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THE CHIRALLY TWISTED NAPHTHALENE CHROMOPHORE IN 1,1'-BINAPHTHYLS

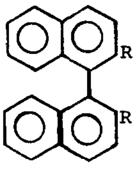
M.M. Harris, P.K. Patel and S.Singh[15]
Bedford College, University of London, NW1 4NS
and (the late) D.L. Marshall
Polytechnic of North East London, West Ham, London E.15

Evidence is here presented that comparison of the CD spectra of a large number of substituted 1,1'-binaphthyls of the same overall configuration reveals a band or bands whose sign can be related, albeit empirically, to the M or P twisted chirality of individual naphthalene units.

CD spectra of 1,1'-binaphthyls substituted in the 2 and 2'-positions[1,2] (I), in the 8 and 8'-positions[2,4] (II), with 2,2'-bridges[1,2] (III), and of 1,1'-binaphthyl itself[3] are already available. We now add the spectra of thirteen 1,1'-binaphthyls bridged across the 8,8'-positions (IV): syntheses of both enantiomers of these (except for IV e, f and g) are published[5,6]. The absolute configuration of all of the 1,1'-binaphthyls has been established by theoretical treatment of the 1,1'-binaphthyl chromophore[2,7,8], by asymmetric reduction[13] by similarity of Cotton Effects[1,4], by anomalous X-ray diffraction[10] and by chemical correlations[5,6,7,9].

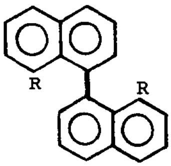
Naphthalene shows three major UV bands[11] in the normally accessible region, λ max 221, 286 and 312 nm. The main characteristics of the CD spectra of 1,1'-binaphthyls are a 'couplet' in the short-wave region, the shorter wavelength lobe being negative for (S) configuration (for conformations of dihedral angle up to ~110°[2,6,8]): they all show chiral absorption near and beyond 280 nm: some of them in addition show a band ~260 nm, interpreted as a conjugation or charge-transfer band[1,2,8].

I



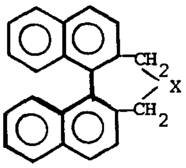
(a) $R=CH_3$
(b) $R=CO_2H$
(c) $R=CO_2Me$
(d) $R=CONH_2$
(e) $R=CH_2Br$
(f) $R=CH_2OH$

II



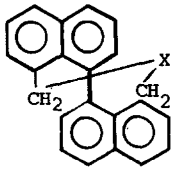
(a) R=H
(b) $R=CH_3$
(c) $R=CO_2H$
(d) $R=CO_2Me$
(e) $R=CH_2Br$
(f) $R=CH_2CN$

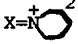
III



(a) X=O
(b) $X=C(CO_2Et)_2$
(c) X=CO
(d) X=CHOH

IV



(a) X=O
(b) $X=SO_2$
(c) X=S
(d) X=Se
(e) $X=\overset{+}{N}Et_2$
(f) 
(g) $X=\overset{+}{N}(allyl)_2$
(h) $X=C(CO_2H)_2$
(i) $X=C(CO_2Me)_2$
(j) $X=C(CO_2Et)_2$
(k) $X=C(CH_2OH)_2$
(l) $X=CHCO_2H$
(m) $X=CHCO_2Me$

Circular Dichroism in the long wave region, Types I, II and III.

I. λnm (ε x 10^{-3}) in dioxane, (S) configuration unless otherwise stated[1].

(+) I(a)	(-) I(b)	(-) I(c)	(-) I(d)	(-) I(e)	(+) I(f)(R)
285(-16)	285(-53)	288(-71)	287(-42)	289(-46)	284(+41)
300(0)	290(-46)	305(-5)	310(0.0)	305(-6)	313(+5)

II. λnm (ε x 10^{-3}) in 95% EtOH[16], (S) configuration[1,2,3].

(+) II(a)	(+) II(b)	(-) II(c)	(-) II(d)	(+) II(e)	(+) II(f)
280-9(-8)	287(-41)	300(-78)	296(-60)	299(-28)	284(-51)
305(-2)	307(+6)	313(-39)	315(-28)		312(+5)

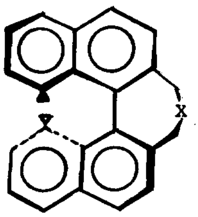
III. λnm (ε x 10^{-3}) in dioxane, (S) configuration unless otherwise stated[1].

(+) III(a)	(+) III(b)	(+)III(c)(R)(in iso-octane)	(-) III(d)(R)
	285(-35)	287(+85)	291 inf.(+37)
305(-51)	305(-69)	293(+105), 300(+155)	305(+54)

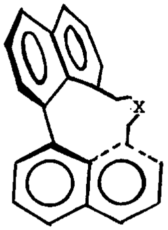
All the above compounds show negative maxima in the 280-315 region, for (S) configuration, a generalisation first noted by Mislow in 1962[1]. In contrast, the Table below shows that (S) 8,8'-bridged compounds have oppositely signed bands in this region. Data for III(a), in 96% ethanol are appended.

IV. λnm (ε x 10^{3}) in 96%[16] EtOH. (S) Configuration. All (+)-.

IV(a)	219(-1020)	232(+1139)	270(+64)	291.5(+59)	302.5(+44)
(b)	222(-1591)	237(+1250)		296.5(+59)	302.5(+60)
(c)	228(-1316)	251(+368)		295.5(+55)	
(d)	232(-749)	256(+199)		297(+72)	
(e)	215(-1125)	228(+903)		294.5(+38)	
(f)	218(-1231)	232.5(+915)		297(+33.5)	
(g)	220(-1511)	234(+940)		298(+50)	
(h)	215-7(-563)	229(+667)		293(+15)	301.5(+15)
(i)	215.5(-492)	228(+1156)		295(+11)	302(+13)
(j)	219(-967)	230.5(+1003)		296.5(+21)	302(+21)
(k)	218(-549)	230(+947)		295(+16.5)	301(+16)
(l)	215(-447)	230(+862)		293(+26)	300.5(+23)
(m)	216(-823)	229(+1252)		294(+23)	302.5(+22)
III(a)	216(-2110)	228(+2340)	262.3(+151)	283 (sh)-51	300(-72)



(S) overall
(P) naphthalene helix



(S) overall
(M) naphthalene helix

Calculated CD spectra of 1,1'-binaphthyls[2,8] have been based on flat naphthalene units although this has long been thought to be an approximation[12]. When flexible models are used it is clear that (S) III-type have naphthalene units with (P) helicity while (S) IV-type have (M). Judging by the sense of the 'couplet (and assuming that the dihedral angles are not greater than ~ 110° [2,6,8]) (S) I and (S) II-types also have naphthalene units of (P) helicity, distortion being brought about by perinaphthalene forces. Consideration of these factors may help to elucidate some of the imbalance and other peculiarities of individual 'couplets'.

Chirally perturbed naphthalene units have been detected by CD spectra in polymers and in (+)-(S)-2-(α-naphthyl)butane[14] which resemble those of types I ⟶ III.

Acknowledgments

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[15] Dr. Shyam Singh's present address is Central Drug Research Institute, Lucknow, U.P., India.

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