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Syntheses and Properties of *m,m'*-Polymethylenebiphenyls

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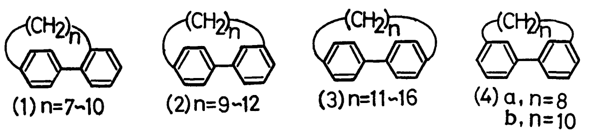
Reports were given on the preparation of three systems of compounds (**1**), (**2**), and (**3**), with varying lengths of polymethylene bridge spanning *o,p'*-, *m,p'*-, and *p,p'*-positions of biphenyl, respectively.[1-3)]



The present communication describes the syntheses and properties of biphenyls (**4**) with *m,m'*-polymethylene bridge.[4)]

Preparation of (**4**) was carried out according to the sequence of reactions illustrated in Chart 1. The usual sequence involving malonic ester synthesis and LAH reduction is extended to the side chains of dibromide (**5a**), *via* (**5b**), and (**5c**), to give the homologous dibromide (**5d**). The malonic ester synthesis applied to the resulting dibromide (**5d**) afforded diester (**5g**), mp 48—49 °C, which was cyclized to acyloin (**6**) by the Prelog-Stoll acyloin condensation. The Clemmensen reduction of (**6**) gave *m,m'*-decamethylenebiphenyl (**4b**), mp 58—59 °C.

Because of severe steric strain in the lower homolog *m,m'*-octamethylenebiphenyl (**4a**), its synthesis was effected only by making a detour through the more flexible intermediates (**7**), (**8**), and (**9**) with saturated biphenyl moiety.

Hydrolysis followed by esterification of dinitrile (**5e**) secured from dibromide (**5d**), afforded diester (**5f**). Catalytic hydrogenation (1 atm, room temperature) over Adams' catalyst of ester (**5f**) in acetic acid gave saturated ester (**7**), which was cyclized by acyloin condensation to yield saturated acyloin (**8**). The Clemmensen reduction of (**8**) afforded saturated hydrocarbon (**9**).

The final step of the synthesis was dehydrogenation of (**9**) by heating with 10% Pd/C catalyst at 260—300 °C for 3 hr yielding *m,m'*-octamethylenebiphenyl (**4a**), mp 73—74 °C. Dehydrogenation under more drastic conditions (360—390 °C for 3 hr) converted (**9**) into perylene (**10**) apparently *via* biphenyl derivative (**4a**).

The electronic spectrum of *m,m'*-polymethylenebiphenyls (**4**) (**4a**: λ_{max} 253 nm, log ε 4.22; **4b**: λ_{max} 253 nm, log ε 4.21 in *n*-hexane) shifts towards longer wavelength with higher intensity compared to the reference compound (3,3'-dimethylbiphenyl: λ_{max} 250 nm, log ε 4.20 in *n*-hexane).

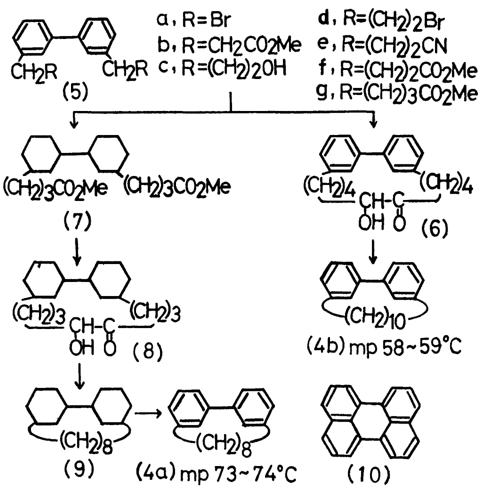


Chart 1

The NMR data of the *m,m'*-polymethylenebiphenyls are shown in Table 1. Absorptions due to the hydrogens of polymethylene bridges appear at lower field than those of the polymethylene in *o,p'*-, *m,p'*-, and *p,p'*-polymethylene bridged biphenyls. Among the *m,m'*-polymethylenebiphenyl derivatives (**4**), the methylene hydrogens of the lower homolog (**4a**) (8.45 τ) absorb at lower field than the higher homolog (**4b**) (8.67 τ).

TABLE 1. NMR SPECTRAL DATA IN CARBON TETRACHLORIDE

Compound	Aromatic protons, τ	Aliphatic protons, τ		
4a	2.62—3.15 (8H)	7.31 (4H)	8.33 (4H)	8.67 (12H)
4b	2.49—3.15 (8H)	7.26 (4H)	8.30 (4H)	8.45 (8H)

The results can be rationalized by assuming that the *m,m'*-polymethylene bridges in the biphenyl derivatives (**4**) are coplanar with the molecular planes as shown by molecular models, and that they are deshielded by the biphenyl moieties, the deshielding being apparently more effective in the shorter bridged compound (**4a**) than in (**4b**).

Experimental

m,m'-Bis-(3-carbomethoxypropyl)-bicyclohexyl (7). Six grams of diester (**5f**) was hydrogenated with 0.6 g of platinum oxide in 45 ml of acetic acid at 40 °C under 1 atmosphere. The reaction stopped after 70 hr when 90% of the theoretical amount of hydrogen had been absorbed. The catalyst was removed by filtration, the solvent was evaporated in a vacuum, and the product was distilled to yield a colorless liquid, bp 142—144 °C/0.05 mmHg, 5.4 g (87%).

1) M. Nakazaki and S. Isoe, *Chem. Ind.* (London), 224 (1965).
2) M. Nakazaki and K. Yamamoto, *ibid.*, 468 (1965).
3) M. Nakazaki, T. Horikawa, and K. Yamamoto, *Tetrahedron Lett.*, **1969**, 4551.
4) R. V. M. Campbell, L. Crombie, B. Tuck, and D. A. Whiting, *Chem. Commun.*, 1206 (1970).

*4-Hydroxy-5-oxo-*m,m'*-octamethylenebicyclohexyl (8).* A solution of 2.7 g of the saturated diester (**7**) in 150 ml of xylene was added to a suspension of 1.2 g of sodium in 400 ml of xylene over 48 hr under nitrogen atmosphere. The usual work-up[5] of the reaction mixture then gave crude acyloin (**8**), 1.2 g (53%).

m,m'*-Octamethylenebicyclohexyl (9).* Amalgamated zinc was prepared by swirling 33 g of zinc with a solution of 1 g of $HgCl_2$ and 1 ml of concd HCl in 100 ml of water. A solution of 1.2 g of acyloin (**8**) in 30 ml of toluene was added to the amalgamated zinc with 100 ml each of concd HCl and acetic acid. The mixture was heated under reflux for 48 hr, during which time four 20 ml-portions of concd HCl were added. After the usual treatment, the crude reaction product was distilled to yield a colorless liquid, bp 116—118 °C/0.1 mmHg, 0.5 g (46%).

Found: C, 86.23; H, 13.19%. Calcd for $C_{20}H_{36}$: C, 86.88; H, 13.12%.

m,m'*-Octamethylenebiphenyl (4a).* Dehydrogenation of 0.5 g of saturated hydrocarbon (**9**) was accomplished by heating with 0.04 g of 10% palladium-on-charcoal at 260—300 °C for 3 hr. The theoretical amount of hydrogen was evolved, the reaction product was taken up in *n*-hexane, filtered free of catalyst and crystallized from ethanol to give 0.3 g (63%) of (**4a**), needles, mp 73—74 °C.

Found: C, 90.71; H, 9.32%. Calcd for $C_{20}H_{24}$: C, 90.80; H, 9.26%.

*5-Hydroxy-6-oxo-*m,m'*-decamethylenebiphenyl (6).* The acyloin reaction was carried out in a manner similar to that described for (**8**). From 11 g of diester (**5g**) was obtained 4.2 g (51%) of the crude acyloin (**6**).

m,m'*-Decamethylenebiphenyl (4b).* Four grams of acyloin (**6**) was converted into hydrocarbon with zinc and acid as described for (**9**). The product was isolated in the usual way and recrystallization from ethanol gave 0.8 g (21%) of (**4b**), needles, mp 58—59 °C.

Found: C, 90.11; H, 10.03%. Calcd for $C_{22}H_{28}$: C, 90.23; H, 9.88%.

5) D. J. Cram and H. Steinberg, *J. Amer. Chem. Soc.*, **73**, 5691 (1951).