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SYNTHESES AND PROPERTIES OF 3,4'-POLYMETHYLENEBIPHENYLS[1]

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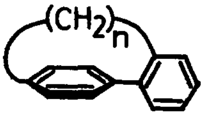
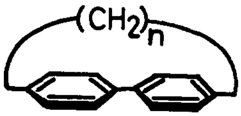
Non-coplanarity[2] of two benzene rings in biphenyl derivatives had been realized only in the biphenyls with bulky groups situated at o,o'-positions.

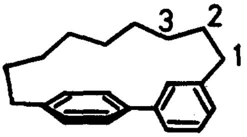
In preceding two papers[3,4], we reported the syntheses of two general systems (1) and (2), which have polymethylene bridges spanning 2,4'- and 4,4'-positions respectively in biphenyl system.



(1) a , n=7
b*, n=8
c , n=9
d*, n=10



(2) a , n=11 d*, n=14
b*, n=12 e , n=15
c , n=13 f , n=16



(3) a , n=9
b , n=10
c , n=11
d , n=12

(* These compounds have been reported in the preceding papers[3,4].)

In the compounds (1)[3,5] with suitable length of polymethylene bridges, the two benzene rings cann't be coplanar and this reflects in their anomalous ultraviolet and n.m.r. spectra. Whereas, completely different situation gives rise in the compounds (2)[4,7] with p,p'-polymethylene bridges which force the molecules to take coplanar conformation.

In this communication, we wish to report the syntheses and properties of another type of biphenyls which have polymethylene bridges spanning 3,4'-position. Examination of molecular models suggests that 3,4'-bridge appears to make the two benzene rings perpendicular more effectively than the 2,4'-bridge, and the lowest member can be made without bond deformation will be (3b), n=10.

Preparation of 3,4'-Polymethylenebiphenyls (3).

The compounds needed for this study were synthesized by the scheme outlined in Chart I. The general approach was analogous to that developed in previous investigations of 2,4'- and 4,4'-polymethylenebiphenyls. Starting from 3-phenylcyclohexylacetate (4), the syntheses of the compounds (3) with even- and odd-numbered polymethylene bridges follow different routs.

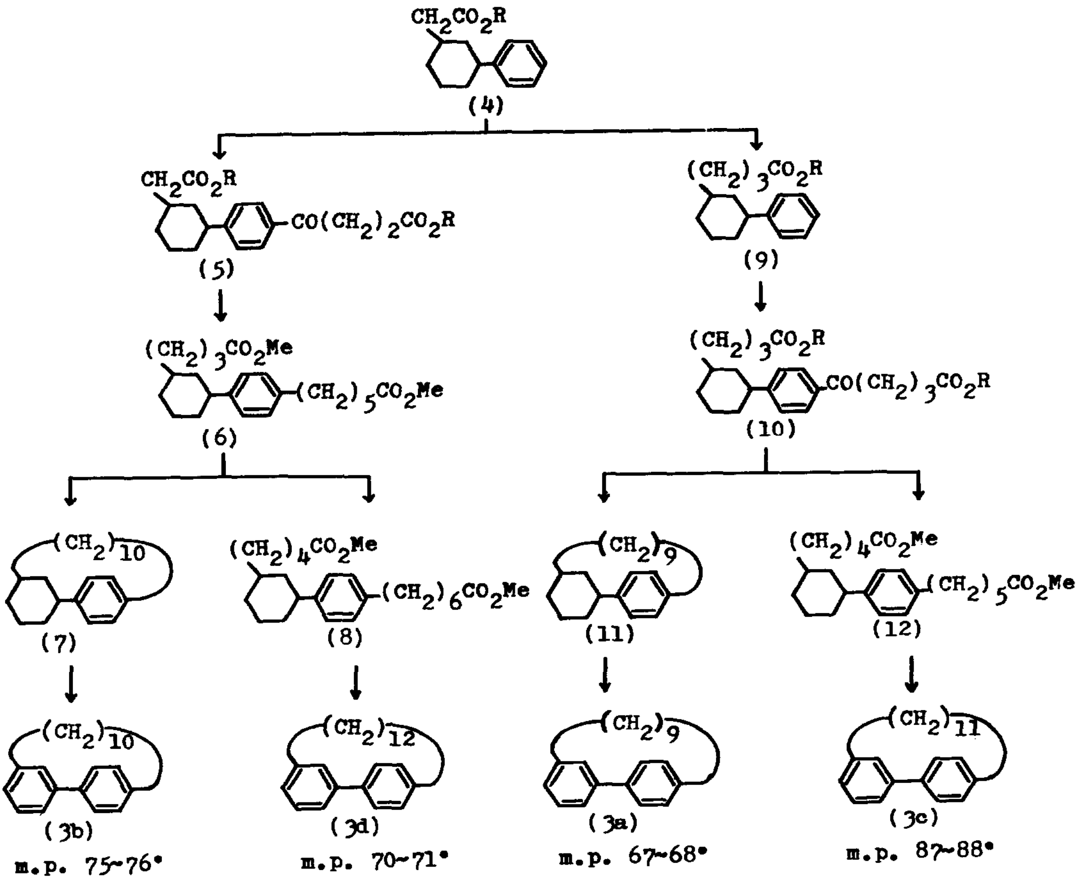
Friedel-Crafts acylation with succinic anhydride gave (5), which was converted into the diester (6) by the series of reactions; a) Wolff-kishner reduction to remove the keto group, b) copper-chromite catalytic hydrogenation to afford glycol, c) conversion to dibromide, d) malonate synthesis.

The hexahydrobiphenyl (7), provided by Prelog-Stollacyloin cyclization of the diester (6) followed by Clemmensen reduction, was heated with 10% Pd/C (320°) to give 3,4'-decamethylenebiphenyl (3b), m.p. 75~76°.

After the side chains of the diester (6) were extended by routine method (Via cyanide), the resulting diester (8) was cyclized by acyloin condensation. Clemmensen reduction, followed by dehydrogenation yielded dodecamethylenebiphenyl (3d), m.p. 70~71°.

For the series of compounds with odd-numbered polymethylene bridges, the side chain of the intermediate (4) was first extended to afford 3-phenylcyclohexylbutyrate (9) which was then treated with γ-carbomethoxybutyryl chloride in carbon tetrachloride to afford the keto-carboxylate(10). By the parallel sequence of reactions with even-numbered polymethylene bridge compounds, the compound (10) was converted into nonamethylenebiphenyl (3a), m.p. 67~68° and undecamethylenebiphenyl (3c), m.p. 87~88°.

CHART I



Ultraviolet Absorption Spectra.

Fig.1 and Table I record the ultraviolet absorption spectra data of these 3,4'-polymethylenebiphenyls with that of 3-butyl-4'-hexylbiphenyl as a reference compound.

Regular shift of absorption maxima toward shorter wavelength with decreasing extinction coefficient going from (3d), n=12 to (3b), n=10, can be rationalized by increasing resonance inhibition.

Anomalous behavior observed in (3a), n=9 suggest the warped benzene rings which can be seen from the molecular model of this compound.

Nuclear Magnetic Resonance Spectra8).

Although general pattern of the nmr spectra of 3,4'-polymethylenebiphenyls (3) appears similar to that of 2,4'-polymethylenebiphenyls (1), the most characteristic feature observed in (3) is the multiplet (4H) centered around 8.4τ which can be assigned to the protons on the carbon atoms 2 and 39) (Fig.2)10). Bridging 3,4'-position, these carbon atoms must surround the perimeter of one of the benzene rings and suffer strong deshielding effect.

These situations should be realized more effectively in 3,3'-polymethylenebiphenyls in which the strain imposed by the tightly drawn polymethylene bridge would cause the biphenyl nucleus to become coplanar, and the polymethylene bridge would also be coplanar with this molecular plane.

Our efforts toward the synthesis of this line of compound have been rewarded by successful preparation of 3,3'-decamethylenebiphenyl, m.p. 58-59° from 3,3'-dimethylbiphenyl, and the details will be the subject of a future communication.

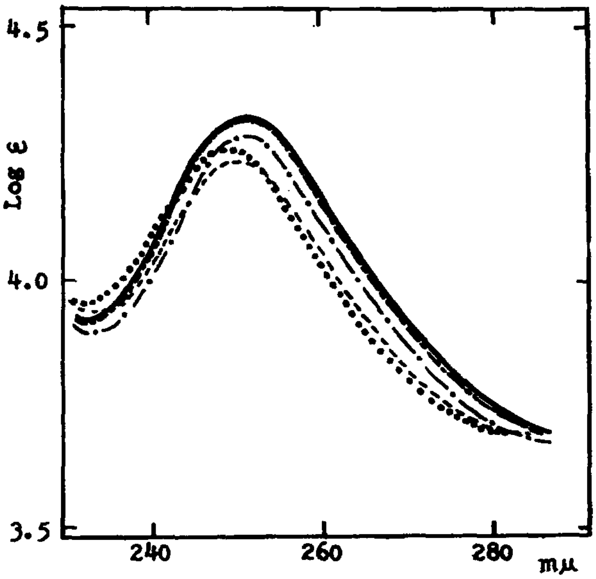


Fig.1. Ultraviolet absorption spectra of (3) in n-hexane: ------,n=9; ....,n=10; —·—·—,n=11; —··—,n=12; ———, 3-butyl-4'-hexylbiphenyl.

Table I
Ultraviolet Absorption Data

compound	λ max (mμ)	ε
(3a)	250	14500
(3b)	248	16700
(3c)	252	18800
(3d)	252	19500
3-butyl-4'-hexylbiphenyl	252	19700

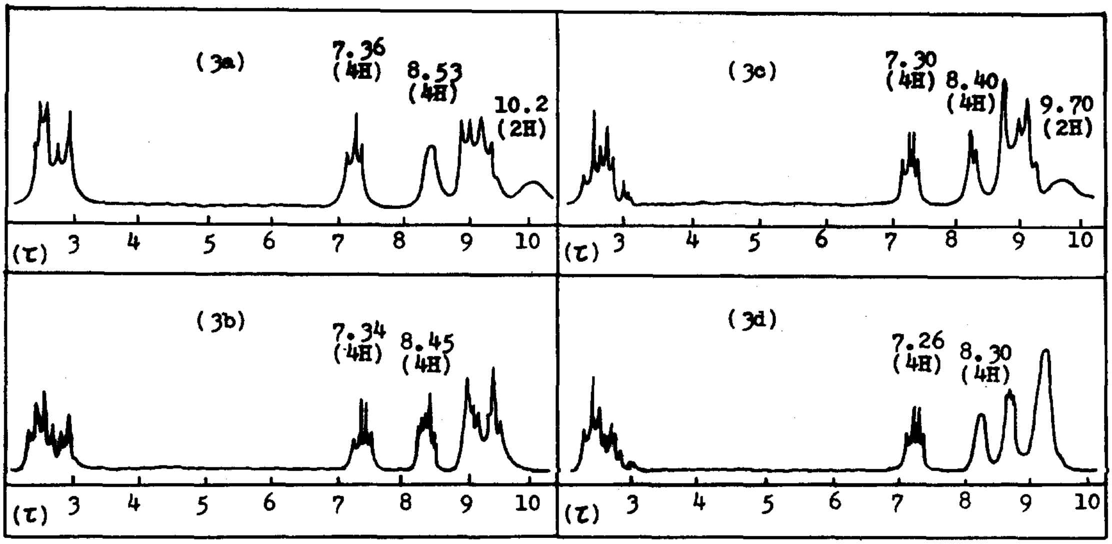


Fig.2. Nuclear magnetic resonance spectra, peak positions reported in τ-value[10].

REFERENCES

1) This material was presented in part before the 20th Annual Meeting of the Chemical Society of Japan, Tokyo, March, 1967.

2) G. H. Beaven, "Steric Effects in Conjugated Systems," Butterworths, London, 1958, p.22.

3) M. Nakazaki and S. Isoe, Chem. & Ind., 224 (1965).

4) M. Nakazaki and K. Yamamoto, ibid., 486 (1965).

5) *Inspection of the Dreiding's molecular model shows that the compound* (1) with heptamethylene bridge is the lowest member can be constructed without bond deformation. We have succeeded to prepare[6] following members of the compounds; (1a), n=7, b.p. 107~109°/10^{-2}Torr, (1d), n=9, m.p. 60.5° whose preparations and properties will be reported elsewhere.

6) *The preliminary account was presented before the 19th Annual Meeting of the* Chemical Society of Japan, Tokyo, March, 1966.

7) Since the preliminary publication[4], the lowest member of (2), n=11, m.p.87° has been synthesized[6] together with higher homologs, (2c), n=13, m.p. 102°, (2e), n=15, m.p. 129° and (2f), n=16, m.p. 111°.

8) The most highly shielded protons (10.2 τ) so far observed in polymethylene-bridged biphenyls are that of 4,4'-polymethylenebiphenyl (2b).

9) The numbering system adopted here is that proposed in B. H. Smith, "Bridged Aromatic Compounds," Academic Press, New York, 1964.

10) The spectra were taken in carbon tetrachloride on a Nucleomagnetic Resonance Spectrometer, JNM-4H-100, Japan Electron-Optics Laboratory Co., Ltd.