) One can say in summarizing, that the organometallic carbonyl reaction presents an efficient method of synthesis for methyl and methoxyl substituted oligophenylenes. The procedure allows, through broad variation of the starting

material, a striving for structures which are not accessible through the Ullmann reaction. Both procedures, however, complement one another excellently. This is natural in so far as both require the same starting compounds. The resulting end-products, however, are different.

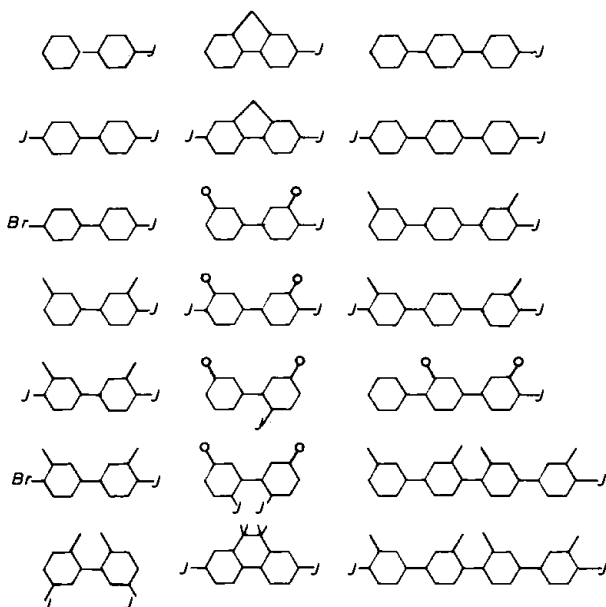
3. Substitution reactions

The possibility of dealing more exhaustively with the two processes of synthesis, depended naturally on making iodine compounds easily accessible.

We occupied ourselves, therefore, very closely with the direct iodination of aromatic compounds. During the investigations, we were able to develop a very efficient iodination process, which provides for the application of iodic acid as oxidant (19).

In this iodination process was found the key to our oligophenylenes (9-11, 16, 17, 20). In Fig. 11 you can see

FIGURE 11



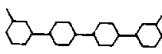
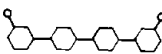
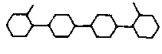
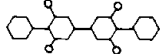
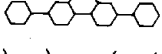
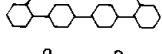

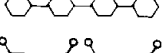
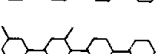
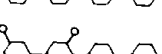
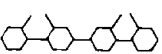
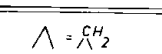
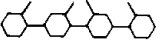
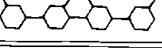
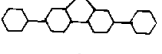
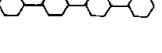
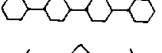
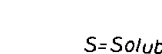
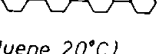


a selection of such iodine compounds, whose constitution is clearly secure. Most of these substances were already used for syntheses. A few of them were previously known.

III. SOME PROPERTIES OF THESE COMPOUNDS

1. Solubility and melting point

All of the p-quaterphenyl derivatives which have been produced up until now, are shown with their solubility and melting point data in Fig. 12. To the left you see the

FIGURE 12

$\text{I} = \text{CH}_3$	S	m.p. [°C]	$\text{I} = \text{OCH}_3$	S	m.p. [°C]
	3,7	213		2	224
	51	150		3	241
	55	176		6	192
	110	139		13	184
	135	142		22	160
	190	116		207	98
	490	96	$\Delta = \text{CH}_2$		
	>500	84		0,3	307
	>500	74		1,4	285
	0,22	320		20	194
				84	159

S=Solubility [g/l] (Toluene, 20°C)

methyl derivatives, in the upper right hand corner the methoxyl derivatives, and to the lower right, the fluorene derivatives. The compounds are arranged according to their solubilities.

This chart shows forcibly that substituted methyl groups have the aptitude to considerably improve the solubility of the *p*-quaterphenyl.

This power depends on the number, as well as on the position of the substituents. The relationships are so complicated, however, that we are not as yet in a position to deduct fixed legitimate associations between structure and solubility, despite the mass of available material. We hope that crystallography will continue to be helpful in solving this problem. Those compounds which are, in general, most soluble contain one methyl group per benzene ring. One can generalize this rule extensively.

The power of the methoxyl group in improving solubility is significantly more limited. When one compares analogous substituted compounds with each other, one can establish the fact, that the effect is weaker by about one order of magnitude. It is interesting, though, that fewer, but unsymmetrically arranged, methoxyl groups cause an enormous increase in the solubility.

In connection with this, one has to submit the question. Why is the solubility of *p*-oligophenylenes so intensely raised by substitution? We can see the cause for that in the destroyed symmetry, which depends on the possibility of rotation of the substituted benzene rings around the longitudinal axis of the molecule. In other words, these molecules can realize more configurations.

According to this conception, a restriction of the rotation with the help of suitable substituents should cause a decrease of the solubility. We synthesized the fluorene derivatives in order to test that and our expectations were confirmed. The solubility of these compounds is very limited, when compared with corresponding methyl derivatives.

While the solubility ascends with increasing degree of substitution, in the same sense the tendency toward crystallization decreases. Therefore, these compounds show a very strong tendency to form supersaturated solutions, and this property makes handling of them especially difficult.

When the solubility increases, the melting point decreases. Solubility and melting point are correlative criteria, since both the occurrence of a solution and melting destroy the lattice. It becomes understandable, therefore, that the tendency toward the formation of a supersaturated solution is connected with the tendency toward the formation of supercooled fusion. In the case of two tetramethyl-*p*-quaterphenyls it appears that a recrystallization of the fusion, which becomes glassy and brittle through cooling, does not take place.

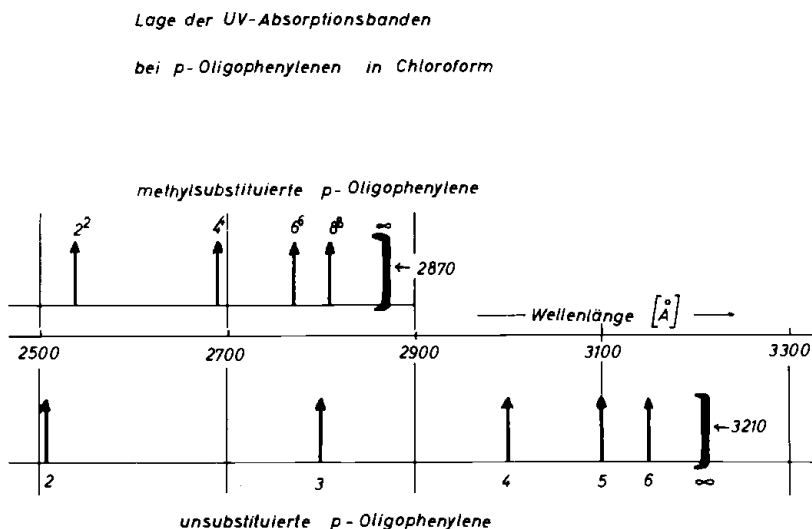
What has been said here about the quaterphenyl derivatives, is also essentially valid for derivatives from other homologs.

2. Ultra-violet spectra

Ultra-violet spectroscopic investigations with unsubstituted oligophenylenes have already been carried out by Gillam and Hey (21).

As is here schematically presented (Fig. 13) (10).

FIGURE 13



These compounds show a broad structureless absorption band, which is displaced toward longer wavelengths when the degree of condensation increases. This displacement takes place, though, in the sense of a converged row with a threshold value of 3210 Å units.

A polyphenylene with a condensation degree of infinity absorbs in the ultraviolet and therefore is colorless.

The absorption behavior of the methyl substituted p-oligophenylenes can also be described with a converged row when one observes the row of the homologous substituted compounds. The range of absorption is much narrower, however, and the threshold value of the corresponding poly-methyl-polyphenylene is 287 Å units.

The substituents produce a hypsochromic effect; they disturb sterically the coplanar adjustment or configuration of the molecule and therefore the interaction of the single chromophores.

The conception that the substituents influence the arrangement of the molecules' frame, receives thereby strong support.

REFERENCES

- (1) W. Kern, *Angew. Chem.* 71:585 (1959).
- (2) W. Kern, M. Seibel and H. O. Wirth, *Makromol. Chem.* 29:164 (1959).
- (3) W. Kern and H. O. Wirth, *Kunststoffe-Plastics* 6:12 (1959).
- (4) W. Kern, H. W. Ebersbach and J. Ziegler, *Makromol. Chem.* 31:154 (1959).
- (5) W. Kern, W. Gruber and H. O. Wirth, *Makromol. Chem.* 37:198 (1960).
- (6) F. Mayer and R. Schiffner, *Ber. deut. chem. Ges.* 65:1337 (1932).
- (7) F. Ullmann and G. M. Meyer, *Ann. Chem. Liebigs*, 332:38 (1904).
- (8) K. A. Heinroth, *Diplomarbeit*, Mainz, 1953.
- (9) H. O. Wirth, *Dissertation*, Mainz, 1956.
- (10) W. Gruber, *Dissertation*, Mainz, 1958.
- (11) K. H. Gönner, *Diplomarbeit*, Mainz, 1960.
- (12) W. Kern and R. J. Rauterkus, *Makromol. Chem.* 28:221 (1958).
- (13) Renate Stück, *Staatsexamensarbeit*, Mainz, 1960.
- (14) M. Seibel, *Dissertation*, Mainz, 1955.
- (15) H. W. Ebersbach, *Dissertation*, Mainz, 1955.

- (16) Irmgard Ziegler, Dissertation, Mainz, 1958.
- (17) O. Königstein, Intended Dissertation, Mainz, 1961.
- (18) W. Heitz, Dissertation, Mainz, 1960.
- (19) H. O. Wirth, O Königstein and W. Kern, Ann. Chem. Liebigs 634:84 (1960).
- (20) H. O. Wirth, Unpublished Investigations.
- (21) A. E. Gillam and D. H. Hey, J. Chem. Soc. (London) 1170 (1939).