lized several times from a toluene–ligroin (3:1) mixture. About 1 g. of fine white crystals, m. p. 302°, was obtained.

Anal. Calcd. for $C_{44}H_{46}N_4O_6$: C, 72.73; H, 6.33; N, 7.71. Found: C, 72.86; H, 6.11; N, 7.95.

A melting point of a mixture of 90% of the lower- and 10% of the higher-melting product showed a depression, m. p. 228–238°.

The higher-melting compound was approximately six times as soluble in toluene as the lower-melting.

Condensation of Adipyl Chloride with 3-Nitro-3′-aminobimesityl.—The procedure used was similar to that described for the isophthalyl derivative. The crude product was crystallized several times from acetone and a single compound was obtained, m. p. 230–231° (corr.). Attempts to isolate a second isomer from the filtrates were unsuccessful. The fractions thus obtained melted over a two or three degree range in the neighborhood of 226°, but mixed melting point with the 230–231° product showed no depression.

Anal. Calcd. for $C_{42}H_{50}N_4O_6$: C, 71.39; H, 7.08. Found: C, 71.70; H, 7.32.

Condensation of Oxalyl Chloride with 3-Nitro-3′-aminobimesityl.—By a procedure similar to those just described one mole of oxalyl chloride was condensed with two of amine. The crude product was obtained in almost quantitative yields. It was fractionally crystallized from dibutyl ether and two fractions obtained, one m. p. 304–307° (corr.), and the other m. p. 273–283° (corr.). The melting point of the lower-melting form could not be improved over the value given, so that it may not have been entirely pure in spite of a satisfactory analysis.

Anal. (High-melting fraction) Calcd. for $C_{38}H_{42}N_4O_6$: N, 8.62. Found: N, 8.83. (Low-melting fraction) Found: N, 8.73.

3-Nitro-3′-isothiocyanobimesityl.—An attempt was made to prepare the thiourea from carbon disulfide and 3-nitro-3′-aminobimesityl. Only an isothiocyano derivative was obtained.

To a solution of 1.5 g. of 3-nitro-3′-aminobimesityl in 10 cc. of ethanol was added 10 cc. of carbon disulfide and 5.5 cc. of alcoholic potassium hydroxide (0.22 *N*). The solution was refluxed for eight hours, evaporated to a small volume and cooled. The product separated and was recrystallized from ethanol to a constant m. p. of 119–120°.

Anal. Calcd. for $C_{19}H_{20}N_2O_2S$: C, 67.05; H, 5.88; S, 9.41; mol. wt., 340. Found: C, 67.49; H, 6.52; S, 9.08; mol. wt. (Rast), 345.

Summary

Two diastereoisomers have been obtained by the condensation of one mole of isophthalyl chloride and two moles of 3-nitro-3′-aminobimesityl. These represent *meso* and racemic isomers due to the presence of two points of restricted rotation in the molecules. They differ from analogous isomers previously prepared in that the points of restricted rotation are widely separated from each other.

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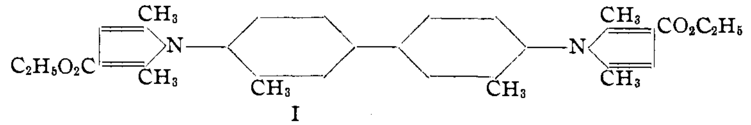
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

Stereochemistry of Biphenyls.[1] XLV. Stereoisomeric Dipyrryl Biphenyls

BY ROGER ADAMS AND R. M. JOYCE, JR.*

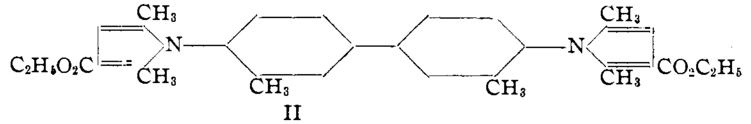
The study of molecules containing two points of restricted rotation[2] has been extended to certain dipyrryl biphenyls. Both *o*-tolidine and dianisidine were condensed with 3-carbethoxy-2,5-hexanedione and in each case two diastereoisomeric forms were isolated. By way of illustration the isomers from *o*-tolidine are shown in I and II. These pairs of isomers represent molecules in which free rotation between the benzene nuclei exists and consequently such molecules are much more mobile than the diphenylpyrroles previously prepared in diastereoisomeric forms.



I

M. p. 172–174°

racemic



II

M. p. 142–144°

meso

The two isomers differ from each other in melting point and solubility. The higher-melting form arbitrarily has been assigned the racemic structure. It is less soluble than the lower-melting form. The difficulty of obtaining easily

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[1] For previous paper in this series see Adams and Joyce, THIS JOURNAL, **60**, 1489 (1938).

[2] Chang and Adams, *ibid.*, **56**, 2084 (1934); Browning and Adams, *ibid.*, **52**, 4098 (1930); Shildneck and Adams, *ibid.*, **53**, 343, 2203 (1931); Knauf, Shildneck and Adams, *ibid.*, **56**, 2109 (1934).

handled acids by saponification of the esters prevented the definite establishment of the configuration the two compounds by resolution studies.

It may be concluded that each point of restricted rotation has an effect upon the stereochemical properties of various organic molecules identical to that of an asymmetric carbon atom. The proximity of the points of restricted rotation has no significance.

Experimental

4,4′-*Bis*-[1-(2,5-dimethyl-3-carbethoxy)-pyrryl]-biphenyl.—A solution of 3.72 g. (0.02 mole) of 3-carbethoxy-2,5-hexanedione in 5 cc. of glacial acetic acid was mixed with a solution of 2.21 g. (0.01 mole) of benzidine in 15 cc. of warm glacial acetic acid and heated for three hours on a steam-bath. It was then cooled, poured into 250 cc. of cold water and the acetic acid neutralized with 10% aqueous sodium hydroxide. The brown precipitate was filtered, dissolved in 100 cc. of hot methanol, treated with Norite, filtered and cooled. The supernatant liquid was decanted from black gummy material which separated and then was concentrated to 40 cc. and cooled. The dark crystalline precipitate was purified by recrystallization first from ligroin and then from methanol. A yield of 0.5 g. of yellow crystals, m. p. 182–183° (corr.), was obtained.

Anal. Calcd. for $C_{30}H_{32}N_2O_4$: N, 5.79. Found: N, 5.87.

Attempts to saponify this ester gave as a product a white powder insoluble in all common organic solvents.

4,4′-*Bis*-[1-(2,5-dimethyl-3-carbethoxy)-pyrryl]-3,3′-dimethylbiphenyl.—A mixture of 12.7 g. (0.06 mole) of *o*-tolidine, 23.5 g. (0.12 mole) of 3-carbethoxy-2,5-hexanedione and 12 g. of freshly fused sodium acetate was dissolved in 100 cc. of warm glacial acetic acid. It was heated on a steam-bath for ten hours, cooled, poured into water and neutralized with dilute aqueous sodium hydroxide. The brown precipitate was filtered, treated with 500 cc. of boiling methanol, the insoluble black gum removed by filtration, the solution concentrated to 200 cc. and cooled.

The crystalline material was filtered and a second crop obtained by concentration of the filtrate to 100 cc.; yield, 5 g. It was dissolved in 300 cc. of boiling ligroin (b. p. 60–100°) and allowed to stand. The granular crystals were filtered and the filtrate concentrated to 75 cc. Upon cooling, a second fraction separated.

The first fraction after three crystallizations from ethanol gave tan granular crystals, m. p. 172–174° (corr.). The slight color was very difficult to remove.

Anal. Calcd. for $C_{32}H_{36}N_2O_4$: C, 75.00; H, 7.03; N, 5.46. Found: C, 75.29; H, 6.96; N, 5.32.

The second fraction after two crystallizations from ethanol gave colorless platelets of constant m. p. 143–144° (corr.).

Anal. Calcd. for $C_{32}H_{36}N_2O_4$: C, 75.00; H, 7.03; N, 5.46. Found: C, 75.40; H, 7.18; N, 5.60.

The melting point of a mixture of 95% of the lower- and 5% of the higher-melting compound showed a depression, m. p. 139–144°. The lower-melting form was about three times as soluble in ligroin or ethanol as the higher-melting.

4,4′-*Bis*-[1-(2,5-dimethyl-3-carbethoxy)-pyrryl]-3,3′-dimethoxybiphenyl.—The procedure was identical to that just described. The yield of crude material from dianisidine and 3-carbethoxy-2,5-hexanedione was about the same as in the case of *o*-tolidine.

The separation of the isomers was difficult. Neither alcohol nor ligroin was very satisfactory. A solution of 2 g. of crude product in 100 cc. of hot ethanol was allowed to cool for a few minutes till 20 to 25 mg. of pinkish platelets had separated. These were filtered immediately and crystallized from ethanol to give a colorless product, m. p. 185–187° (corr.).

Anal. Calcd. for $C_{32}H_{36}N_2O_6$: C, 70.59; H, 6.63; N, 5.15. Found: C, 70.70; H, 6.44; N, 5.28.

The filtrate was concentrated to 25 cc. and cooled. The crystalline product which separated, obviously a mixture of the two isomers, was filtered. Further concentration to 12 cc. gave still more of the crystalline mixture. This filtrate was then concentrated to 5 cc., whereupon a single crystalline form separated as flower-like rosets. By recrystallization from ethanol, they were brought to constant m. p. 168–170° (corr.).

Anal. Calcd. for $C_{32}H_{36}N_2O_6$: C, 70.59; H, 6.63; N, 5.15. Found: C, 70.51; H, 6.68; N, 5.17.

A mixture of 80% of the higher-melting and 20% of the lower-melting form showed a depressed melting point of 162–170°. The lower-melting form is about 1.5 times as soluble in ethanol as the higher-melting.

Summary

o-Tolidine and dianisidine have been condensed with 3-carbethoxy-2,5-hexanedione. In each case two diastereoisomeric dipyrryl biphenyls were isolated. These represent examples of molecules containing two points of restricted rotation, each between a pyrrole and benzene ring. The restricted points are farther removed from each other than in the dipyrryl benzene derivatives previously studied.

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