

Anal. Calcd. for $C_{18}H_{18}O_2$: C, 81.17; H, 6.81. Found: C, 81.44; H, 6.94.

The (+)-isomer ($[\alpha]^{25}_D + 25^\circ$ (c 0.9, chloroform)) was obtained by decomposition of the salt ($[\alpha]^{25}_D - 68^\circ$ (c 1.0, chf.)) which precipitated from (\pm)-I and quinine in acetone. The product was not further investigated.

Racemization Experiments. A.—A 1% solution of (–)-I in benzene was heated under reflux for 1 hour. The residue was crystallized from cyclohexane to give 89% of I,

m.p. 139–141.5°, infrared spectrum identical with that of starting material, $[\alpha]^{25}_D 0.0^\circ$ (c 1.1, l 2, benzene).

B.—Thermostated solutions (1%) of (–)-I in redistilled *o*-xylene were examined polarimetrically (2-dm. tube) over a period of at least one half-life. Readings were taken at 435 $m\mu$ and the results were plotted as $\log \alpha_t$ vs. time. Excellent straight-line relationships resulted from the minimum of fifteen readings which were obtained for each run. The values of k obtained from the slopes of the curves are listed in Table I.

[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY OF NEW YORK UNIVERSITY, NEW YORK 53, N. Y., AND OF STANFORD UNIVERSITY, STANFORD, CALIF.]

Configuration, Conformation and Rotatory Dispersion of Optically Active Biaryls^{1,2}

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RECEIVED AUGUST 8, 1961

Ultraviolet and optical rotatory dispersion data have been gathered for the body of dissymmetric biaryls of known absolute configuration. The O.R.D.-curves have been found dependent on conformation and configuration. The change from open to 2,2'-bridged seven-membered ring biaryls gives rise to characteristic changes in the O.R.D. which are interpreted as reflecting changes in conformation. The absolute configuration uniquely determines the sign of the Cotton effect curves: the long-wave length Cotton effect of 2,2'-bridged biphenyls having the (*R*)-configuration is positive for the 1,1'-binaphthyls, 6,6'-dimethylbiphenyls and 6,6'-dichlorobiphenyls, and it is negative for the 6,6'-dinitrobiphenyls. The long-wave length Cotton effect of the 2,2'-bridged biaryls is generally accompanied by a Cotton effect at shorter wave lengths of opposite sign and greater amplitude, which often dominates the sign of rotation in the visible. The intense Cotton effect centered at the conjugation band of simple 2,2'-bridged biphenyls reflects the dissymmetric biphenyl chromophore, and the sign of the Cotton effect is characteristic of the absolute sense of twist of biphenyl. An amide rule has been formulated on which is based the assignment of absolute configurations to the biphenyl derivatives in the class of ellagitannins. 2,2'-Bridged seven-membered ring biaryls containing a carbonyl group in the non-conjugated position have been shown to exhibit a strengthened $n \rightarrow \pi^*$ transition akin to that of β, γ -unsaturated ketones as well as a corresponding Cotton effect curve whose amplitude is unusually high and whose sign is characteristic of the absolute sense of twist of the biaryl.

Examination of the optical rotatory power of the large body of biaryls whose absolute configuration had been secured^{3–8} suggested the formulation of some generalizations. In particular, an optical displacement rule (Bridge rule) was tentatively advanced,⁶ according to which the shift in optical rotation in the visible region accompanying bridging of the 2,2'-positions is diagnostic of configuration (*e.g.*, the (*R*)-configuration⁹ for a negative shift). A theoretical basis for this rule was provided⁶ in terms of the change in quadrant of polarizable groups attached to the biphenyl nucleus which accompanies bridging.

(1) Paper XI in the series (by K. M.) "Configurational Studies in the Biphenyl Series" and paper LXVIII in the series (by C. D.) "Optical Rotatory Dispersion Studies." Communicated in preliminary form in *J. Am. Chem. Soc.*, **82**, 4740 (1960).

(2) Grants and fellowships by the Alfred P. Sloan Foundation (K. M.), The Truhek Laboratories (R. E. O., P. R.), the National Cancer Institute (C. D., grant No. CRTY-5061) and the National Science Foundation (K. M., grant No. G-15746; C. D., grant No. G-6579) are gratefully acknowledged.

(3) P. Newman, P. Rutkin and K. Mislow, *J. Am. Chem. Soc.*, **80**, 465 (1958).

(4) M. Siegel and K. Mislow, *ibid.*, **80**, 473 (1958).

(5) F. A. McGinn, A. K. Lazarus, M. Siegel, J. E. Ricci and K. Mislow, *ibid.*, **80**, 476 (1958).

(6) D. D. Fitts, M. Siegel and K. Mislow, *ibid.*, **80**, 480 (1958).

(7) K. Mislow and F. A. McGinn, *ibid.*, **80**, 6036 (1958); K. Mislow, V. Prelog and H. Scherrer, *Helv. Chim. Acta*, **41**, 1410 (1958).

(8) K. Mislow and P. A. Grasemann, *J. Org. Chem.*, **23**, 2027 (1958).

(9) The configurational designation proposed by R. S. Cahn, C. K. Ingold and V. Prelog, *Experientia*, **12**, 81 (1956), will be used in this paper. The O.R.D. of constitutionally symmetrical doubly bridged biphenyls, which cannot be named by this system (K. Mislow and M. A. W. Glass, *J. Am. Chem. Soc.*, **83**, 2780 (1961)), will be discussed in another connection.

Subsequent work revealed⁷ a counter instance (XXXIX) to the rule, and it was recognized¹⁰ that scrutiny of the optical rotatory dispersions would be likely to furnish correlative information of greater general significance: the usefulness of O.R.D. in this connection had been established¹¹ in the series of classically asymmetric (asymmetric carbon¹²) compounds. Accordingly, spectral (ultraviolet and O.R.D.) information was gathered for a series of suitably substituted biaryls. The data are now presented in Tables I–VII and Figs. 1–24.

As indicated in the tables, the absolute configurations of the majority of compounds studied are known; the configurational assignments have been summarized.¹⁰ In the case of certain compounds synthesized for the purpose of this study (Experimental part), the absolute configuration follows from that of the starting materials¹⁰; such cases are indicated by the double bracket (*e.g.*, ((*S*))). Of the newly reported syntheses, the conversion of (*R*)-XXII into (+)-(*R*)-VII by the Sandmeyer reaction is of interest in demonstrating that the replacement of both amino groups by bromo groups in the blocking positions proceeds without significant racemization, as had previously been observed⁵ for similar replacements by cyano and

(10) K. Mislow, *Angew. Chem.*, **70**, 683 (1958).

(11) C. Djerassi, "Optical Rotatory Dispersion," McGraw-Hill Book Co., Inc., New York, N. Y., 1960.

(12) Recent extensions to asymmetric sulfur (W. Klyne, J. Day and A. Kjaer, *Acta Chem. Scand.*, **14**, 215 (1960)) and asymmetric silicon (L. H. Sommer, C. L. Frye, M. C. Musolf, G. A. Parker, P. G. Rodewald, K. W. Michael, Y. Okaya and R. Pepinsky, *J. Am. Chem. Soc.*, **83**, 2210 (1961)) are noted.

TABLE I

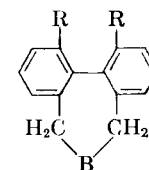


No.	R	R'	Config.	Solvent	Ultraviolet spectrum ¹	Optical data
I	NO ₂	CONH ₂	(R)	Methanol	260, 300 (4.03, 3.47)	$[\alpha]_{700} + 120^\circ$, $[\alpha]_{589} + 250^\circ$, $[\alpha]_{378} + 3070^\circ$, $[\alpha]_{310} - 4690^\circ$, $[\alpha]_{287} - 2960^\circ$, $[\alpha]_{240} - 10,660^\circ$ ($C = 0.10-0.0025$)
II	NO ₂	CH ₂ Br	(R)	Dioxane	260, 300 (4.04, 3.51)	$[\alpha]_{700} + 5^\circ$, $[\alpha]_{589} + 25^\circ$, $[\alpha]_{380} + 770^\circ$, $[\alpha]_{325} - 1810^\circ$, $[\alpha]_{305} - 780^\circ$, $[\alpha]_{253} - 10,100^\circ$, $[\alpha]_{240} - 8600^\circ$ ($C = 0.11-0.0027$)
III	NO ₂	COOH	(R)	Dioxane	260, 300 (4.02, 3.51)	$[\alpha]_{700} + 50^\circ$, $[\alpha]_{589} + 140^\circ$, $[\alpha]_{376} + 2100^\circ$, $[\alpha]_{304} - 2600^\circ$, $[\alpha]_{297} - 2400^\circ$, $[\alpha]_{271} - 8000^\circ$, $[\alpha]_{260} + 2400^\circ$ ($C = 0.10-0.0025$)
IV	NO ₂	COOCH ₃	(S)	Dioxane	228, 253, 300 (4.55, 4.05, 3.40)	$[\alpha]_{700} - 90^\circ$, $[\alpha]_{589} - 130^\circ$, $[\alpha]_{399} - 1270^\circ$, $[\alpha]_{375} - 1630^\circ$, $[\alpha]_{301} + 2660^\circ$, $[\alpha]_{290} + 2780^\circ$, $[\alpha]_{281} + 8990^\circ$, $[\alpha]_{245} + 1410^\circ$ ($C = 0.10-0.0026$)
V	NO ₂	CH ₂ OH	(S)	Dioxane	259, 300 (4.01, 3.56)	$[\alpha]_{700} - 50^\circ$, $[\alpha]_{589} - 60^\circ$, $[\alpha]_{372} - 1500^\circ$, $[\alpha]_{328} + 190^\circ$, $[\alpha]_{307} - 1010^\circ$, $[\alpha]_{267} + 3280^\circ$, $[\alpha]_{250} - 1550^\circ$ ($C = 0.10-0.0052$)
VI	NO ₂	CH ₃	(S)	Dioxane	263, 300 (3.88, 3.49)	$[\alpha]_{700} - 26^\circ$, $[\alpha]_{589} - 30^\circ$, $[\alpha]_{375} - 792^\circ$, $[\alpha]_{333} + 508^\circ$, $[\alpha]_{313} - 1250^\circ$, $[\alpha]_{265} + 4690^\circ$, $[\alpha]_{235} - 6840^\circ$ ($C = 0.10-0.0020$)
VII	CH ₃	Br	(R)	Hexane	213, 270, 277 (4.46, 2.76, 2.62)	$[\alpha]_{700} + 5^\circ$, $[\alpha]_{589} + 10^\circ$, $[\alpha]_{278} + 762^\circ$, $[\alpha]_{273} + 317^\circ$, $[\alpha]_{272} + 347^\circ$, $[\alpha]_{240} - 149^\circ$ ($C = 0.51-0.10$)
VIII	CH ₃	Cl	(R)	Hexane	215, 269, 277 (4.40, 2.73, 2.59)	$[\alpha]_{700} + 30^\circ$, $[\alpha]_{589} + 45^\circ$, $[\alpha]_{277} + 1040^\circ$, $[\alpha]_{272} + 742^\circ$, $[\alpha]_{270} + 742^\circ$, $[\alpha]_{245} - 74^\circ$ ($C = 0.47-0.094$)
IX	CH ₃	I	(S)	Hexane	212, 234, 265, 280 (4.53, 4.28, 3.20, 2.99)	$[\alpha]_{700} + 5^\circ$, $[\alpha]_{589} + 35^\circ$, $[\alpha]_{345} + 812^\circ$, $[\alpha]_{282} - 450^\circ$, $[\alpha]_{258} + 1190^\circ$, $[\alpha]_{245} + 7030^\circ$ ($C = 0.50-0.020$)
X	CH ₃	CH ₂ OH	(R)	Dioxane	266, 275 (2.89, 2.77)	$[\alpha]_{700} + 18.2^\circ$, $[\alpha]_{589} + 26.6^\circ$, $[\alpha]_{280} + 231^\circ$, $[\alpha]_{250} + 163^\circ$ ($C = 0.52-0.10$)
XI	CH ₃	CH ₂ CN	(S)	Dioxane	264, 272 (2.89, 2.81)	$[\alpha]_{700} + 11.5^\circ$, $[\alpha]_{589} + 21.4^\circ$, $[\alpha]_{315} + 72.2^\circ$, $[\alpha]_{274} - 315^\circ$, $[\alpha]_{250} + 463^\circ$ ($C = 0.54-0.12$)
XII	CH ₃	CONH ₂	((R))	Dioxane	275 (3.28)	$[\alpha]_{700} + 12.3^\circ$, $[\alpha]_{589} + 37.7^\circ$, $[\alpha]_{265} + 6000^\circ$, $[\alpha]_{240} - 7500^\circ$ ($C = 0.18-0.020$)
XIII	CH ₃	CN	(S)	Dioxane	232, 239, 270, 278, 287 (4.27, 4.15, 3.31; 3.54, 3.62)	$[\alpha]_{589} - 16.7^\circ$, $[\alpha]_{297} + 481^\circ$, $[\alpha]_{275} - 760^\circ$, $[\alpha]_{253} + 2180^\circ$, $[\alpha]_{240} - 30,900^\circ$ ($C = 1.35-0.015$)
XIV	CH ₃	NHAc	(R)	Dioxane	240, 285 (4.26, 3.18)	$[\alpha]_{700} - 3.9^\circ$, $[\alpha]_{589} - 15.8^\circ$, $[\alpha]_{289} - 1800^\circ$, $[\alpha]_{248} + 12,200^\circ$, $[\alpha]_{240} + 4400^\circ$ ($C = 0.10-0.020$)
XV	CH ₃	COOCH ₃	(R)	Dioxane	237, 285 (4.10, 3.51)	$[\alpha]_{700} - 23.9^\circ$, $[\alpha]_{589} - 34.0^\circ$, $[\alpha]_{299} - 667^\circ$, $[\alpha]_{286} - 250^\circ$, $[\alpha]_{268} - 1290^\circ$, $[\alpha]_{245} + 3960^\circ$ ($C = 0.12-0.0048$)
XVI	CH ₃	COOH	(R)	Dioxane	236, 286 (4.13, 3.53)	$[\alpha]_{700} - 20^\circ$, $[\alpha]_{589} - 33^\circ$, $[\alpha]_{300} - 1020^\circ$, $[\alpha]_{289} - 245^\circ$, $[\alpha]_{273} - 1130^\circ$, $[\alpha]_{248} + 6270^\circ$, $[\alpha]_{245} + 5100^\circ$ ($C = 0.10-0.0026$)
XVII	CH ₃	CH ₂ Br	(R)	Dioxane	240, 274, 284 (4.10, 3.31, 3.20)	$[\alpha]_{700} - 54^\circ$, $[\alpha]_{589} - 63.4^\circ$, $[\alpha]_{261} - 1500^\circ$, $[\alpha]_{245} - 270^\circ$, ($C = 0.42-0.022$)
XVIII	Cl	CONH ₂	(S)	Dioxane	277 (3.20)	$[\alpha]_{700} - 70^\circ$, $[\alpha]_{589} - 96^\circ$, $[\alpha]_{276} - 6290^\circ$, $[\alpha]_{253} + 1350^\circ$, $[\alpha]_{245} + 6770^\circ$ ($C = 0.10$)
XIX	Cl	COOH	(S)	Dioxane	235, 288, 295 (4.16, 3.54, 3.50)	$[\alpha]_{700} - 10^\circ$, $[\alpha]_{589} - 15^\circ$, $[\alpha]_{307} - 537^\circ$, $[\alpha]_{268} 0^\circ$, $[\alpha]_{250} - 5160^\circ$, $[\alpha]_{245} + 8600^\circ$ ($C = 0.11-0.0021$)
XX	Cl	CH ₂ OH	(R)	Dioxane	268, 276 (2.84, 2.73)	$[\alpha]_{700} + 53^\circ$, $[\alpha]_{589} + 58^\circ$, $[\alpha]_{273} + 719^\circ$, $[\alpha]_{245} + 236^\circ$ ($C = 0.23-0.081$)
XXI	Cl	CH ₂ Br	(R)	Dioxane	277, 285 (3.15, 3.09)	$[\alpha]_{700} + 32.7^\circ$, $[\alpha]_{589} + 40.2^\circ$, $[\alpha]_{287} + 430^\circ$, $[\alpha]_{280} + 680^\circ$, $[\alpha]_{250} + 1030^\circ$ ($C = 0.21-0.063$)
XXII	NH ₂	CH ₃	(R)	Dioxane	240, 295 (4.25, 3.82)	$[\alpha]_{700} + 73^\circ$, $[\alpha]_{589} + 115^\circ$, $[\alpha]_{339} + 670^\circ$, $[\alpha]_{310} - 682^\circ$, $[\alpha]_{293} + 10,100^\circ$, $[\alpha]_{270} - 1100^\circ$, $[\alpha]_{261} + 6200^\circ$, $[\alpha]_{247} + 3100^\circ$ ($C = 0.16-0.0013$)
XXIII	NH ₂ ⁺	CH ₃	(R)	0.1 N HCl	262.5, 270, 290 (3.01, 2.97, 2.13)	$[\alpha]_{700} - 40^\circ$, $[\alpha]_{589} - 47^\circ$, $[\alpha]_{273} - 703^\circ$, $[\alpha]_{262} - 185^\circ$, $[\alpha]_{230} - 4440^\circ$ ($C = 0.11-0.027$)

¹ Wave lengths in mμ, maxima in italics, shoulders in roman, figures in parentheses give log ε.

TABLE II

DATA ON BIARYLS XXIV-XXXVII OF FORMULA TYPE

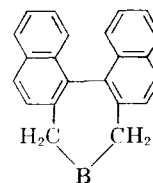


No.	R	B	Config.	Solvent	Ultraviolet spectrum ^a	Optical data	
						Optical rotatory dispersion	
XXIV	NO ₂	CO	(S)	Dioxane	231, 276, 300 (4.32, 3.84, 3.73)	[α] ₇₀₀ +56°, [α] ₅₈₉ +98°, [α] ₃₈₀ +4860°, [α] ₃₂₁ -24,300°, [α] ₃₁₆ -22,100°, [α] ₃₁₂ -24,200°, [α] ₂₉₃ +13,400°, [α] ₂₆₃ 0°, [α] ₂₄₅ +8530° (C = 0.071-0.0016)	
XXV	NO ₂	CHOH	(S)	Dioxane	228, 270, 300 (4.35, 3.90, 3.70)	[α] ₇₀₀ +590°, [α] ₅₈₉ +770°, [α] ₃₇₀ +7870°, [α] ₃₁₁ -13,800°, [α] ₂₉₀ -8230°, [α] ₂₇₃ -13,200°, [α] ₂₅₀ -2940° (C = 0.048-0.0017)	
XXVI	NO ₂	N ⁺ [(CH ₂) ₅]Br ⁻	(R)	Water	232, 270, 300 (4.35, 3.92, 3.62)	[α] ₇₀₀ -50°, [α] ₅₈₉ -400°, [α] ₃₆₅ -7060°, [α] ₃₀₀ +16,300°, [α] ₂₉₄ +15,700°, [α] ₂₇₄ +24,800°, [α] ₂₄₃ -18,000°, [α] ₂₂₅ -30,000° (C = 0.082-0.0020)	
XXVII	NO ₂	C(COOC ₂ H ₅) ₂	(R)	Dioxane ^b	230, 267, 300 (4.37, 3.93, 3.69)	[α] ₇₀₀ 0°, [α] ₅₈₉ -170°, [α] ₃₆₅ -4930°, [α] ₃₀₃ +10,400°, [α] ₂₉₆ +7980°, [α] ₂₇₂ +15,900°, [α] ₂₃₉ -17,200°, [α] ₂₃₀ -11,100° (C = 0.049-0.0099)	
XXVIII	NH ₂	C(COOC ₂ H ₅) ₂	(R)	Dioxane	227, 250, 307 (4.48, 4.12, 3.94)	[α] ₅₈₉ -22°, [α] ₃₄₅ -242°, [α] ₃₃₂ +82° (C = 0.097)	
XXIX	NH ₃ ⁺	C(COOC ₂ H ₅) ₂	(R)	0.1 N HCl	227, 250, 298 (4.34, 3.94, 3.61)	[α] ₅₈₉ +80°, [α] ₃₁₅ +1410° (C = 0.095)	
XXX	CH ₃	C(COOC ₂ H ₅) ₂	((R))	Dioxane	243, 271, 281 (4.20, 3.14, 2.85)	[α] ₅₈₉ +85°, [α] ₂₈₃ +3410°, [α] ₂₇₉ +3290°, [α] ₂₅₃ +19,100°, [α] ₂₃₁ -1560°, [α] ₂₂₅ -12,700° (C = 0.15-0.0048)	
XXXI	CH ₃	CHOH	((S))	Isooctane	242, 270, 280 (4.09, 2.99, 2.70)	[α] ₅₈₉ +62°, [α] ₂₈₅ -3100°, [α] ₂₇₇ -1630°, [α] ₂₅₃ -19,600°, [α] ₂₃₀ +30,100°, [α] ₂₂₅ +23,400° (C = 1.06-0.0024)	
XXXII	CH ₃	O	(S)	Dioxane	244, 270, 281 (4.05, 3.29, 2.95)	[α] ₅₈₉ +40°, [α] ₄₀₀ +140°, [α] ₂₅₂ -13,700°, [α] ₂₂₉ +30,000°, [α] ₂₂₅ +26,700° (C = 0.10-0.0012)	
XXXIII	CH ₃	CH ₂	((S))	Isooctane	240, 274 (4.06, 2.78)	[α] ₇₀₀ +123°, [α] ₅₈₉ +175°, [α] ₂₉₃ -1450°, [α] ₂₇₈ -770°, [α] ₂₆₄ -20,200°, [α] ₂₃₀ +38,100°, [α] ₂₂₅ +29,400° (C = 0.11-0.0023)	
XXXIV	Cl	C(COOC ₂ H ₅) ₂	((R))	Isooctane	244, 275, 285 (4.01, 3.13, 2.98)	[α] ₇₀₀ -80.4°, [α] ₅₈₉ -118°, [α] ₃₇₀ -180°, [α] ₂₉₀ +1170°, [α] ₂₈₃ -3000°, [α] ₂₇₉ -2230°, [α] ₂₇₇ -2350°, [α] ₂₆₇ +9530°, [α] ₂₂₇ -20,300°, [α] ₂₂₃ -26,200° (C = 0.12-0.0012)	
XXXV	Cl	N ⁺ [(CH ₂) ₅]Br ⁻	(R)	Water	245, 276, 285 (3.94, 3.50, 3.26)	[α] ₇₀₀ 0°, [α] ₅₈₉ -50°, [α] ₃₇₀ -191°, [α] ₂₉₄ +508°, [α] ₂₈₆ -707°, [α] ₂₅₅ +15,800°, [α] ₂₃₇ -3330°, [α] ₂₃₂ -2080°, [α] ₂₂₀ -49,400° (C = 0.12-0.0012)	
XXXVI	CH ₃	CO	((R))	Isooctane	245, 272, 289.5, 297.5, 307, 317 (3.99, 3.17, 2.88, 2.88, 2.76, 2.41)	[α] ₅₈₉ +575°, [α] ₃₂₀ +27,600°, [α] ₃₁₆ +18,000°, [α] ₃₁₀ +27,700°, [α] ₂₈₄ -30,150°, [α] ₂₆₇ -15,800° (C = 0.02)	
XXXVII	CH ₃	CO	((S))	Isooctane	Identical with XXXVI	[α] ₅₈₉ -657°, [α] ₃₂₀ -29,600°, [α] ₃₁₆ -19,500°, [α] ₃₁₀ -28,000°, [α] ₂₈₇ +33,450°, [α] ₂₇₂ +21,800° (C = 0.027)	
A				Isooctane	Identical with XXXVI	[α] ₅₈₉ -723°, [α] ₃₁₈ -32,350°, [α] ₃₁₃ -25,800°, [α] ₃₀₉ -28,900°, [α] ₂₈₄ +32,000°, [α] ₂₈₀ +30,200°, [α] ₂₇₅ +29,000°, [α] ₂₅₆ +5070°, [α] ₂₂₉ +73,400°, [α] ₂₂₅ +71,000° (C = 0.29-0.0024)	
B				Dioxane	246, 274, 287, 295, 304, 315 (3.97, 3.19, 2.90, 2.88, 2.75, 2.40)	[α] ₅₈₉ -726°, [α] ₃₁₅ -35,400°, [α] _{312.5} +35,400°, [α] ₂₇₇ +31,200° (C = 0.112-0.0044)	
C				95% EtOH	246.5, 274, 289, 296, 305, 315 (3.92, 3.26, 2.92, 2.87, 2.70, 2.24)	[α] ₅₈₉ -726°, [α] ₃₁₅ -35,400°, [α] _{312.5} +35,400°, [α] ₂₇₇ +31,200° (C = 0.112-0.0044)	

^a See footnote a, Table I. ^b Ultraviolet spectrum in 95% ethanol.

TABLE III

DATA ON BIARYLS XXVIII-XLIII OF FORMULA TYPE

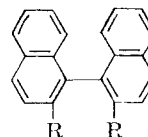


No.	B	Config.	Solvent	Optical data	
				Ultraviolet spectrum ^a	Optical rotatory dispersion
XXXVIII	—	(<i>S</i>)	Dioxane	220, 240, 280, 320, 335, 348, (5.17, 4.72, 3.61, 4.09, 4.16, 4.15)	$[\alpha]_{589} + 925^\circ$, $[\alpha]_{410} + 2145^\circ$, $[\alpha]_{350} - 5200^\circ$, $[\alpha]_{262} + 224,000^\circ$, $[\alpha]_{244} - 336,000^\circ$, $[\alpha]_{230} - 120,000^\circ$ ($C = 0.09-0.00025$)
XXXIX	CO	(<i>R</i>)	Isooctane	218, 235, 245, 265, 274, 289, 303, 315, 320, 328, (4.79, 4.65, 4.52, 3.58, 3.61, 3.79, 3.93, 3.81, 3.74, 3.43)	$[\alpha]_{589} + 471^\circ$, $[\alpha]_{330} + 37,050^\circ$, $[\alpha]_{323} + 14,420^\circ$, $[\alpha]_{321} + 17,620^\circ$, $[\alpha]_{277} - 76,450^\circ$, $[\alpha]_{255} - 32,000^\circ$, $[\alpha]_{239} - 196,000^\circ$, $[\alpha]_{230} + 136,000^\circ$ ($C = 0.005-0.0005$)
XL	CHOCOCOC ₆ H ₅	(<i>R</i>)	Dioxane		$[\alpha]_{589} - 98^\circ$, $[\alpha]_{375} 0^\circ$, $[\alpha]_{325} + 6800^\circ$, $[\alpha]_{275} - 34,000^\circ$, $[\alpha]_{255} - 12,000^\circ$, $[\alpha]_{235} - 286,000^\circ$, $[\alpha]_{225} + 1,040,000^\circ$ ($C = 0.05-0.0001$)
XLI	CHOH	(<i>R</i>)	Dioxane	220, 232, 266, 275, 293, 305, 324 (5.02, 4.90, 3.77, 3.84, 4.03, 4.12, 3.92)	$[\alpha]_{589} - 226^\circ$, $[\alpha]_{380} - 775^\circ$, $[\alpha]_{327} + 9000^\circ$, $[\alpha]_{322} + 3600^\circ$, $[\alpha]_{318} + 3200^\circ$, $[\alpha]_{280} - 55,000^\circ$, $[\alpha]_{277} - 42,000^\circ$, $[\alpha]_{271} - 49,600^\circ$, $[\alpha]_{255} - 20,000^\circ$, $[\alpha]_{240-38} - 200,000^\circ$, $[\alpha]_{235} - 220,000^\circ$, $[\alpha]_{227} + 3,000,000^\circ$ ($C = 0.08-0.0005$)
XLII	C(COOC ₂ H ₅) ₂	((<i>S</i>))	Dioxane	220, 232, 266, 275, 295, 306, 316, 321 (5.05, 4.87, 3.79, 3.82, 4.03, 4.10, 4.00, 3.97)	$[\alpha]_{589} + 133^\circ$, $[\alpha]_{400} + 388^\circ$, $[\alpha]_{327} - 9200^\circ$, $[\alpha]_{280} + 31,600^\circ$, $[\alpha]_{275} + 30,800^\circ$, $[\alpha]_{271} + 32,800^\circ$, $[\alpha]_{260} + 12,000^\circ$, $[\alpha]_{237} + 160,000^\circ$ ($C = 0.05-0.001$)
XLIII	O	((<i>S</i>))	Dioxane	218, 231, 266, 278, 293, 306, 320 (5.03, 4.86, 3.75, 3.86, 4.04, 4.14, 4.01)	$[\alpha]_{589} + 562^\circ$, $[\alpha]_{375} + 1428^\circ$, $[\alpha]_{323} - 7200^\circ$, $[\alpha]_{280} + 53,400^\circ$, $[\alpha]_{277} + 51,200^\circ$, $[\alpha]_{274} + 52,400^\circ$, $[\alpha]_{265-63} + 18,000^\circ$, $[\alpha]_{250} - 14,000^\circ$, $[\alpha]_{230} + 280,000^\circ$, $[\alpha]_{225} - 400,000^\circ$ ($C = 0.05-0.0002$)

^a See footnote *a*, Table I.

TABLE IV

DATA ON BIARYLS XLIV-LII OF FORMULA TYPE



No.	R	Config.	Solvent	Optical data	
				Ultraviolet spectrum ^a	Optical rotatory dispersion
XLIV	CH ₂ OH	(<i>R</i>)	Dioxane	226, 264, 274, 285, 295, 317, 322 (5.11, 3.91, 4.05, 4.15, 4.08, 3.05, 2.99)	$[\alpha]_{589} + 110^\circ$, $[\alpha]_{318} + 3400^\circ$, $[\alpha]_{312} + 2200^\circ$, $[\alpha]_{300} + 5000^\circ$, $[\alpha]_{240} - 104,000^\circ$ ($C = 0.05-0.0005$)
XLV	CH ₃	(<i>S</i>)	Dioxane	226, 276, 285, 292, 307, 313, 323 (5.18, 4.04, 4.10, 4.06, 3.55, 3.29, 3.40)	$[\alpha]_{589} + 6^\circ$, $[\alpha]_{300} - 2400^\circ$, $[\alpha]_{235} + 168,000^\circ$ ($C = 0.1-0.0005$)
XLVI	COOH	(<i>S</i>)	Dioxane	236, 275, 285, 296, 325, 338 (4.95, 4.08, 4.16, 4.08, 3.57, 3.62)	$[\alpha]_{589} - 4^\circ$, $[\alpha]_{336} - 3200^\circ$, $[\alpha]_{320} - 800^\circ$, $[\alpha]_{298} - 4800^\circ$, $[\alpha]_{282} + 72,000^\circ$, $[\alpha]_{235} - 210,000^\circ$, $[\alpha]_{232} - 120,000^\circ$ ($C = 0.09-0.0002$)

XLVII	COOCH ₃	(S)	Dioxane	235, 275, 285, 296, 325, 338 (5.02, 4.06, 4.14, 4.06, 3.52, 3.59)	[α] ₅₈₉ - 49°, [α] ₃₃₈ - 2200°, [α] ₃₁₈ + 1400°, [α] ₃₀₁ - 1200°, [α] ₂₈₃ + 100,000°, [α] ₂₇₁ - 130,000°, [α] ₂₂₈ 0° (C = 0.09-0.0002)
XLVIII	CONH ₂	((S))	Dioxane	225, 275, 285, 295, 325 (5.08, 4.03, 4.07, 4.04, 3.10)	[α] ₅₈₉ - 204°, [α] ₂₇₇ - 11,600°, [α] ₂₅₅ + 34,000°, [α] ₂₄₄ 0° (C = 0.10-0.0005)
XLIX	CH ₂ Br	(S)	Dioxane	232, 276, 285, 297, 321, 329 (4.97, 4.15, 4.19, 4.11, 3.21, 3.09)	[α] ₅₈₉ - 147°, [α] ₃₀₀ - 6000°, [α] ₂₅₀ + 52,000° (C = 0.08-0.001)
L	NH ₂	(R)	Dioxane	243, 274, 283.5, 294, 352 (4.99, 4.06, 4.14, 4.00, 3.80)	[α] ₅₈₉ + 168°, [α] ₃₁₈₋₁₀ - 2400°, [α] ₃₀₅ - 3200°, [α] ₂₈₀ + 3600°, [α] ₂₅₀ - 12,000° (C = 0.02-0.005)
LI ^b	NH ₂ ⁺	(R)	1 N HCl	276, 285, 293 (4.01, 4.09, 4.05)	[α] ₅₈₉ + 5°, [α] ₃₅₆ + 12,500°, [α] ₃₂₀ - 16,800°, [α] ₃₀₀ - 5600°, [α] ₂₅₅ - 140,000° [α] ₂₄₅ + 280,000° [α] ₂₃₀ 0° (C = 0.13-0.0001)
LII	N(CH ₂) ₂	((R))	Dioxane	220, 257, 295 (5.35, 4.76, 4.21)	[α] ₅₈₉ - 50°, [α] ₃₉₅ - 1400°, [α] ₃₀₆ + 3000°, [α] ₃₂₅ + 800°, [α] ₃₁₀ + 5600°, [α] ₂₈₀ - 33,600°, [α] ₂₅₉ + 76,800°, [α] ₂₅₄ 0° (C = 0.05-0.000625)
LIII	⁺ N(CH ₂) ₂ H	((R))	0.1 N HCl	224, 286, 306, 314, 320, 333 (5.06, 4.08, 3.67, 3.29, 3.19, 2.53)	[α] ₅₈₉ + 50°, [α] ₃₂₀ - 797°, [α] ₃₁₆ - 619° (C = 0.095)

^a See footnote a, Table I. ^b Ultraviolet spectrum from ref. 42.

TABLE V

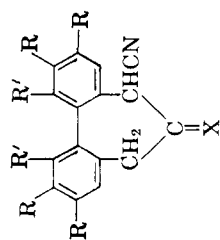


No.	R	R'	Config.	Solvent	Optical data	
					Ultraviolet spectrum ^a	Optical rotatory dispersion
LIV	OCH ₃	COOH	L	Dioxane	220, 258, 300 (4.80, 4.44, 3.80)	[α] ₅₈₉ - 63°, [α] ₃₅₅ - 115°, [α] ₃₂₅ + 880°, [α] ₃₀₅ - 3000°, [α] ₂₈₅ - 1200°, [α] ₂₈₀ - 1600° (C = 0.05-0.01)
LV	OCH ₃	COOCH ₃	L	Dioxane	222, 265, 300 (4.78, 4.66, 3.78)	[α] ₅₈₉ - 97°, [α] ₃₇₀ - 213°, [α] ₃₂₇ + 960°, [α] ₃₀₄ - 2800°, [α] ₂₉₀ - 1600°, [α] ₂₆₇ - 7200°, [α] ₂₃₇ + 44,000°, [α] ₂₃₅ + 24,000° (C = 0.03-0.0005)
LVI	OCH ₃	CONH ₂	L	Methanol	215, 290 (4.67, 3.48)	[α] ₅₈₉ + 35°, [α] ₃₁₀ + 1920°, [α] ₂₇₀ - 800°, [α] ₂₃₇ + 53,300°, [α] ₂₃₀ + 33,400° (C = 0.03-0.0006)
LVII	OCH ₂ C ₆ H ₅	COOH	D	Dioxane	227, 260, 300 (4.83, 4.37, 3.83)	[α] ₅₈₉ - 35°, [α] ₃₃₀ - 500°, [α] ₃₁₀ + 1250°, [α] ₂₈₅ - 2800°, [α] ₂₇₀ + 1600°, [α] ₂₄₈ - 8000° (C = 0.09-0.002)
LVIII	OCH ₂ C ₆ H ₅	COOCH ₃	D	Dioxane	227, 260, 300 (4.82, 4.36, 3.82)	[α] ₅₈₉ - 16°, [α] ₃₃₀ - 320°, [α] ₃₁₀ + 1040°, [α] ₂₈₀ - 2000°, [α] ₂₆₅ + 4000°, [α] ₂₆₂ + 800° (C = 0.095-0.005)
LIX	OCH ₂ C ₆ H ₅	CONH ₂	L	Methanol	213, 290 (5.10, 3.64)	[α] ₅₈₉ + 177°, [α] ₃₁₀ + 1500°, [α] ₂₉₅ + 1200°, [α] ₂₄₀ + 19,000°, [α] ₂₃₂ 0° (C = 0.14-0.002)
LX	OCH ₂ C ₆ H ₅	CH ₂ OH	D	Dioxane		[α] ₅₈₉ - 34°, [α] ₂₆₀ - 4360° (C = 0.101-0.0101)
LXI	OCH ₂ C ₆ H ₅	CH ₂ Br	D	Dioxane	232, 260, 295 (4.74, 4.30, 3.70)	[α] ₅₈₉ - 21°, [α] ₃₀₈ + 360°, [α] ₂₉₀ - 300°, [α] ₂₈₀ + 400° (C = 0.1-0.02)

^a See footnote a, Table I.

TABLE VI

DATA ON BIARVLS LXII-LXV OF FORMULA TYPE

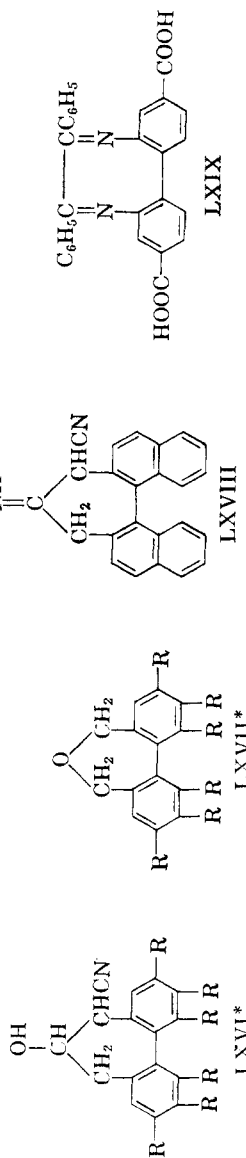


No.	R	R'	X	Config. ^b	Solvent	Ultraviolet spectrum ^a		Optical data	
						λ	ε	λ	[α] _D
LXII	OCH ₂ C ₆ H ₅	OCH ₂ C ₆ H ₅	NH	D	Dioxane	265, 308 (4.59, 4.08)		[α] ₅₈₉ -60°, [α] ₄₇₀ -3200°, [α] ₃₈₀ 0°, [α] ₃₃₀ -8000° [α] ₂₈₅ +16,000°, [α] ₂₄₀ +10,000° (C = 0.10-0.001)	
LXIII	OCH ₂ C ₆ H ₅	OCH ₂ C ₆ H ₅	O	D	Dioxane	238, 265 (4.63, 4.35)		[α] ₅₈₉ +151°, [α] ₄₇₀ +8000°, [α] ₃₇₀ -12,000°, [α] ₃₁₀ +24,000° (C = 0.05-0.001)	
LXIV	H	CH ₃	NH	(S)	Dioxane	226, 244, 264, 298, (4.38, 4.35, 4.09, 4.12)		[α] ₅₈₉ +580°, [α] ₄₇₀ +24,000°, [α] ₃₇₀ -40,000°, [α] ₃₁₀ +72,000° (C = 0.1-0.0033)	
LXV	H	NO ₂	NH	(S)	Dioxane	222, 250, 280 (4.58, 4.23, 4.21)		[α] ₅₈₉ +820°, [α] ₄₇₀ +11,500°, [α] ₃₇₀ -34,000°, [α] ₃₁₀ -26,000° (C = 0.02-0.001)	

^a See footnote a, Table I. ^b Configuration refers to biphenyl moiety only.

TABLE VII

DATA ON BIARVLS LXVI-LXIX



No.	Config. ^b	Solvent	Ultraviolet spectrum ^a		Optical data	
			λ	ε	λ	[α] _D
LXVI	D	Dioxane	235, 265 (4.65, 4.34)		[α] ₅₈₉ +92°, [α] ₄₇₀ +8000°, [α] ₃₇₀ +7000°, [α] ₃₂₀ +16,000°, [α] ₂₇₀ -17,000°, [α] ₂₃₂ -10,000° (C = 0.11-0.02)	
LXVII	D	Dioxane	235, 266 (4.68, 4.35)		[α] ₅₈₉ +80°, [α] ₄₇₀ +4120° (C = 0.085-0.0034)	
LXVIII	(R)	Dioxane	228, 246, 272, 284, 294, 320 (4.93, 4.44, 4.39, 4.46, 4.43, 4.15)		[α] ₅₈₉ -742°, [α] ₄₇₀ -2500°, [α] ₃₇₀ -1205°, [α] ₃₁₀ -19,600°, [α] ₂₇₀ -25,000°, [α] ₂₃₀ +112,000°, [α] ₁₇₀ -120,000° (C = 0.02-0.0005)	
LXIX	Dioxane	240, 260, 310, (4.66, 4.69, 4.00)			[α] ₅₈₉ -1166°, [α] ₄₇₀ -13,600°, [α] ₃₇₀ +35,200°, [α] ₃₁₀ +96,000°, [α] ₂₇₀ +36,800°, [α] ₂₃₀ -16,000° (C = 0.037-0.0005)	

^a See footnote a, Table I. ^b Configuration refers to biphenyl moiety only. * R = OCH₂C₆H₅.

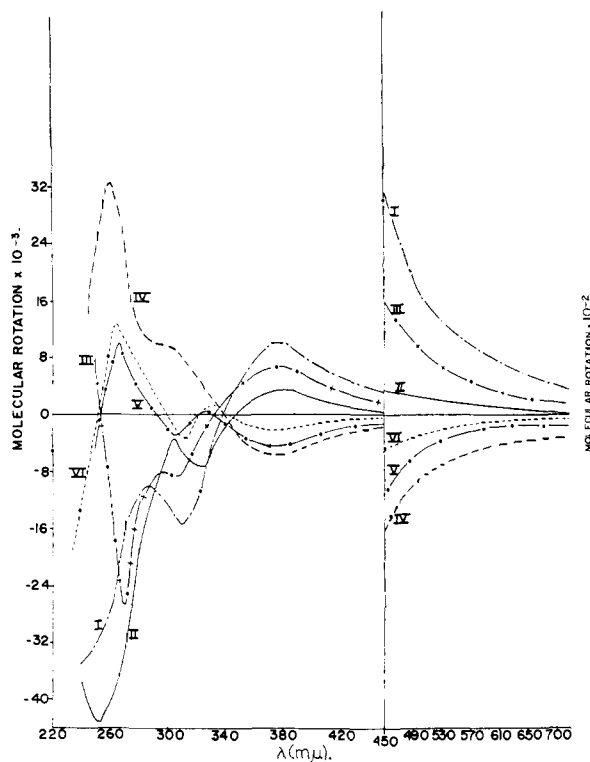


Fig. 1.

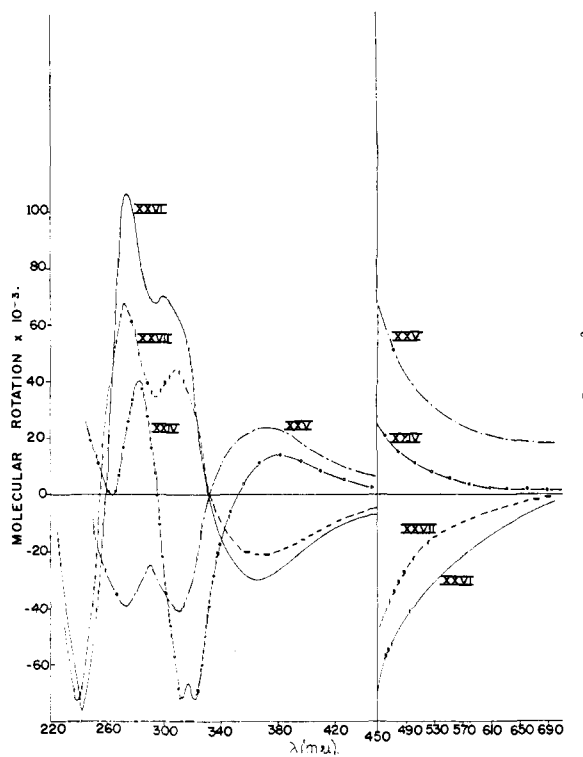


Fig. 2.

chloro groups. Mix¹³ has reported the conversion of presumably optically pure (-)-6-amino-6'-nitro-2,2'-dimethylbiphenyl¹⁴ via (+)-6-bromo-6'-nitro-2,2'-dimethylbiphenyl to (+)-6-amino-6'-bromo-2,2'-dimethylbiphenyl, $[\alpha]_D +8.5^\circ$. Since (-)-6-amino-6'-bromo-2,2'-dimethylbiphenyl, $[\alpha]_D -5.32^\circ$ (and therefore at most 63% optically pure), has been converted¹⁵ to the enantiomer of VII, $[\alpha]_D -6.2^\circ$, the optically pure dibromide has a *minimum* $[\alpha]_D +9.9^\circ$, in reasonable agreement with the value ($[\alpha]_D +11.7^\circ$) for VII found in the present work. The above correlation incidentally establishes the configuration of (-)-(*R*)-6-amino-6'-nitro-2,2'-dimethylbiphenyl, an atropisomeric substance which is resolvable by chromatography on lactose.¹⁶

The configurations of LIV-LXIII, LXVI and LXVII are only known relatively. As indicated in the tables, the convention is adopted of referring all configurations in the interrelated series to the parent substance, D(+)-4,5,6,4',5',6'-hexahydroxy-2,2-diphenic acid.¹⁷

Results

Inspection of the data reveals that the pattern of O.R.D. curves is dependent on the type of substituent in the biphenyl nucleus. The chromophore responsible for the observed Cotton effect curves

evidently varies with each structural type. It is therefore convenient to discuss the rotatory power of each structural group in separate sections.

2,2'-Dinitrobiphenyls.—The dinitrobiphenyls exhibit two Cotton effects (Figs. 1 and 2) of *opposite* signs centered near 260 and 330 $m\mu$, respectively. The effect at 260 $m\mu$ very likely corresponds to the nitrobenzene B-band; in the case of the long-wave length Cotton effect, the pertinent transition would appear to be the long wave length nitrobenzene band commonly found at 330 $m\mu$ ($\log \epsilon \text{ ca. } 2.2$).^{18,19} The ultraviolet spectra of the dinitrobiphenyls do not reveal this transition, which is masked by the strong end absorption of the bands at shorter wave lengths.

The dinitrobiphenyls can now be readily classified according to their ultraviolet and O.R.D. spectral characteristics. The *unbridged* dinitrobiphenyls I-VI have maxima or shoulders near 259 $m\mu$ ($\log \epsilon 4.0$) and 300 $m\mu$ ($\log \epsilon 3.5$); a *positive* 330 $m\mu$ Cotton effect curve corresponds to the (*R*)-configuration (Fig. 1). In contrast, *bridged* dinitrobiphenyls XXIV-XXVII have maxima or shoulders near 271 $m\mu$ ($\log \epsilon 3.9$) and 300 $m\mu$ ($\log \epsilon 3.7$). Examination of the O.R.D. curves (Fig. 2) reveals that the Cotton effect at shorter wave lengths has undergone a red-shift, that the amplitudes of both Cotton effects have been significantly enhanced by bridging, and that the signs of *both* effects have been inverted. Consequently, a *negative* 330 $m\mu$ Cotton effect corresponds to the (*R*)-configuration.

(13) H. Mix, *Ann.*, **592**, 146 (1955).

(14) Rotations refer to 96% ethanol; m.p. of racemate, 123-124°; m.p. of pure enantiomer, 111° (H. Mix, private communication). The m.p. previously reported for the enantiomer by A. Angeletti and P. Guala, *Gazz. chim. ital.*, **61**, 651 (1931), is 122-123°.

(15) A. Angeletti and C. Migliardi, *ibid.*, **65**, 819 (1935).

(16) G. Di Modica and A. Angeletti, *Ricerca sci.*, **22**, 715 (1952); *Chem. Zentr.*, **125**, 10228 (1954).

(17) O. Th. Schmidt and K. Demmler, *Ann.*, **586**, 179 (1954).

(18) E.g., G. Scheibe, *Ber.*, **59**, 2617 (1926); L. Dede and A. Rosenberg, *ibid.*, **67**, 147 (1934); R. A. Morton and A. McGookin, *J. Chem. Soc.*, 901 (1934); K. L. Wolf and W. Herold, *Z. physik. Chem.*, **13B**, 201 (1931).

(19) M. Godfrey and J. N. Murrell, *Proc. Chem. Soc. (London)*, **173** (1961).

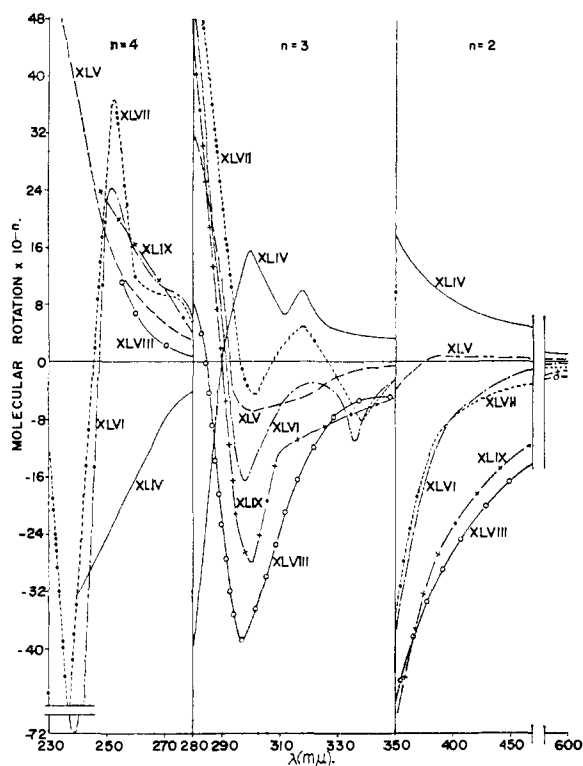


Fig. 3.

The ultraviolet spectral results in the unbridged series confirm prior findings.²⁰⁻²³ The observation that compounds of this type have spectra closely resembling those of the two halves (e.g., *m*-nitrobenzoic acid compared to III) has been made the basis for the suggestion²⁰⁻²² that the absorption spectrum, taken as a classical criterion²⁴ for non-coplanarity, demonstrates the near-orthogonality of the nitrophenyl moieties, as confirmed by dipole moment²⁵ and Kerr constant²⁶ measurements; indeed, it has been concluded^{27,28} from dipole moment measurements that the nitro groups in 2,2'-dinitrobiphenyl are inclined toward each other (i.e., dihedral angle (θ) less than 90° , or *cis* conformation).

The structural feature of bridging fixes the molecule in the *cis* conformation. The marked redshift of the B-band^{20,29} and more especially the reversal of the sign of the Cotton effects which

(20) E. J. Moriconi, W. F. O'Connor, F. T. Wallenberger and W. F. Forbes, *J. Am. Chem. Soc.*, **81**, 5950 (1959).

(21) L. W. Pickett, M. Groth, S. Duckworth and J. Cuncliffe, *ibid.*, **72**, 44 (1950).

(22) B. Williamson and W. H. Rodebush, *ibid.*, **63**, 3018 (1941).

(23) W. Kuhn and R. Rometsch, *Helv. Chim. Acta*, **27**, 1080 (1944).

The O.R.D. curves of III and of XXIII reported by these authors are in accord with those determined in the present work. Concerning the absolute configuration deduced in this paper, cf. ref. 5.

(24) L. W. Pickett, G. F. Walter and H. France, *J. Am. Chem. Soc.*, **58**, 2296 (1936); M. Calvin, *J. Org. Chem.*, **4**, 256 (1939); private communication by G. B. Kistiakowsky to L. W. Pickett, *et al.*, above.

(25) R. J. W. LeFevre and H. Vine, *J. Chem. Soc.*, 967 (1938).

(26) J. Y. H. Chan, C. G. LeFevre and R. J. W. LeFevre, *ibid.*, 2666 (1939).

(27) E. Bergmann and L. Engel, *Z. Physik. Chem.*, **8B**, 111 (1930).

(28) A. C. Littlejohn and J. W. Smith, *J. Chem. Soc.*, 2552 (1954).

(29) 2,2'-Dinitrobiphenyls may be formally viewed as *ortho*-substituted nitrobenzenes. Bulky *o*-substituents have the effect of quenching the B-band [W. G. Brown and H. Reagan, *J. Am. Chem. Soc.*, **69**, 1032 (1947); B. M. Wepster, *Rec. trav. chim.*, **76**, 335 (1957)].

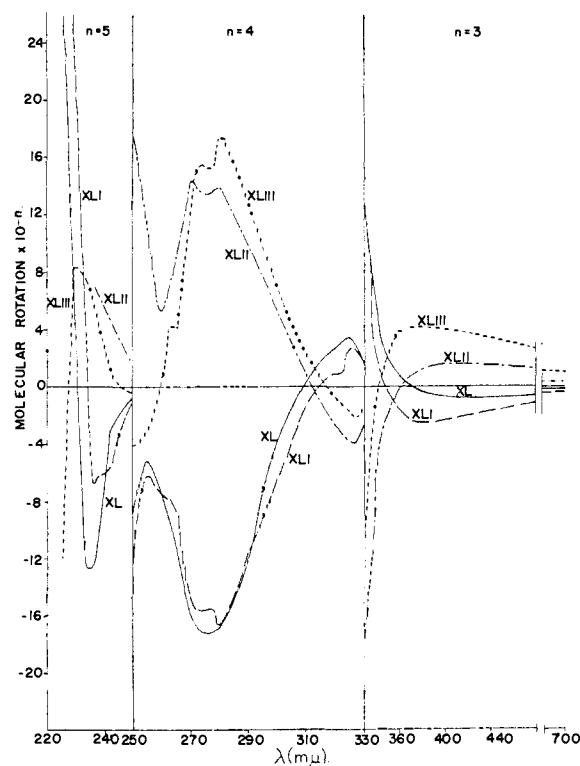


Fig. 4.

accompanies the change from an open to a bridged system is taken as *prima facie* evidence for a change in quadrant of the biphenyl conformation, in analogy to the argument⁶ advanced for XXII. Accordingly, we now tentatively assign the *trans* conformation ($\theta > 90^\circ$) to I-VI.

1,1'-Binaphthyls.—The complex absorption spectra of *unbridged* binaphthyls are dominated by maxima at 285 and ca. 230 $m\mu$.³⁰ Correspondingly, the complex O.R.D. curves of XLIV-XLIX (Fig. 3) are dominated by two Cotton effects centered at 285 and below 250 $m\mu$, respectively. In all cases, a *positive* 285 $m\mu$ Cotton effect corresponds to the (*R*)-configuration.

In contrast, the O.R.D. curves of 1,1'-binaphthyls *bridged* by a three-atom chain in the 2,2'-positions (XL-XLIII) have absorption spectra which are dominated by maxima at 220, 232 and 306 $m\mu$. Conceivably, the represents a red-shift as a result of bridging; *cf.* the related argument for the 2,2'-dinitrobiphenyls. There is evidence of a red-shift also in the O.R.D. curves (Fig. 4) which now feature two Cotton effects of *opposite* sign, centered near 300 and below 240 $m\mu$, respectively. A *positive* 300 $m\mu$ Cotton effect corresponds to the (*R*)-configuration. The generally enhanced rotations (compared to the unbridged series) are particularly noteworthy for the short-wave length Cotton effect, whose tail raises or lowers the inflection point of the long-wave length Cotton effect (amplitude ca. 200,000°) by ca. 60,000°, and whose sign completely dominates the rotation in the visible region.

(30) 1,1'-Binaphthyl exhibits maxima at 285 and 295 $m\mu$; see V. L. Frampton, J. D. Edwards, Jr., and H. R. Henze, *J. Am. Chem. Soc.*, **70**, 2284 (1948).

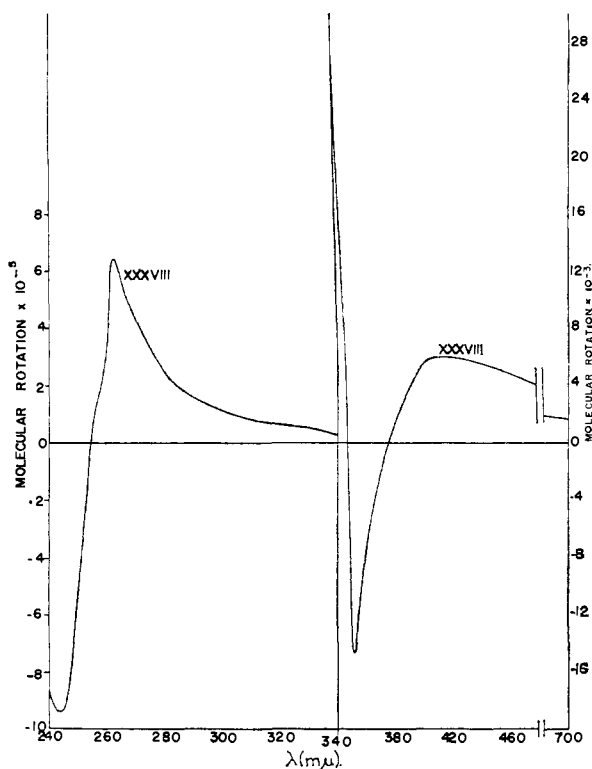


Fig. 5.

The structural feature of shortening the 2,2'-bridge has important ultraviolet and O.R.D. consequences. The ultraviolet spectrum³¹ of XXXV-III is altered significantly, particularly in the appearance of a group of prominent long-wave length bands at 320, 335 and 348 mμ. This red-shift is also reflected in the O.R.D. spectrum (Fig. 5) of the optically active³² (*S*)-compound⁷: a positive Cotton effect of enormous amplitude (1,570,000°), centered near 250 mμ, swamps the long-wave length negative Cotton effect (itself red-shifted to *ca.* 340 mμ) and completely dominates the visible region.

1,2,3,4-Dibenzcyclohepta-1,3-diene-6-ones.—The absorption spectrum of XXXIX, a 1,1'-binaphthyl bridged in the 2,2'-positions by a three-atom chain, fits the general pattern for this group of substances (preceding section). The O.R.D. curve (Fig. 6), however, is in a different category: there is now no sign in the visible of a background rotation and the whole region above 260 mμ is dominated by a multiple positive Cotton curve centered near 300 mμ whose large molecular amplitude³³ significantly exceeds that of the other bridged binaphthyls. The identity of the optically active chromophore responsible for this phenomenon emerges upon comparison of the O.R.D. curves of XXXIX and of XXXVI (Fig. 6). The O.R.D. curve of XXXVI is similarly characterized

(31) E. D. Bergmann and J. Szmuszkovicz, *J. Am. Chem. Soc.*, **73**, 5153 (1951). We have confirmed the long-wave length band group reported by these authors.

(32) D. M. Hall and E. E. Turner, *J. Chem. Soc.*, 1242 (1955).

(33) This effect, the result of further penetration into the ultraviolet, had not been uncovered at the time that our preliminary results were communicated.¹ It was then believed that XXXIX conformed in type to the other bridged binaphthyls.

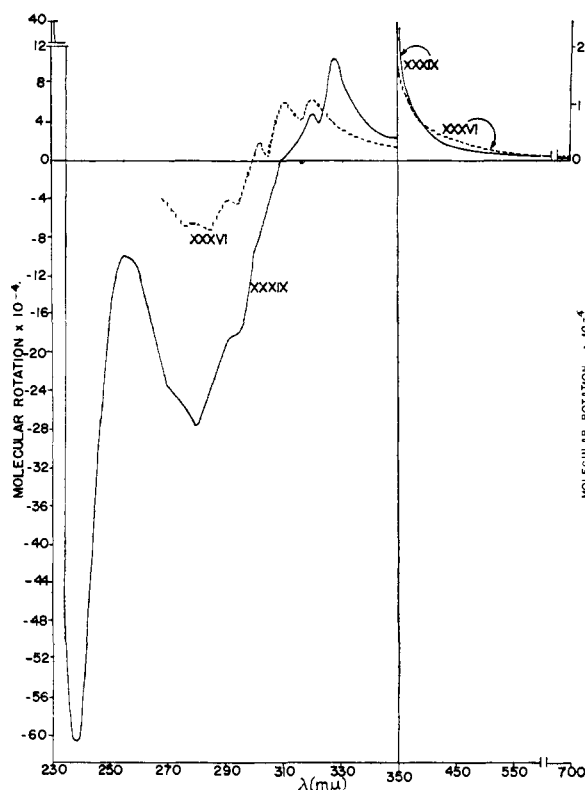


Fig. 6.

by an extraordinary amplitude and by fine structure. The disproportionate depth of the trough in the O.R.D. curve of XXXIX arises from the incursion of the negative background curve associated with the (*R*)-configuration of bridged binaphthyls.

The new optically active chromophore which gives rise to the effect just discussed cannot be adequately studied with XXXIX in whose absorption spectrum the group of bands associated with the optically active transition is masked by the intense binaphthyl absorption. This objection is overcome in XXXVI, where the intensity of the end absorption of the biphenyl conjugation band at 245 mμ (log ϵ 3.99) is quite moderate; the carbonyl bands in the region 285–320 mμ now stand clearly revealed. Since XXXVI has proved to be a key compound in this and related investigations (Discussion), we have taken some pains in ascertaining its structure beyond any doubt.

The usual elemental analyses (Experimental) demonstrate that XXXVI can only be either the ketone shown or the 5-keto isomer, since structures requiring 9,10-dihydrophenanthrene or fluorene nuclei are ruled out by the position of the biphenyl conjugation band. The 5-ketone is ruled out in a number of ways. First, deuterium exchange of racemic XXXVI gives a *d*₄-derivative, whereas a *d*₂-derivative would be expected for the 5-keto isomer. Second, the ultraviolet spectrum of XXXVI is virtually identical with that of the parent 1,2,3,4-dibenzcyclohepta-1,3-diene-6-one (Table VIII, Discussion), and entirely different from that of the 5-one (Experimental). Third, both XXXVI and the parent compound show a split carbonyl doublet in the infrared spectrum

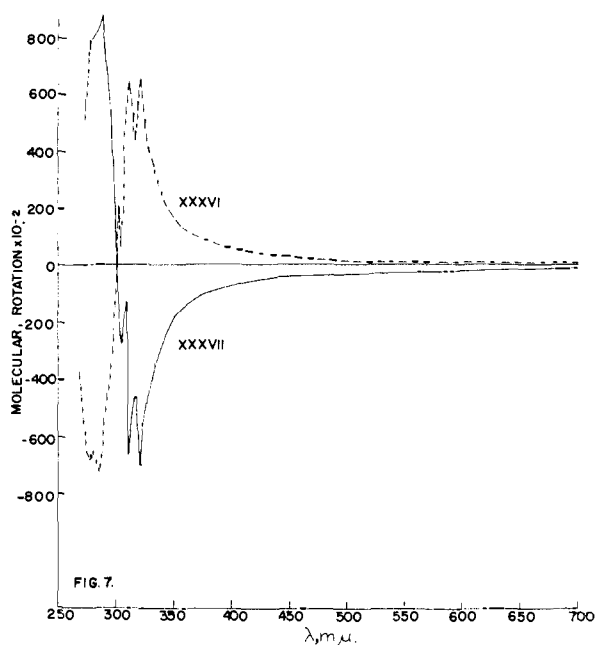


Fig. 7.

(KBr or chf.) at 1715 and 1705 cm^{-1} , whereas 1,2,3,4-dibenzocyclohepta-1,3-diene-5-one has a carbonyl band at 1670 (1665 shoulder) cm^{-1} . The identity of the parent compound is further confirmed by the n.m.r. spectrum in CDCl_3 which

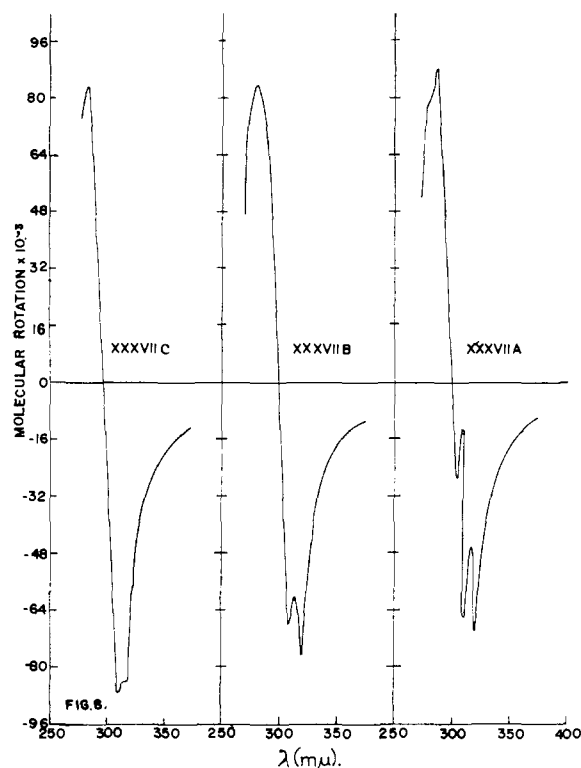


Fig. 8.

3,4-dibenzocyclohepta-1,3-diene-6-carboxylic acid.³⁴

We note that the split carbonyl band in the infrared is solvent-dependent. In CCl_4 , a shift to higher frequencies and a coalescence of peaks is observed (1724, (1718 shoulder) cm^{-1}). The deuterated derivative shows a greater split (1715 and 1695 cm^{-1} in chf.; 1721 (1700 sh.) cm^{-1} in CCl_4) as a result of a 10–20 cm^{-1} shift of the low frequency branch to yet lower frequency; the various interactions which may be responsible have been discussed in related cases.³⁵

Additional evidence for the reality of the fine structure in the O.R.D. curve of XXXVI is provided by the curve of the enantiomer XXXVII (independently prepared) which matches that of XXXVI in every detail (Fig. 7). The multiplicity is solvent dependent: in going from a non-polar to a polar solvent (isoöctane to dioxane to ethanol), the fine structure is progressively lost (Fig. 8), as has been observed in other cases.^{11,36} It is noteworthy that the change in solvent polarity appears to produce no marked change in wave length of any of the bands in the ultraviolet or O.R.D. spectrum.

2,2'-Biphenyldiamines.—The rotatory power of XXII has been a subject of recent interest.^{6,23,37} An inversion of the long-wave length sign of rotation of XXII and of L with protonation has been discussed^{6,37} in terms of a change in quadrant of

(34) J. W. Cook, G. T. Dickson and J. D. Loudon, *J. Chem. Soc.*, 746 (1947), and references cited; cf. also Z. B. Papanastassiou, Ph.D. Dissertation, West Virginia University, 1954.

(35) G. Allen, P. S. Ellington and G. D. Meakins, *J. Chem. Soc.*, 1909 (1960), and references cited therein.

(36) C. Djerassi, R. Riniker and B. Riniker, *J. Am. Chem. Soc.*, **78**, 6377 (1956).

(37) H. Musso and G. Sandrock, *Angew. Chem.*, **72**, 322 (1960).

TABLE VIII

ULTRAVIOLET SPECTRA^a OF SOME β,γ -BENZO-KETONES IN ISOÖCTANE

	Benzene bands	Carbonyl bands
	245 (3.99)	289.5 (2.88)
	272 (3.17)	297.5 (2.88)
		307 (2.76)
		317 (2.41)
	249.5 (4.20) ^b	287.5 (2.88)
		296 (2.81)
		305 (2.64)
		316 (2.24)
	244 (2.23)	287 (2.33)
	249 (2.37)	294 (2.37)
	254.5 (2.51)	302 (2.35)
	259.5 (2.60)	311 (2.21)
	266 (2.53)	322 (1.81)
		288 (2.69)
	266 (2.77)	297.5 (2.85)
	273.5 (2.79)	308 (2.90)
		321 (2.70)
		287 (2.72)
	253 (2.91)	296.5 (2.85)
	261 (2.87)	307.5 (2.87)
	266.5 (2.99)	307.5 (2.87)
	273.5 (2.99)	319 (2.65)

^a See footnote a, Table I. ^b Z. B. Papanastassiou (ref. 35) reports $\lambda_{\text{max}}^{\text{cyclohexane}}$ 252 (4.20). ^c Reported⁹² $\lambda_{\text{max}}^{\text{EtOH}}$ 210 (4.03), 264 (2.76), 273 (2.78), 300 (2.92). ^d Ref. 91.

shows in addition to the aromatic hydrogens only a single aliphatic proton peak at $\delta = 3.52$ p.p.m. (211 c.p.s.) with the relative integrated intensities (aromatic: aliphatic = 2:1) expected for this substance. In addition, the parent compound has been structurally correlated (*via* the 6-amine) with 1,2-

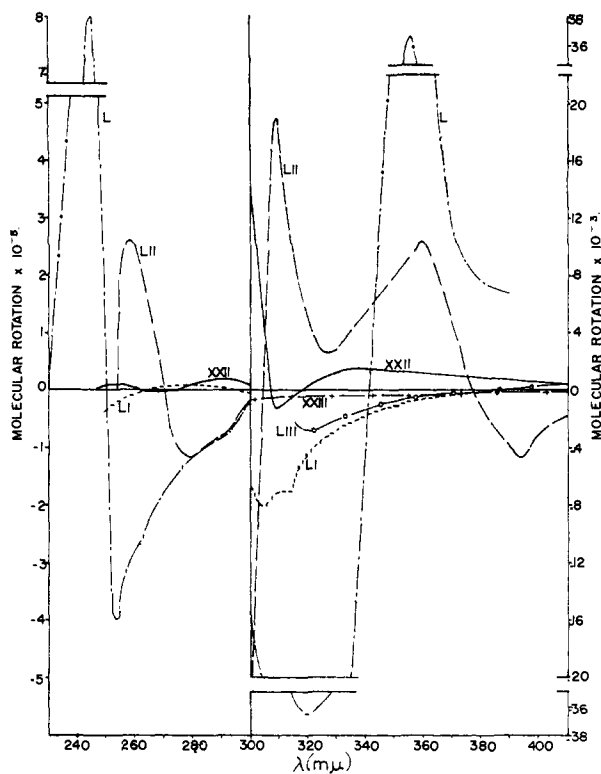


Fig. 9.

the biphenyl nucleus. On the other hand, it has been pointed out⁶ that 1,1'-bianthracene-2,2'-diamine³⁸ does not behave in a fashion analogous to XXII and L. An investigation of the O.R.D. behavior of unbridged biphenyldiamines (Fig. 9) is thus of obvious relevance.

It has been previously observed that the long-wave length band near 290 $m\mu$ in 2-aminobiphenyl,³⁹ 2,2'-diaminobiphenyl²² and XXII^{21,23} is quenched on protonation and that a new band appears near 260 $m\mu$ which may be a benzene band; further, the absorption spectra of unprotonated and protonated amines resemble those of aniline and anilinium ion, suggesting²⁴ near-orthogonality of the aminophenyl moieties. In this connection, it is noted that dipole moment measurements yield values of 79° for 2,2'-diaminobiphenyl,²⁷ 67° for XXII⁴⁰ and 120° for 2,2'-bis-(dimethylamino)-biphenyl.⁴¹ Similarly, Jones⁴² has found that the absorption spectra of L and protonated L (*i.e.*, LI) closely resemble those of 2-naphthylamine and 2-naphthylammonium (or 2-methylnaphthalene), respectively, and that protonation quenches the band near 350 $m\mu$.

The O.R.D. curves appear to reflect these changes in the spectra. Compound XXII may be regarded as having a positive Cotton effect curve⁴³

(38) K. Lauer, R. Oda and M. Miyawaki, *J. prakt. Chem.*, **148**, 310 (1937).

(39) M. Pestemer and E. Mayer-Pitsch, *Monatsh.*, **70**, 104 (1937).

(40) E. Bergmann and L. Engel, *Z. physik. Chem.*, **15B**, 85 (1931). However, this value has been questioned by A. Weissberger, *ibid.*, **15B**, 97 (1931), and by H. Hillemann, *Angew. Chem.*, **50**, 435 (1937), footnote 3.

(41) M. Lumbroso, *Bull. soc. chim. France*, **16**, D 387 (1949).

(42) R. N. Jones, *J. Am. Chem. Soc.*, **67**, 2127 (1945).

(43) The O.R.D. curve of XXII reported by A. Wortmann, Ph.D.

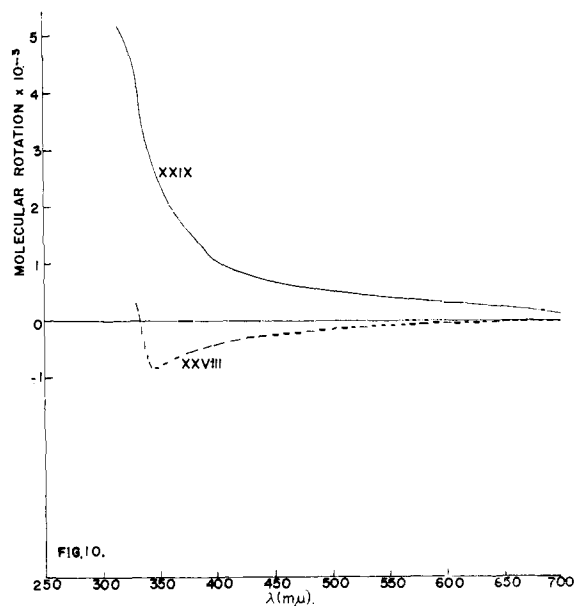


Fig. 10.

with a first extremum near 340 $m\mu$ and intersecting the zero-axis at 320 $m\mu$, which may correspond to the aniline chromophore at 295 $m\mu$. The quenching of that chromophore produces XXIII, which now exhibits a flat plain *negative* curve.⁴⁴ The complexity of the changes which are occurring is pointed up by L and LII. An apparent positive Cotton effect curve for L (probably ascribable to the 2-naphthylamine chromophore at 352 $m\mu$) is completely removed on protonation (LI). We have found that even the long-wave length sign of LI is concentration dependent: $[\alpha]^{22D}$ (*N* HCl) is -58° (*c* 2.0) and $+3^\circ$ (*c* 0.2).

The unbridged biphenyldiamines may in principle assume a variety of conformations. In contradistinction, a change of quadrants is precluded in XXVIII and XXXIX by the presence of the bridge. Nevertheless, the change of XXVIII to XXIX corresponds to a change of sign of rotation in the visible region (Fig. 10). Since no change in quadrant is possible, the earlier postulates^{6,37} will have to be re-examined.

The change in the absorption spectrum of XXVIII on protonation to compound XXIX appears to consist mainly of a 20 $m\mu$ hypsochromic shift in the 307 $m\mu$ (aniline) band.⁴⁵ The O.R.D. curve of (*R*)-XXVIII (Fig. 10) reveals a positive curve intersecting the zero-axis at 335 $m\mu$, which is superimposed on a negative background curve.⁴⁶

Dissertation, Kiel, 1939 (cited in ref. 23), is in agreement with that determined in the present work.

(44) This appears to be the tail of a negative Cotton effect curve.²³

(45) 2,2'-Biphenyldiamines may be viewed as *o*-substituted anilines. No *ortho*-effect is apparent in the absorption spectra of appropriately substituted anilines (B. M. Wepster, *Rec. trav. chim.*, **76**, 357 (1957)). The small change in the absorption spectrum may be regarded a direct consequence of the disposition of the two amino-groups, which are forcibly held in close proximity by the bridge, and for which the extent of double protonation will therefore be predictably minute.

(46) These observations, the result of further penetration into the ultraviolet, had not been made at the time that our preliminary results were communicated.¹ It was then believed that the negative background curve in XXVIII corresponded to a Cotton effect.

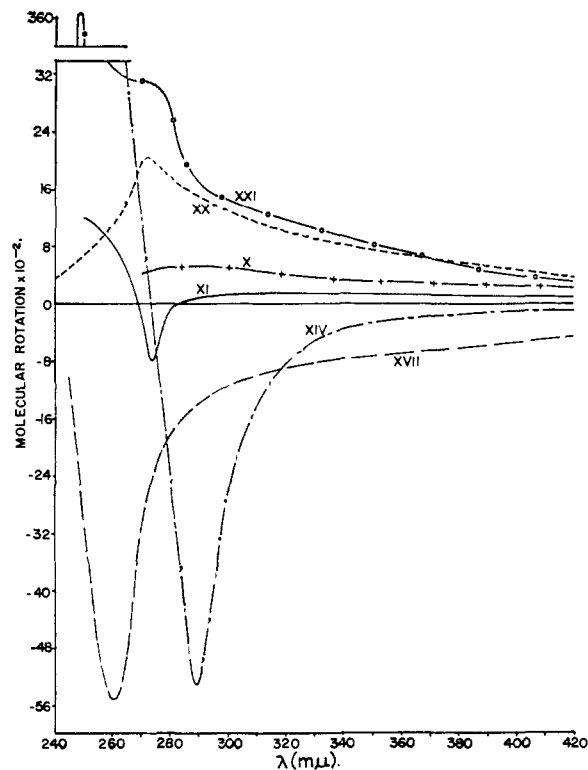


Fig. 11.

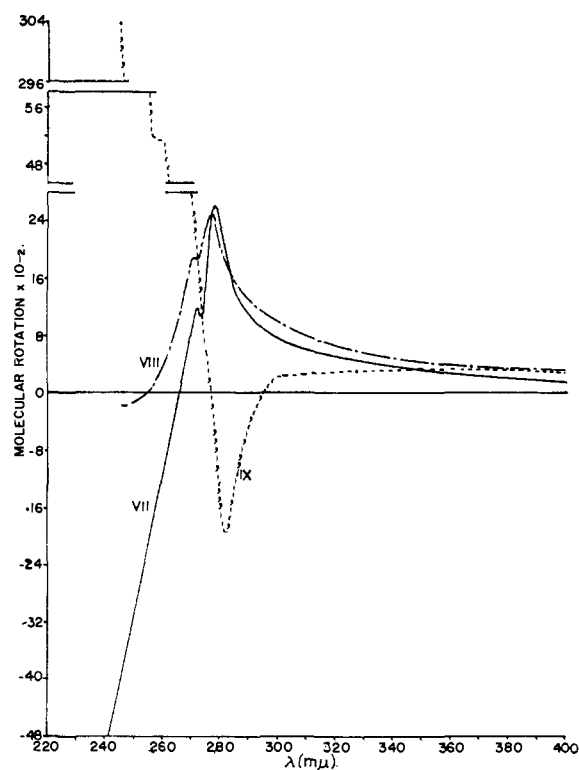


Fig. 12.

Protonation results in disappearance of the background rotation.

2,2'-Dimethyl- and 2,2'-Dihalobiphenyls.—By far the largest class of biphenyls investigated consists of compounds with no marked chromophoric substituents. *Unbridged* compounds in this category are VII–XXI. The absorption spectra of the related 2,2'-dialkyl- and 2,2'-dihalogenobiphenyls have been adequately discussed^{47,48} in terms of average conformations in which the biphenyl moieties are nearly perpendicular. Dipole moment,^{27,28,41,49} electron diffraction⁵⁰ and n.m.r.⁵¹ evidence suggests that compounds in this category assume conformations nearer *cis* than *trans*, presumably because secondary valence (*e.g.*, London dispersion) forces hold the blocking substituents in van der Waals contact; analogous explanations have been adduced for the preferred *cis* conformation^{52,53} of *n*-propyl halides and of 1,1,2-tetra-

haloethanes, for the preferred *cis* conformation^{53,54} of 1-halo-1-propenes and of 1,2-dihaloethenes, for the unexpectedly high stability⁵⁵ of axial (relative to equatorial) cyclohexyl bromide, and for the preferred *cis* conformation of 1,1'-bis-(4-chlorophenyl)-ferrocene⁵⁶ and of 1,6-dichloro-1,5-cyclooctadiene.⁵⁷

A number of the O.R.D. curves (*e.g.*, Fig. 11) do not seem to offer features of sufficient interest for extensive discussion at this time. The 6,6'-dihalo-2,2'-dimethylbiphenyls VII–IX (Fig. 12) constitute an interesting subgroup in which a positive Cotton effect centered at 260–270 $m\mu$ corresponds to the (*R*)-configuration. In the case of IX, the sign of rotation in the visible is governed by a background effect: this is no doubt the result of the incursion of the strong iodobenzene chromophore at 234 $m\mu$ which Beaven and Hall⁴⁷ have observed in the absorption spectrum of 2,2'-diiodobiphenyl. The background effect in XIII (Fig. 13) may be similarly explained if the benzonitrile chromophore⁵⁸ at 232 $m\mu$ is held responsible.

Among the diphenic acids and their derivatives (Fig. 13), the amides (XII and XVIII) form an important subgroup: broad long-wave length extrema near 270 $m\mu$ of high intensity dominate the whole region above 270 $m\mu$; a positive Cotton effect corresponds to the (*R*)-configuration.

(54) H. G. Viehe, *Chem. Ber.*, **92**, 1697 (1960), and references cited therein.

(55) E. L. Eliel and R. G. Haber, *J. Am. Chem. Soc.*, **81**, 1249 (1959); V. A. Atkinson and K. Lunde, *Acta Chem. Scand.*, **14**, 2139 (1960).

(56) D. A. Semenov and J. D. Roberts, *ibid.*, **79**, 2741 (1957).

(57) J. D. Roberts, *ibid.*, **72**, 3300 (1950).

(58) K. L. Wolf and O. Strasser, *Z. physik. Chem.*, **21B**, 389 (1933); R. C. Hirt and F. T. King, *J. Phys. Chem.*, **20**, 1821 (1952).

(47) M. T. O'Shaughnessy and W. H. Rodebush, *J. Am. Chem. Soc.*, **62**, 2906 (1940); P. M. Everitt, D. M. Hall and E. E. Turner, *J. Chem. Soc.*, 2286 (1956); G. H. Beaven and D. M. Hall, *ibid.*, 4637 (1956); G. H. Beaven, in G. W. Gray, "Steric Effects in Conjugated Systems," Academic Press, Inc., New York, N. Y., 1958, Ch 3; G. H. Beaven and E. A. Johnson, in "Institute of Petroleum Hydrocarbon Research Group Conference on Molecular Spectroscopy," ed. by E. Thornton and H. W. Thompson, Pergamon Press, New York, N. Y., 1959, pp. 78–92.

(48) G. H. Beaven, D. M. Hall, M. S. Lesslie, E. E. Turner and G. R. Bird, *J. Chem. Soc.*, 131 (1954).

(49) G. C. Hampson and A. Weissberger, *J. Am. Chem. Soc.*, **58**, 2111 (1936); T. Sato, *Bull. Chem. Soc. Japan*, **33**, 501 (1960).

(50) O. Bastiansen, *Acta Chem. Scand.*, **4**, 926 (1950); O. Bastiansen and L. Smedvik, *ibid.*, **8**, 1593 (1954).

(51) S. Brownstein, *J. Am. Chem. Soc.*, **80**, 2300 (1958).

(52) N. Sheppard, *Adv. in Spectroscopy*, **1**, 288 (1959), and references cited therein; Y. Morino and K. Kuchitsu, *J. Chem. Phys.*, **28**, 175 (1958); *cf.* also G. J. Szasz, *ibid.*, **23**, 2449 (1955).

(53) W. G. Lee and S. I. Miller, *J. Am. Chem. Soc.*, **82**, 2463 (1960), and references cited therein.

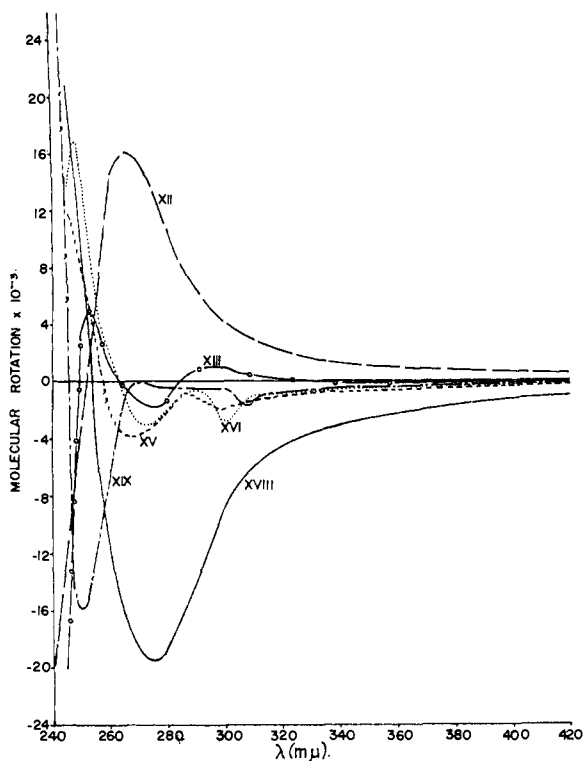


Fig. 13.

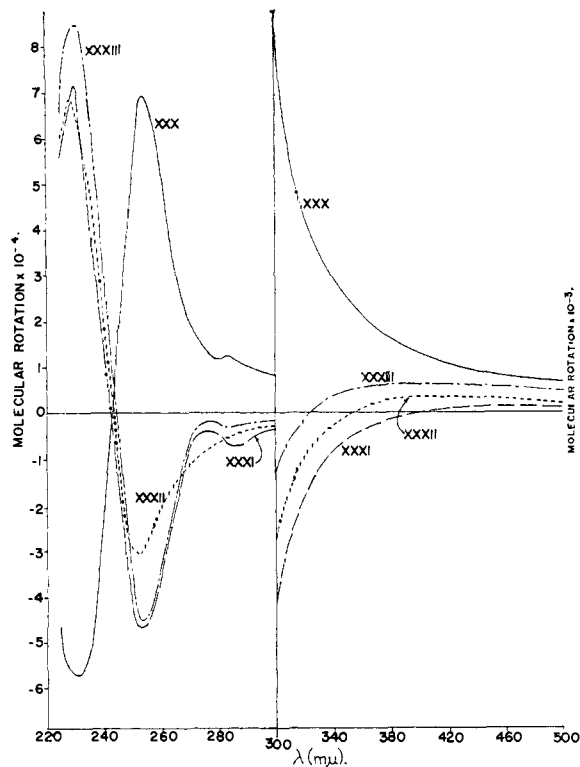


Fig. 14.

Bridging of 2,2'-dimethyl- (Fig. 14) and 2,2'-dichloro- (Fig. 15) biphenyls produces a notable change in the character of the O.R.D. curves. Cotton effects of appreciable amplitude (order of magnitude 10^5) centered near $245 \text{ m}\mu$ are in striking evidence; a *positive* effect corresponds to the (*R*)-configuration. Superimposed on all but one (XXX) of the Cotton curves is a background curve of *opposite* sign which dominates the whole visible region. In all but one (XXXII) of the curves a Cotton effect of very low amplitude also appears near $280 \text{ m}\mu$; the sign of this effect is the same as that of the $245 \text{ m}\mu$ effect.

The absorption spectra of the bridged compounds (including XXXVI and XXXVII) feature a biphenyl conjugation band in the range $240\text{--}246 \text{ m}\mu$ ($\log \epsilon \text{ ca. } 4.0$). The position of this band is characteristic of the size of the bridge. It has been shown that in the series of 2,2'-bridged biphenyls⁵⁹ the conjugation band is a reflection of angle of torsion and hence of bridge length. Specifically, six-membered ring 2,2'-bridged biphenyls substituted^{60,61} or unsubstituted^{62,63} in the 6,6'-positions have λ_{max} $260\text{--}264 \text{ m}\mu$; seven-membered ring 2,2'-bridged alicyclic^{64,64-66} or hetero-

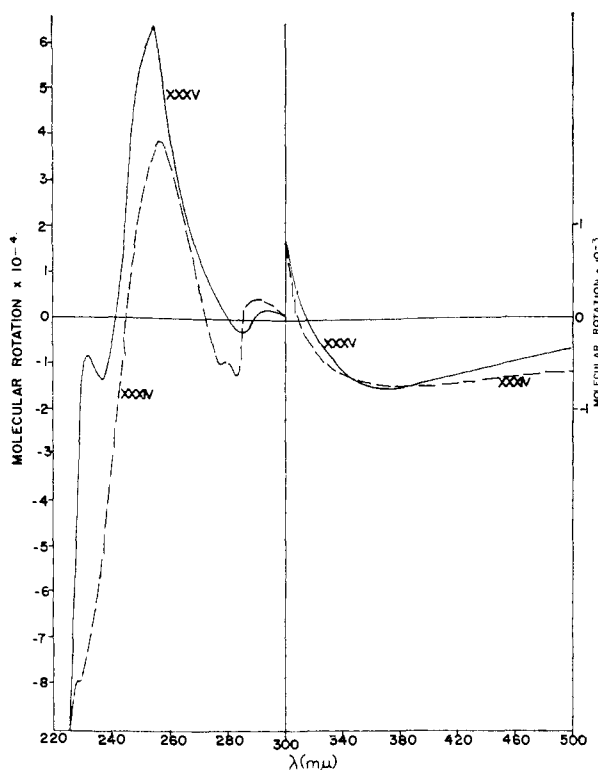


Fig. 15.

(59) Fluorene (one-carbon bridge) is not included since (owing to angle strain) the long biphenyl axis is not linear (G. M. Brown and M. H. Bartner, *Acta Cryst.*, **7**, 139 (1954); D. M. Burns and J. Iball, *Nature*, **173**, 635 (1954)).

(60) E. D. Bergmann and Z. Pelchowicz, *J. Am. Chem. Soc.*, **75**, 2663 (1953).

(61) G. Wittig and H. Zimmermann, *Chem. Ber.*, **86**, 629 (1953).

(62) F. A. Askew, *J. Chem. Soc.*, 512 (1935); R. N. Jones, *J. Am. Chem. Soc.*, **63**, 1658 (1941).

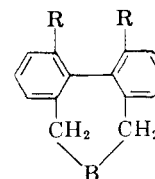
(63) G. H. Beaven, D. M. Hall, M. S. Lesslie and E. E. Turner, *J. Chem. Soc.*, 854 (1952).

(64) D. C. Iffland and H. Siegel, *J. Org. Chem.*, **21**, 1056 (1956); *J. Am. Chem. Soc.*, **80**, 1947 (1958).

(65) A. C. Cope and R. D. Smith, *ibid.*, **78**, 1012 (1956); G. H. Beaven, G. R. Bird, D. M. Hall, E. A. Johnson, J. E. Ladbury, M. S. Lesslie and E. E. Turner, *J. Chem. Soc.*, 2708 (1955).

(66) G. H. Beaven and E. A. Johnson, *ibid.*, 651 (1957); D. M. Hall, J. E. Ladbury, M. S. Lesslie and E. E. Turner, *ibid.*, 3475 (1956).

TABLE IX

CONJUGATION BAND ^a IN XMAIAMBridged BIPHENYLS OF FORMULA TYPE

R/B	CH ₂	C(COOEt) ₂	CO	CHCOOH	$\dot{N}R_2^+Br^-$	O
H	247 (4.20)E ⁶⁶	249 (4.23)E ⁶⁴	249.5 (4.20)H	249 (4.22)E ⁶⁷	248 (4.18)W ⁶⁸	250 (4.22)H ⁶³
CH ₃	240 (4.06)H	243 (4.05)D	245 (3.99)H ^b	242 (4.05)E	242 (3.96)E ⁶¹	244 (4.05)D ^d
Cl	244 (4.01)H	245 (3.94)W ^c

^a Data taken from present work unless otherwise indicated; E = ethanol, H = hexane or isoöctane, D = dioxane, W = water. Figure in parentheses gives log ϵ ; wave length in m μ . Superscripts refer to footnote in text. ^b Cf. Table VIII. ^c Lit.⁶⁸ 247 (4.00)E. ^d Lit.⁶¹ 242 (4.04)E.

cyclic^{48,63,67} biphenyls unsubstituted or substituted^{61,68} in the 6,6'-positions have λ_{max} 243–256 m μ , near the conjugation band of biphenyl itself⁶⁹; eight-membered ring 2,2'-bridged bi-

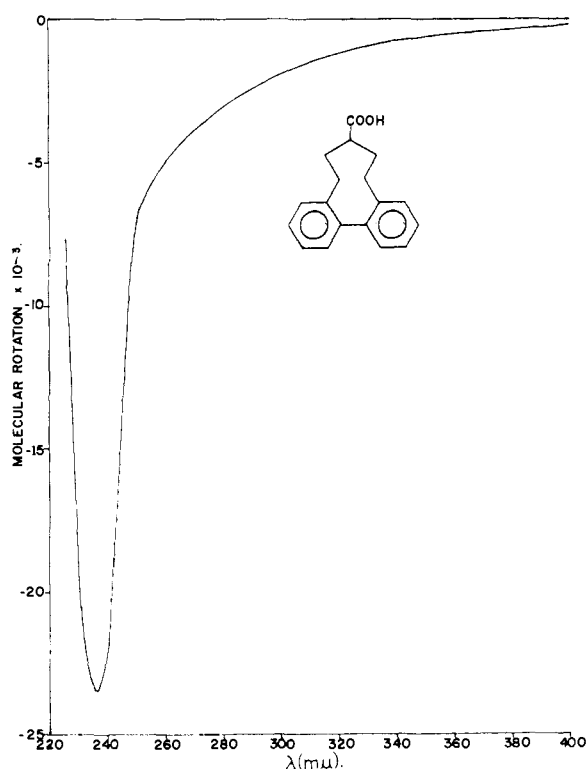


Fig. 16.

phenyls unsubstituted in the 6,6'-positions⁶⁵ have λ_{max} 235–239 m μ , and the nine-membered ring

(67) W. E. Truce and D. D. Emrick, *J. Am. Chem. Soc.*, **78**, 6130 (1956).

(68) S. R. Ahmed and D. M. Hall, *J. Chem. Soc.*, 4165 (1960).

(69) Although the angle of torsion θ of biphenyl in the solid state is 0° (A. Hargreaves, S. H. Rizvi and J. Trotter, *Proc. Chem. Soc.*, 122 (1961) and references cited therein; J. B. Robertson, *Nature*, **191**, 593 (1961); J. Trotter, *Acta Cryst.*, **14**, 1135 (1961)), it is about 45° in the gaseous state (O. Bastiansen, *Acta Chem. Scand.*, **3**, 408 (1949)). In solution, θ has been estimated at 20–30° (H. Suzuki, *Bull. chem. soc., Japan*, **32**, 1340 (1959), and references cited therein). The coincidence in the position of the conjugation bands in biphenyl, λ_{max}^{EtOH} 249 m μ ⁶⁹ and in the seven-membered ring bridged biphenyls does not reflect similar angles of torsion: the value of θ for the seven-membered ring bridged biphenyls has been variously estimated at 43–49° based on spectral data (H. Suzuki, *ibid.*, **32**, 1357 (1959)) and, independently, based on the usual bond distances and angles.⁷⁰

(70) D. M. Hall and F. Minhaj, *J. Chem. Soc.*, 4584 (1957).

analog⁷¹ has λ_{max} 231 m μ . The stability of the twisted conformation has been demonstrated by the optical activation^{64,71,72} of appropriate 2,2'-bridged biphenyls unsubstituted in the 6,6'-positions. In the present case, the maxima are on the low side of the range for seven-membered ring 2,2'-bridged biphenyls; indeed, λ_{max} for XXXIII (240 m μ) is the lowest heretofore reported for this type of structure, even taking into account the slight (1–2 m μ) correction which may apply for non-polar solvents.⁶³ This and related information is gathered in Table IX. It now appears that seven-membered ring 2,2'-bridged biphenyls with homo- or heterocyclic bridges and λ_{max} 249 \pm 2 m μ (log ϵ 4.2) suffer both a *blue-shift* and a *lowering in extinction* to λ_{max} 242 \pm 2 m μ (log ϵ 4.0) on substitution in the 6,6'-positions by either methyl or chlorine; this generalization has not heretofore been possible on the basis of more limited data.⁷³

It is therefore concluded that the optically active transition responsible for the Cotton effect centered near 245 m μ (Fig. 14 and 15) is the biphenyl conjugation band (Table IX). In support of this contention, the corresponding Cotton effect of (–)-1,2,3,4-dibenzocyclonona-1,3-diene-7-carboxylic acid (Fig. 16) was found to have suffered a blue-shift paralleling that of the ultraviolet maximum (λ_{max}^{EtOH} 231 m μ).⁷¹ Only the long-wave length extremum at 236 m μ was instrumentally accessible. The magnitudes of the rotations are not comparable since the optical purity of the acid is unknown.⁷¹

2,3,4,2',3',4'-Hexakis-(benzyloxy)-biphenyls.—

Interest in the absolute configuration of this class of compounds arises from the fact that these

(71) K. Mislow, S. Hyden and H. Schaefer, *Tetrahedron Letters*, No. 12, 410 (1961); *J. Am. Chem. Soc.*, **84**, 1449 (1962).

(72) L. V. Dvorken, R. B. Smyth and K. Mislow, *ibid.*, **80**, 486 (1958); S. R. Ahmed and D. M. Hall, *J. Chem. Soc.*, 3383 (1959).

(73) Truce and Emrick⁶⁷ have suggested in a speculative vein that the introduction of 6,6'-methyl groups may cause electroic interactions with the biphenyl nucleus which should (for purposes of comparison with the parent substance) be corrected for by subtracting ca. 8 m μ from λ_{max} of the 6,6'-dimethyl derivative. Since 4,4'-dimethyl-⁶⁷ and 4,4'-dichlorobiphenyl⁷⁰ have λ_{max} 254.5 m μ (log ϵ 4.32) and 259 m μ (log ϵ 4.40), we feel that a similar correction for the 6,6'-dichloro derivatives of ca. 11 m μ may be in order. It is seen that the corrected values for 6,6'-dimethyl and 6,6'-dichloro derivatives will be very similar and that the net effect on the conjugation band in the two series will therefore also be comparable. Any steric effects on the conjugation band, though probably negligible,⁷⁰ are in any case expected to be of comparable magnitude in the two series since methyl and chlorine are approximately isosteric.

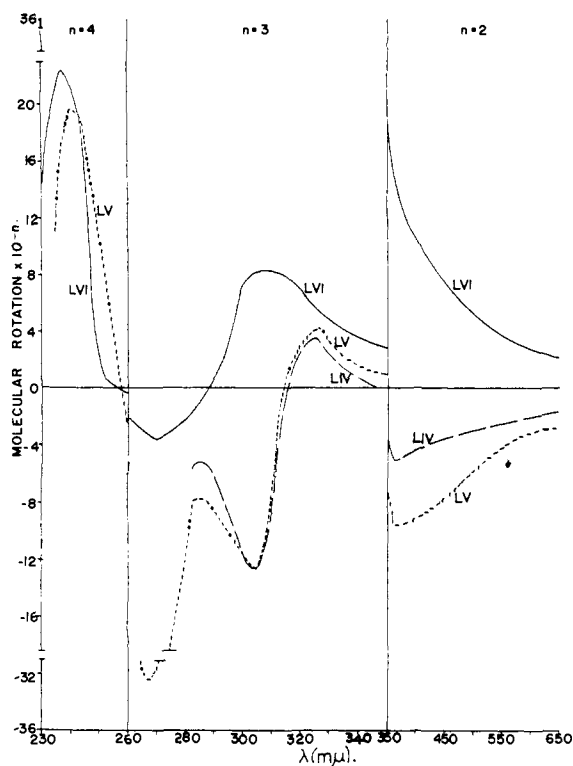


Fig. 17.

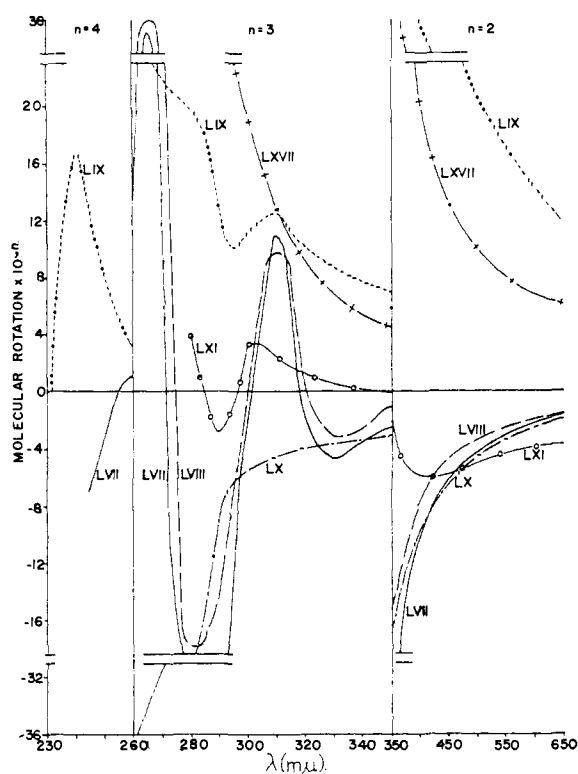


Fig. 18.

derivatives⁷⁴ of the naturally occurring ellagitannins⁷⁴ owe their dissymmetry to restricted rotation around a single bond, an attribute rarely encountered among the natural products.⁷⁵

A direct approach to a solution of this problem by an asymmetric synthesis of the type employed in the biphenyl³- and binaphthyl⁷-series founded on the failure of attempts to prepare the appropriate bridged ketone analogous to XXIV, XXXVI and XXXIX: under the conditions (heating in a phosphoric-acetic acid mixture) which were successful in the hydrolysis of the corresponding imino-nitriles LXV, LXIV and LXVIII, the hydrolysis of LXII resulted in extensive decomposition, presumably by acid-catalyzed debenzoylation.⁷⁶ Under milder conditions (heating in a phosphoric acid-dioxane mixture) only the imino-group was hydrolyzed⁷⁷: LXII gave LXIII and racemic LXIV gave the analogous bridged ketonitrile (Experimental Part). The products were char-

(74) O. Th. Schmidt, in "Progress in the Chemistry of Organic Natural Products," Vol. 13, ed. L. Zechmeister, Springer-Verlag Vienna, 1956, pp. 70-136; O. Th. Schmidt and W. Mayer, *Angew. Chem.*, **68**, 103 (1956); O. Th. Schmidt and H. H. Grünwald, *Ann.*, **603**, 183 (1957); cf. also the ellagittannin isolated by L. Jurd, *J. Am. Chem. Soc.*, **80**, 2249 (1958).

(75) The aporphine alkaloids have a twisted biphenyl moiety whose stereochemistry is governed by the asymmetric carbon in the 2,2'-bridge (S. Goodwin, J. N. Shoolery and J. F. Johnson, *Proc. Chem. Soc.*, 306 (1958)). The absolute configuration of a member of the group, bulbocapnine, has been established by X-ray diffraction (R. Pepinsky, private communication) and the O.R.D. curves of such aporphines have been recorded by C. Djerassi, K. Mislow and M. Shamma, *Experientia*, in press.

(76) O. Th. Schmidt, H. Voigt, W. Puff and R. Köster, *Ann.*, **586**, 165 (1954).

(77) In this connection, cf. K. Ziegler, H. Eberle and H. Ohlinger, *ibid.*, **504**, 94 (1933); S. M. McElvain and R. D. Mullineaux, *J. Am. Chem. Soc.*, **74**, 1812 (1952); A. Dornow, I. Kühlicke and F. Baxmann, *Chem. Ber.*, **82**, 254 (1949).

acterized by the weak split band near 2260 and 2230 cm.^{-1} which is typical of β -ketonitriles.⁷⁸

A constitutionally symmetrical, bridged optically active derivative in this series (oxepin LXVII) was obtained. The O.R.D. curves of LXVII, of some unbridged analogs (LVII-LXI) and of several related hexamethoxy derivatives (LIV-LVI) are shown in Figs. 17 and 18. The synthetic routes intercorrelate all of these compounds, designated by the family notation¹⁷ D and L. For the group of hexamethoxy compounds (Fig. 17), a positive long-wavelength Cotton effect signalizes the L-configuration. On the other hand, the hexakisbenzyloxy derivatives (Fig. 18) do not form a pattern on which we wish to comment in detail at this time—other than to note that the very similar curves (in the 260-350 μ range) for LX and LXI nevertheless refer to opposite configurations. The problem of the responsible chromophores is very complex; most of the absorption spectra feature bands near 215 μ ($\log \epsilon$ 4.7-5.1), 260-265 μ ($\log \epsilon$ 4.3-4.7) and 290-300 μ ($\log \epsilon$ 3.5-3.8). The band at 260-265 μ is a familiar feature in the structurally related colchinal and isocolchinal derivatives⁷⁹ and may be the conjugation band as affected by the combined presence of 2,2', 3,3'- and 4,4'-substituents.^{48,63,70}

Iminonitriles.—The compounds thus far discussed are constitutionally symmetrical and de-

(78) M. E. Kuehne, *J. Am. Chem. Soc.*, **81**, 5400 (1959).

(79) H. T. Huang, D. S. Tarbell and H. R. V. Arnstein, *ibid.*, **70**, 4181 (1948); R. Horowitz, G. E. Ulyot, E. C. Horning, M. G. Horning, J. Koo, M. S. Fish, J. A. Parker and G. N. Walker, *ibid.*, **72**, 4330 (1950); H. Rapoport, A. R. Williams and M. E. Cisney, *ibid.*, **73**, 1414 (1951); H. Rapoport, R. H. Allen and M. E. Cisney, *ibid.*, **77**, 670 (1955).

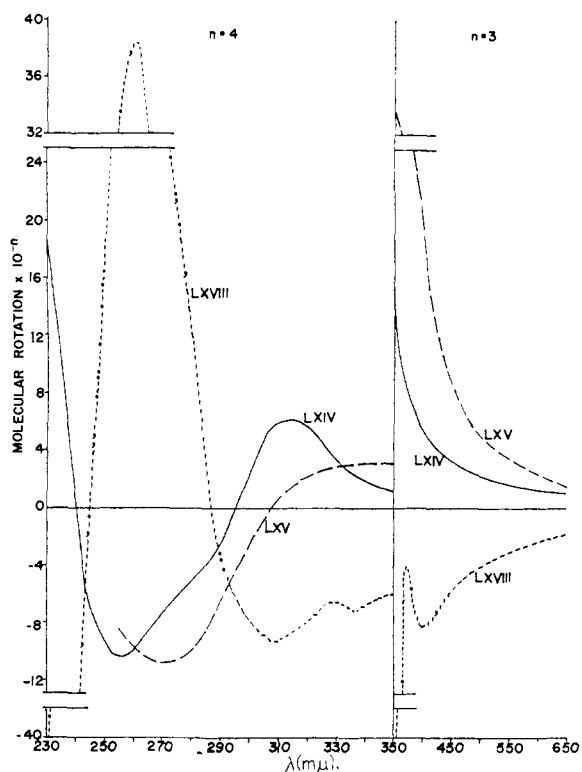


Fig. 19.

void of asymmetric atoms. The iminonitriles obtained as intermediates in synthesis are neither. Interpretation of O.R.D. curves must thus necessarily be on a more speculative plane. Nevertheless, the curves feature traits which we believe interesting enough to point out at this time.

The O.R.D. of iminonitriles reveals high amplitude Cotton effects centered near $300 \text{ m}\mu$ (Fig. 19). While in LXV and LXVIII the long-wave length nitro- respectively naphthyl-chromophores may render interpretation ambiguous, this is not the case for LXIV, where the long-wave length Cotton effect surely corresponds to the band at $298 \text{ m}\mu$. It is remarkable that the amplitude ($166,000^\circ$) of the effect and the position of the long-wave length extremum ($315 \text{ m}\mu$) are very similar to the corresponding quantities in XXXVII ($147,000^\circ$, $318 \text{ m}\mu$), but that for the same absolute configuration of the biphenyl moiety the signs of the two effects are opposite. Clearly a new chromophore has been introduced, as can also be demonstrated (Fig. 20) in the series LXII (iminonitrile), LXIII (ketonitrile) and LXVI (alcohol-nitrile): though the biphenyl nucleus has the same configuration (D) in the three compounds, the three curves differ markedly.

Discussion

The results obtained in the present investigation provide the first instance of conformational and configurational correlations in the class of atropisomers (*i.e.*, compounds owing their stereoisomerism to restricted rotation around a single bond) by the method¹¹ of optical rotatory dispersion. In the course of this work a multiplicity of optically active chromophores was recognized; for this

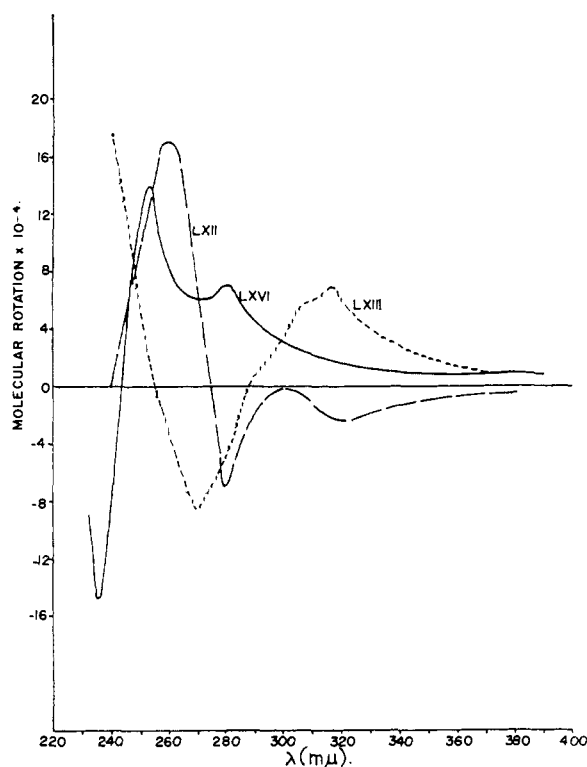


Fig. 20.

reason, we prefer to limit generalizations to particular classes of compounds.

Conformations.—In the biphenyls, the problem of conformation arises; as discussed for the specific cases of 2,2'-dinitro-, 2,2'-dimethyl- and 2,2'-dihalobiphenyls, the overwhelming evidence from a variety of types of measurements leads to the conclusion that in these compounds the *cis* is preferred over the *trans* conformation. Nevertheless, in the case of *tetra*-substituted biphenyls a new factor is introduced, since attractive secondary forces between 2-X: 6'-Y and 2'-X: 6-Y may come into play and result in a preference for the *trans* conformation. In addition, the actual deviation from orthogonality cannot be very great in the *tetra*-substituted biphenyls (*e.g.*, *cf.* the absorption spectra) and in the open binaphthyls, and it is therefore more profitable to focus our discussion at this time principally on those biphenyls in which the conformation and torsional angle are fixed and known, *i.e.*, on the *bridged* biphenyls.

The effect of bridging on the O.R.D. characteristics of the biphenyls is striking in all of the classes investigated. In the 2,2'-dinitrobiphenyls, bridging results in a reversal of the *sign* of the Cotton effect which, together with the red-shift of the B-band, we take to signal a change in quadrant. In the 1,1'-binaphthyls, the change from (a) unbridged to (b) seven-membered ring bridged to (c) six-membered ring bridged (XXXVIII) 1,1'-binaphthyls is accompanied in the absorption spectrum by red-shifts. The O.R.D. behavior reflects this shift, which is also accompanied by a substantial enhancement in amplitude. The amplitude of the short-wave length Cotton effect in XXXVIII has been commented on (above).

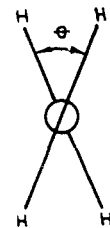
In the group of 2,2'-dimethyl- and 2,2'-dichlorobiphenyls, conversion to the bridged structures gives rise to the appearance of a high-amplitude Cotton effect centered at the biphenyl conjugation band. It has been demonstrated (above) that the position of this Cotton effect changes (along with the relevant absorption maximum) with change of θ . Biphenyl itself is dissymmetric and optically active in all but two of its conformations; the Cotton effect just referred to pertains to the twisted ($0^\circ < \theta < 90^\circ$) conformation of biphenyl. *The present work provides the first experimental demonstration of the inherently dissymmetric biphenyl chromophore.*⁸⁰

Configurations.—The factor of variable conformation can be eliminated by going to the seven-membered ring 2,2'-bridged biphenyls and binaphthyls. The angle of torsion in this group of compounds is fixed⁶⁹ in the *cis* conformation near 43–49°.

For each set of compounds, two or three Cotton effects were observed, corresponding to various groups of bands in the ultraviolet spectrum. The Cotton effects at shorter wave lengths were found generally to have the higher amplitudes. It was found that the absolute configuration uniquely determines the sign of each Cotton effect. The signs of the several Cotton effects in each O.R.D. curve are usually not the same, so that *the transition (or band group) associated with the particular Cotton effect must be specified for the purpose of configurational assignment.* Accordingly, we summarize the salient results as follows: *For 2,2'-bridged biaryls having the (R)-configuration, the sign of the long-wave length Cotton effect is negative for 6,6'-dinitro derivatives, positive for 6,6'-dimethyl- and 6,6'-dichloro-derivatives, and positive for 1,1'-binaphthyls.*

In a number of studies the absolute configuration of biphenyls has been related to the sign of rotation in the visible and near ultraviolet regions.^{6,23,31,32} The conformational rigidity of XXXVIII in particular has rendered this structure attractive for theoretical calculations.^{6,32} We are now able to report that the sign of rotation at the D-line on which conclusions relative to XXXVIII are based is the sign of a Cotton effect curve centered near 250 m μ , which dominates the entire visible region but which is opposite in sign to the long-wave length Cotton effect curve centered at ca. 340 m μ .

With the identification of the dissymmetric biphenyl chromophore (above), the further statement is now possible that *the conformation of biphenyl which has the absolute configuration shown ($\theta = \text{ca. } 45^\circ$) will have a positive*



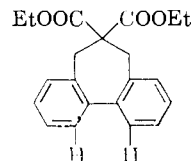
(80) The concept of "inherently dissymmetric chromophores" has been discussed by A. Moscovitz, Chapter 12, ref. 11; *Tetrahedron*, **13**, 48 (1961).

(81) E. Wasserman, Ph.D. Dissertation, Harvard University, 1958; E. Wasserman, *Revs. Modern Phys.*, **32**, 443 (1960).

(82) H. Looyenga, Ph.D. Dissertation, University of Leiden, 1955. The expression for $D_{12}S_{12}$ on p. 36 of the thesis should read $-1/2 \sin 4\alpha$ ($S_{12} = -\cos \alpha/64$). This leads to the conclusion that (+)-XXXVIII has the (S)-configuration, in harmony with independent calculations.⁶ We are indebted to Professor D. D. Fitts and Dr. H. Looyenga for helpful correspondence.

Cotton effect (amplitude order of magnitude 10^5) centered at 240–250 m μ .

The empirical basis for the Bridge rule⁶ now becomes clear. In the case of the dinitrobiphenyls, the sign of the long-wave length Cotton effect curve dominates the visible region; in the case of almost all of the other biphenyls and of the binaphthyls, the *background* rotation dominates the visible region. In either case, it would be concluded that the (R)-configuration corresponds to a negative rotation in the visible. Exceptions to the rule thus occur when there is a change of the chromophore responsible for the long-wave length Cotton effect, or when the sign of the background rotation no longer dominates the visible region. As an example of the first type, (+)-XXXVI and (+)-XXXIX have the (R)-configuration: the rotation in the visible is here governed by the dissymmetric chromophore to be discussed in the next section. As an example of the second type, (+)-XXX has the (R)-configuration: though the Cotton effect curve is of the same sign as in related (XXXI–XXXIII) 2,2'-bridged (R)-biphenyls, the background rotation in this case does *not* dominate the visible region. The last example demonstrates that *the generalizations based on rotatory dispersion are more encompassing than the earlier monochromatic rule.* In connection with the behavior exhibited by XXX, we note that (+)-(R)-XXIX, which may be regarded as isoelectronic with XXX, also shows no background curve and would therefore constitute another exception to the monochromatic bridge rule. The same may be said of the parent compound:⁶⁴



The (–)-isomer has the (S)-configuration³; granting a negative Cotton effect curve (in analogy to the (S)-6,6'-dimethyl- and (S)-6,6'-dihalo-2,2'-bridged biphenyls), the sign in the visible is thus again *not* dominated by an opposite background rotation. We conclude that this exceptional behavior is a particular function of the carboxylic grouping which is the common structural feature of all of these substances—including the nine-membered ring in Fig. 16.

The recognition that either the sign of the Cotton effect curve or the sign of the background curve may predominate in the visible, depending on the chromophore appropriate for the structural type, renders extensions of the above generalizations to systems not included in the present study unwarranted. The earlier conclusions,^{6,10} concerning bridged biaryls which possess other chromophores, e.g., the bridged derivatives of the diaryl-2,2'-disulfonic acids³³ and the interesting bridged

(83) W. L. F. Armarego and E. E. Turner, *J. Chem. Soc.*, 3668 (1956); 13 (1957). In particular, it has been shown (C. Djerassi, A. Fredga and B. Sjöberg, *Acta Chem. Scand.*, **15**, 417 (1961)) that the disulfide chromophore is optically active and that the sign of corresponding Cotton effect curves is configuration dependent.

TABLE X
 [M]D OF SOME DIPHENIC ACIDS, ESTERS AND AMIDES^a

Con-figuration	(S) ^b				D ^c			D ^d
R								
COOCH ₃	-346°	-20°	+128°	-67°	+187°	+167° ^e	-301° ^f	+415°
COOH	-422	-22	+70	-116	+93	+116	-423	+366°
CONH ₂	-958	-368	0	-776	-113	-432°	-1138°	+147

^a In methanol unless otherwise specified. ^b Present work and ref. 6. ^c Ref. 17. ^d Ref. 86. ^e In ethanol. ^f In acetone.

compound (LXIX) reported by Bell⁸⁴ (Fig. 21), must therefore remain at best tentative.

Amide Rule.—The tentative proposal⁶ of an Amide rule in the biaryl series may now be re-examined in the light of the present results. Scrutiny of the O.R.D. curves of amides I (Fig. 1), XII (Fig. 13), XVIII (Fig. 13), XLVIII (Fig. 3), LVI (Fig. 17) and LIX (Fig. 18) reveals that *in the entire visible region constitutionally symmetrical biaryl amides having the (R)-configuration suffer a marked shift in the positive direction, relative*

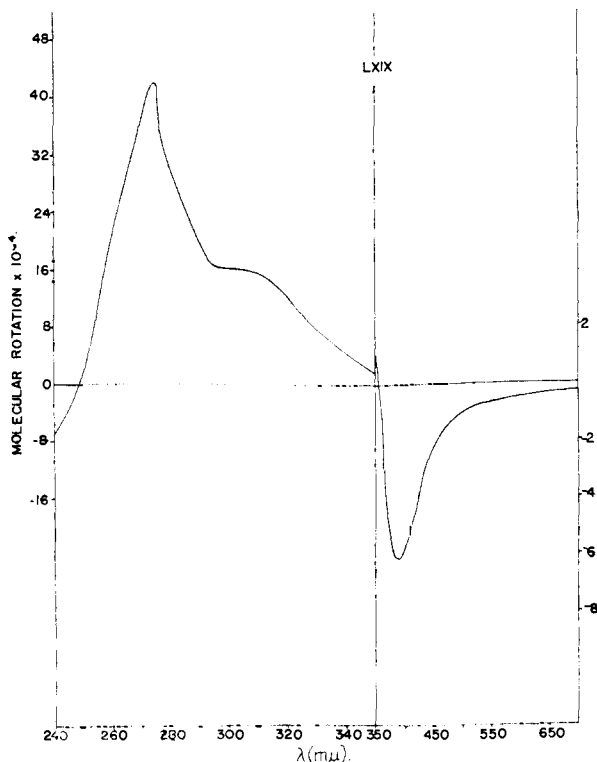


Fig. 21.

to the corresponding esters and acids. The dominance of the amide rotation appears strikingly in Fig. 13, where the O.R.D. curves of amides XII and XVIII exceed by far in intensity all the other curves in the region above 270 μ . Taking the D-line as a representative wave length in the visible region, the pertinent information is collected in Table X.⁸⁵

(84) F. Bell, *J. Chem. Soc.*, 1527 (1952).

(85) Although almost all of the reported rotations refer to methanol, the trend appears not to be appreciably solvent dependent. Thus,

The (S)-biaryls are seen to follow the *Amide rule* (above).⁸⁶ The intercorrelated ellagic acid derivatives belonging to the D-family¹⁷ as well as the simpler D-6,6'-dimethoxy-2,2'-diphenic acid derivatives⁸⁷ show precisely the same trend. Accordingly we now tentatively assign the (S)-configuration to the D-family of biaryls in Table X,⁸⁸ and to the corresponding optically active biphenyl moieties in the precursor ellagitannins.⁷⁴ In particular, *naturally occurring corilagin corresponds to the stereoformula on the right ((S)) in Fig. 22*. It is interesting to note that the unnatural diastereomer ((R)) (Fig. 22) can also be accommodated in a strainless model.⁸⁹

β,γ -Benzo-ketones.—The carbonyl group in XXXVI and in the parent 1,2,3,4-dibenzocyclohepta-1,3-diene-6-one is formally unconjugated; the shift toward longer wave lengths and the high intensity of the carbonyl bands therefore appear to be out of the ordinary. These phenomena, as shown in Table VIII, are matched by a number of other β,γ -benzo-ketones, and to such a similar extent that the same cause may properly be sought in accounting for the effect in all of the compounds, despite their structural diversity.

Exaltation and red-shift of the carbonyl $\pi \rightarrow \pi^*$ transition characterize the absorption spectra of variously substituted phenylacetones⁹⁰ and α -phenylcyclohexanones,⁹⁰ as well as of bicyclic benzoketones⁹¹⁻⁹³; even a β -ketoparacyclophane

we find for the series of (R)-6,6'-dimethyl-2,2'-diphenic acid derivatives:

Solvent	[α] ₄₄₀ , compound XV	[α] ₄₄₀ , compound XVI	[α] ₄₄₀ , compound XII
Chloroform	-40°	-97°	+41°
Dioxane	-49	-32	+58
Methanol	-55	-27	+6
Acetone	-44	-15	+26

(86) K. Freudenberg, F. Brauns and H. Siegel, *Ber.*, **56**, 193 (1923), established an *amide rule* in the series of α -hydroxy acids which owe their asymmetry to the presence of an asymmetric carbon.

(87) W. M. Stanley, E. McMahon and R. Adams, *J. Am. Chem. Soc.*, **55**, 706 (1933); numerical data tabulated refer to the (-)-form which was obtained in a higher state of optical purity.

(88) Similar conclusions arrived at⁶ for the (+)-1,1'-bianthrils may require further confirmation.

(89) O. Th. Schmidt, D. M. Schmidt and J. Herok, *Ann.*, **587**, 67 (1954).

(90) W. D. Kumler, I. A. Strait and E. L. Alpen, *J. Am. Chem. Soc.*, **72**, 1463 (1950); E. L. Alpen, W. D. Kumler and I. A. Strait, *ibid.*, **72**, 4588 (1950); D. J. Cram and J. D. Knight, *ibid.*, **74**, 5839 (1952); W. B. Bennett and A. Burger, *ibid.*, **75**, 84 (1953); A. C. Huitric and W. D. Kumler, *ibid.*, **78**, 614 (1956).

(91) W. E. Noland, M. S. Baker and H. I. Freeman, *ibid.*, **78**, 2233 (1956); R. C. Cookson and N. Lewin, *Chemistry & Industry*, 985 (1956); H. Birnbaum, R. C. Cookson and N. Lewin, *J. Chem. Soc.*, 1224 (1961).

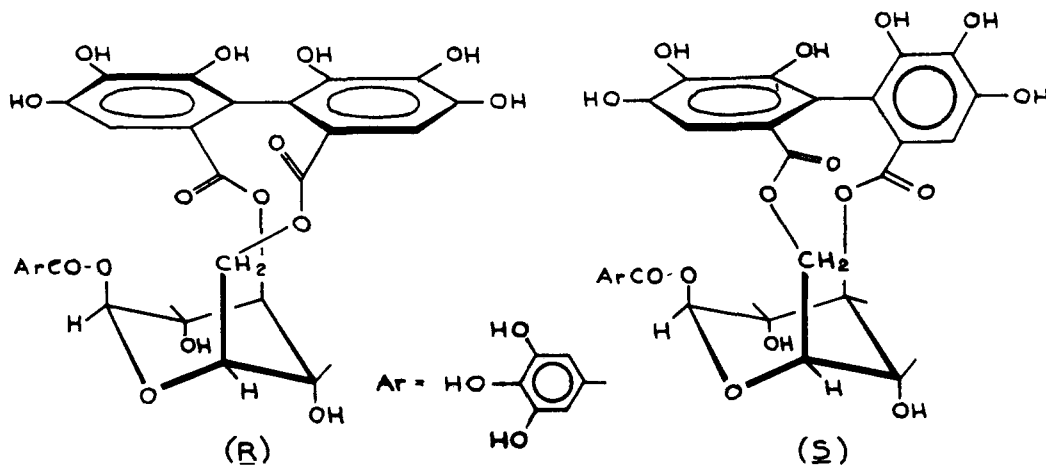


Fig. 22.—Diastereomeric corilagins.

belongs in this category.⁹⁴ Kumler, *et al.*,⁹⁰ recognized that an interaction between the carbonyl and phenyl groups, taking place directly through space, might account for the result. The view is now generally accepted that these and related observations in the β,γ -unsaturated ketones^{95–97} are the result of an interaction between the π -electrons of the benzene ring (or double bond) and the non-bonding p-orbital of the carbonyl oxygen.⁹⁸ This overlapping can take place only when the π - and p_n -electrons have a common component in space; β,γ -unsaturated ketones in which π - and p_n -electrons are orthogonal exhibit normal carbonyl absorptions.^{99,100}

The carbonyl absorption of XXXVI and of the parent compound fully conforms to the preceding picture of a strengthened $n \rightarrow \pi^*$ transition; models show that the p_n -orbital is properly disposed relative to the benzene π -electrons for effective overlapping. The fine structure observed is a reflection of the (much weaker) fine structure of simple aldehydes¹⁰¹ and ketones¹⁰² in non-polar

solvents. The vibrational contour of maxima (or shoulders) near 288, 297, 307 and 317 $m\mu$ in isoöctane is particularly noticeable in the strengthened $n \rightarrow \pi^*$ transition; the same behavior is also exhibited by simple prototypes.^{96,98}

The optically active chromophore in XXXVI (and XXXIX) has thus been fully identified. The unusual amplitude of the 300 $m\mu$ Cotton effect curve arises from the enhancement in rotational strength of the chromophore.¹⁰³ The solvent-dependent fine structure reflects ultraviolet behavior in this respect. The sign of the curve (positive for derivatives of (R)-1,2,3,4-dibenzocyclohepta-1,3-diene-6-one) is a reflection of the handedness (absolute configuration) of twist of the essential β,γ -unsaturated ketone chromophore.^{103,104} This dissymmetric chromophore is the subject of further investigation.¹⁰⁵

A complete O.R.D. curve of XXXVIIIB is shown superimposed on the ultraviolet spectrum in Fig. 23. The two high-amplitude Cotton effects of the same (negative) sign correspond to the strengthened $n \rightarrow \pi^*$ transition of dissymmetric β,γ -unsaturated ketones (λ_0 299 $m\mu$) and to the conjugation band of dissymmetric seven-membered ring biphenyls (λ_0 243 $m\mu$). *In the inherently dissymmetric chromophore represented by this molecule, the sign of each Cotton effect separately reflects the absolute configuration of the biphenyl.* A strong positive background curve is in evidence.

The presence of individually contributing chromophores may also be revealed by algebraic analysis. Thus, the deviation of the O.R.D. curve of dinitroketone XXIV from the pattern followed by the other bridged dinitrobiphenyls (Fig. 2) is the result of the added carbonyl group: the curve of XXIV is closely similar to the curve calculated for an equimolar mixture of dimethyl ketone XXXVIIIB and dinitro alcohol XXV (Fig. 24).

A Note on the Designation of Cotton Effects.

In most instances, both extrema of the Cotton effects are realizable and little doubt attaches to the nature of the responsible transitions. In some

(92) P. D. Bartlett and W. P. Giddings, *J. Am. Chem. Soc.*, **82**, 1240 (1960).

(93) E. Wenkert and T. E. Stevens, *ibid.*, **78**, 2318 (1956); E. Adler, J. Dahlén and G. Westin, *Acta Chem. Scand.*, **14**, 1580 (1960); A. S. Kende and P. MacGregor, *J. Am. Chem. Soc.*, **83**, 4197 (1961).

(94) D. J. Cram and K. C. Dewhirst, *ibid.*, **81**, 5963 (1959).

(95) J. Meinwald, S. L. Emerman, N. C. Yang and G. Büchi, *ibid.*, **77**, 4401 (1955); R. C. Cookson and N. S. Waryiar, *J. Chem. Soc.*, 2302 (1956), and references cited therein; S. L. Emerman and J. Meinwald, *J. Org. Chem.*, **21**, 375 (1956); J. Meinwald and G. A. Wiley, *J. Am. Chem. Soc.*, **79**, 2569 (1957); N. J. Leonard and F. H. Owens, *ibid.*, **80**, 6039 (1958); J. J. Hurst and G. H. Whitham, *Proc. Chem. Soc.*, 160 (1959); *J. Chem. Soc.*, 2864 (1960); G. Büchi and E. M. Burgess, *J. Am. Chem. Soc.*, **82**, 4333 (1960); C. H. DePuy and P. R. Story, *ibid.*, **82**, 627 (1960); H. M. Fales and W. C. Wildman, *ibid.*, **82**, 197 (1960); C. A. Grob and A. Weiss, *Helv. Chim. Acta*, **43**, 1390 (1960).

(96) P. D. Bartlett and B. E. Tate, *J. Am. Chem. Soc.*, **78**, 2473 (1956).

(97) Possibly also in γ,δ -unsaturated ketones (S. F. Marsocci and S. MacKenzie, *ibid.*, **81**, 4513 (1959)).

(98) H. Labhart and G. Wagnière, *Helv. Chim. Acta*, **42**, 2219 (1959).

(99) S. Winstein, L. DeVries and R. Orloski, *J. Am. Chem. Soc.*, **83**, 2020 (1961).

(100) R. C. Cookson, R. R. Hill and J. Hudec, *Chemistry & Industry*, 589 (1961).

(101) C. N. R. Rao, C. K. Goldman and A. Balasubramanian, *Can. J. Chem.*, **38**, 2508 (1960).

(102) G. Förster, R. Skrabal and J. Wagner, *Z. Elektrochem.*, **43**, 290 (1937).

(103) K. Mislow, M. A. W. Glass, A. Moscovitz and C. Djerassi, *J. Am. Chem. Soc.*, **83**, 2771 (1961).

(104) K. Mislow and C. Djerassi, *ibid.*, **82**, 5247 (1960).

(105) A. Moscovitz, K. Mislow, M. A. W. Glass and C. Djerassi, *ibid.*, in press; K. Mislow and J. G. Berger, *ibid.*, in press.

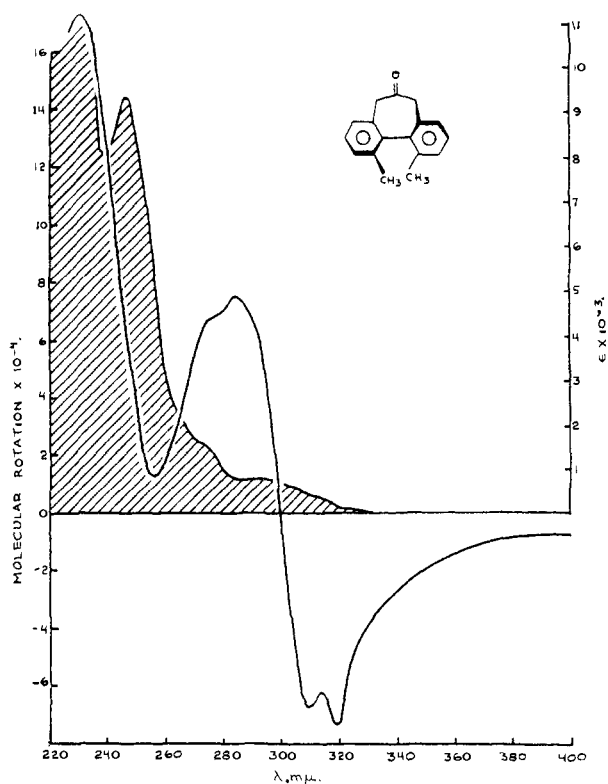


Fig. 23.

of the other cases discussed above, only the first extremum has been observable with present instrumentation. In these cases we have discussed the results on the assumption that the observed maximum or minimum does in fact represent the first extremum of a Cotton effect curve. It must be stressed, however, that quite possibly such observations can also be accommodated by Cotton effect curves overlapped by extremely intense background curves of *opposite* sign whose magnitude is sufficient to wash out the first extremum altogether: what then appears to be the first extremum of a Cotton effect curve is in fact the *second* extremum of a Cotton effect curve of *opposite* sign.

These reservations can be resolved only by further polarimetric penetration into the ultraviolet and by unequivocal identification of the optically active transitions, preferably through circular dichroism measurements.

Experimental Part¹⁰⁶

The following compounds had been previously prepared in these laboratories³⁻⁸ and were thus immediately accessible: I-VI, VIII, X, XI, XIII, XIV, XVI, XIX-XXVI, XXXV, XXXIX-XLI, XLIV-XLVII, XLIX-LI, LXIV, LXV, LXVIII.

We are indebted to the following individuals for making available to us samples of optically active compounds prepared in their laboratories: Prof. D. D. Iffland and Dr. H. Siegel, for XXXVII-XXXIX⁸⁴; Prof. F. Bell, for LXIX⁸⁴; Prof. D. M. Hall, for XXXVII³²; Prof. O. Th. Schmidt, for LIV-LVI and for LIX.¹⁷ Compound LII (LIII), supplied by Prof. V. Prelog, had been prepared¹⁰⁷ from L by

(106) Microanalyses by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. Deuterium analysis by J. Nemeth, Urbana, Ill., by the falling drop method. Spectropolarimetry in part by Mrs. T. Nakano and Mrs. Ruth Records using an automatically recording Rudolph spectropolarimeter.

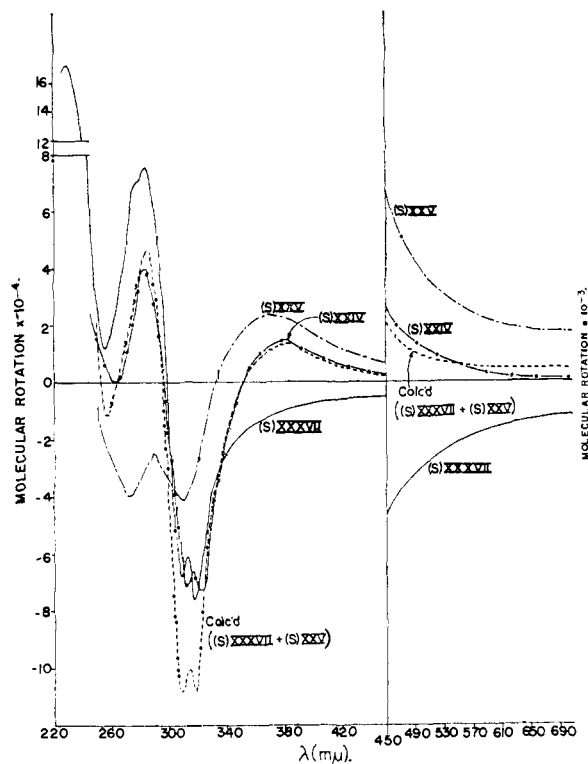


Fig. 24.

N-methylation; the product has m.p. 252.5-256°, $[\alpha]^{20D} -186^\circ$ (benzene), $[\alpha]^{20D} +65^\circ$ (0.1 N HCl).

The remaining compounds listed in Tables I-VII and related compounds which were prepared for the purpose of this study are described in the following sections.

(+)-6,6'-Dibromo-2,2'-dimethylbiphenyl (VII).¹⁰⁸—A solution of 6,6'-dimethyl-2,2'-biphenyldiamine (4.5 g., m.p. 158.5-160.5°, $[\alpha]^{20D} -35.9^\circ$ (N HCl)) in 48% hydrobromic acid (12.6 ml.) was tetrazotized through addition at ice-bath temperatures of sodium nitrite (2.94 g.) in water (5.5 ml.). The cold solution of tetrazonium salt was added in small portions to a boiling suspension of cuprous bromide (3.32 g.) in 48% hydrobromic acid (6.5 ml.). The reaction mixture was steam distilled and the first liter of distillate filtered. The residue (2.0 g., m.p. 79-92°) was purified by chromatography on silica gel (benzene as eluent) and recrystallization from ethanol to give product, m.p. 108.5-110° (lit.¹⁵ m.p. 109-110°), $[\alpha]^{30D} +11.7^\circ$ (c 0.6, ethanol) (lit.¹⁶ $[\alpha]_D -6.2^\circ$, ethanol).

Anal. Calcd. for $C_{14}H_{12}Br_2$: C, 49.44; H, 3.56. Found: C, 49.46; H, 3.71.

(+)-6,6'-Diiodo-2,2'-dimethylbiphenyl (IX).¹⁰⁹—Tetrazotization of 6,6'-dimethyl-2,2'-biphenyldiamine (m.p. 161-162°, $[\alpha]^{20D} +37.1^\circ$ (N HCl)) and conversion to the diiodo compound according to Bell¹⁰⁹ gave product, m.p. 93.5-94.5° (lit.¹⁰⁹ m.p. 84°), $[\alpha]^{82D} +20.8^\circ$ (c 0.6, ethanol) after two recrystallizations from absolute ethanol.

Anal. Calcd. for $C_{14}H_{12}I_2$: C, 38.74; H, 2.79. Found: C, 38.86; H, 3.38.

(+)-6,6'-Dimethyl-2,2'-biphenyldicarboxamide (XII).—A mixture of (-)-6,6'-dimethyl-2,2'-diphenic acid (1.3 g., m.p. 206-212°, $[\alpha]^{20D} -22.5^\circ$ (c 1.0, methanol)), thionyl chloride (15 ml.) and pyridine (0.6 ml.) was heated under reflux for 30 minutes. Solvent was removed under reduced pressure and the remaining solid was leached with boiling carbon tetrachloride. Evaporation of the carbon tetrachloride left 1.3 g. of a cream colored solid, m.p. 59-64°, which was transformed to a white solid on treatment with 7 ml. of cold concd. aq. ammonia. The amide was washed

(107) Unpublished result by Dr. J. H. Rassweiler (private communication).

(108) Kindly prepared by Mr. P. A. Grasemann.

(109) F. Bell, *J. Chem. Soc.*, 835 (1934).

with water and the crude product (1.1 g., m.p. 238–247°) recrystallized from methanol to give solid, m.p. 248–250°, $[\alpha]^{25D} +37^\circ$ (*c* 0.7, dioxane), $[\alpha]^{25D} 0.0^\circ$ (*c* 4.0, *l* 2, methanol), $[\alpha]^{34,366} +144^\circ$ (methanol).

Anal. Calcd. for $C_{16}H_{16}O_2N_2$: C, 71.62; H, 6.01; N, 10.44. Found: C, 71.92; H, 6.09; N, 10.14.

(–)-6,6'-Dimethyl-2,2'-diphenic acid dimethyl ester (XV) was prepared from (–)-6,6'-dimethyl-2,2'-diphenic acid (m.p. 210–211°, $[\alpha]^{25D} -23^\circ$ (*c* 1.8, methanol)) and ethereal diazomethane. The product was eluted from silica gel with 1:1 benzene-chloroform and was obtained as a colorless oil, $[\alpha]^{25D} -46^\circ$ (*c* 1.8, methanol) (lit.⁶¹ $[\alpha]^{25D} +44.0^\circ$ and -31.4° (methanol)). The compound resisted all attempts at crystallization.

(–)-6,6'-Dichloro-2,2'-biphenyldicarboxamide (XVIII) was prepared, as described for the enantiomer,⁶ from (–)-6,6'-dichloro-2,2'-diphenic acid (m.p. 264–265.5°, $[\alpha]^{25D} -4.2^\circ$ (methanol)). After recrystallization from chloroform the product had m.p. 239–239.5°, $[\alpha]^{25D} -79^\circ$ (*c* 0.80, methanol).

Anal. Calcd. for $C_{14}H_{10}Cl_2O_2N_2$: C, 54.38; H, 3.26; N, 9.07; Cl, 22.94. Found: C, 53.97; H, 3.62; N, 9.01; Cl, 22.74.

(+)- and (±)-4',1''-Dimethyl-1,2,3,4-dibenzcyclohepta-1,3-diene-6,6-dicarboxylic Acid Diethyl Ester (XXX).—A solution of (–)-6,6'-dimethyl-2,2'-bis-(bromomethyl)-biphenyl (XVII),¹⁰ 1.0 g., m.p. 53.5–55°, $[\alpha]^{30D} -51.3^\circ$ (*c* 1.0, benzene) in 6 ml. of ether was added to a solution of sodium (0.136 g.) and diethyl malonate (0.47 g.) in 6 ml. of ethanol. The mixture was heated under reflux for 2.5 hours and the resulting suspension was filtered hot. The residual solid was washed with water, dried and recrystallized from ethanol to give 0.85 g. of the desired product, m.p. 130.5–132°, $[\alpha]^{25D} +88^\circ$ (*c* 2.0, benzene).

Anal. Calcd. for $C_{28}H_{26}O_4$: C, 75.38; H, 7.15; mol. wt., 366. Found: C, 75.34; H, 7.36; mol. wt., 346.

The (±)-form, similarly prepared from (±)-6,6'-dimethyl-2,2'-bis-(bromomethyl)-biphenyl (m.p. 68–69°), had m.p. 134.5–136°.

Anal. Calcd. for $C_{28}H_{26}O_4$: C, 75.38; H, 7.15. Found: C, 74.91; H, 7.24.

(+)-4',1''-Dimethyl-2,7-dihydro-3,4,5,6-dibenzoxepin (XXXII) was prepared from (–)-6,6'-dimethyl-2,2'-bis-(hydroxymethyl)-biphenyl (m.p. 119–122°, $[\alpha]^{25D} -31^\circ$ (*c* 2.3, methanol)) according to the procedure of Wittig and Zimmerman.⁶¹ Following elution from neutral alumina (grade III) with 3:5 hexane-benzene and recrystallization from ligroin, the product had m.p. 136–138.5°, $[\alpha]^{25D} +112^\circ$ (*c* 1.9, benzene); lit.⁶¹ m.p. 130–131°, $[\alpha]^{20D} +114^\circ$ (benzene).

(–)-4',1''-Dichloro-1,2,3,4-dibenzcyclohepta-1,3-diene-6,6-dicarboxylic Acid Diethyl Ester (XXXIV).—A solution of (+)-6,6'-dichloro-2,2'-bis-(bromomethyl)-biphenyl (0.95 g., m.p. 69.5–71°, $[\alpha]^{25D} +78^\circ$ (*c* 1.6, benzene)) in 3 ml. of ether was added to a solution of sodium (0.1 g.) and diethyl malonate (0.37 g.) in 6 ml. of ethanol. The mixture was heated under reflux for 2.5 hours and the resulting suspension was filtered hot. The residual solid was washed with water and dried. The crude material (0.65 g., m.p. 160–165°) was recrystallized from ethanol to yield the desired product, m.p. 165–167°, $[\alpha]^{25D} -101^\circ$ (*c* 1.7 benzene).

Anal. Calcd. for $C_{21}H_{20}Cl_2O_4$: C, 61.93; H, 4.95; Cl, 17.41. Found: C, 61.75; H, 5.07; Cl, 17.29.

(–)- and (±)-4',1''-Dimethyl-5-cyano-1,2,3,4-dibenzcyclohepta-1,3-diene-6-imine was prepared from (–)-6,6'-dimethyl-2,2'-bis-(bromomethyl)-biphenyl (XVII) via (–)-6,6'-dimethyl-2,2'-bis-(cyanomethyl)-biphenyl as described² for the enantiomer LXIV. After recrystallization from acetonitrile, the product had m.p. 256–258° dec., $[\alpha]^{25D} -502^\circ$ (*c* 2.2, pyridine), infrared spectrum identical with that of the enantiomer.

Anal. Calcd. for $C_{18}H_{18}N_2$: C, 83.04; H, 6.20; N, 10.76. Found: C, 82.93; H, 6.05; N, 10.49.

The (±)-form, similarly prepared from (±)-6,6'-dimethyl-2,2'-bis-(bromomethyl)-biphenyl, melted at 211–214°.

Anal. Calcd. for $C_{18}H_{18}N_2$: C, 83.04; H, 6.20; N, 10.76. Found: C, 82.93; H, 6.25; N, 10.58.

(±)-4',1''-Dimethyl-5-cyano-1,2,3,4-dibenzcyclohepta-1,3-diene-6-one.—A mixture of (±)-4',1''-dimethyl-5-cyano-1,2,3,4-dibenzcyclohepta-1,3-diene-6-imine (0.43 g.), phosphoric acid (85%, 12 ml.) and purified¹¹ dioxane (36 ml.) was refluxed under nitrogen for 2 hours. The mixture was poured onto ice and the resulting precipitate was dissolved in benzene. The benzene solution was washed with 5% sodium bicarbonate and water, dried and evaporated. The crude product (0.38 g.) was chromatographed on neutral alumina (act. grade III). Elution with 1% ether in benzene resulted in a product, m.p. 126.7–127° after recrystallization from hexane. The infrared spectrum (KBr wafer) featured a band at 1720 cm^{-1} (CO) and a weak split band at 2260 and 2230 cm^{-1} (CN). The ultraviolet spectrum (dioxane) exhibited maxima at 243 $m\mu$ ($\log \epsilon$ 4.12) and 274 $m\mu$ ($\log \epsilon$ 3.62) and shoulders at 300 $m\mu$ ($\log \epsilon$ 3.04) and 312 $m\mu$ ($\log \epsilon$ 2.63).

Anal. Calcd. for $C_{18}H_{16}ON$: C, 82.73; H, 5.79; N, 5.36; mol. wt., 261; neut. equiv., 261. Found: C, 82.73; H, 5.99; N, 5.07; mol. wt., 251; neut. equiv., 263 (toward strong base).

(+)-, (–)- and (±)-4',1''-Dimethyl-1,2,3,4-dibenzcyclohepta-1,3-diene-6-one (XXXVI and XXXVII).—A mixture of (–)-4',1''-dimethyl-5-cyano-1,2,3,4-dibenzcyclohepta-1,3-diene-6-imine (1.3 g.), 35 ml. of 85% phosphoric acid and 35 ml. of glacial acetic acid was heated under reflux for 5 hours. The cooled mixture was poured into 1 l. of ice-cold water and the precipitated beige oil was extracted with benzene. The organic layer was washed with water, 5% sodium bicarbonate and water until neutral to Hydrion paper. After drying (magnesium sulfate) and removal of solvent, the residual light yellow oil was chromatographed on neutral alumina (act. grade III), using 1:4 benzene-hexane as eluent. The combined eluted fractions were evaporated to give 0.58 g. of the desired ketone XXXVI, m.p. 61–63°, $[\alpha]^{25D} +617^\circ$ (*c* 1.65, benzene), $[\alpha]^{25,355} +1882^\circ$ (*c* 1.65, benzene). The product was analytically free of nitrogen. The infrared spectrum featured a carbonyl doublet at 1705 and 1715 cm^{-1} .

Anal. Calcd. for $C_{17}H_{16}O$: C, 86.40; H, 6.83. Found: C, 86.26; H, 6.90.

The (–)-isomer XXXVII was similarly prepared from (+)-4',1''-dimethyl-5-cyano-1,2,3,4-dibenzcyclohepta-1,3-diene-6-imine⁹ (m.p. 253.5–257° dec., $[\alpha]^{25D} +498^\circ$ (*c* 1.3, pyridine)). After recrystallization from ligroin or aqueous methanol the product had m.p. 62.5–63.5°, $[\alpha]^{25D} -628^\circ$ (*c* 1.0, benzene), $[\alpha]^{25,355} -1907^\circ$ (*c* 1.0, benzene), $[\alpha]^{25,365} -5298^\circ$ (*c* 1.0, benzene), $[\alpha]^{25,365} -4940^\circ$ (*c* 1.0, acetone), and was analytically free of nitrogen. The infrared spectrum was identical with that of the (+)-form.

Anal. Calcd. for $C_{17}H_{16}O$: C, 86.40; H, 6.83. Found: C, 86.45; H, 6.88.

The (±)-form, similarly prepared from (±)-4',1''-dimethyl-5-cyano-1,2,3,4-dibenzcyclohepta-1,3-diene-6-imine, melted at 61–63°. A mixture of the (±)- and the (–)-form melted at 50.5–62.5°. The compound was analytically free of nitrogen, phosphorus, active hydrogen and olefinic unsaturation (as tested by catalytic hydrogenation). The infrared spectrum of a 10% chloroform solution (identical in every respect with that of the (–)-form) and of a KBr wafer featured the carbonyl doublet at 1705 and 1715 cm^{-1} .

Anal. Calcd. for $C_{17}H_{16}O$: C, 86.40; H, 6.83; mol. wt., 236. Found: C, 86.24; H, 6.98; mol. wt., 230.

The identical (infrared, mixture m.p.) compound was also obtained upon hydrolysis of (±)-4',1''-dimethyl-5-cyano-1,2,3,4-dibenzcyclohepta-1,3-diene-6-one under the conditions of the hydrolysis of (±)-4',1''-dimethyl-5-cyano-1,2,3,4-dibenzcyclohepta-1,3-diene-6-imine.

(±)-4',1''-Dimethyl-1,2,3,4-dibenzcyclohepta-1,3-diene-6-one-5,7-d₂.—A mixture of (±)-4',1''-dimethyl-1,2,3,4-dibenzcyclohepta-1,3-diene-6-one (1.01 g.), 99.5% deuterium oxide (1.50 g.), anhydrous sodium carbonate (18.0 mg.) and 5.0 ml. of redistilled dioxane was refluxed under nitrogen for 12 hours. The ketone was recovered, dried, and exchanged as described in the foregoing three more times. The final product was purified by chromatography on silica gel (5% acetone-benzene as eluent) and

(110) M. Siegel, Ph.D. dissertation, New York University, 1957.

(111) K. Hess and H. Frahm, *Ber.*, **71**, 2627 (1938).

recrystallization from ligroin to give faintly yellow rosettes, m.p. 59.5–61°, ultraviolet spectrum identical with that of undeterated ketone.

Anal. Calcd. for $C_{17}H_{12}D_4O$: 25.00 at. % excess D [4.00 D/molecule]. Found: 23.33 at. % excess D [3.72 D/molecule].

(-), (+)- and (\pm)-4',1''-Dimethyl-1,2,3,4-dibenzocyclohepta-1,3-diene-6-ol (XXXI).—A solution of (+)-4',1''-dimethyl-1,2,3,4-dibenzocyclohepta-1,3-diene-6-one (XXXVI) (0.49 g.) in 10 ml. of anhyd. ether was added to a solution of 0.07 g. of lithium aluminum hydride in 10 ml. of anhyd. ether. The mixture was heated under reflux for 30 minutes. The product, worked up in the usual manner, was purified by chromatography on neutral alumina (act. grade III) using benzene as eluent. There was thus obtained 0.24 g. of the desired alcohol, m.p. 77–79° after recrystallization from hexane, $[\alpha]^{25}_D -135^\circ$ (c 1.3, benzene), $[\alpha]^{25}_{435} -198^\circ$ (c 1.3, benzene). The infrared spectrum was devoid of carbonyl absorption.

Anal. Calcd. for $C_{17}H_{18}O$: C, 85.67; H, 7.61. Found: C, 85.94; H, 7.48.

The (+)-isomer XXXI was similarly prepared from (-)-4',1''-dimethyl-1,2,3,4-dibenzocyclohepta-1,3-diene-6-one (XXXVII). The product had m.p. 79–81°, $[\alpha]^{27}_D +141^\circ$ (c 1.0, benzene), $[\alpha]^{27}_{435} +209^\circ$ (c 1.0, benzene), $[\alpha]^{27}_{365} +131^\circ$ (c 1.0, benzene), $[\alpha]^{27}_D +24.9^\circ$ (c 0.97, acetone), $[\alpha]^{27}_{435} -30.0^\circ$ (c 0.97, acetone), $[\alpha]^{27}_{365} -240^\circ$ (c 0.97, acetone). The infrared spectrum was identical with that of the enantiomer.

Anal. Calcd. for $C_{17}H_{18}O$: C, 85.67; H, 7.61. Found: C, 85.55; H, 7.53.

The (\pm)-form, similarly prepared from (\pm)-4',1''-dimethyl-1,2,3,4-dibenzocyclohepta-1,3-diene-6-one, melted at 121–122° after recrystallization from cyclohexane. The infrared spectrum of a 10% solution in chloroform was identical with that of the (+)-form.

Anal. Calcd. for $C_{17}H_{18}O$: C, 85.67; H, 7.61; act. H, 0.42; mol. wt., 238. Found: C, 86.15; H, 7.63; act. H, 0.54; mol. wt., 216.

(+)- and (\pm)-4',1''-Dimethyl-1,2,3,4-dibenzocyclohepta-1,3-diene (XXXIII).—A solution of (-)-4',1''-dimethyl-1,2,3,4-dibenzocyclohepta-1,3-diene-6-one (XXXVII, 2.0 g.) in 30 ml. of abs. ethanol was added dropwise to a stirred, refluxing mixture of water (5.0 ml.), ethanol (15.0 ml.), concd. hydrochloric acid (8.0 ml.) and amalgamated zinc (prepared from 9.7 g. of zinc, 5.9 mg. of mercuric chloride and 25 ml. of 5% aq. hydrochloric acid). Heating under reflux was continued for 5 hours while concd. hydrochloric acid (30.0 ml.) and ethanol (40.0 ml.) was added intermittently. After dilution with 100 ml. of water, the aqueous phase was extracted with ether and the ether layer was washed until neutral to Hydrion paper, dried (potassium carbonate) and evaporated to dryness. The residual white solid (1.6 g.) had m.p. 61.5–62.5°; the infrared spectrum exhibited no carbonyl band but had a strong olefin peak at 820 cm^{-1} .

Hydrogenation at 23° over 5% Pd-C in ethanol resulted in the uptake of 2.1 mmoles of hydrogen. The recovered white solid (1.56 g.) had m.p. 61.5–63°. Elution on neutral alumina (grade I) with *n*-hexane afforded a white solid (1.49 g.), m.p. 63–64°, mixture m.p. with (-)-4',1''-dimethyl-1,2,3,4-dibenzocyclohepta-1,3-diene-6-one, 45–51°. Recrystallization from methanol-water gave 1.2 g. of long needles, m.p. 63–64°, $[\alpha]^{23}_D +243^\circ$ (c 2.1, benzene). The infrared spectrum of this product was identical with that of crude prehydrogenation material except for the absence of the peak at 820 cm^{-1} .

Anal. Calcd. for $C_{17}H_{18}$: C, 91.84; H, 8.16; mol. wt., 222. Found: C, 92.05; H, 8.38; mol. wt., 203.

The (\pm)-form, similarly prepared from (\pm)-4',1''-dimethyl-1,2,3,4-dibenzocyclohepta-1,3-diene-6-one, could not be obtained as a solid. Distillation (bath temp. 115–120°, 0.25 mm.) yielded a liquid, n^{25}_D 1.5978, infrared spectrum (chloroform) identical with that of the (+)-form.

Anal. Calcd. for $C_{17}H_{18}$: C, 91.84; H, 8.16; mol. wt., 222. Found: C, 91.83; H, 8.23; mol. wt., 201.

(+)-2',1':1,2;1'',2'':3,4-Dinaphthocyclohepta-1,3-diene-6,6-dicarboxylic Acid Diethyl Ester (XLII).—A solution of (-)-2,2'-bis-(bromomethyl)-1,1'-binaphthyl (1.1 g.), m.p.

183–188°, $[\alpha]^{25}_D -164^\circ$ (c 1.5, benzene) in 3 ml. of ether was added to a solution of sodium (0.11 g.) and of diethyl malonate (0.37 g.) in 9 ml. of ethanol. The mixture was heated under reflux for 2.5 hours and the resulting suspension was filtered hot. The residual solid was washed with water, dried and recrystallized from ethanol to give 0.35 g. of the desired product, m.p. 163–166°, $[\alpha]^{25}_D +314^\circ$ (c 1.2, benzene).

Anal. Calcd. for $C_{29}H_{26}O_4$: C, 79.43; H, 5.98. Found: C, 79.58; H, 6.04.

(\pm)- and (+)-2,7-Dihydro-2',1';3,4;1'',2'':5,6-dinaphthoxepin (XLIII).—A solution of (\pm)-2,2'-bis-(hydroxymethyl)-1,1'-binaphthyl (3.0 g., m.p. 191–192.5°) and *p*-toluenesulfonic acid monohydrate (0.40 g.) in benzene (150 ml.) was heated under reflux for 28 hours. The water produced (0.2 ml.) was continuously collected in a trap. The benzene solution was washed with sodium carbonate and water, dried and evaporated. The residue was chromatographed on neutral alumina (act. grade III) using 1:1 hexane-benzene. Two recrystallizations from 95% ethanol yielded solid, m.p. 188–188.5°; mixture m.p. with starting diol, 166–186°.

Anal. Calcd. for $C_{22}H_{16}O$: C, 89.14; H, 5.45. Found: C, 88.99; H, 5.49.

The (+)-oxepin, similarly prepared from (-)-1,1'-binaphthalene-2,2'-dicarboxylic acid *via* the diol, had m.p. 152–153°, $[\alpha]^{25}_D +687^\circ$ (c 1.4, benzene). The infrared spectrum (chloroform) was identical with that of the (\pm)-form.

Anal. Calcd. for $C_{22}H_{16}O$: C, 89.14; H, 5.45; mol. wt., 296. Found: C, 89.57; H, 5.53; mol. wt., 303.

(-)-1,1'-Binaphthalene-2,2'-dicarboxamide (XLVIII). A mixture of (-)-1,1'-binaphthalene-2,2'-dicarboxylic acid (1.1 g., $[\alpha]^{25}_D -100^\circ$ (0.1 *N* sodium hydroxide), m.p. 140–145°), 10 ml. of thionyl chloride and 0.4 ml. of anhyd. pyridine was heated under reflux for 30 minutes. Solvent was removed by distillation and the residue was leached with carbon tetrachloride to give 1.1 g. of substance, m.p. 170–174°; recrystallization from carbon tetrachloride gave (-)-1,1'-binaphthalene-2,2'-dicarboxylic acid dichloride, m.p. 171.5–172.5°, $[\alpha]^{25}_D -30^\circ$ (c 2.0, *chf.*).

Anal. Calcd. for $C_{22}H_{12}Cl_2O_2$: Cl, 18.70. Found: Cl, 19.12.

The acid chloride (0.9 g.) was stirred with 6 ml. of cold concd. aq. ammonia. The resulting solid was washed with water, dried, leached with hot hexane and again dried to give 0.84 g. of the desired product, m.p. 271–272°, $[\alpha]^{24}_D -228^\circ$ (c 0.85, methanol).

Anal. Calcd. for $C_{22}H_{16}O_2N_2$: C, 77.63; H, 4.74; N, 8.23. Found: C, 77.70; H, 5.00; N, 8.10.

(-)-4,5,6,4',5',6'-Hexakis-(benzyloxy)-2,2'-diphenic acid (LVII) was prepared and resolved according to Schmidt and Demmler.¹⁷ The product had m.p. 147–148°, lit.¹⁷ m.p. 147°; $[\alpha]^{21}_D -63.5^\circ$ (c 2.0, chloroform), $[\alpha]^{21}_D -45^\circ$ (c 1.0, acetone), lit.¹⁷ $[\alpha]^{20}_D -63.6^\circ$ (c 2, *chf.*).

(-)-4,5,6,4',5',6'-Hexakis-(benzyloxy)-2,2'-diphenic acid dimethyl ester (LVIII) was prepared from (-)-4,5,6,4',5',6'-hexakis-(benzyloxy)-2,2'-diphenic acid and diazomethane in the usual manner. The product had m.p. 117.5–118.5°, $[\alpha]^{22}_D -37^\circ$ (c 0.9, *chf.*); lit.¹⁷ m.p. 117.5°, $[\alpha]^{20}_D -33^\circ$ (c 0.9, acetone).

(\pm) and (-)-2,2'-Bis-(hydroxymethyl)-4,5,6,4',5',6'-hexakis-(benzyloxy)-biphenyl (LX).—Lithium aluminum hydride (7.69 g.) was added to a stirred solution of (\pm)-4,5,6,4',5',6'-hexakis-(benzyloxy)-2,2'-diphenic acid¹⁶ (40.0 g.) in anhydrous ether (2.1 l.). The reaction mixture was heated under reflux for 1 hour, benzene (250 ml.) was added, and the products were decomposed by the addition of water and 10% sulfuric acid. The organic phase was separated and the aqueous phase was extracted with benzene. The combined organic layers were washed successively with water, 0.05% potassium hydroxide (no ppt. on acidification) and water. The solvent was evaporated and the residual sirup (33 g., 85%) was induced to crystallize by scratching under hexane. Recrystallization from methylcyclohexane yielded the desired product, m.p. 99–101°. The infrared spectrum (5% in carbon tetrachloride) showed no carbonyl absorption.

Anal. Calcd. for $C_{46}H_{50}O_8$: C, 79.04; H, 5.92; act. H, 0.236. Found: C, 79.49; H, 5.92; act. H, 0.22.

Similar reduction of (-)-4,5,6,4',5',6'-hexakis-(benzyloxy)-2,2'-diphenic acid yielded a sirup which resisted all attempts at crystallization. The analytical sample was prepared by chromatography on acid-washed alumina (Merck), using 2:1 benzene-ether as eluent, and had $[\alpha]_D^{25} -60.2^\circ$ (*c* 3.2, benzene). The infrared spectrum was identical with that of the (\pm)-form.

Anal. Calcd. for $C_{56}H_{50}O_8$: C, 79.04; H, 5.92; act. H, 0.235. Found: C, 78.97; H, 5.83; act. H, 0.22.

(\pm)- and (-)-2,2'-Bis-(bromomethyl)-4,5,6,4',5',6'-hexakis-(benzyloxy)-biphenyl (LXI).—Phosphorus tribromide (8.5 ml.) was added dropwise to a stirred solution of (\pm)-2,2'-bis-(hydroxymethyl)-4,5,6,4',5',6'-hexakis-(benzyloxy)-biphenyl (21.6 g.) in dry benzene (750 ml.) at room temperature. Stirring was continued at room temperature for 20 minutes and at $55 \pm 5^\circ$ for an additional 20 minutes. The reaction mixture was then cooled in an ice-bath, and rapidly washed three times with ice-cold saturated sodium chloride solution. The last wash was neutral to Hydrion paper. The organic phase was dried over sodium sulfate, concentrated to 200 ml. and eluted through acid-washed alumina (Merck) with benzene. Removal of the benzene left 22.5 g. (90%) of crude product, most of which crystallized spontaneously. It was found possible by slow cooling of a benzene-hexane solution of the dibromide to grow hexagonal prisms 15 mm. on the side which had m.p. 91–92°. Recrystallization from this solvent pair did not raise the melting point.

Anal. Calcd. for $C_{58}H_{48}Br_2O_6$: C, 68.85; H, 4.95; Br, 16.36. Found: C, 69.24; H, 5.02; Br, 16.68.

The (-)-isomer, similarly prepared from (-)-2,2'-bis-(hydroxymethyl)-4,5,6,4',5',6'-hexakis-(benzyloxy)-biphenyl, had m.p. 79.5–80.5°, $[\alpha]_D^{25} -19.3^\circ$ (*c* 2.1, benzene) after two recrystallizations from hexane. The infrared spectrum (5% in carbon tetrachloride) was identical with that of the (\pm)-form.

Anal. Calcd. for $C_{58}H_{48}Br_2O_6$: C, 68.85; H, 4.95; Br, 16.36. Found: C, 69.18; H, 4.58; Br, 16.21.

(\pm)-2,2'-Bis-(methoxymethyl)-4,5,6,4',5',6'-hexakis-(benzyloxy)-biphenyl.—Several recrystallizations of (\pm)-2,2'-bis-(bromomethyl)-4,5,6,4',5',6'-hexakis-(benzyloxy)-biphenyl from methanol gave a product which had a constant m.p. 87.6–89.1°. It was analytically free of bromine. The ultraviolet spectrum (dioxane) exhibited shoulders at 259 ($\log \epsilon$ 3.88), 264 ($\log \epsilon$ 3.74), 269 ($\log \epsilon$ 3.62) and 283 m μ ($\log \epsilon$ 3.46).

Anal. Calcd. for $C_{58}H_{54}O_8$: C, 79.25; H, 6.19. Found: C, 79.53; H, 6.20.

(\pm)- and (+)-2',3',4',1'',2'',3''-Hexakis-(benzyloxy)-2,7-dihydro-3,4,5,6-dibenzoxepin (LXVII).—A solution of crude (\pm)-2,2'-bis-(bromomethyl)-4,5,6,4',5',6'-hexakis-(benzyloxy)-biphenyl (prepared from (\pm)-2,2'-bis-(hydroxymethyl)-4,5,6,4',5',6'-hexakis-(benzyloxy)-biphenyl as described above) in benzene-hexane was seeded with pure dibromide. After separation of the resulting crop of pure dibromide, the filtrate was concentrated and cooled. A second crop of white crystals deposited, m.p. 116.5–117°. The material was analytically free of bromine.

Anal. Calcd. for $C_{56}H_{48}O_7$: C, 80.75; H, 5.81. Found: C, 80.73; H, 5.73.

The (+)-isomer was obtained from the tail fractions of the chromatography of crude (-)-2,2'-bis-(bromomethyl)-4,5,6,4',5',6'-hexakis-(benzyloxy)-biphenyl on alumina. The product was a sirup which could not be induced to crystallize; $[\alpha]_D^{25} +65^\circ$ (*c* 2.0, benzene). The infrared spectrum (5% in carbon tetrachloride) was identical with that of the (\pm)-form. The substance was analytically free of bromine.

Anal. Calcd. for $C_{56}H_{48}O_7$: C, 80.75; H, 5.81. Found: C, 80.23; H, 5.81.

(\pm)- and (-)-2',3',4',1'',2'',3''-Hexakis-(benzyloxy)-5-cyano-1,2,3,4-dibenzocyclohepta-1,3-diene-6-imine (LXII). A solution of (\pm)-2,2'-bis-(bromomethyl)-4,5,6,4',5',6'-hexakis-(benzyloxy)-biphenyl (22.5 g.) and sodium cyanide (4.5 g.) in 300 ml. of anhydrous dimethylformamide was kept at 60° for 3 hours under a nitrogen atmosphere. The cooled solution was poured into saturated sodium chloride and the resulting mixture was extracted with benzene. The washed combined benzene layers were evaporated and the residue was extracted into 1.7 l. of abs. ethanol (a

small amount of brown gum remains). After addition of a solution of 0.64 g. of sodium in 16.2 ml. of ethanol, the combined ethanolic extracts were refluxed for 3 hours, concentrated to 250 ml. and filtered from the precipitated solid. The residue was washed with water and recrystallized from 1:1 benzene-hexane to yield 7.0 g. of product, m.p. 184.8–186.4°. The infrared spectrum exhibited bands at 2150 and 2270 cm^{-1} ($\text{C}\equiv\text{N}$), 1610 cm^{-1} ($\text{C}=\text{N}$) and near 3300 cm^{-1} ($\text{N}-\text{H}$).

Anal. Calcd. for $C_{58}H_{48}O_6N_2$: C, 80.16; H, 5.57; N, 3.22. Found: C, 79.80; H, 5.42; N, 2.76.

The (-)-isomer, similarly prepared from (-)-dibromide, had m.p. 191.6–192.2°, $[\alpha]_D^{25} -110^\circ$ (*c* 0.85, C_6H_6), $[\alpha]_D^{25} -84^\circ$ (*c* 1.6, pyridine), infrared spectrum identical with that of the racemic modification.

Anal. Calcd. for $C_{58}H_{48}O_6N_2$: C, 80.16; H, 5.57; N, 3.22. Found: C, 80.37; H, 5.41; N, 3.72.

(\pm)- and (+)-2',3',4',1'',2'',3''-Hexakis-(benzyloxy)-5-cyano-1,2,3,4-dibenzocyclohepta-1,3-diene-6-one (LXIII).—A mixture of (\pm)-2',3',4',1'',2'',3''-hexakis-(benzyloxy)-5-cyano-1,2,3,4-dibenzocyclohepta-1,3-diene-6-imine (2.1 g.), purified dioxane¹¹¹ (52 ml.) and phosphoric acid (85%, 17 ml.) was heated under reflux in a nitrogen atmosphere for 2 hours. The cooled solution was poured into water and the precipitated solid was recrystallized from benzene-hexane to give 1.9 g. of product, m.p. 134.3–135.4°. The infrared spectrum (10% solution in chloroform) showed the expected carbonyl peak at 1720 cm^{-1} , but the nitrile peaks were apparent only as a weak doublet (2260 and 2220 cm^{-1}) at a concentration of 10% in KBr.

Anal. Calcd. for $C_{58}H_{47}O_7N$: C, 80.07; H, 5.45; N, 1.61. Found: C, 80.05; H, 5.46; N, 1.77.

The (+)-isomer, similarly obtained from (-)-iminonitrile, had m.p. 115.5–116.5° after recrystallization from cyclohexane, ethyl acetate-hexane or benzene-hexane, $[\alpha]_D^{25} +329^\circ$ (*c* 1.3, benzene), infrared spectrum (chloroform) identical with that of the racemic modification.

Anal. Calcd. for $C_{58}H_{47}O_7N$: C, 80.07; H, 5.45; N, 1.61; act. H, 0.12; mol. wt., 870; neut. equiv., 870. Found: C, 80.08; H, 5.56; N, 1.95; act. H, 0.16; mol. wt., 858; neut. equiv., 874.¹¹²

The rotation of this compound in 86 wt. % ethanol-water was $[\alpha]_D^{25} +29^\circ$ (*c* 0.4). In the presence of one equivalent of 0.01 *N* sodium hydroxide in 86 wt. % ethanol the rotation was $[\alpha]_D^{25} -62^\circ$ (*c* 0.6), unchanged on standing at room temperature.

(\pm)- and (+)-2',3',4',1'',2'',3''-Hexakis-(benzyloxy)-5-cyano-1,2,3,4-dibenzocyclohepta-1,3-diene-6-ol (LXVI).—A mixture of (\pm)-2',3',4',1'',2'',3''-hexakis-(benzyloxy)-5-cyano-1,2,3,4-dibenzocyclohepta-1,3-diene-6-one (0.37 g.), aluminum *t*-butoxide (0.33 g.) and purified¹¹¹ dioxane (9 ml.) was heated under reflux in a nitrogen atmosphere for 1.5 hours. The cooled solution was decomposed with 2 *N* hydrochloric acid. The product was extracted with benzene and purified by chromatography on silica gel using 1:4 ether-benzene as eluent. There was thus obtained 0.33 g. of solid, m.p. 154–155° after two recrystallizations from cyclohexane, infrared spectrum free of carbonyl absorption.

Anal. Calcd. for $C_{58}H_{49}O_7N$: C, 79.88; H, 5.66; N, 1.61; act. H, 0.11. Found: C, 79.91; H, 5.79; N, 1.78; act. H, 0.13.

The (+)-isomer, similarly prepared from (+)-ketonitrile, had m.p. 153.5–155° after recrystallization from cyclohexane, $[\alpha]_D^{25} +109^\circ$ (*c* 1.7, benzene), infrared spectrum (chloroform) identical with that of the racemic modification.

Anal. Calcd. for $C_{58}H_{49}O_7N$: C, 79.88; H, 5.66; N, 1.61; act. H, 0.11. Found: C, 80.07; H, 5.90; N, 1.88; act. H, 0.11.

(\pm)-4',1''-Dimethyl-1,2,3,4-dibenzocyclohepta-1,3-diene-6-carboxylic Acid.—A mixture of (\pm)-4',1''-dimethyl-1,2,3,4-dibenzocyclohepta-1,3-diene-6,6-dicarboxylic acid diethyl ester (5.0 g.), potassium hydroxide (10 g.) and 250 ml. of 95% ethanol was heated under reflux for 2.5 hours. The solution was worked up as usual to yield 4.0 g. of a white solid, m.p. 152–156° dec. The solid was heated for 0.5 hour in a bath at 195° (temperature of melt 170°). At that time foaming had completely subsided. Recrystallization of the residue from aqueous ethanol yielded solid,

(112) Titration with 0.01 *N* NaOH in 86 wt. % ethanol.

m.p. 155.5–156.5°; $\lambda_{\text{max}}^{\text{EIOH}}$ 242 (log ϵ 4.05), 270 (log ϵ 3.02), 280 $m\mu$ (log ϵ 2.72).

Anal. Calcd. for $C_{12}H_{16}O_2$: C, 81.17; H, 6.81; neut. equiv., 266. Found: C, 81.10; H, 7.03; neut. equiv., 267.

1,2,3,4-Dibenzcyclohepta-1,3-diene-5-one.—A sample¹¹³ (44.3 mg.) was purified by chromatography on neutral alumina (grade I). Elution with 1:1 ether–benzene gave a colorless, crystalline solid, m.p. 86–87° (lit. m.p. 85–86°,¹¹⁴ 85–86°,⁸⁵ yellow prisms); $\lambda_{\text{max}}^{\text{isoctane}}$ 255.5 (log ϵ 4.03), 283 (log ϵ 3.30), 295 $m\mu$ (log ϵ 3.32).

1,2,3,4-Dibenzcyclohepta-1,3-diene-6-one was prepared by hydrolysis¹¹⁵ of 5-cyano-1,2,3,4-dibenzcyclohepta-1,3-diene-6-imine¹¹⁶ (m.p. 191.5–193°) as described for the 4',1''-

(113) Kindly provided by Prof. H. Rapoport.

(114) H. Rapoport and A. R. Williams, *J. Am. Chem. Soc.*, **71**, 1774 (1949).

(115) T. Sakan and M. Nakagazi, *J. Inst. Polytech., Osaka City Univ.*, **1**, No. 2, 23 (1950); *C. A.*, **46**, 5036 (1952).

dimethyl derivative. The product, purified by elution with 1:1 hexane–benzene on neutral alumina (grade III) and recrystallization from aq. methanol, had m.p. 78–79.5°; lit. m.p. 78–79°.¹¹⁶ 78–79.8°.⁸⁵

1,3-Diphenyl-2-propanone (Eastman Kodak Co.) was recrystallized three times from chloroform–ligroin to constant m.p. 34.5–35.5°, lit.⁸⁰ m.p. 36–37°.

2-Benznorbornenone was freshly prepared by Oppenauer oxidation of *endo*-benznorbornenol¹¹⁷ as described⁹² for the *exo* isomer. The product was purified by elution with 30% benzene–ether on neutral alumina (grade I) followed by distillation (bath temp. 40–60°, 0.02 mm.). The infrared spectrum was identical in all respects with that reported⁹² for the ketone.

Anal. Calcd. for $C_{11}H_{16}O$: C, 83.51; H, 6.37. Found: C, 83.75. H, 6.76.

(116) J. Kenner and E. G. Turner, *J. Chem. Soc.*, 2101 (1911).

(117) Kindly provided by Prof. P. D. Bartlett.

[CONTRIBUTION FROM THE RICHARD B. WETHERILL LABORATORY OF PURDUE UNIVERSITY, LAFAYETTE, IND.]

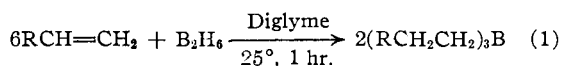
Hydroboration. XIV. Rates and Stoichiometry of the Hydroboration of Some Representative Hindered Olefins

BY HERBERT C. BROWN AND A. W. MOERIKOFER¹

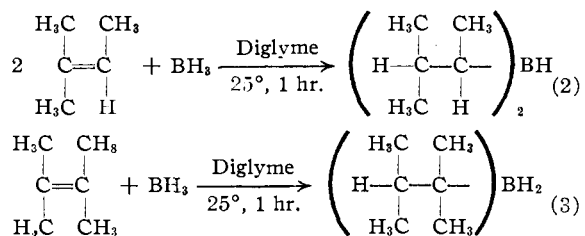
RECEIVED SEPTEMBER 5, 1961

A quantitative study was made of the rates and stoichiometry of the hydroboration of a number of representative hindered olefins in order to establish convenient procedures for the synthesis of mono- and dialkylboranes. Among the trisubstituted aliphatic olefins, 2-methyl-2-butene reacts readily at 0° to form bis-3-methyl-2-butylborane (disiamylborane), whereas the reaction of 2,4,4-trimethyl-2-pentene may be controlled to produce a monoalkyl derivative, 2,4,4-trimethyl-3-pentylborane. Similarly, the reaction of the tetrasubstituted olefin, 2,3-dimethyl-2-butene may be controlled to yield the related derivative, 2,3-dimethyl-2-butylborane (thexylborane). In the case of the simple cyclic olefins, the reaction of cyclopentene is not readily controlled short of the tricyclopentyl stage. However, cyclohexene is readily converted into dicyclohexylborane. 1-Methylcyclopentene, 1-methylcyclohexene and α -pinene, all trisubstituted olefins, are readily converted into the corresponding dialkylboranes, although diisopinocampheylborane (from α -pinene) exhibits some tendency toward a reversible dissociation. Finally, the possible synthesis of the corresponding dialkylboranes from 2-methyl-1-propene, 2-methyl-1-butene, 2,4,4-trimethyl-1-pentene and β -pinene was explored. Addition of the olefins to a solution of the theoretical quantity of diborane in tetrahydrofuran at 0° give yields of 60–70% of the desired dialkylboranes, 10% of free borane and 20% of the corresponding trialkylborane. Consequently, this investigation has opened up convenient synthetic procedures for the synthesis of a number of mono- and dialkylboranes of interest as selective hydroborating and reducing agents.

In our initial exploration of the scope of the hydroboration reaction, we observed that the great majority of olefins reacted readily under the standard conditions, 1 hr. at 25°, to yield the corresponding trialkylborane (1).² However, in the



case of certain highly substituted olefins, such as 2-methyl-2-butene and 2,3-dimethyl-2-butene, the reaction appeared to stop short of this stage, yielding the corresponding dialkylborane (2) and monoalkylborane (3).



(1) Post-doctorate research associate, 1960–1961, on a Research Award (585-C) provided by the Petroleum Research Fund of the American Chemical Society.

(2) H. C. Brown and B. C. Subba Rao, *J. Am. Chem. Soc.*, **81**, 6428 (1959).

Since that time the product from 2-methyl-2-butene, bis-3-methyl-2-butylborane or disiamylborane,^{3,4} has proven of major value as a selective hydroborating^{5–7} and reducing agent.⁸ Similarly, the trimethylamine addition compound of *t*-butylborane has been utilized as a hydroborating agent.⁹ Consequently, it appeared desirable to explore in more detail the reaction of a number of representative hindered olefins with diborane in the hope of defining conditions which would permit the convenient synthesis of monoalkyl- and dialkylboranes.

Results and Discussion

The olefins included in this study, grouped according to structural type, are listed below.

(3) It is convenient to discuss these compounds as derivatives of borane, BH_3 , even though both borane and these alkyl derivatives normally exist as dimers.⁴ Similarly, it is convenient to discuss the reactions in terms of the molecules of olefin reacting under the indicated conditions with each borane (BH_3) or borane equivalent ($3/4NaBH_4 + BF_3$).

(4) H. C. Brown and G. J. Klender, *Inorg. Chem.*, **1**, in press (1962).

(5) H. C. Brown and G. Zweifel, *J. Am. Chem. Soc.*, **83**, 1241 (1961).

(6) H. C. Brown and G. Zweifel, *ibid.*, **83**, 2544 (1961); G. Zweifel, K. Nagase and H. C. Brown, *ibid.*, **84**, 190 (1962).

(7) H. C. Brown and A. Moerikof, *ibid.*, **83**, 3417 (1961).

(8) H. C. Brown and D. B. Bigley, *ibid.*, **83**, 486 (1961).

(9) M. F. Hawthorne, *ibid.*, **83**, 2541 (1961).