2,2′-Bridged Biphenyls with 12-Membered Heterocyclic Bridging Rings. Part 1. Tetrabenzo[*b,d,h,j*][1,6]diazacyclododecines

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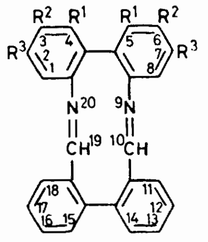
Four tetrabenzo[*b,d,h,j*][1,6]diazacyclododecines and their tetrahydro-derivatives have been prepared. ^{1}H N.m.r. and u.v. spectroscopy are used to determine the geometry of the tetrabenzodiazadodecines. It is concluded that they have the *EE* configuration, with dihedral angles in the biphenyl moieties of 55—60° and with angles of twist about the Ar_C–CH=N and Ar_N–N=CH single bonds of 10—20 and 80—70° respectively. N.m.r. spectra in the presence of chiral lanthanide shift reagents show that at least two of the compounds are chiral.

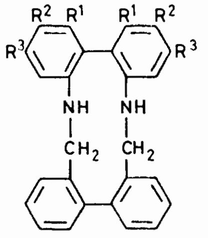
THE preparation of tetrabenzo[*b,d,h,j*][1,6]diazacyclododecine (1) by the interaction of 2,2′-diaminobiphenyl and biphenyl-2,2′-dicarbaldehyde has been described previously,[1,2] but little is known about its molecular shape and conformational stability. We have now prepared a series [(1)—(4)] of these large-ring compounds and of their tetrahydro-derivatives [(5)—(8)] and have investigated the geometry of the former series by ^{1}H n.m.r. and u.v. spectroscopy.

RESULTS AND DISCUSSION

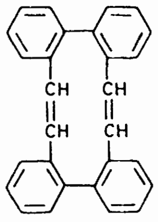
Preparation.—The dialdehyde reacted readily with the appropriate diaminobiphenyls in ethanol solution to give the diazacyclododecines in good yield. However it failed to react with 2,2′-diamino-4,6,4′,6′-tetramethylbiphenyl. Bindra and Elix [2] reduced (1) with sodium borohydride in methanol and obtained a product with m.p. 158 °C. We were unable to repeat their reduction but obtained the tetrahydro-compound (5) in good yield and with m.p. 174—176 °C by using (dimethylamino)-borane in acetic acid, a reagent used by Billman and McDowell [3] to reduce benzylideneanilines. Compounds (2) and (3) were reduced similarly but compound (4) needed hydrogen and a platinum catalyst.



(1) $R^1 = R^2 = R^3 = H$
(2) $R^1 = R^2 = H,\ R^3 = CO_2Me$
(3) $R^1 = R^3 = H,\ R^2 = OMe$
(4) $R^2 = R^3 = H,\ R^1 = CO_2Me$



(5) $R^1 = R^2 = R^3 = H$
(6) $R^1 = R^2 = H,\ R^3 = CO_2Me$
(7) $R^1 = R^3 = H,\ R^2 = OMe$
(8) $R^2 = R^3 = H,\ R^1 = CO_2Me$



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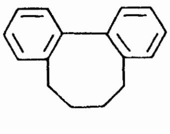

(10)

The two compounds [(2) and (6)] with ester groups *para* to the biphenyl link appeared in two distinct crystalline forms. It is noteworthy that the precursor, dimethyl 2,2′-diaminobiphenyl-4,4′-dicarboxylate, and the corresponding ethyl ester also show dimorphism.[4] Reduction of dimethyl 2,2′dinitrobiphenyl-6,6′-dicarboxylate with hydrazine–Raney nickel gave a high-melting solid, presumably the bis-lactam (lit.,[5] m.p. >330 °C). Hydrogenation over platinum gave the required diamino-ester, which changed on melting into the bis-lactam.

Geometry of the Tetrabenzo[b,d,h,j][1,6]*diazacyclododecine Ring System.*—The 12-membered ring comprises two twisted biphenyl units which may have (*R*) or (*S*) chirality and two –CH=N– units which may have the *syn* (*Z*) or *anti* (*E*) configuration. It is convenient to refer to the aromatic rings attached to the C=N group as Ar_C and Ar_N respectively.

It is possible to construct Dreiding models for the *ZZ*, the *ZE*, and the *EE* configurations. The analogous homocyclic compound (9) has been obtained as three geometrical isomers [6] and the configurations of two of them (*ZE* and *EE*) have been established by *X*-ray crystallography. We found no evidence of the presence of a second isomer with any of the compounds (1)—(4). As all of them gave a single signal for the aldimine proton in their ^{1}H n.m.r. spectra the *ZE* isomer, which requires the two aldimine protons to be in different environments, can be ruled out.

Benzylideneanilines which are not part of larger ring systems exist as the stable *E* isomers at normal temperatures.[7-10] Unstable *Z* isomers are produced photochemically at low temperatures [8,9] but revert to the *E* isomers above −70 °C. At room temperature the *Z* isomers have a thermal relaxation time (→*E*) of *ca.* 1 s.[10] Nevertheless the constraints of the rest of the molecule in (1)—(4) might stabilise the *ZZ* configuration and so both *ZZ* and *EE* configurational possibilities have to be considered.

For the *ZZ* configuration the model shows a rigid structure in which one biphenyl unit is (*R*) and the other (*S*), each of them having a dihedral angle of *ca.* 65°.

These chiralities are reversed in the enantiomer. The plane of CH=N is different from either plane of the attached aromatic rings, both Ar_C and Ar_N having been rotated through *ca.* 75° with respect to the CH=N plane.

For the *EE* configuration the Dreiding model shows flexibility, within limits, although most of the flexibility is lost in models of the space-filling type. Both biphenyl units have the same sense of twist and the dihedral angle appears to be *ca.* 55°. Flexibility involves twisting about the Ar_C–C and Ar_N–N bonds and in all conformations the sum of these two dihedral angles is *ca.* 90°. In benzylideneaniline itself these angles are *ca.* 10 and 55° respectively in the crystal[11] (0 and *ca.* 52° in the gas phase[12]) and are probably very similar in solution, since there is extensive Ar_C–CH=N conjugation but much reduced Ar_N–N=CH conjugation (see below). It thus seems likely that if the compounds (1)—(4) exist in the *EE* form, they will adopt a conformation in which the 90° is distributed unequally between the two dihedral angles, the angle of twist at Ar_N–N being much larger than that at Ar_C–C. Either the conformation of both Ar_C–CH=N–Ar_N units must be the same or else any exchange of the situations by conformational changes must be rapid on the n.m.r. time scale since the two aldimine protons give a single signal in the ^1H n.m.r. spectrum.

TABLE 1

^1H N.m.r. data (p.p.m. from $SiMe_4$ for $CDCl_3$ solutions)

Compd.	Me	CH=N	H^1	H^2	H^3	H^4	H^{15}	H^{16}	H^{17}	H^{18}
(1)		7.93(s)	6.61—6.65(m)	7.20——7.32(m)		7.34—7.46(m)	7.56(d)	7.56(d)	7.34—7.46(m)	7.68(d)
(2)	3.86(s)	7.96(s)	7.34(s)		7.90—7.94(m)	7.47—7.51(m)	7.57(d)	7.57(d)	7.41—7.47(m)	7.65(d)
(3)	3.81(s)	7.88(s)	6.55(d)	6.78—6.83(m)		7.00(d)	7.53(d)	7.53(d)	7.33—7.45(m)	7.65(d)
(4)	3.59(s)	7.77(s)	6.80(d)	7.24—7.35(m)	7.73(d)		7.53——7.55(m)		7.36—7.45(m)	7.71(d)

Neither the *ZZ* nor the *EE* model can be converted into its enantiomer without breaking bonds.

On the basis of the ^1H n.m.r. spectra and the electronic spectra, discussed below, we favour the *EE* configuration in which Ar_C–C is twisted through 10—20° and Ar_N–N is twisted through 80—70°.

^1H *N.M.R. Spectra.*—The spectra determined at 220 MHz are summarised in Table 1. The aldimine protons (at δ 7.77 and 7.96) are shielded in comparison with those in benzylideneanilines,[13] in which the signal at δ 8.42 is sensitive to *para*-substitution in the Ar_C ring but not to *para*-substitution in the Ar_N ring. However, *ortho*-substituents in the Ar_N ring have a shielding effect, giving values of δ 8.08 and 8.09 for the aldimine proton in compounds made from 2,4,6-trimethylaniline. This shielding effect is attributed[13] to the increased twisting of the N–Ar_N bond from *ca.* 50 to nearly 90° thus removing the deshielding effect which the ring was previously having on the aldimine proton.

In compounds (1)—(4) the *EE* model described above would produce a similar shielding effect on the aldimine protons, provided that the angle Ar_N–N is of the order of 80°. In addition the aldimine proton experiences some shielding by the second ring of its own Ar_C–Ar_C biphenyl unit; the two effects together would account for the observed shift. The *ZZ* model would also give rise to shielding resulting from increased twisting of the N–Ar_N bond but this alone would be insufficient to account for the full effect observed, and in this configuration the aldimine proton is not exposed to any additional shielding.

Small variations in the chemical shift of the aldimine protons on substitution in the Ar_N rings are observed, the largest being for compound (4) where the ester substituents, although *meta* to the nitrogens, are *ortho* to the biphenyl link and can thus have an effect on the overall conformation of the molecule by increasing the dihedral angle in one biphenyl unit. In this case, the effect is to increase shielding of the aldimine protons, probably by reducing the angle between Ar_C and CH=N.

A striking feature of the spectra of compounds (1), (3), and (4) is the presence of two strongly shielded aromatic protons. These are the protons H^1 and H^8, *ortho* to the nitrogen atoms. In the benzylideneanilines protons *ortho* to the nitrogen show only very slight shielding, but in the cyclic compounds the increase in the angle Ar_N–N means a corresponding increase in the overlap of the nitrogen lone-pair orbital with the π orbitals of the ring, with a consequent shielding effect which, for the *ortho* protons, is similar to that observed with *NN*-dimethylaniline. In compound (2) the 2,7-methoxycarbonyl groups counteract the shielding effect and bring the signal downfield to δ 7.34.

In the benzylideneanilines the protons *ortho* to CH=N in the Ar_C ring are deshielded by the double bond and shifted downfield by *ca.* 0.6 p.p.m. The corresponding protons (H^{11} and H^{18}) in the cyclic compounds show a smaller downfield shift of *ca.* 0.4 p.p.m., which may indicate that the Ar_C–C angle of twist is a little larger here than in the acyclic compounds. In compound (4) the shift is *ca.* 0.45, again indicating the consequences throughout the molecule of the steric effect of the substituent groups. The ester groups in compound (4) show shielding of the methyl signals and also have a smaller deshielding effect on the neighbouring protons H^3 and H^6 (δ 7.73) than the ester groups in (2) have on the same protons (δ *ca.* 7.92). Therefore the methoxycarbonyl groups in (4) must themselves be twisted out of the ring plane.

The spectrum of compound (3) was examined at temperatures down to −60 °C and showed no evidence of change of conformation or of conformational heterogeneity.

At 60 MHz the spectra of these compounds are much less clearly resolved but for compounds (2)—(4) the use of lanthanide shift-reagents separates some of the signals,

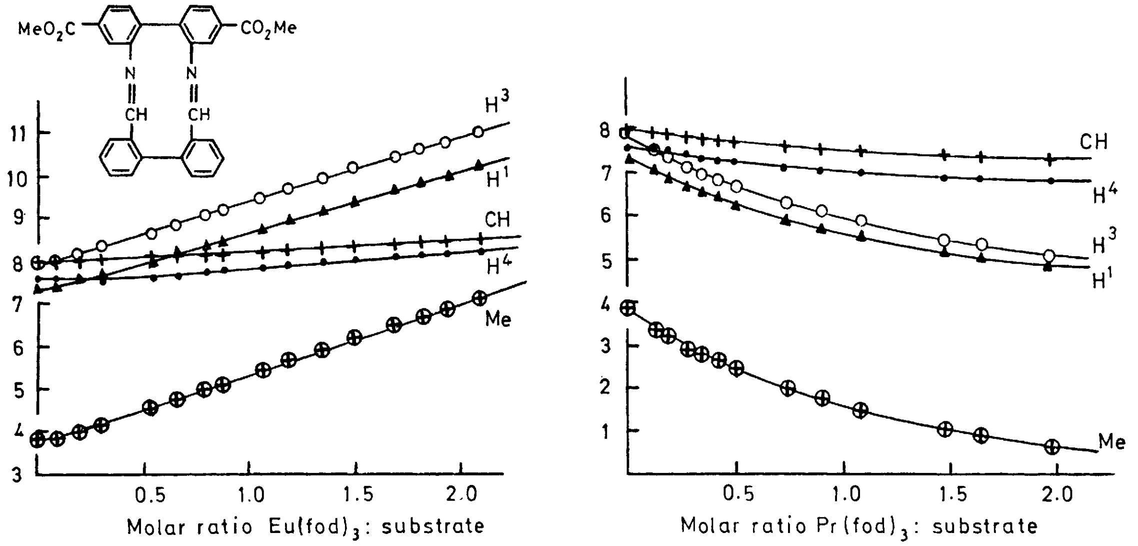

FIGURE 1 Hydrogen-1 chemical shifts for compound (2) in $CDCl_3$ in the presence of $Eu(fod)_3$ or $Pr(fod)_3$

provides further confirmation of some assignments and supports the configuration and conformation discussed above.

Compound (1) shows no change in its spectrum on addition of successive amounts of either $Eu(fod)_3$ or $Pr(fod)_3$. Imines are reported [14] to be unaffected by lanthanide shift-reagents and in this case the electron density at nitrogen is considered to be unusually low.

In compound (3) the methoxy-groups provide sites for weak complexing with $Eu(fod)_3$ or $Pr(fod)_3$. Delocalisation of the oxygen lone-pair electrons into the aromatic ring makes aromatic ethers much less effective than aliphatic ethers as electron donors [15] and the induced shifts observed here (for OMe, CH=N, H^1, H^2, H^4, H^{11}) are very small.

The ester groups in compounds (2) and (4) are much more effective co-ordination sites and moderate shifts are induced for a number of the protons (Figures 1 and 2). For compound (2) the induced shifts are in accordance with the proposed geometry; in addition to the protons shown in Figure 1, H^{11} undergoes a small shift but the signal is hidden by others in many of the spectra. Compound (4) is interesting in that H^1 and H^2 move *downfield* in the presence of $Pr(fod)_3$; the other protons undergo a normal upfield shift. However in the presence of $Eu(fod)_3$ all the induced shifts are downfield. For axially symmetric complexes the pseudocontact shift is proportional to $(3\cos^2\theta_i - 1)/r_i^3$ where θ_i is the angle between the principal magnetic axis and the distance vector, r_i, joining the particular nucleus, i, in the complexed substrate to the metal. The direction of shift is therefore reversed for values of θ between 54.7 and 125.3°. While the complex formed with (4) is very unlikely to be axially symmetrical, the induced shift will still have an angular dependence and, since steric overcrowding round the ester groups may impose severe limits on conformations able to co-ordinate to the metal,

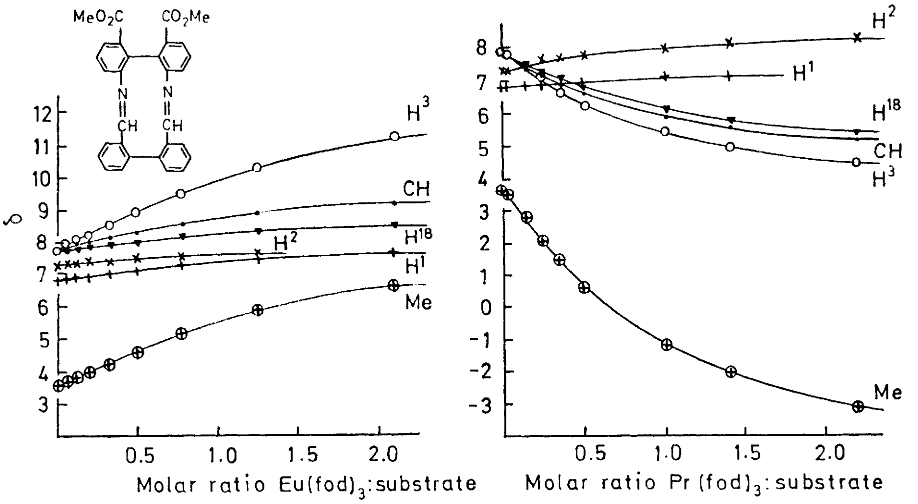

FIGURE 2 Hydrogen-1 chemical shifts for compound (4) in $CDCl_3$ in the presence of $Eu(fod)_3$ or $Pr(fod)_3$

it is quite likely that θ for particular protons will differ considerably in the two complexes.

Electronic Spectra.—Partial conjugation within the tetrabenzodiazacyclododecine molecule may be expected within each biphenyl unit and within the $\mathrm{Ar_C}$-CH=N-$\mathrm{Ar_N}$ moieties but the extent to which conjugative effects develop will depend on the relevant dihedral angles.

Biphenyl in 96% ethanol has a strong band (ε 17 300) at 249 nm which persists [16] without much change for dihedral angles of up to nearly 50°. The spectrum of benzylideneaniline (Table 2) shows broad and overlapping bands. The band at 262 nm is attributed [17–24] to conjugation between $\mathrm{Ph_C}$ and CH=N but full conjugation through the two rings is prevented by twisting of $\mathrm{Ph_N}$ out of the plane of CH=N. The broad long-wave band at *ca.* 311 nm (in ethanol) is considered [19, 20, 22, 24–26] to result from the residual conjugation through the whole π system ($\mathrm{Ar_C}$-C=N-$\mathrm{Ar_N}$), hypsochromically shifted and of low intensity in comparison with *e.g. trans*-stilbene. Protonation in concentrated sulphuric acid removes the lone pair and thus the driving force for twisting [22, 23] of N-$\mathrm{Ar_N}$, and the spectrum becomes that of an approximately planar and fully conjugated system, with an intense band [22] at 340 nm (ε 21 000).

Table 2

Electronic spectrum of benzylideneaniline (wavelengths in parentheses denote inflections)

								Long-wave band		
$\lambda_{max.}$	$\varepsilon_{max.}$	$\lambda_{max.}$	$\varepsilon_{max.}$	$\lambda_{max.}$	$\varepsilon_{max.}$	$\lambda_{max.}$	$\varepsilon_{max.}$	$\lambda_{max.}$	$\varepsilon_{max.}$	Solvent
211	14 000	220	13 800	236	10 800	262	17 000	315	7 360 [a]	Cyclohexane [b]
		218	15 000	(238)	8 900	262	16 700	311	9 000 [c]	Ethanol [d]

[a] B. Scheuer-Lamalle and G. Durocher, *Canad. J. Spectroscopy*, 1976, **21**, 165, $\lambda_{max.}$ 322.5 ($\varepsilon_{max.}$ 7 000) for the long-wave band in cyclohexane. [b] E. Haselbach and E. Heilbronner, *Helv. Chim. Acta*, 1968, **51**, 16. [c] 'U.V. Atlas of Organic Compounds,' Butterworths–Verlag Chemie, 1966, C6/1; $\lambda_{infl.}$ 312 ($\varepsilon_{infl.}$ 8 000) for the long-wave band in ethanol. [d] M. A. El-Bayoumi, M. El-Aasser, and F. Abdel-Halim, *J. Amer. Chem. Soc.*, 1971, **93**, 586.

The spectrum of compound (1) in 96% ethanol shows a broad band at 234 nm (ε 39 400) with a shoulder at *ca.* 250 nm and a very broad long-wave band which, in the unsubstituted compound, does not have a true maximum; ε is *ca.* 5 600 at 315 nm, rising to 6 400 at 300 nm. Since each chromophore appears twice in the structure the observed intensities should be roughly halved in order to relate them to features in the spectra of biphenyl or benzylideneaniline.

The low intensity of the long-wave band shows that conjugation through the entire $\mathrm{Ar_C}$-C=N-$\mathrm{Ar_N}$ chromophore is yet further reduced in comparison with benzylideneaniline itself. This indicates further twisting within the chromophore consistent with the *EE* configuration in a conformation in which the $\mathrm{Ar_N}$-N twist is large. It is noteworthy that in the *Z* photoisomer of benzylideneaniline, in which the angle of twist about $\mathrm{Ar_N}$-N is considered to be 90°, the intensity of this band is reduced by *ca.* 75% from its value in the *E* isomer.

The overlapping high intensity bands at 234—250 nm in the spectrum of (1) are probably the 238 and 262 nm bands of the $\mathrm{Ar_C}$-C=N-$\mathrm{Ar_N}$ structure with a residue of the biphenyl band, shifted to shorter wavelength, superimposed on them. A biphenyl [27] (10) in which the dihedral angle is *ca.* 60° (ref. 28) has the conjugation band at 235 nm with ε *ca.* 10 000. On this basis ε_{234} for compound (1) should be *ca.* 20 000 + (2 × ε_{238} for benzylideneaniline) = *ca.* 38 000, which is close to the observed value of 39 000. This indicates that the 238-nm band of benzylideneaniline is fully developed and thus supports a conformation for (1) in which the dihedral angle for the biphenyl units is $\ngtr$60°. On the other hand the 262-nm band of benzylideneaniline appears to be of lower intensity in (1) since ε_{262} at 25 000 is less than twice ε_{262} for benzylideneaniline (34 000); possibly there has also been a slight hypsochromic shift. It seems possible that there is some increased twisting about the $\mathrm{Ar_C}$-C bond but not sufficient to cause substantial loss of conjugation between $\mathrm{Ar_C}$ and C=N. The *ZZ* configuration in which this angle of twist is *ca.* 75° would be expected to have very much lower absorption in this region.

Substituent effects on the spectra are complex because of band overlapping. In compound (2) the ester groups should not affect the overall conformation of the molecule and, since they are *meta* to the nitrogen atoms, should not much affect the N-$\mathrm{Ar_N}$ interaction but as they are *para* to the biphenyl link they can be expected to exert their normal bathochromic effect on the biphenyl conjugation; this is observed in the long-wave shift of one of the biphenyl conjugation bands so that there is now a distinct band at 253 nm (biphenyl conjugation superimposed on the $\mathrm{Ar_C}$-CH=N band at 262 nm). On the short-wave side of this band absorption is still high since the other biphenyl band and the $\mathrm{Ar_N}$-N unit absorb there (Figure 3).

para-Substitution by methoxy in the $\mathrm{Ar_N}$ ring in benzylideneaniline produces long-wave shifts in the 238- and 311-nm bands and a general increase in intensity.[23] In compound (3) overlapping bands obscure any wavelength changes but there is a marked increase in intensity in the 235-nm band and in the long-wave band.

Compound (4) differs from the others in that the substituent ester groups have a steric effect on their biphenyl unit, so that one biphenyl conjugation band undergoes a further hypsochromic shift (*cf.* the effect of *ortho* substituents on the conjugation band in bridged biphenyls [16]). As a result the combined band appears at 227 nm and has a misleadingly high intensity because it is now overlapping the steep side of the very intense band at *ca.* 203 nm. In this spectrum the band at 253 nm, although still an inflection, is more obviously a separate band than in the spectra of (1) and (3) because it no longer has quite such intense absorption on its short-wave side.

From the chemical shift of the aldimine proton in compound (4) it was postulated that as a result of increased twisting of a biphenyl unit the angle between Ar_C and CH=N is slightly reduced in this compound in comparison with the others. This is supported by an increase in ε_{262} to *ca.* 29 000 from 25 000 in compound (1) and by an increase in the intensity of the long-wave band.

Chirality.—In discussing the geometry of the tetrabenzodiazacyclododecines we have used twisted biphenyl units as parts of the structure. Models suggest that inversion of configuration will have a high energy barrier but they might be misleading and it was desirable to demonstrate the overall chirality of the structure if possible.

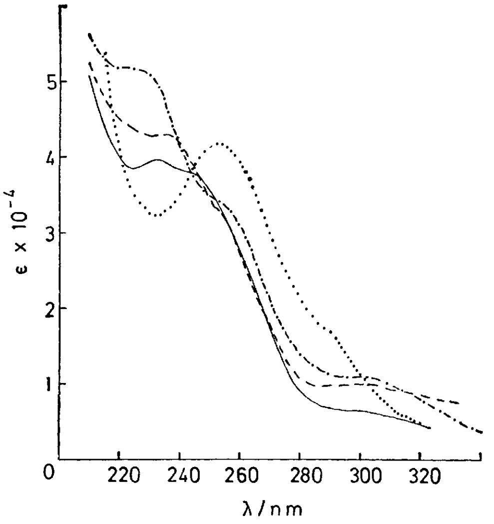

FIGURE 3 U.v. absorption spectra in 96% EtOH of tetrabenzodiazacyclododecines; (——), compound (1); (· · · ·), compound (2); (– – – –), compound (3); (— · — · —), compound (4)

We have shown earlier[29] that chiral shift-reagents, present in high molar ratio, can be used to show the presence of enantiomers in racemic, optically stable biphenyls in which methoxycarbonyl groups are available for co-ordination to the lanthanide. The addition of tris[3-trifluoromethylhydroxymethylene-(+)-camphorato]europium(III) [Eu(tfc)$_3$][30] to solutions of compounds (2) or (4) in deuteriochloroform produced a doubling of the methyl proton resonances at 60 MHz, the separation being 0.02 p.p.m. (at a molar ratio of 8.79 : 1) for compound (2) and 0.04 p.p.m. (at a molar ratio of 9.99 : 1) for compound (4). Compound (3) appeared to show a slight separation of the methoxy-proton signals in the presence of Eu(tfc)$_3$, but owing to the low complexing power of the methoxy-groups the induced shifts were small and the demonstration of chirality less certain with this compound than with (2) and (4).

The Tetrahydro-compounds.—Reduction of the C=N double bonds removes much of the rigidity of the molecules. Spectral evidence, especially from ^{13}C n.m.r., suggests that more than one conformation is present, and further investigations are in progress.

EXPERIMENTAL

U.v. spectra were determined in 96% ethanol on a Perkin-Elmer 124 spectrophotometer. ^{1}H N.m.r. spectra were determined for CDCl$_3$ solutions by the P.C.M.U., Harwell (220 MHz) or on a Perkin-Elmer R 12 (60 MHz) spectrometer. I.r. spectra were determined on Perkin-Elmer 457 or Unicam SP 200 spectrophotometers. Melting points above 120 °C were determined on a Electrothermal melting point apparatus.

Lanthanide-induced shifts were measured at 60 MHz after introducing successive weighed amounts of the shift-reagent into a solution of the substrate in dry CDCl$_3$.

Tetrabenzo[b,d,h,j][1,6]*diazacyclododecine* (1).—(*With Dr. H. Y. Hwang*). This had m.p. 312—313 °C after crystallisation from benzene (lit.,[2] 326 °C); $\nu_{C=N}$ 1 625 cm^{-1}; $\lambda_{max.}$ 234 ($\varepsilon_{max.}$ 39 400); $\lambda_{infl.}$ 250 ($\varepsilon_{infl.}$ 35 700); $\lambda_{infl.}$ *ca.* 310 nm ($\varepsilon_{infl.}$ 5 750).

9,10,19,20-*Tetrahydrotetrabenzo*[b,d,h,j][1,6]*diazacyclododecine* (5).—The above diazacyclododecine (1.0 g) was suspended in glacial acetic acid (2 ml) and (dimethylamino)borane (0.412 g) in acetic acid (2 ml) added slowly, the temperature being kept at 20 °C. A further 1 ml of acetic acid was added and the mixture heated at 50—53 °C for 7 min. Precipitation at room temperature with water gave a solid (0.985 g, 97%), m.p. 168—172.5 °C raised to 174—176 °C after one crystallisation from methanol (lit.,[2] m.p. 158 °C) (Found: C, 86.2; H, 6.1; N, 7.6. Calc. for $C_{26}H_{22}N_2$: C, 86.15; H, 6.1; N, 7.7%). The compound became brown during storage and measurements were made as soon as possible after purification.

Dimethyl Tetrabenzo[b,d,h,j][1,6]*diazacyclododecine*-2,7-*dicarboxylate* (2).—Biphenyl-2,2′-dicarbaldehyde[31] (1.05 g) and dimethyl 2,2′-diaminobiphenyl-4,4′-dicarboxylate[4] (1.5 g) were heated together in ethanol (60 ml) for 3 h. Crystals (2.3 g, 97%), m.p. 251—255 °C, separated after the cooled solution had been allowed to stand for 2 d, and were recrystallised from benzene–light petroleum (b.p. 60—80 °C), giving pale yellow diamond-shaped *plates*, m.p. 261—261.5 °C, and pale yellow *rods*, m.p. 262—263 °C (Found: C, 76.1; H, 4.6; N, 5.6. $C_{30}H_{22}N_2O_4$ requires C, 75.9; H, 4.7; N, 5.9%); $\nu_{C=N}$ 1 632 cm^{-1}. Initially plates were always obtained; in some recrystallisations plates predominated, in others rods were the major form; $\lambda_{max.}$ 253 ($\varepsilon_{max.}$ 41 500); $\lambda_{infl.}$ 290 ($\varepsilon_{infl.}$ 17 500).

Dimethyl 9,10,19,20-*Tetrahydrotetrabenzo*[b,d,h,j][1,6]*diazacyclododecine*-2,7-*dicarboxylate* (6).—Reduction of the above compound (0.5 g) in acetic acid (1.5 ml) with (dimethylamino)borane (0.165 g) in acetic acid was carried out at 20 °C, with subsequent heating at *ca.* 50 °C for 7 min. The product was precipitated with cold water and gave, on crystallisation from ethanol, predominantly pale yellow *rods*, m.p. 238—239 °C, together with a small quantity of yellow hexagonal *plates*, m.p. 237—238 °C (Found: C, 74.7; H, 5.4; N, 5.6. $C_{30}H_{26}N_2O_4$ requires C, 75.3; H, 5.5; N, 5.85%) (total yield 0.45 g, 89%).

2,2′-*Diamino*-5,5′-*dimethoxybiphenyl*.— 5,5′-Dimethoxy-2,2′-dinitrobiphenyl, m.p. 148—149 °C (lit.,[32] 148—149 °C), obtained by the action of copper bronze on 3-chloro-4-

nitroanisole,[33] was reduced with hydrogen in the presence of 5% Pd–C catalyst in tetrahydrofuran solution at 13—17 °C. The diamine was crystallised from light petroleum (b.p. 80—100 °C) and had m.p. 105—106 °C (Found: C, 69.0; H, 6.9; N, 10.7. $C_{14}H_{16}N_2O_2$ requires C, 68.8; H, 6.6; N, 11.5%).

3,6-*Dimethoxytetrabenzo*[b,d,h,j][1,6]*diazacyclododecine* (3).—Biphenyl-2,2′-dicarbaldehyde (0.525 g) and 2,2′-diamino-5,5′-dimethoxybiphenyl (0.611 g) were heated together in ethanol (35 ml) for 1 h. Solid (0.99 g, 95%), m.p. 286—287.5 °C, was collected after the solution had been left overnight. Crystallisation from dry benzene gave pale yellow prisms, m.p. 288.5—289.5 °C (Found: C, 80.5; H, 5.3; N, 6.3. $C_{28}H_{22}N_2O_2$ requires C, 80.35; H, 5.3; N, 6.7%); $\nu_{C=N}$ 1 630 cm^{-1}; $\lambda_{infl.}$ 235 ($\varepsilon_{infl.}$ 43 200); $\lambda_{infl.}$ 255 ($\varepsilon_{infl.}$ 32 000); $\lambda_{max.}$ 300 nm ($\varepsilon_{max.}$ 9 800).

3,6-*Dimethoxy*-9,10,19,20-*tetrahydrotetrabenzo*[b,d,h,j]-[1,6]*diazacyclododecine* (7).—The above compound (0.50 g) was reduced with (dimethylamino)borane in glacial acetic acid under the usual conditions. The secondary *amine* crystallised from ethanol in pale yellow hexagonal plates, m.p. 164.5—165 °C (69%) (Found: C, 79.8; H, 6.3; N, 6.5. $C_{28}H_{26}N_2O_2$ requires C, 79.6; H, 6.2; N, 6.6%).

Dimethyl 2,2′-*Diaminobiphenyl*-6,6′-*dicarboxylate*.—Dimethyl 2,2′-dinitrobiphenyl-6,6′-dicarboxylate[34] (4.0 g) in tetrahydrofuran solution and Adams' platinum oxide catalyst (1.40 g) were shaken with hydrogen at *ca.* 4 atm and at 13—15 °C. The *diamine* crystallised from ethanol in pale yellow prisms, m.p. 127—128 °C, changing after melting to a white solid, which did not melt up to 340 °C (the bis-lactam[5] has m.p. >330 °C) (Found: C, 63.9; H, 5.4; N, 9.2. $C_{16}H_{16}N_2O_4$ requires C, 64.0; H, 5.4; N, 9.3%).

Dimethyl Tetrabenzo[b,d,h,j][1,6]*diazacyclododecine*-4,5-*dicarboxylate* (4).—Biphenyl-2,2′-dicarbaldehyde (0.525 g) and dimethyl 2,2′-diaminobiphenyl-6,6′-dicarboxylate (0.751 g) were allowed to react in ethanol (50 ml) at room temperature during 2 d. The pale yellow product (81%) was obtained, after crystallisation from ethanol, with m.p. 276—277 °C (Found: C, 75.6; H, 4.7; N, 5.6. $C_{30}H_{22}N_2O_4$ requires C, 75.9; H, 4.7; N, 5.9%); $\nu_{C=N}$ 1 626 cm^{-1}; $\lambda_{max.}$ 227 ($\varepsilon_{max.}$ 49 700); $\lambda_{infl.}$ 256 ($\varepsilon_{infl.}$ 33 300); $\lambda_{infl.}$ 300 ($\varepsilon_{infl.}$ 11 000).

Dimethyl 9,10,19,20-*Tetrahydrotetrabenzo*[b,d,h,j][1,6]*diazacyclododecine*-4,5-*dicarboxylate* (8).—The above compound (0.2 g) in tetrahydrofuran (100 ml) was shaken with hydrogen in the presence of Adams' platinum oxide catalyst at *ca.* 3 atm and 17 °C. After filtration, the solvent was removed at <30 °C and water added. The *tetrahydro-ester* crystallised from ethanol in needles, m.p. 214—214.5 °C (73%) (Found: C, 74.95; H, 5.8; N, 5.9. $C_{30}H_{26}N_2O_4$ requires C, 75.3; H, 5.5; N, 5.85%).

2,2′-*Diamino*-4,6,4′,6′-*tetramethylbiphenyl*.—The dinitro-compound[35] was reduced with hydrogen in glacial acetic acid–ethanol solution in the presence of Adams' platinum oxide catalyst. The *diamine*, crystallised from light petroleum (b.p. 60—80 °C), had m.p. 180—181.5 °C (Found: C, 79.9; H, 8.5; N, 11.7. $C_{16}H_{20}N_2$ requires C, 80.0; H, 8.4; N, 11.7%) (3.5 g, 87%).

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