

Optically Active 8,8'-Disubstituted 1,1'-Binaphthyls: Electronic Absorption Spectra and Cotton Effects: Assignment of Absolute Configuration

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Determination of the absolute configuration of 1,1'-binaphthyls by the use of Cotton effects associated with the short wave band of the electronic absorption spectra is discussed and applied to examples with substituents in the 8- and 8'-positions. Racemisation parameters are determined for 1,1'-binaphthyl-8,8'-diacetic acid in 0.1N-aqueous sodium hydroxide solution.

THE 1,1'-binaphthyl system was cited by Mislow and his co-workers in 1962¹ as an example of an inherently dissymmetric chromophore:² the relationship between the u.v. absorption spectra, o.r.d. spectra, and c.d. of some of its 2,2'-disubstituted derivatives was discussed³ and the generalisation proposed that a positive Cotton effect centred near 285 nm in this series corresponds with the *R*-configuration. Recently this study has been extended to 1,1'-binaphthyl itself,⁴ observations being made over a larger range of wave-length than was previously available: the Mislow generalisation is affirmed in the parent compound, there being a small negative Cotton effect in the 285 nm region in the *S*-(+)-enantiomer. However, a pair of Cotton effects of opposite signs and of high rotational strengths which appear in the short wave region, would, if common to the series, provide a more useful criterion for assigning chirality to the binaphthyl skeleton: the present work examines this possibility with particular respect to some 8,8'-disubstituted 1,1'-binaphthyls of previously unassigned absolute configuration.

Table 1 lists the main features of the u.v. absorption spectra in 96% ethanol of some 8,8'-disubstituted, 8-substituted, and 2,2'-disubstituted 1,1'-binaphthyls.

† D.M.S. is an abbreviation of 'Documentation of Molecular Spectra, U.V. Atlas of Organic Compounds,' Butterworths, London, 1966, *et seq.*

¹ K. Mislow, M. A. W. Glass, R. E. O'Brien, P. Rutkin, D. H. Steinberg, J. Weiss, and C. Djerassi, *J. Amer. Chem. Soc.*, 1962, **84**, 1456.

² A. Moscovitz, *Tetrahedron*, 1971, **13**, 48; see also C. Djerassi, 'Optical Rotatory Dispersion,' McGraw-Hill, New York, 1960, ch. 12.

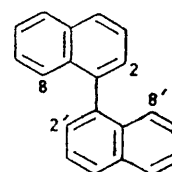
³ K. Mislow, E. Bunnenberg, R. Records, K. Wellman, and C. Djerassi, *J. Amer. Chem. Soc.*, 1963, **85**, 1342.

⁴ P. A. Browne, M. M. Harris, R. Z. Mazengo, and S. Singh, *J. Chem. Soc. (C)*, 1971, 3990.

⁵ D. M. Hall, *Progr. Stereochem.*, 1969, **4**, 1.

⁶ Y. Badar, A. S. Cooke, and M. M. Harris, *J. Chem. Soc.*, 1965, 1412.

The principles governing the position and intensity of bands in u.v. spectra of hindered biaryls have recently been reviewed.⁵



	8	8'	2	2'
(I) ⁴	H	H	H	H
(II) ⁶	Me	Me	H	H
(III) ⁷	CO ₂ H	CO ₂ H	H	H
(IV) ^{7,12}	CO ₂ Me	CO ₂ Me	H	H
(V) ⁶	CH ₂ OH	CH ₂ OH	H	H
(VI) ⁶	CH ₂ Br	CH ₂ Br	H	H
(VII)	CH ₂ CN	CH ₂ CN	H	H
(VIII)	CH ₂ CO ₂ H	CH ₂ CO ₂ H	H	H
(IX)	CH ₂ CO ₂ Et	CH ₂ CO ₂ Et	H	H
(X)	CH ₂ C ₆ H ₅ [†] N ⁻	CH ₂ C ₆ H ₅ [†] N ⁻	H	H
(XI) ⁸	Me	CO ₂ H	H	H
(XII) ⁹	Me	H	H	H
(XIII) ⁷	CO ₂ H	H	H	H
(XIV) ^{10,11}	H	H	Me	Me
(XV) ^{13,14}	H	H	CO ₂ H	CO ₂ H
(XVI) ^{13,14}	H	H	CH ₂ OH	CH ₂ OH

The u.v. spectrum of 9,10-dihydro-3,4:5,6-dibenzo-phenanthrene has been recorded,^{14,15} † and a comparison

⁷ A. S. Cooke and M. M. Harris, *J. Chem. Soc.*, 1963, 2365 and references therein.

⁸ M. M. Harris, R. Z. Mazengo, and A. S. Cooke, *J. Chem. Soc. (C)*, 1967, 2575.

⁹ A. S. Cooke and M. M. Harris, *J. Chem. Soc. (C)*, 1967, 988.

¹⁰ D. D. Fitts, M. Siegel, and K. Mislow, *J. Amer. Chem. Soc.*, 1958, **80**, 480.

¹¹ W. Dixon, M. M. Harris, and R. Z. Mazengo, *J. Chem. Soc. (B)*, 1971, 775.

¹² D. M. Hall, S. Ridgwell, and E. E. Turner, *J. Chem. Soc.*, 1954, 2498.

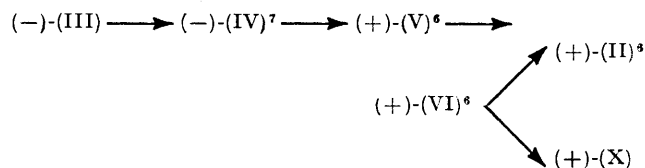
¹³ D. M. Hall and E. E. Turner, *Chem. and Ind.*, 1953, 1177 and references therein.

¹⁴ D. M. Hall and E. E. Turner, *J. Chem. Soc.*, 1955, 1242.

¹⁵ D. M. Hall and R. Z. Mazengo, D.M.S., E1/47.

between the spectra of this compound and 1,1'-binaphthyl is interesting. The former compound shows three distinct major bands [220 (ϵ 121,000), 229.9 (31,000), 239.5 (42,000), 273.5 (2700), 279.5 (3300), 320 (11,000), 334.5 (13,000), and 347 nm (13,400)] the one at 239.5 nm being attributed to conjugation between the naphthalene rings (dihedral angle *ca.* 20°). Such a band occurs in the spectrum of the relatively unhindered 2,2'-binaphthyl,¹⁶ but is missing from that of 1,1'-binaphthyl. All the substituted 1,1'-binaphthyls in Table I lack this band, except for the 8,8'-dicarboxylic acid (III) and its ester (IV). Complications arise in (III) and (IV) which are not yet elucidated in detail: naphthalene and 1-methylnaphthalene have λ_{\max} 221 (hexane) and 224 nm (ethanol) respectively, while the corresponding 1,1'-binaphthyls (I) and (II) absorb at

The absolute configuration of (+)-(I) is already established as *S*;¹⁸ (+)-(XIV) is *S*;^{3,10,19} (-)-(XV) is *S*,^{1,3,10} and (+)-(XVI) is *R*.^{1,3} Among the 8,8'-disubstituted compounds, the following are linked to the optically active precursor (-)-(III) by chemical reactions which do not involve the chiral axis and hence they are all of the same chirality (Scheme).



Enantiomers of (VIII) were prepared by optical resolution of the (\pm)-compound: esterification gave

TABLE I

U.v. absorption spectra^a (λ /nm; ϵ /l mol⁻¹ cm⁻¹)

Compound	Short wave band				Long wave band									
	λ_{\max}	ϵ_{\max}	λ_{\min}	ϵ_{\min}	λ	ϵ	λ	ϵ	λ	ϵ	λ	ϵ	λ	ϵ
(I) <i>b</i>	220	101,000	249	4760	262inf	6210	272inf	9900	283	13,400	293	13,000	313sh	2950
(II)	221.5	85,000	256	5600	280sh	11,000	290	14,000	300	13,000				
(III) <i>c, f</i>	219.5	60,000	267.5	4800	309	13,800	332	9400						
(IV)	239.5	44,000												
	219.5	65,000	266.5	5700	305	13,000	320sh	9400						
	255sh	47,000												
(V) <i>d</i>	223.5	80,000	258	5800	279inf	10,000	291	13,000	300	12,600	322.5inf	5000		
(VI)	224.5	76,000	258.5	5800	280inf	10,000	290	13,000	300	12,000	322.5	4900		
(VII)	224.5	54,800	265	5000	280inf	7890	302	12,370						
(VIII)	222.5	83,100	257	5500	269	7300	279	10,000	290	12,700	301	12,000	324	1430
(IX)	223	87,300	257	5550	267	7300	277	9900	290	13,100	301	12,100	324	2200
(X)	221.5	139,400	274	11,200	285	12,560	293	13,400						
(XI)	225.5	70,000	264.5	5500	303	11,000	330sh	6900						
(XII)	221	90,000	253.5	5000	287.5	13,000	296	13,000						
(XIII)	221.5	69,000	261.5	4800	296	11,000	325sh	5800						
(XIV) <i>e</i>	225.5	140,000	248	4400	265inf	8200	275inf	11,000	285	13,000	292	12,000	307.5	3000
													314	2000
(XV) <i>c, f</i>	230	69,000	263.5	7200	275sh	9400	285.5	12,000	297sh	9200				
(XVI) <i>e</i>	225	135,000	250	5100	260inf	8500	275sh	11,600	284	14,000	292	12,200	305.5	2900

^a Solvent 96% ethanol. ^b M. M. Harris and R. Z. Mazengo D.M.S. E1/44; see also ref. 16. ^c Ref. 12 and D.M.S. E1/46. ^d M. M. Harris and R. Z. Mazengo D.M.S. E1/14. ^e Ref. 1 previously determined in dioxan. ^f While we were engaged in this work Professor S. F. Mason kindly allowed us to see his unpublished spectra for these two compounds: our results are in substantial agreement.

220 and 221.5 nm (both in ethanol): 1-naphthoic acid has λ_{\max} 224 nm (methanol) but the corresponding 1,1'-binaphthyl (III) has peaks at 219 and 239.5 nm in this region. The simple additivity which would be expected to follow from largely inhibited conjugation between the naphthalene rings¹⁶ is shown in (I) and (II) but is modified in (III).

Absence of a distinct conjugation band suggests that the dihedral angle between the main planes of the two naphthalene nuclei is $>60^\circ$,⁵ and indeed, models indicate that the bulky substituents in many of the compounds keep the planes at even higher mutual angles. However, Lefèvre¹⁷ and his co-workers have calculated the dihedral angle in 1,1'-binaphthyl itself, in solution, from molecular Kerr constants, and obtained a result of 48°. At this angle a weak conjugation band would be expected: if it exists it must be masked by the strong short wave band at λ_{\max} 220 nm; this conclusion could apply to some of the other substances in Table I.

¹⁶ R. A. Friedel, M. Orchin, and L. Reggel, *J. Amer. Chem. Soc.*, 1948, **70**, 199.

¹⁷ R. J. W. Lefèvre, A. Sundaram, and K. M. S. Sundaram, *J. Chem. Soc.*, 1963, 3180.

enantiomers (IX). Details of o.r.d. spectra in 96% ethanol for compounds (II)–(VI), (VIII), (X), and (XIV), and of c.d. data in 95% ethanol for compounds (II), (III), (VI), (VIII), (X), and (XIV) are given in the Experimental section.

In Table 2 are shown the wave-lengths at which the negative and positive extrema of the observed c.d. occur, in the region of the short wave band of the u.v. spectrum: data for five optically active 8,8'-disubstituted 1,1'-binaphthyls are given, together with those for (+)-1,1'-binaphthyl and (+)-2,2'-dimethyl-1,1'-binaphthyl as standards of comparison.

The patterns of the spectra of compounds (+)-(I), (+)-(II), (+)-(VIII), (+)-(X), and (+)-(XIV) are closely similar, the negative and positive c.d. bands correspond in sign and $[\theta] = 0$ at a wave-length equal or near to λ_{\max} of the u.v. spectrum: it seems reasonable therefore to assign the *S*-configuration to (+)-(II), (+)-(VIII), and (+)-(X). Compounds (III) and (VI) are

¹⁸ H. Akimoto, T. Shioiri, Y. Iitaka, and S. Yamada, *Tetrahedron Letters*, 1968, 97.

¹⁹ S. Yamada and H. Akimoto, *Tetrahedron Letters*, 1968, 3967.

less straightforward; in (–)-(III) the change of sign of the c.d. corresponds with neither of the u.v. maxima, and in (+)-(VI) also there is a marked difference. In addition to the unspecified factors which introduce complexity into the u.v. spectrum of (III), both (III) and (VI) may have contributions to their c.d. spectra from chiral bands of low rotational strength which arise because of the rotation of the CO₂H and CH₂Br groups is restricted. However, as (–)-(III) and (+)-(VI) must have the same configuration as (+)-(II), it is probable that the major bands considered do arise from similar structural features and in spite of minor modifications are characteristic of the *S*-configuration. All the compounds in Table 2

parameters and transition state theory functions for its racemisation calculated. The results are given in Table 3, with selected examples for comparison: the CH₂CO₂[–] group is apparently the bulkiest in the list, the nearest to it in effective blocking size being CH₂OH. However, the order of the free energies of activation for racemisation is substantially modified by entropy factors which suggest that the two acids are solvated.

Fragmentation of (VIII) under electron impact as revealed in the mass spectrum is clearly interesting but not easy to interpret unless divergent pathways are assumed. The carboxy-groups are sufficiently stable for the molecular ion to appear: C₂₀H₁₂ probably represents

TABLE 2

Correlation of configuration through c.d. (λ/nm; [θ] in parentheses) in the short wave (λ 214–240 nm) region

Compound	(I)	(II)	(III) ^a	(VI)	(VIII)	(X)	(XIV)
Sign of rotation at 589 nm	(+)	(+)	(–)	(+)	(+)	(+)	(+)
Negative extremum	214 (–590,000)	218 (–320,000)	223 (–5000,000)	228 (–760,000)	220 (–340,000)	[214] ^a (–940,000)	221 (–590,000)
Wave-length at [θ] = 0	220	222.5	232.5	238	226	222.5	224.5
Positive extremum	225 (+825,000)	229.5 (+1200,000)	240 (+420,000)	241 (+142,000)	230 (+135,000)	231 (+280,000)	228.5 (+1240,000)
Configuration previously assigned	<i>S</i> ^b						<i>S</i> ^c
Configuration by c.d. correlation	<i>S</i>	<i>S</i>	<i>S</i>	<i>S</i>	<i>S</i>	<i>S</i>	<i>S</i>

^a Limit of observation. ^b Refs. 4 and 18. ^c Refs. 3 and 10. ^d See note *f*, Table 1.

TABLE 3

Arrhenius parameters and transition state theory functions for racemisation of some 8,8'-disubstituted 1,1'-binaphthyls

Compound	Solvent	<i>E</i> /kcal mol ^{–1}	log ₁₀ <i>A</i>	Δ <i>F</i> [‡] /kcal mol ^{–1}	Δ <i>H</i> [‡] /kcal mol ^{–1}	Δ <i>S</i> [‡] /cal mol ^{–1} K ^{–1}
(VIII)	0.1 <i>N</i> aq. NaOH	32	14.3	29.6	31.2	+3.6
(III) ^a	0.1 <i>N</i> aq. NaOH	26	15.2	22.5	25.5	+9.2
(V) ^b	<i>NN</i> -Dimethylformamide	29.2	12.6	29.8	28.4	–3.4
(II) ^b	<i>NN</i> -Dimethylformamide	27.6	11.0	30.4	26.8	–9.4

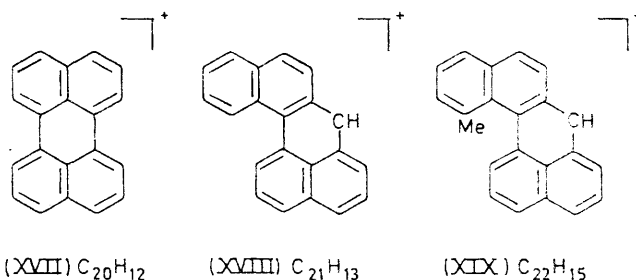
^a M. M. Harris and A. S. Mellor, *Chem. and Ind.*, 1959, 949. ^b Ref. 6.

show the negative Cotton effect of medium to low rotational strength near 285 nm, as Mislow³ found in the 2,2'-disubstituted series. The diagnostic value attributed to the two prominent short wave c.d. bands falls into line with observations made by Badger²⁰ and theoretical deductions made by Mason²¹ for compounds in the 1,1'-binaphthyl series.

1,1'-Binaphthyl-8,8'-diacetic acid (VIII) was synthesised by alkaline hydrolysis of 8,8'-biscyanomethyl-1,1'-binaphthyl, itself prepared from 8,8'-bisbromomethyl-1,1'-binaphthyl⁶ by heating it for some hours with aqueous ethanolic potassium cyanide. Neither of these successive reactions was suitable for preserving the optical activity of atropisomers, had the optically active dibromo-compound been used: therefore the racemic acid was made from racemic precursors and resolved subsequently by crystallisation of its quinine salt from acetone. The acid is optically stable at room temperature but is optically labile at higher temperatures: its racemisation in sodium hydroxide solution was followed polarimetrically at four temperatures, and the Arrhenius

²⁰ G. M. Badger, R. J. Drewler, and G. E. Lewis, *J. Chem. Soc.*, 1962, 4268.

a perylenium radical (XVII). The structure of the major fragment, C₂₁H₁₃, and the next in abundance, C₂₂H₁₅, are a matter for conjecture: (XVIII) and (XIX) are worthy of consideration.



EXPERIMENTAL

U.v. spectra were determined on a Unicam SP 500 spectrophotometer in 96% ethanol: 2 mm cell used normally, 1 cm for some of the longer wave-lengths. Polarimeter

²¹ R. Grinter and S. F. Mason, *Trans. Faraday Soc.*, 1964, 60, 274, see also S. F. Mason 'Optical Rotatory Dispersion and Circular Dichroism in Organic Chemistry,' ed. G. Snatzke, Heyden, London, 1967, ch. 4.

readings in the region 365–578 nm were made on a Zeiss photoelectric polarimeter with a thermostatically controlled polarimeter tube $l = 0.5$ or 1 dm. O.r.d. spectra were determined on a Perkin-Elmer P23 spectrophotopolarimeter. C.d. data for compounds (II), (III), (VI), (X), and (XIV) were measured on a Fica Spectropol I, and for (VIII) on a Jouan Dichrographe. Mass spectra were taken with an A.E.I. MS902 double-focusing mass spectrometer at 70 eV. N.m.r. spectra, at 60 MHz, refer to tetramethylsilane as standard.

8,8'-Biscyanomethyl-1,1'-binaphthyl (VII).—8,8'-Bisbromomethyl-1,1'-binaphthyl (VI) (7.3 g) suspended in 95% aqueous ethanol (100 ml) was added gradually during 2 h to a boiling solution of potassium cyanide (2.6 g, 2.4 mol) in H₂O (6 ml) and EtOH (17.3 g) and boiled for 3 h. After cooling, water was added until precipitation was complete; the precipitate crystallised from benzene in dark red prisms (4.5 g, 77.5%), m.p. 218–223° (decomp.), m.p. in apparatus pre-heated to 220°, 230–232° [Found: C, 86.4; H, 4.9; N, 8.5%; M , 332.1313 (mass spectrum). C₂₄H₁₆N₂ requires C, 86.7; H, 4.8; N, 8.4%; M , 332.1314], ν_{\max} (Nujol) 2250s cm⁻¹ (C≡N str.), τ (CDCl₃) 2.00–2.75 (12H, complex m, aromatic), and 5.83–6.08 (4H, q, CH₂CN, J 10 Hz).

1,1'-Binaphthyl-8,8'-diacetic Acid (VIII).—8,8'-Biscyanomethyl-1,1'-binaphthyl (5 g) was boiled with 50% aqueous ethanolic potassium hydroxide (100 ml) until there was no further evolution of ammonia; the potassium salt which separated on cooling was filtered off, dissolved in water, purified by boiling with charcoal, and acidified with 3*N*-hydrochloric acid. The precipitated acid was crystallised from methanol (4.5 g, 82%), m.p. 320° (decomp.) (Found: C, 77.7; H, 5.0; O, 17.2%; M^+ , 370.1195. C₂₄H₁₈O₄ requires C, 77.8; H, 4.9; O, 17.3%; M , 370.1205), ν_{\max} (Nujol) 1700s cm⁻¹ (CO₂H), poor solubility precluded the observation of a reliable n.m.r. spectrum, m/e 370 (28%), 352 (8), 326 (8), 325 (10), 324 (14), 323 (8), 281 (12), 280 (16), 279 (56), 278 (24), 277 (28), 276 (20), 267 (20), 266 (36), 265 (100), 264 (12), 263 (16), 253 (8), 252 (20), 239 (8), 140 (8), 139 (24), and 138 (24), high resolution m/e 370.1195 (C₂₄H₁₈O₄ requires 370.1205), 324.1158 (C₂₃H₁₆O₂ requires 324.1150), 279.1171 (C₂₂H₁₅ requires 279.1174), 277.1013 (C₂₂H₁₃ requires 277.1017), 265.1017 (C₂₁H₁₃ requires 265.1017), and 252.0941 (C₂₀H₁₂ requires 252.0939).

Optically Active 1,1'-Binaphthyl-8,8'-diacetic Acid.—The (±)-acid was resolved by crystallising its monoquinine salt from acetone; the less soluble diastereoisomeric salt was decomposed to give the (+)-acid, m.p. 308–310°, $[\alpha]_{546}^{20} + 249^\circ$ (c 0.18; l 0.5 dm; *NN*-dimethylformamide) (Found: C, 78.1; H, 5.1%). The more soluble salt gave the (–)-acid, $[\alpha]_{546}^{20} - 245^\circ$ (c 0.212; *NN*-dimethylformamide) (Found: C, 77.7; H, 5.0; O, 17.3%).

Racemisation in Aqueous Sodium Hydroxide.—The (+)-acid (0.1868 g) was dissolved in 0.1*N* aqueous sodium hydroxide (50 ml) and portions of the solution were sealed in ampoules, kept in an oil thermostat at a series of suitable temperatures, withdrawn at measured time intervals, cooled immediately to room temperature, and the optical rotation measured. The chemical identity of racemised solutions was confirmed spectroscopically. First-order rate constants for racemisation were calculated for each temperature and racemisation parameters derived from them by the procedure previously described:²² $k_{\text{rac}}^{111^\circ} 9.15 \times 10^{-5}$, $k_{\text{rac}}^{123^\circ} 2.8 \times 10^{-4}$, $k_{\text{rac}}^{133^\circ} 7.3 \times 10^{-4}$, $k_{\text{rac}}^{137^\circ} 1.4 \times 10^{-3}$ s⁻¹; $E = 32.0$ kcal mol⁻¹; $\log_{10} A = 14.3$; $\Delta F^\ddagger = 29.6$ kcal

mol⁻¹; $\Delta H^\ddagger = 31.2$ kcal mol⁻¹; $\Delta S^\ddagger = 3.6$ cal mol⁻¹ K⁻¹ (average for the temperature range).

8,8'-Bismethoxycarbonylmethyl-1,1'-binaphthyl.—The acid (VIII) (1 g) was added to a cold ethereal solution of diazomethane (0.3 g): the dimethyl ester crystallised from benzene, m.p. 125–127°, yield ca. 100% (Found: C, 78.55; H, 5.8. C₂₈H₂₂O₄ requires C, 78.4; H, 5.6%) τ (CDCl₃) 2.00–3.00 (4H and 8H, complex m, aromatic), 6.74 (4H, s, naphthyl-CH₂), and 6.83 (6H, s, CO₂CH₃).

8,8'-Bisethoxycarbonylmethyl-1,1'-binaphthyl (IX).—The acid (VIII) (1 g) was boiled for 3 h with thionyl chloride (0.5 ml) in benzene (100 ml) and then cooled, ethanol (5 ml) was added dropwise, and boiling was resumed for a further 1 h. Normal work-up gave the diethyl ester (1 g, 87%), m.p. 95–96° (Found: C, 78.7; H, 6.1; O, 15.0%; M^+ , 426.1820. C₂₈H₂₆O₄ requires C, 78.9; H, 6.1; O, 15.0%; M , 426.1831), ν_{\max} (Nujol) 1740–1725s cm⁻¹ (CO₂Et), τ (CDCl₃) 2.00–3.00 (4 and 8H, complex m, aromatic), 6.75 (4H, s, naphthyl-CH₂), 6.36 (4H, q, CH₂CH₃, J 7 Hz), 9.04 (6H, t, J 7 Hz, CH₃CH₂), m/e 426 (6%), 381 (5), 380 (13), 353 (11), 352 (24), 323 (23), 305 (11), 280 (13), 279 (54), 278 (46), 277 (43), 276 (19), 266 (16), 265 (100), 264 (8), 252 (11), and 139 (8), $m^* 339 = 380^2/426$.

8,8'-Bis-(1-pyridiniomethyl)-1,1'-binaphthyl Di-iodide (X).—8,8'-Bisbromomethyl-1,1'-binaphthyl (VI) (1 g) was stirred with an excess of hot, dry pyridine; the solid bromide which separated was very hygroscopic and failed to crystallise. By the action of hot concentrated potassium iodide solution it was converted into the iodide which formed yellow crystals of the di-iodide dihydrate when crystallised from a concentrated aqueous solution (1.4 g, 87.5%), m.p. 196° (decomp.), m.p. after losing water ca. 165° (Found: C, 52.9; H, 4.2; N, 3.8; I, 34.8. C₃₂H₂₆I₂N₂·2H₂O requires C, 52.7; H, 4.1; N, 3.8; I, 34.8%).

Optically Active Di-iodide (X).—Repeating the above procedure on a sample of (–)-8,8'-bisbromomethyl-1,1'-binaphthyl, $[\alpha]_{546}^{20} - 180^\circ$, gave (–)-(X), $[\alpha]_{546}^{18} - 27.7^\circ$ (c 0.396; 95% ethanol) (Found: C, 52.9; H, 4.2; N, 3.8; I, 35.2%).

Use of the (+)-8,8'-bisbromomethyl-1,1'-binaphthyl, $[\alpha]_{546}^{20} + 348.7^\circ$, gave (+)-(X), $[\alpha]_{546}^{18} + 202.0^\circ$.

O.r.d.—The sign of rotation in the title of each compound refers to α_D . Most of the compounds are optically labile and are made from optically labile precursors; thus they are not optically pure: c = concentration in g l⁻¹; wave-length in nm, $[\alpha]$ in parentheses, $t = 21$ °C unless otherwise stated solvent 95% ethanol.

(i) (+)-8,8'-Dimethyl-1,1'-binaphthyl (II). $c = 0.14 - 0.028$, $t = 22$ °C, 215 (–48,000°), 220–222.5 (–35,000°), 228 (0°), 235 (+85,700°), 265 (+27,800°), 288 (0°), and 291 (–4,600°). The band at ca. 265 nm changed in specific rotation on heating to 60 °C and did not return to the same value on cooling.

(ii) (–)-1,1'-Binaphthyl-8,8'-dicarboxylic acid (III). $c = 1.3 - 0.01$, 215 (–295,000°), 230 (–537,000°), 233 (–564,000°), 242 (0°), 249.5 (+16,000°), 159 (+4600°), 270 (+10,800°), 304.5 (0°), 312 (–3900°), 320 (–2500°), 340 (–5800°), 400 (–2000°), and 546 (–839°).

(iii) (+)-1,1'-Binaphthyl-8,8'-dicarboxylic acid (III). $c = 0.496 - 0.03$, 215 (+55,000°), 230 (+116,000°), 242 (0°), 249 (–50,000°), 258 (–9000°), 280 (–25,000°), 304 (0°), 312.5 (+8000°), 345 (+10,000°), and 400 (+3300°).

(iv) (–)-8,8'-Bismethoxycarbonyl-1,1'-binaphthyl (IV).

²² D. M. Hall and M. M. Harris, *J. Chem. Soc.*, 1960, 490.

$c = 1.28-0.128$, 215 ($-13,300^\circ$), 232 ($-33,000^\circ$), 237 (0°), 243 ($+13,500^\circ$), 251 (0°), 258 (-2300°), 259.5 (0°), 275 ($+14,000^\circ$), 301.5 (0°), 337 (-2500°).

(v) (+)-8,8'-Bishydroxymethyl-1,1'-binaphthyl (V). $c = 2.36-0.056$, 218 (-2000°), 228 (-9000°), 231.5 (0°), 245 ($+14,000^\circ$), 260 ($+6000^\circ$), 268 ($+7000^\circ$), 303 ($+2000^\circ$), 308 ($+2300^\circ$), 330 ($+700^\circ$).

(vi) (+)-8,8'-Bisbromomethyl-1,1'-binaphthyl (VI). $c = 0.30-0.018$, 220 ($-46,700^\circ$), 227 ($-93,000^\circ$), 235-238 ($-82,000^\circ$), 248 (0°), 255 ($+23,500^\circ$), 258 ($+25,000^\circ$), 285 ($+14,000^\circ$), 320 (1000°), and 546 ($+348^\circ$).

(vii) (-)-1,1'-Binaphthyl-8,8'-diacetic acid (VIII). $c = 0.51-0.02$, 217.5 (0°), 220 ($+22,000^\circ$), 228 ($+134,000^\circ$), 239 (0°), 248 ($-55,300^\circ$), 250 ($-49,000^\circ$), 254 ($-48,000^\circ$), 268 ($-16,500^\circ$), 280 ($-11,300^\circ$), 293 (0°), 307 (1700°), 310 (0°), 330 (-2300°), and 546 (-307°).

(viii) (+)-1,1'-Binaphthyl-8,8'-diacetic acid (VIII). $c = 0.51-0.02$, 213 ($-36,600^\circ$), 227 ($-80,500^\circ$), 239 (0°), 247.5 ($+37,000^\circ$), 252 ($+20,500^\circ$), 269 ($+10,000^\circ$), 280 ($+7,300^\circ$), 291 (0°), 300 (-600°), 308 (0°), 328 ($+2100^\circ$), and 546 ($+227^\circ$).

(ix) (-)-8,8'-Bis-(1-pyridiniomethyl)-1,1'-binaphthyl Diiodide (X). $c = 0.31-0.025$, 215 ($+4000^\circ$), 223 ($+16,000^\circ$), 231.5 (0°), 250 (-6000°), 260-275 (-4000°), 298 (0°), 305 ($+500^\circ$), 315 (0°), and 320 (-400°).

(x) (+)-8,8'-Bis-(1-pyridiniomethyl)-1,1'-binaphthyl Diiodide (X). $c = 0.5-0.03$, 210 ($-40,000^\circ$), 217 ($-48,000^\circ$), 231.5 (0°), 250 ($+34,000^\circ$), 270-275 ($+10,700^\circ$), 290 ($+7300^\circ$), 301 (0°), 304 (-400°), 315 (0°), 328 ($+1300^\circ$), and 546 (202°).

(xi) (-)-2,2'-Dimethyl-1,1'-binaphthyl (XIV). $c = 0.55-0.01$, $t = 30^\circ\text{C}$, 215 ($-31,000^\circ$), 218 (0°), 224.5 ($+300,000^\circ$), 231 (0°), 234 ($-84,000^\circ$), 253 ($+54,000^\circ$), 264 (0°), 272 ($+31,000^\circ$), 280-285 ($+22,000^\circ$), 315 (0°), 319 (-450°), and 321.5 ($+1800^\circ$). The region between 260 and 290 nm is sensitive to concentration and to temperature, e.g., $[\alpha]_{272}^{30^\circ} = +31,000^\circ$, $[\alpha]_{272}^{50^\circ} = +3600^\circ$; the change is reversed on cooling.

(xii) (+)-2,2'-Dimethyl-1,1'-binaphthyl (XIV). $c = 0.45-0.009$, $t = 30^\circ\text{C}$, 214 ($+74,000^\circ$), 218 (0°), 223 ($-365,000^\circ$), 229 (0°), 235 ($+141,000^\circ$), 302 (0°), 303 (-1000°), 309 (-800°), 318 (0°), 319 ($+450^\circ$), 321 (0°), 322 ($+1400^\circ$), and 546 ($+22^\circ$).

C.d.— c = concentration in g l^{-1} , wavelength in nm, molar ellipticity θ in parentheses, $t = 21.5^\circ$, solvent 95% ethanol.

(i) (+)-8,8'-Dimethyl-1,1'-binaphthyl (II). $c = 0.23-$

0.0046 , 210 (0°), 215 ($-220,000^\circ$), 218 ($-320,000^\circ$), 220 ($-200,000^\circ$), 222.5 (0°), 229.5 ($+120,000^\circ$), 250 ($+33,000^\circ$), 255.5-257.5 ($+32,000^\circ$), 269.5 (0°), 285 ($-35,000^\circ$), 287 ($-35,000^\circ$), 290 ($-26,000^\circ$), 300 (-1600°), 302 (0°), 306.5 ($+3200^\circ$), 313 ($+800^\circ$), 316 ($+1000^\circ$), 318 ($+800^\circ$), 321 ($+1600^\circ$), 323 (0°), 325.5 (-4400°), 330 (-1400°), and 335 (0°).

(ii) (-)-1,1'-Binaphthyl-8,8'-dicarboxylic acid (III). $c = 0.6-0.024$, 214 (0°), 223 ($-500,000^\circ$), 232.5 (0°), 240 ($+420,000^\circ$), 250 ($+140,000^\circ$), 251 ($+35,000^\circ$), 270 ($+176,000^\circ$), 281 (0°), 289-296 ($-50,500^\circ$), 324 ($-32,000^\circ$), 326 ($-37,000^\circ$), 330 ($-33,800^\circ$), 334 ($-32,000^\circ$), and 340 ($-20,000^\circ$).

(iii) (+)-8,8'-Bisbromomethyl-1,1'-binaphthyl (VI). $c = 0.5-0.02$, 218 ($-380,000^\circ$), 220 ($-436,000^\circ$), 224 ($-762,000^\circ$), 228 ($-760,000^\circ$), 234 ($-109,000^\circ$), 238 (0°), 241 ($+142,000^\circ$), 260 (0°), 265 ($-26,000^\circ$), 270 ($-22,000^\circ$), 300 ($-35,000^\circ$), and 340 (0°).

(iv) (+)-1,1'-Binaphthyl-8,8'-diacetic acid (VIII). $c = 0.54-0.054$, 214 ($-130,000^\circ$), 220 ($-340,000^\circ$), 226 (0°), 230 ($+135,000^\circ$), 250 (0°), 280-286 ($-18,000^\circ$), and 310 (-1700°).

(v) (-)-1,1'-Binaphthyl-8,8'-diacetic acid (VIII). $c = 0.4-0.04$, 217 (0°), 220 ($+250,000^\circ$), 222 ($+260,000^\circ$), 226 (0°), 231 ($-110,000^\circ$), 250 (0°), 270 ($+13,000^\circ$), 280-284 ($+10,000^\circ$), and 300 (0°).

(vi) (+)-8,8'-Bis-(1-pyridiniomethyl)-1,1'-binaphthyl Diiodide (X). $c = 0.71-0.142$, 214 ($-940,000^\circ$), 220 ($-280,000^\circ$), 222.5 (0°), 231 ($+280,000^\circ$), 234 ($+260,000^\circ$), 266 (0°), 286 ($-55,000^\circ$), 293 ($-35,000^\circ$), 296 ($-40,000^\circ$), 320 (-5000°), and 340 (0°).

(vii) (+)-2,2'-Dimethyl-1,1'-binaphthyl (XIV). $c = 0.42-0.0084$, 213 (0°), 221 ($-590,000^\circ$), 222 ($-545,000^\circ$), 224.5 (0°), 228.5 ($+1240,000^\circ$), 259 (0°), 280 ($-29,000^\circ$), 283 ($-30,000^\circ$), 304 (-2200°), 306 (-2500°), 312 (-700°), 320 (-3000°), 325-335 (-200°), and 340 (0°).

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