831. *The Synthesis of Polycyclic Aromatic Hydrocarbons. Part II.* Optical Rotatory Dispersion Studies of* 1,1′-*Bianthryls.*

By G. M. BADGER, R. J. DREWER, and G. E. LEWIS.

The optical rotatory dispersion characteristics of three " hindered " 1,1′-bianthryls have been determined. Each curve shows *two* Cotton effects (of opposite sign). (—)-9,10-Dihydrodinaphtho(2′,3′-3,4:2″,3″-5,6)phenanthrene (III) and the configurationally related (—)-bianthryls have been assigned the *R*-configuration.

ABSOLUTE configurations of hindered biaryls have been determined by chemical interconversions,[1] by analysis of the phase diagram for a mixture of a compound of known and one of unknown configuration,[2] and by analysis based on the polarisability theory of optical activity.[3] More recently, Mislow and his co-workers [4] have used optical rotatory dispersion and have related the absolute configurations of biphenyls and binaphthyls to the sign of their Cotton effect curves: a positive long-wavelength Cotton effect was found to indicate the *R*-configuration, and a negative effect the *S*-configuration in the series examined. It therefore seemed of interest to attempt to determine the absolute configuration of some hindered 1,1′-bianthryls.

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* Part I, *J.*, 1957, 1837.

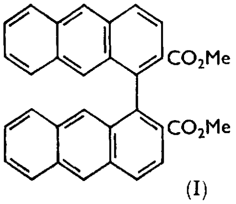
[1] Newman, Rutkin, and Mislow, *J. Amer. Chem. Soc.*, 1958, **80**, 465; Mislow and McGinn, *ibid.*, p. 6036; McGinn, Lazarus, Siegel, Ricci, and Mislow, *ibid.*, p. 476; Mislow, *Angew. Chem.*, 1958, **70**, 683.

[2] Siegel and Mislow, *J. Amer. Chem. Soc.*, 1958, **80**, 473.

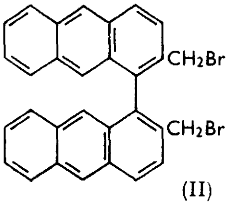
[3] Fitts, Siegel, and Mislow, *J. Amer. Chem. Soc.*, 1958, **80**, 480.

[4] Mislow, Glass, O'Brien, Rutkin, Steinberg, and Djerassi, *J. Amer. Chem. Soc.*, 1960, **82**, 4740.

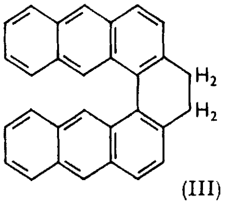
(—)-9,10-Dihydrodinaphtho(2′,3′-3,4:2″,3″-5,6)phenanthrene (III) has already been synthesised by cyclisation of (—)-2,2′-bisbromomethyl-1,1′-bianthryl (II), itself prepared from (—)-dimethyl 1,1′-bianthryl-2,2′-dicarboxylate (I).[5] These compounds are therefore configurationally related; and as the bridged compound is far more lævorotatory



(I)



(II)



(III)

than the unbridged compounds, the *R*-configuration has been tentatively assigned to them.[3] Similarly, (+)-9,10-dihydrodinaphtho(2′,3′-3,4:2″,3″-5,6)phenanthrene has been synthesised from the corresponding dextrorotatory bianthryls, and these compounds have been tentatively assigned the *S*-configuration.

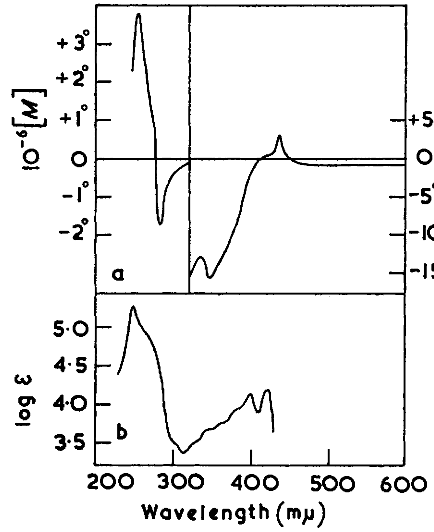


FIG. 1.

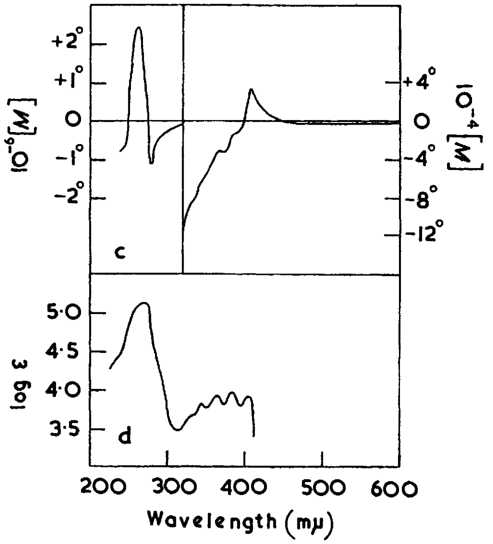


FIG. 2.

FIG. 1. (a) Optical rotatory dispersion curve and (b) ultraviolet absorption curve of (—)-9,10-dihydrodinaphtho(2′,3′-3,4:2″,3″-5,6)phenanthrene (III), both in cyclohexane–dioxan.

FIG. 2. (c) Optical rotatory dispersion curve and (d) ultraviolet absorption curve of (—)-dimethyl 1,1′-bianthryl-2,2′-dicarboxylate (I), both in cyclohexane–dioxan.

The optical rotatory dispersion curve given by (—)-9,10-dihydrodinaphtho(2′,3′-3,4:2″,3″-5,6)phenanthrene (III) has been found to exhibit *two* Cotton effects (Fig. 1). There is a positive Cotton effect with λ_{mean} 390 mμ, and a much larger negative Cotton effect with λ_{mean} 269 mμ. The optical rotatory dispersion curve given by (—)-dimethyl 1,1′-bianthryl-2,2′-dicarboxylate (I) showed even more fine structure, including a positive Cotton effect with λ_{mean} 377 mμ, and a large negative Cotton effect with λ_{mean} 271 mμ (Fig. 2). (+)-Bisbromomethyl-1,1′-bianthryl (II) was found to be very labile, and a satisfactory optical rotatory dispersion curve could not be obtained. Nevertheless, a small negative Cotton effect was demonstrated between 340 and 430 mμ, and a large positive

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[5] Badger, Jefferies, and Kimber, *J.*, 1957, 1837.

Cotton effect between 250 and 300 mμ. These compounds exhibit very large rotations at some wavelengths: at 254 mμ, for example, (—)-9,10-dihydrodinaphtho(2′,3′-3,4:2″,3″-5,6)phenanthrene has a molecular rotation of $+3{\cdot}8 \times 10^6$ degrees.

As all these curves showed two Cotton effects (of opposite sign), assignment on the basis of the rules enunciated by Mislow and his co-workers [4] requires further discussion. It is necessary, for example, to decide which absorption band is responsible for each Cotton effect.

Benzene has three regions of absorption in its ultraviolet spectrum: intense absorption at 179 mμ (group I band); intense absorption around 200 mμ (group II band); and a region of low-intensity absorption around 260 mμ (group III band).[6] With the bridged biphenyls, λ_{mean} of the long-wavelength Cotton effects is around 280—300 mμ,[4] and it seems that the group III absorption is mainly responsible for this. Similarly, naphthalene has absorption around 221 mμ (group I), around 285 mμ (group II), and around 310 mμ (group III).

Recent work by Mislow and his co-workers [7] has shown that the bridged binaphthyl, (*S*)-(+)-9,10-dihydro-3,4:5,6-dibenzophenanthrene, exhibits a small negative Cotton effect (λ_{mean} *ca.* 330 mμ) and a much larger positive Cotton effect (λ_{mean} *ca.* 250 mμ). The ultraviolet absorption spectrum [8] of this compound has a group I band at 239 mμ, group II bands at 320, 336, and 348 mμ, and a group III band of low intensity at 357 mμ. It seems likely, therefore, that the smaller Cotton effect is associated with the group II bands and that the close proximity of the weak group III band to the much stronger group II bands may be sufficient reason for the absence of a Cotton effect due to group III absorption. The group I absorption is undoubtedly responsible for the larger Cotton effect, and for configurational correlation with the 1,1′-bianthryls this observation is important.

Anthracene absorbs at 251 mμ (group I bands) and around 374 mμ (group II bands), but the group III bands are " hidden " under the group II bands. The small Cotton effect (λ_{mean} 390 mμ) given by (—)-9,10-dihydrodinaphtho(2′,3′-3,4:2″,3″-5,6)phenanthrene could be assigned either to the group II or to the " hidden " group III bands; but the group II assignment is the more probable owing to the marked similarity between the small Cotton effects of the bridged (—)-bianthryl (III) and (*R*)-(—)-9,10-dihydro-3,4:5,6-dibenzophenanthrene. The large negative Cotton effect (λ_{mean} 269 mμ) of the (—)-bianthryl (III) can be assigned with confidence to the group I absorption. By analogy with (*R*)-(—)-9,10-dihydro-3,4:5,6-dibenzophenanthrene, it may be concluded that a negative Cotton effect associated with a group I absorption band indicates *R*-configuration, and a positive effect here an *S*-configuration. Hence, (—)-9,10-dihydrodinaphtho(2′,3′-3,4:2″,3″-5,6)phenanthrene (III) and the related (—)-bianthryls (I, II) must have *R*-configuration; and their enantiomorphs must have the *S*-configuration. As the unbridged *R*-(—)-compounds (I,II) have the same sign for their Cotton effects as the bridged *R*-(—)-compound (III), they must also have the *syn*-conformation.[3,4]

EXPERIMENTAL

Cyclohexane.—A mixture of cyclohexane (3·6 l.; Fluka), concentrated sulphuric acid (500 ml.), and concentrated nitric acid (400 ml.) was stirred and refluxed for 9 hr. The resulting product was washed with aqueous sodium hydroxide and water, dried ($CaCl_2$), and fractionally distilled over sodium. The forerun was discarded.

Dioxan.—A mixture of dioxan (2 l.) and N-hydrochloric acid (200 ml.) was refluxed under nitrogen for 7 hr. The resulting dioxan was dried (KOH) and then refluxed over anhydrous stannous chloride (25 g.) for 0·5 hr. It was distilled, refluxed over sodium for 12 hr., and finally fractionally distilled over sodium. The fraction of b. p. 101—101·3° was collected.

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[6] Badger, " The Structures and Reactions of the Aromatic Compounds," Cambridge Univ. Press, London, 1954, p. 392.

[7] Mislow, Glass, O'Brien, Rutkin, Steinberg, Weiss, and Djerassi, *J. Amer. Chem. Soc.*, 1962, **84**, 1455; Mislow, *Ann. New York Acad. Sci.*, 1962, **93**, 457.

[8] Bergmann and Szmuszkovicz, *J. Amer. Chem. Soc.*, 1951, **73**, 5153.

Ultraviolet Spectra.—The spectra were determined with an Optica CF4 recording spectrophotometer for cyclohexane–dioxan solutions with the proportion of dioxan ranging from 0·1 to 20% v/v.

Optical Rotatory Dispersion.—The optical rotatory dispersion measurements were made with a Rudolph photoelectric model 200AS spectropolarimeter fitted with a standard xenon lamp, a Philips HP 125-w. mercury–quartz burner, and a 12 v, 50-w tungsten lamp operated from a 12-v accumulator. Djerassi's method [9] was modified in order to avoid inaccuracies due to time-variations in the null point of the instrument. At each wavelength for which a reading was required (whether that of a solution or the pure solvent) the null points were determined with the tube successively in and out of the polarimeter trough. Secondly, it was found that the symmetrical angle settings above 5° increased the experimental error far more than changes in concentration. Solutions of higher dilution were accordingly used in wavelength regions of strong absorption.

Molecular rotations determined on solutions of different concentration at the same wavelength were generally found to be in good agreement. With (—)-9,10-dihydrodinaphtho-(2′,3′-3,4:2″,3″-5,6)phenanthrene, a maximum variation of 10% was observed; and with (—)-dimethyl 1,1′-bianthryl-2,2′-dicarboxylate, the maximum variation was 20%.

The compounds examined were sparingly soluble in cyclohexane, and cyclohexane–dioxan solutions were accordingly used. The stock solution was prepared in dioxan and, as optical rotatory dispersion could not be measured in this solvent below 275 mμ, the solution was diluted as required with the more transparent cyclohexane. For dihydrodinaphthophenanthrene, no significant difference in either ultraviolet absorption or optical rotatory dispersion was detected between solutions in dioxan and in cyclohexane–dioxan.

(—)-9,10-*Dihydrodinaphtho*(2′,3′-3,4:2″,3″-5,6)*phenanthrene.*—This compound had been prepared by Badger, Jefferies, and Kimber.[5] Its ultraviolet spectrum showed $\lambda_{\text{max.}}$ (log ε values in parentheses): 248 (5·3), sh 328 (3·5), sh 344 (3·6), sh 362 (3·7), sh 379 (3·9), 400 (4·1), and 422 mμ (4·2). For the O.R.D. measurements the following concentrations were used for the wavelengths given: 1·1 × 10^{-4}M (20% dioxan), 580—426 mμ; 3·3 × 10^{-5}M (10% dioxan), 420—320 mμ; 1·1 × 10^{-5}M (2% dioxan), 313—289 mμ; 1·1 × 10^{-6}M (1% dioxan), 288—258 mμ; and 3·3 × 10^{-7}M (1% dioxan), 258—248 mμ. It showed a large negative Cotton effect: peak, 254 mμ; trough, 283 mμ; λ_{mean} 269 mμ; and a small positive Cotton effect: peak, 436 mμ; trough 345 mμ; and λ_{mean} 390 mμ. Optical activity decreased on prolonged exposure to ultraviolet light, and fresh solutions were made up as required. A solution exposed to sunlight for some hours lost its optical activity completely.

(—)-*Dimethyl* 1,1′-*Bianthryl*-2,2′-*dicarboxylate.*—This compound had been prepared by Badger, Jefferies, and Kimber.[5] Its ultraviolet spectrum showed $\lambda_{\text{max.}}$ (log ε values in parentheses): 268 (5·1), sh 329 (3·6), 343 (3·8), 364 (3·9), 383 (4·0), and 404 mμ (3·9). For the O.R.D. measurements the following concentrations were used for the wavelengths given: 1·05 × 10^{-4}M (10% dioxan), 580—414 mμ; 3·1 × 10^{-5}M (10% dioxan), 412—302 mμ; 1·05 × 10^{-6}M (0·1% dioxan), 297—283 mμ; and 3·1 × 10^{-7}M (0·1% dioxan), 281—238 mμ. It showed a large negative Cotton effect: peak, 262 mμ; trough, 280 mμ; and λ_{mean} 271 mμ; and a small positive Cotton effect: peak, 408 mμ; trough (?), 345 mμ; and λ_{mean} 377 mμ.

(+)-*Bisbromomethyl*-1,1′-*bianthryl.*—This compound was available from the earlier work. Its ultraviolet spectrum showed $\lambda_{\text{max.}}$ (log ε values in parentheses): 262 (5·1), sh 317 (3·6), sh 334 (3·7), 348 (3·9), 367 (4·0), and 386 mμ (4·0). For the O.R.D. measurements, the following concentrations were used for the wavelengths given: 1·15 × 10^{-4}M (10% dioxan), 580—405 mμ; 3·4 × 10^{-5}M (10% dioxan), 313—302 mμ; 1·15 × 10^{-5}M (1% dioxan), 366—334, 297 mμ; 3·4 × 10^{-6}M (1% dioxan), 293—280 mμ; 1·15 × 10^{-6}M (1% dioxan), 275—248 mμ. It showed a large positive Cotton effect between 250 and 300 mμ, and a small negative Cotton effect between 340 and 430 mμ. The low optical activity of this compound in comparison with its absorption precluded accurate determination of the O.R.D. curve. This compound underwent photochemical change, whose nature is under investigation.

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[9] Djerassi, " Optical Rotatory Dispersion," McGraw-Hill, New York, 1960, pp. 21—25.