tion; the organic layer was separated, dried over potassium hydroxide and distilled, giving 2-octanol, b.p. 84–86° (28 mm.), $[\alpha]^{26}_{\rm D}$ +9.10° (homogeneous), $n^{26}_{\rm D}$ 1.4236.

The solid residue was leached with a total of 62 ml. of hot ethyl acetate, and the leachings, combined with 186 ml. of benzene, were chromatographed on 137 g. of silica gel. (+)-DNDBCH-6-one (0.120 g., $[\alpha]^{26}_{\rm D}$ +52° (*c* 1.1, ethyl acetate)) and (−)-DNDBCH-6-ol (0.427 g., $[\alpha]^{26}_{\rm D}$ −54° (*c* 4.2, ethyl acetate)) were recovered as described for the previous experiment. Both fractions had infrared spectra (KBr wafer) identical with authentic materials. Reduction of 0.100 g. of the (+)-DNDBCH-6-one and isolation of product DNDBCH-6-ol (0.061 g., 61%, $[\alpha]^{26}_{\rm D}$ +212° (*c* 0.24, ethyl acetate), infrared spectrum (KBr wafer) identical with authentic alcohol) followed the procedure described in the previous section.

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NEW YORK 53, N. Y.

[CONTRIBUTION FROM THE WM. H. NICHOLS CHEMICAL LABORATORY, NEW YORK UNIVERSITY]

The Configurational Intercorrelation of Optically Active Biphenyls by Thermal Analysis[1]

BY MAURICE SIEGEL AND KURT MISLOW[2]

RECEIVED JULY 1, 1957

The configurations of 6,6′-dinitro-, 6,6′-dichloro- and 6,6′-dimethyl-2,2′-diphenic acid have been correlated by the method of thermal analysis, in the first application of any indirect method to intercorrelations in the biphenyl series. In conjunction with previous work,[1] the *S*-configuration has thence been assigned to (−)-6,6′-dichloro- and to (+)-6,6′-dimethyl-2,2′-diphenic acid. The method has been extended successfully to the correlation of 6,6′-dichloro- and 6,6′-dimethyl-2,2′-bis-(hydroxymethyl)-biphenyl.

While absolute configuration may now be assigned to key compounds in the series of optically active biphenyls through use of the general method earlier developed,[1] the same purpose also may be served by configurational intercorrelation within the series, employing *S*(−)-6,6′-dinitro-2,2′-diphenic acid as the absolute standard. Anticipating the difficulties which are likely to be encountered in direct chemical interconversions, we were particularly concerned with developing a physical method for achieving the desired end.

Scrutiny of the literature disclosed that in most instances the melting points of the enantiomeric forms of the hindered biphenyls lie below those of the racemic modifications[3]: racemate formation appears to be the general case. This observation encouraged investigation of the method of thermal analysis[4] as a means for arriving at configurational relationships within the biphenyl series.

Optically Active 2,2′-Diphenic Acids.—A major limitation of the method, as applied to hindered biphenyls, was recognized at the outset: for optically unstable biphenyls, the relatively high temperatures involved in the establishment of solid–liquid equilibria are likely to cause enantiomeric interconversions and consequent vitiation of results. The compounds which were employed in testing the method, 6,6′-dinitro-, 6,6′-dichloro- and 6,6′-dimethyl-2,2′-diphenic acid, are, however, optically stable[5]; furthermore (a) they are similarly constituted dicarboxylic acids, *i.e.*, expected on the basis of previous work[4] to exhibit significant differences in phase behavior, and (b) the absolute configuration of one of their number is known.[1]

Thermal analysis of mixtures of the three racemates with the corresponding optically active forms revealed no peculiarities. The phase diagrams each exhibit simple eutectics, with some evidence of partial solid solution formation, and no evidence of partial racemate formation[6]; the only compound formed between the enantiomeric species is the 1:1 racemate.

The phase diagrams of (+)-6,6′-dimethyl-2,2′-diphenic acid *vs.* (+)- and (−)-6,6′-dichloro-2,2′-diphenic acid (Fig. 1, curves A and B, respectively), (+)-6,6′-dimethyl-2,2′-diphenic acid *vs.* (+)- and (−)-6,6′-dinitro-2,2′-diphenic acid (Fig. 2, curves A and B, respectively) and (+)-6,6′-dichloro-2,2′-diphenic acid *vs.* (−)- and (+)-6,6′-dinitro-2,2′-diphenic acid (Fig. 3, curves A and B, respectively) serve as unambiguous evidence for the desired configurational correlation. In each case, one, the quasi-enantiomeric, pair forms a congruent and pronounced 1:1 compound (quasi-racemate; arrow, curves A),[7] while the other, configurationally related, pair exhibits continuous solid solution formation (curves B). This type of a difference in phase behavior provides a measure of internal consistency,

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[1] Configurational Studies in the Biphenyl Series II. Part I, P. Newman, P. Rutkin and K. Mislow, THIS JOURNAL, **80**, 465 (1958).

[2] To whom correspondence regarding the article should be addressed.

[3] Among the several exceptions: (±)-methyl 6,6′-dinitro-2,2′-diphenate, m.p. 132–133° (J. Kenner and W. V. Stubbings, *J. Chem. Soc.*, 593 (1921)), (+)- and (−)-forms, m.p. 141–142° (Part I (ref. 1)); 6,6′-dimethyl-2,2′-biphenyldiamine, m.p. 136°, (+)- and (−)-forms, m.p. 156° (J. Meisenheimer and M. Höring, *Ber.*, **60**, 1425 (1927)).

[4] The method, introduced by J. Timmermans (*Rec. trav. chim.*, **48**, 890 (1929)), has been brilliantly exploited by A. Fredga ("The Svedberg," Almqvist and Wiksells, Uppsala, 1944, p. 261) and his collaborators at Uppsala. For incisive reviews, *cf.* especially J. Timmermans, *J. chim. phys.*, **49**, 162 (1952); H. Lettré, *Erg. Enzymforsch.*, **9**, 1 (1943); and, more recently, K. Petterson, *Arkiv Kemi*, **10**, 297 (1956). For previous work in this Laboratory, *cf.* K. Mislow and M. Heffler, THIS JOURNAL, **74**, 3668 (1952); K. Mislow and W. C. Meluch, *ibid.*, **78**, 5920 (1956). Thus far, only centrally asymmetric compounds have been correlated by this powerful method.

[5] (a) R. Kuhn and O. Albrecht, *Ann.*, **455**, 272 (1927), have reported on the extreme stability of 6,6′-dinitro-2,2′-diphenic acid. (b) The optical stability of methyl 6,6′-dimethyl-2,2′-diphenate has been commented on by D. Aziz and J. G. Breckenridge, *Can. J. Research*, **28B**, 26 (1950). (c) The interference radius of Cl (1.89) is intermediate between that of NO_2 (1.92) and CH_3 (1.73) (G. W. Wheland, "Advanced Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1949, p. 210), hence (*cf.* a and b) 2,2′-dichloro-2,2′-diphenic acid is also optically stable.

[6] M. Bergmann and M. Lissitzin, *Ber.*, **63**, 310 (1930); *cf.* however M. Tomita and Y. Seiki, *J. Biochemistry (Japan)*, **30**, 101 (1939).

[7] The maximum in curve 1A is far less satisfactorily expressed and defined than are those in curves 2A and 3A. The possibility of, for example, incongruent melting cannot be unequivocally ruled out on the basis of the present data. Our conclusions remain unaffected.

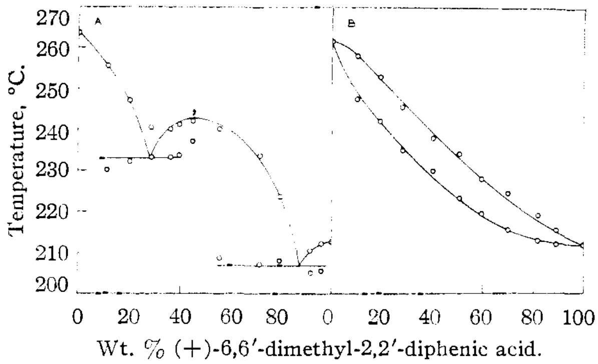

Fig. 1.—Phase diagrams of (+)-6,6′-dimethyl-2,2′-diphenic acid *vs.* (+)- and (−)-6,6′-dichloro-2,2′-diphenic acid (curves A and B, resp.).

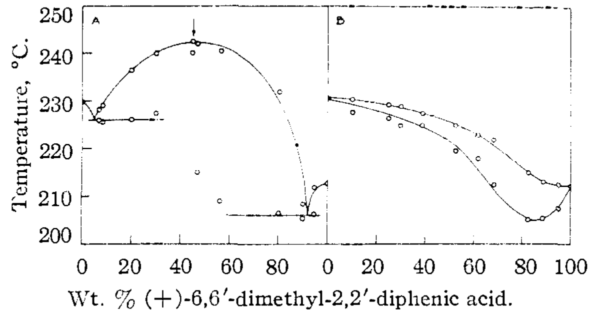

Fig. 2.—Phase diagrams of (+)-6,6′-dimethyl-2,2′-diphenic acid *vs.* (+)- and (−)-6,6′-dinitro-2,2′-diphenic acid (curves A and B, resp.).

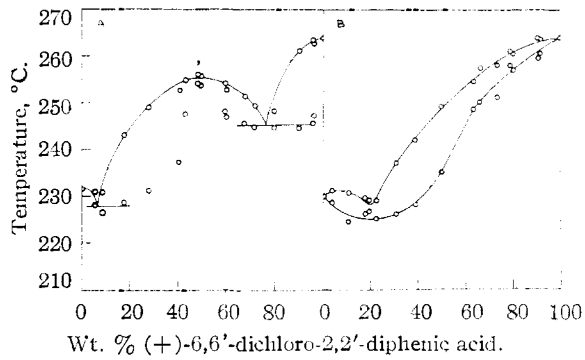

Fig. 3.—Phase diagrams of (+)-6,6′-dichloro-2,2′-diphenic acid *vs.* (−)- and (+)-6,6′-dinitro-2,2′-diphenic acid (curves A and B, resp.).

since either compound formation or solid solution formation alone, coupled with simple eutectic formation in the diastereomeric mixture, would ordinarily suffice to establish a configurational relationship.[4] The apparent isomorphism of the three 6,6′-substituents is not surprising.[8]

The first two phase diagrams (Figs. 1 and 2) lead to the conclusion that (+)-6,6′-dimethyl-, (−)-6,6′-dichloro- and (−)-6,6′-dinitro-2,2′-diphenic acids have the same configuration; this inference is reinforced by the independent evidence of the third phase diagram (Fig. 3). Accordingly,[1] (+)-6,6′-dimethyl- and (−)-6,6′-dichloro-2,2′-diphenic acid have the *S*-configuration, and the absolute configuration of all compounds related to these acids is automatically established. In addition to (+)-6,6′-dichloro-2,2′-bis-(hydroxymethyl)-biphenyl (see below) this includes the series of compounds recently investigated by Wittig and Zimmermann.[9]

Optically Active 2,2′-Bis-(hydroxymethyl)-biphenyls.—The method described above is limited to chemically stable and stoichiometrically well defined compounds; consequently 1,1′-binaphthalene-2,2′-dicarboxylic acid cannot be correlated in this fashion.[10] Since 2,2′-bis-(hydroxymethyl)-1,1′-binaphthyl does not share the peculiarities of its acid precursor,[10b] the phase behavior of the above-mentioned diol, 6,6′-dimethyl-2,2′-bis-(hydroxymethyl)-biphenyl and 6,6′-dichloro-2,2′-bis-(hydroxymethyl)-biphenyl was studied, in the hope of assigning absolute configuration to the series of 2,2′-substituted 1,1′-binaphthyls.

Thermal analysis of mixtures of the three racemates with the corresponding optically active forms showed that but a single 1:1-racemate is formed in each case. However, racemate formation appears to be less pronounced in this series than in the series of dicarboxylic acids, as judged (a) by the difference in melting point of racemates and enantiomeric components, and (b) by the "branching" of the curves, measured as the distance (in percentage composition) between the two symmetrical eutectic points; the greater differences in melting point (Δ m.p.) and the more extensive branching reflects the greater stability of the racemates of the diacids, as compared with the racemates of the diols (see Table I). Independently, since the acids melt *ca.* 100° above the m.p. of the diols, stronger intermolecular bonding in the crystal lattice is indicated for the former, as might be expected from the nature of the substituent groups.

These considerations serve in part to explain the phase diagrams of (+)-6,6′-dichloro-2,2′-bis-(hydroxymethyl)-biphenyl *vs.* (−)- and (+)-6,6′-dimethyl-2,2′-bis-(hydroxymethyl)-biphenyl (Fig. 4, curves A and B, respectively); while the quasi-

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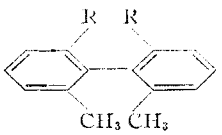
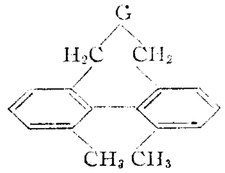
(8) The isomeric toluic acids form continuous solid solutions with the corresponding positional isomers of chlorobenzoic acid (H. Lettré, H. Barnbeck and W. Lege, *Ber.*, **69**, 1151 (1936)); o-nitrobenzoic acid forms solid solutions with o-methyl- and o-chlorobenzoic acids (H. Lettré, *ibid.*, **73**, 386 (1940)); the interference radii (*i.e.*, approximate sizes) of the three substituents are of comparable magnitude.[5c]

(9)



Ia, R = $COOCH_3$
b, R = CH_2OH
c, R = CH_2Br
d, R = CH_2CN



IIa, G = O
b, G = $\overset{+}{N}(CH_3)_2$

(+)-Ia, (−)-Ib, (+)-Ic, (+)-IIa and (+)-IIb were prepared starting from (+)-6,6′-dimethyl-2,2′-diphenic acid (G. Wittig and H. Zimmermann, *Chem. Ber.*, **86**, 629 (1953)). Further, (+)-Id and the derived iminonitrile were prepared from (+)-Ic.[1] Accordingly, all of these compounds possess the *S*-configuration.

(10) (a) R. Kuhn and O. Albrecht (*Ann.*, **465**, 282 (1928)) and (b) D. M. Hall and E. E. Turner (*J. Chem. Soc.*, 1242 (1955)) as well as the present authors, observed that the optically active dicarboxylic acid melts at *ca.* 135° with apparent decomposition, while the racemate melts at 273° without decomposition; the enantiomeric forms appear to crystallize with molecules of solvation ((b) above) which are tenaciously retained even under heating *in vacuo*.

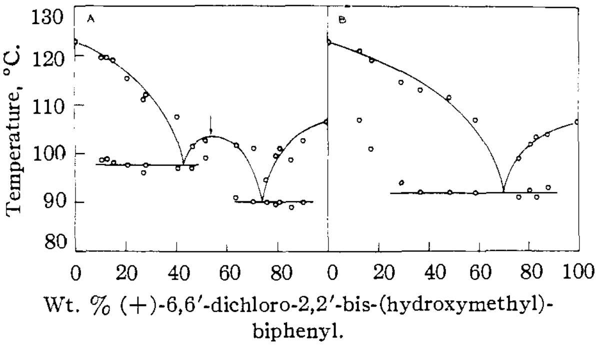


Fig. 4.—Phase diagrams of (+)-6,6′-dichloro-2,2′-bis-(hydroxymethyl)-biphenyl *vs.* (−)- and (+)-6,6′-dimethyl-2,2′-bis-(hydroxymethyl)-biphenyl (curves A and B, resp.).

enantiomers[11] form a congruent 1:1 compound (arrow, curve A), the maximum is not nearly so well expressed as it is for the quasi-racemates of the diacids. The configurationally related pair[11] exhibits a simple eutectic, with possible solid solution formation at concentrations below 30% of the dichlorodiol (curve B).

TABLE I

MELTING BEHAVIOR OF SOME RESTRICTED BIARYLS

2,2′-Substituent	6,6′-Dimethylbiphenyl	6,6′-Dichlorobiphenyl	6,6′-Dinitrobiphenyl	1,1′-Binaphthyl
–COOH				
M.p. racemic form, °C.	237	291	267	273
M.p. active form, °C.	213	264	231	(*ca.* 135)
Δ m.p., °C.	24	27	36	..
Branching, %	86	86	*ca.* 98	..
–CH_2OH				
M.p. racemic form, °C.	123	120	144	191
M.p. active form, °C	123	107	121	165
Δ m.p., °C.	0	13	23	26
Branching, %	60	78		*ca.* 84

Since the method of thermal analysis was proven applicable to the series of 2,2′-bis-(hydroxymethyl)-biphenyls, the phase behavior of mixtures of (−)-2,2′-bis-(hydroxymethyl)-1,1′-binaphthyl with the (+)- and (−)-6,6′-dimethyl-2,2′-bis-(hydroxymethyl)-biphenyl was investigated. It was found (Fig. 5) that the phase diagrams are indistinguishable, simple eutectics being formed in both cases. The comparison substances evidently differ in structure and geometry to a degree which renders fruitless the application of a method which is based on over-all similarities in size and shape. The limitations of the method thereby have been demonstrated.

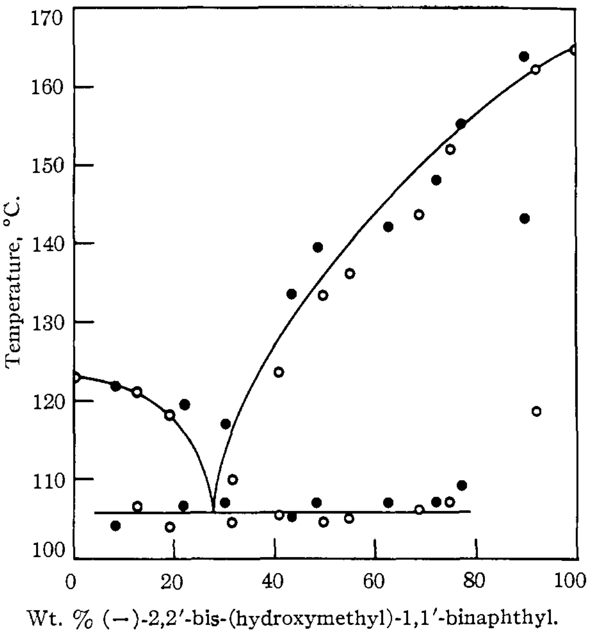


Fig. 5.—Phase diagrams of (−)-2,2′-bis-(hydroxymethyl)-1,1′-binaphthyl *vs.* (+)- and (−)-6,6′-dimethyl-2,2′-bis-(hydroxymethyl)-biphenyl (solid and open circles, resp.).

Experimental Part[12]

Optically Active 2,2′-Diphenic Acids.—These materials were required for use in thermal analysis and as precursors for the preparation of optically active 2,2′-bis-(hydroxymethyl)-biphenyls. Resolution[13a] with (−)-α-phenethylamine[13b] of (±)-**6,6′-dinitro-2,2′-diphenic acid**, m.p. 265.5–267°, gave the (−)-form, m.p. 230–231.5°, $[\alpha]^{29}D$ −127° (*c* 1.6, methanol) and the enantiomer, m.p. 229–230.5°, $[\alpha]^{25}D$ +127° (*c* 2.4, methanol). Resolution[14] with brucine of (±)-**6,6′-dichloro-2,2′-diphenic acid**, m.p. 289.5–291°, gave the (+)-form, m.p. 263–264.5°, $[\alpha]^{29}D$ +7.3° (*c* 4.3, methanol) and the enantiomer, m.p. 261–263°, $[\alpha]^{29}D$ −7.2° (*c* 4.1, methanol). Resolution[5b,9,15] with morphine of (±)-**6,6′-dimethyl-2,2′-diphenic acid**, m.p. 236–237.5°, yielded the (+)-form, m.p. 211.5–213.5°, $[\alpha]^{31}D$ +25° (*c* 1.2, methanol) $[\alpha]^{31}_{546}$ +27.5° (*c* 1.2, methanol) (lit.[15] $[\alpha]D$ +15° (methanol); lit.[9] $[\alpha]^{25}D$ +20.4° (methanol), m.p. 205–207°; lit.[5b] $[\alpha]^{25}_{546}$ +23.2° (methanol), m.p. 211–212.5°) and the enantiomer, m.p. 207–211°, $[\alpha]^{23}D$ −22° (*c* 1.0, methanol). Resolution[10a,b] with quinine of (±)-**1,1′-binaphthalene-2,2′-dicarboxylic acid**, m.p. 269.5–273°, gave the (−)-form, m.p. *ca.* 135° dec., $[\alpha]^{30}D$ −84° (*c* 0.46, 0.1 *N* NaOH), $[\alpha]^{22}_{546}$ −123° (*c* 1.4, 0.1 *N* NaOH) (lit.[10a] m.p. *ca.* 135° dec., $[\alpha]^{22}D$ −101.6°; lit.[10b] m.p. *ca.* 120° dec., $[\alpha]^{22}_{546}$ −125.2°).

Optically Active 2,2′-Bis-(hydroxymethyl)-biphenyls.—All of these materials were prepared by lithium aluminum hydride reduction of the acids described in the preceding section. Thus (±)-, (−)- and (+)-**6,6′-dimethyl-2,2′-bis-(hydroxymethyl)-biphenyl**, all melting at 122–123.5° and having $[\alpha]^{24}D$ 0°, −30° (*c* 2.3, methanol), +31° (*c* 3.1, methanol), respectively, were prepared[9,16] from (±)-, (+)- and (−)-6,6′-dimethyl-2,2′-diphenic acid, respectively. (±)-**2,2′-Bis-(hydroxymethyl)-1,1′-binaphthyl**, m.p. 190.5–191.5°, and the (−)-form, m.p. 163.5–165.5°, $[\alpha]^{24}_{546}$ −84° (*c* 1.6, acetone), were prepared[10b,17] from (±)- and (−)-1,1′-binaphthalene-2,2′-dicarboxylic acid, respectively. **6,6′-Dichloro-2,2′-bis-(hydroxymethyl)-biphenyl** was prepared by lithium aluminum hydride reduction of 6,6′-dichloro-2,2′-diphenic acid. The procedure followed was that employed for the preparation of the methyl analog.[9,16] From racemic acid there was obtained a solid, m.p. 119–120° after recrystallization from benzene.

Anal. Calcd. for $C_{14}H_{12}Cl_2O_2$: C, 59.4; H, 4.3; Cl, 25.0. Found: C, 59.5; H, 4.4; Cl, 25.3.

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[11] (+)-6,6′-Dichloro-2,2′-bis-(hydroxymethyl)-biphenyl was obtained from (+)-6,6′-dichloro-2,2′-diphenic acid and therefore (see above) has the *R*-configuration; (−)- and (+)-6,6′-dimethyl-2,2′-bis-(hydroxymethyl)-biphenyl have the *S*- and *R*- configuration, respectively (ref. 9).

[12] Microanalyses by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

[13] (a) A. W. Ingersoll and J. R. Little, THIS JOURNAL, **56**, 2123 (1934); (b) W. Theilacker and H. G. Winkler, *Chem. Ber.*, **87**, 690 (1954).

[14] G. H. Christie, C. W. James and J. Kenner, *J. Chem. Soc.*, 1948 (1923).

[15] F. Bell, *ibid.*, 835 (1934).

[16] E. D. Bergmann and Z. Pelchowicz, THIS JOURNAL, **75**, 2663 (1953).

[17] E. D. Bergmann and J. Szmuszkovicz, *ibid.*, **73**, 5153 (1951).

The product similarly obtained from the (+)-acid had m.p. 106–107°, $[\alpha]^{30}_{D}$ +75° (*c* 0.63, methanol), $[\alpha]^{30}_{D}$ +141° (*c* 0.91, benzene).

Anal. Calcd. for $C_{14}H_{12}Cl_2O_2$: C, 59.4; H, 4.3; Cl, 25.0. Found: C, 59.2; H, 4.0; Cl, 25.4.

Melting Points of Mixtures.—Weighed amounts of the component acids or alcohols were thoroughly mixed and ground. Melting points were determined by the capillary method with a Hershberg melting point apparatus; the heating rate was 1–2°/min. The initial thawing temperatures and the final melting temperatures were recorded, respectively, as points on the solidus and the liquidus curves, Figs. 1–5.

Acknowledgment.—This work was supported in part by a grant from The Trubek Laboratories.

New York 53, N. Y.

[Contribution from the Wm. H. Nichols Chemical Laboratory, New York University]

Direct Configurational Intercorrelation of 6,6′-Dinitro-, 6,6′-Dichloro- and 6,6′-Dimethyl-2,2′-diphenic Acid. Absolute Configuration of 6,6′-Dimethyl-2,2′-biphenyldiamine[1]

By Francis A. McGinn, Allan K. Lazarus,[2] Maurice Siegel, John E. Ricci and Kurt Mislow[3]

Received July 1, 1957

6,6′-Dinitro-2,2′-bis-(bromomethyl)-biphenyl, 6,6′-dichloro-2,2′-bis-(hydroxymethyl)-biphenyl and 6,6′-dimethyl-2,2′-diphenic acid have each been related by chemical paths to 6,6′-dimethyl-2,2′-biphenyldiamine (I) and therefore to each other. The results serve as unequivocal confirmation of those obtained by the indirect method of thermal analysis and also provide an absolute configurational assignment for I which is in conflict with the results[15] of certain theoretical considerations. The optical sign of I is solvent dependent. Evidence is presented that the *monoprotonated* form in 50 wt.% dioxane has a sign opposite to that of the unprotonated diamine in the same medium. Approximate values are calculated for the ionization constants and for the specific rotations of the unprotonated and monoprotonated species.

The method of thermal analysis has served in the configurational correlation of (−)-6,6′-dinitro-, (−)-6,6′-dichloro- and (+)-6,6′-dimethyl-2,2′-diphenic acid.[4] It was felt desirable to confirm these results by independent, completely unambiguous means. In the biphenyl series, the most unequivocal method is the chemical one, for retention of optical activity in a chemical transformation involving the blocking substituents can only imply retention of configuration: the possibility of racemization is the sole alternative.

The desired chemical correlation was achieved by transformation of 6,6′-dinitro-2,2′-diphenic acid into 6,6′-dimethyl-2,2′-biphenyldiamine (I), and conversion of the latter into 6,6′-dichloro- and 6,6′-dicyano-2,2′-dimethylbiphenyl, obtained from 6,6′-dichloro- and 6,6′-dimethyl-2,2′-diphenic acid, respectively. Certain attractive alternative paths were excluded on the basis of previous information: (a) chemical reduction[5] or catalytic hydrogenation (*cf.* Experimental) of 6,6′-dinitro-2,2′-diphenic acid yields the (inactive) dilactam of 6,6′-diamino-2,2′-diphenic acid as does hydrolysis of the diacetyl derivative of the latter[5,6] and (b) it has been reported[7] that compound I cannot successfully be prepared by the Curtius and Hofmann rearrangements in attempts at conversion from 6,6′-dimethyl-2,2′-diphenic acid.

S(−)-6,6′-Dinitro-2,2′-diphenic acid has been converted[8] to *S*(−)-6,6′-dinitro-2,2′-bis-(hydroxymethyl)-biphenyl. Judging by the observation that *p*-nitrobenzyl alcohol can be smoothly hydrogenated to *p*-toluidine, it was anticipated that the dinitrodiol could be hydrogenolyzed directly to I. Contrary to expectations, reduction ceased after absorption of six moles of hydrogen, yielding *S*(−)-6,6′-bis-(hydroxymethyl)-2,2′-biphenyldiamine. The twisted geometry of the molecule apparently prevents the required orientation for adsorption on the catalytic surface of the hydroxymethyl, but not of the nitro groups; to our knowledge similar observations do not appear to have been reported previously.[9]

The route chosen, as a consequence, involved preparation[8] of *S*(−)-6,6′-dinitro-2,2′-bis-(bromomethyl)-biphenyl from the dinitrodiol, followed by reduction with $NaBH_4$–$AlCl_3$[10] to (−)-6,6′-dinitro-2,2′-dimethylbiphenyl and catalytic reduction of the latter to (−)-I,[11] which must therefore have the *S*-configuration.

S(−)-I[11] was converted, *via* the Sandmeyer reaction, to *S*(−)-6,6′-dichloro-2,2′-dimethylbiphenyl. (+)-6,6′-Dichloro-2,2′-bis-(hydroxymethyl)-biphenyl, prepared[4] from (+)-6,6′-dichloro-2,2′-diphenic acid, was converted to (+)-6,6′-dichloro-2,2′-bis-(bromomethyl)-biphenyl, reduction of which afforded *R*(+)-6,6′-dichloro-2,2′-dimethylbiphenyl. The starting acid must therefore have the *R*-configuration.

Finally, *R*(+)-I[11] was converted, *via* the Sandmeyer reaction, to *R*(+)-6,6′-dicyano-2,2′-dimethylbiphenyl. Since (+)-6,6′-dimethyl-2,2′-diphenic acid could be derivatized to *S*(−)-6,6′-dicyano-2,2′-dimethylbiphenyl, the starting acid has the *S*-configuration.

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[1] Configurational Studies in the Biphenyl Series III. Part II, preceding paper.

[2] Allied Chemical and Dye Fellow, 1956–1957.

[3] To whom correspondence regarding the article should be addressed.

[4] M. Siegel and K. Mislow, This Journal, **80**, 473 (1958).

[5] J. Kenner and W. V. Stubbings, *J. Chem. Soc.*, 593 (1921).

[6] J. Meisenheimer and M. Höring, *Ber.*, **60**, 1425 (1927).

[7] F. Bell, *J. Chem. Soc.*, 835 (1934).

[8] P. Newman, P. Rutkin and K. Mislow, This Journal, **80**, 465 (1958).

[9] For a summary of hydrogenolysis reactions, *cf.* W. H. Hartung and R. Simonoff, "Organic Reactions," Vol. VII, John Wiley and Sons, Inc., New York, N. Y., 1953, p. 263.

[10] This reagent mixture has been successfully employed in similar reductions by H. C. Brown and B. C. S. Rao, This Journal, **78**, 2582 (1956).

[11] Sign of rotation refers to solvent ethanol; *cf.* Table I.