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THE SYNTHESIS AND SPECTROSCOPIC PROPERTIES OF SOME SUBSTITUTED AND BRIDGED BIPHENYLS

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Abstract—A series of tetramethoxybiphenyls and bridged tetramethoxybiphenyls have been prepared and their UV spectra investigated. The substituted biphenyls show short- and long-wavelength bands while the bridged biphenyls and the parent 3,3',4,4'-tetramethoxybiphenyl in addition show conjugation bands. The significance of these findings is discussed. The NMR spectra of the bridged biphenyls show that, with one exception, conformational inversion in this series is rapid at 35°.

Substituted biphenyls and bridged biphenyls have been the subject of extensive spectroscopic study.[1–11] To a large extent this work relates to compounds unsubstituted except in the *ortho* positions. In connection with other work we had occasion to prepare a range of both types in which each benzene ring is substituted by two OMe groups. Previous work has shown that there is a correlation between the maximum of the conjugation band of the UV absorption and the angle θ between the planes of the benzene rings, i.e. as θ increases so the band shifts to shorter wavelength and decreases in intensity.[2,3,11] UV spectroscopic measurements on the present series confirm this and show that where there is also present a long-wavelength band a similar relationship holds.

Preparation. The substituted tetramethoxybiphenyls (I–IV) were prepared as described by Cromartie *et al.*[12] The dinitrile (VI) was obtained from the diamide (III) by treatment with thionyl chloride, and the dialcohol (IV) was converted into the dichloride (V) with thionyl chloride and pyridine in benzene. Dieckmann cyclization of the diester (II) gave the β-ketoester (XII) which was hydrolysed and decarboxylated to the ketone (XIII) by treatment with boiling n-butanol-conc hydrochloric acid. From this ketone were prepared the oxime (XIV), the alcohol (XVI) and the Wolff-Kischner reduction product (XV). Beckmann rearrangement of the oxime proceeded only with difficulty, the best yields (10–14%) of the expected amide (XVIII) being obtained with phosphorus pentachloride in benzene. The major product of this reaction was the chloronitrile (VIII), resulting from ring cleavage due to attack by chloride ion on the highly-strained ring system (XIX).

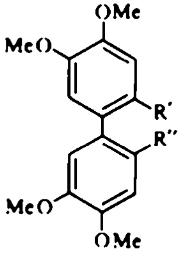
UV spectra. Table 1 records the UV spectroscopic data for these compounds and for ethyl 3,4-dimethoxyphenylacetate (XX), together with the figures reported by Matarasso-Tchiroukhine[13] for the related compounds (IX, X, XI and XVII). Data quoted by Beaven *et al.*[4,5] and by Braude and Forbes[6] show that the presence of two OMe groups per molecule in the biphenyl series causes an increase in intensity and a shift to longer wavelength of the long-wavelength band. In this series of compounds, the presence of four OMe groups per molecule further intensifies and shifts to the red the long-wavelength bands. These long-wavelength bands show clearly the relationship between λ_{max}, ε_{max} and the angle θ described by Beaven *et al.*[3] and

TABLE 1. UV SPECTRA OF SOME SUBSTITUTED AND BRIDGED BIPHENYLS IN ETHANOL

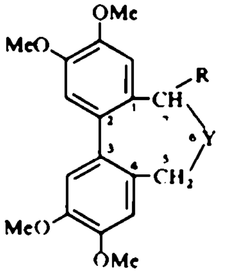
Compound	Short-wave band λ_{max} mμ	Conjugation band λ_{max} mμ	Long-wave band λ_{max} mμ
I	233 (s) (4·25)[b]		287 (3·88)
II	234 (s) (4·24)		288 (3·91)
III	236 (s) (4·21)		287 (3·87)
V	232 (s) (4·29)		285 (3·90)
VI	235 (s) (4·22)		287 (3·89)
VII	229 (4·66)		282 (3·97)
VIII	235 (s) (4·28)		284 (3·89)
IX[a]			286 (4·10)
X[a]			290 (4·09)
XI[a]		273 (4·30)	291 (4·23)
XII	246 (4·38)	261 (4·27)	289 (4·20)
XIII	243 (s) (4·19)		288 (4·12)
XIV	241 (s) (4·20)	272 (4·17)	291 (4·14)
XV	not visible	265 (4·18)	292 (4·14)
XVI	239 (s) (4·16)	266 (4·18)	291 (4·13)
XVII[a]		274 (4·20)	297 (4·10)
XVIII	235 (s) (4·21)	261 (3·93)	282 (3·89)
XX	229 (3·84)		279 (3·49)

[a] Reported in Ref. 13, no short-wave band figures given.

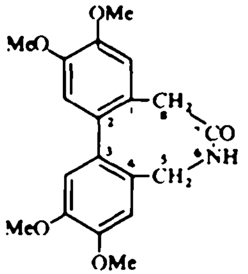
[b] (s) = shoulder. Figures in brackets refer to $\log_{10} \epsilon_{max}$.



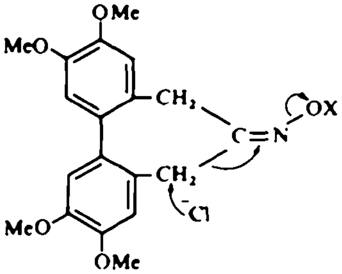
I: R′ = R″ = CH_2CO_2H
II: R′ = R″ = CH_2CO_2Me
III: R′ = R″ = CH_2CONH_2
IV: R′ = R″ = CH_2CH_2OH
V: R′ = R″ = CH_2CH_2Cl
VI: R′ = R″ = CH_2CN
VII: R′ = R″ = CH_2CH_2OCOPh
VIII: R′ = CH_2Cl, R″ = CH_2CN
IX: R′ = R″ = Me
X: R′ = R″ = CH_2Cl
XI: R′ = R″ = H



XII: R = CO_2Me Y = C=O
XIII: R = H Y = C=O
XIV: R = H Y = C=NOH
XV: R = H Y = CH_2
XVI: R = H Y = CHOH
XVII: R = H Y = O



XVIII



XIX

Mislow *et al.*,[8] among others, and discussed by Jaffé and Orchin[2] and Suzuki[11] for the *conjugation* band of less highly substituted biphenyls. Thus, for those compounds I–VIII which have bulky groups in the 2- and 2′-positions, the values of θ are greater than that for the parent compound XI and this is reflected in the shorter wavelengths and lower intensities of the absorption bands.*

Formation of the 7-membered ring bridge (compounds XII–XVII) forces the aromatic rings into a more nearly coplanar situation and the decrease in θ results in higher intensities of absorption at slightly higher wavelength. Expansion of the 7-membered ring system to an 8-membered ring in the amide XVIII allows greater flexibility in the system and thus a higher value for θ; the absorption band shifts to shorter wavelength with lower intensity.

The conjugation bands in this series also show this relationship; expansion of the ring of XIV from 7 to 8 members in XVIII causes a decrease in the intensity and the wavelength.

The non-bridged, 2,2′-disubstituted compounds (I–X) do not show bands in the 260–275 mμ region, the high angle of torsion preventing effective conjugation. Interestingly, the spectrum of the ketone XIII also does not appear to have a conjugation band, despite the fact that the position and intensity of the long-wavelength absorption are similar to those of the other bridged compounds, indicating comparable values of θ. Mislow *et al.*[8] have noted that, for another series of bridged biphenyls, the presence of a ketonic CO in the 6-position is associated with a small shift (5–10 mμ) to longer wavelength of the conjugation band, and this is attributed to interaction between the benzene and CO π-systems in the electronically excited state. This was confirmed by observation of strengthened $n-\pi^*$ transitions at longer wavelength. It may be that a similar effect is operating in the present example and that the conjugation band has been modified to such an extent that it is not clearly visible, being masked by the intense long-wavelength absorption. It is unlikely that we would observe in this system the strengthened $n-\pi^*$ transitions which might accompany this effect.

NMR spectra. Table 2 shows the NMR data for some bridged biphenyls. On the whole the spectra agree well with those reported by Mislow *et al.*[8] and Sutherland

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* The extinction coefficients reported by Matarasso-Tchiroukhine (Ref. 13) for compounds IX and X appear to be a little higher than might be expected on comparison with the figures quoted here for similar compounds, although the values for λ_{max} are in fair agreement with ours.

TABLE 2. NMR SPECTRA OF BRIDGED BIPHENYLS IN DEUTEROCHLOROFORM
Chemical shift at 35° (τ-scale)

Compound	Aromatic H	Methoxyl H	5H	6H	7H	8H	Other
XII	3·0 3·3 [4] (m)	6·10 [12] (d) 6·31 [3] (s) (ester)	6·85 [2] (s)	—	6·46 [1] (broad)		
XIII	3·13 [2] (s) 3·41 [2] (s)	6·16 [6] (s) 6·20 [6] (s)	6·62 [4] (s)	-	as 5H		
XIV	3·20 [2] (s) 3·36 [2] (s)	6·14 [14] (s)	6·72 [2] (s) (anti)		(syn : included with methoxyl H)	—	
XV	3·30 [2] (s) 3·43 [2] (s)	6·20 [12] (s)	7·5–8·0 [6] (m)	as 5H	as 5H		
XVI	3·24 [2] (s) 3·38 [2] (s)	6·17 [12] (s)	$\underbrace{7{\cdot}49\ [4]\ (o),\ 5{\cdot}63\ [1]\ (t)}_{ABX\ (J_{AB} = 13\ c/s)}$		as 5H	-	8·0 [1] (s)
XVIII	3·33 [2] (s) 3·40 [2] (s)	6·20 [14] (s)	6·80 [2] (d)	8·75 [1] (s)	—	(included with methoxyl H)	--

s = Singlet, d = doublet, t = triplet, m = multiplet, o = octet. Figures in square brackets refer to integrated proton count.

and Ramsey.[10] At the temperature used, only the alcohol XVI shows clearly the non-equivalence of the benzylic protons which is to be expected in a rigid system where conformational inversion is slow. An ABX system is observed with J_{AB} = 13 c/s. A range of 11–15·2 c/s is quoted in Ref. 8.

EXPERIMENTAL

UV spectra were recorded on a Cary 14 Recording Spectrophotometer and on a Unicam SP800 Spectrophotometer. IR spectra were obtained with a Perkin–Elmer Model 337 instrument and NMR spectra were recorded using a Varian A-60 spectrometer operating at 60 mc/s.

2,2'-Bis-β-chloroethyl-4,4',5,5'-tetramethoxybiphenyl (V). A soln of $SOCl_2$ (0·35 ml) in benzene (10 ml) was added to a soln of IV (374 mg) in benzene (50 ml). Pyridine (0·40 ml) was added and the mixture was heated under reflux (1 hr) and then poured into ice-conc HCl. This mixture yielded to benzene the *dichloride* V (373 mg) which was crystallized from benzene pet. ether, m.p. 144 145°. (Found: C, 60·5; H, 5·9; Cl, 17·8. $C_{20}H_{24}Cl_2O_4$ requires: C, 60·2; H, 6·0; Cl, 17·8%).

The dibenzoyl derivatives (VII) of IV crystallized from EtOH as rhombs., m.p. 105–106°, ν_{max} (CH_2Cl_2) 1725 cm^{-1} (ester CO). (Found: C, 71·6; H, 5·9. $C_{34}H_{34}O_8$ requires: C, 71·6; H, 6·0%).

Dieckmann cyclization. Finely-chopped Na (4·3 g) was added to a soln of II (10 g) in benzene, followed by MeOH (1 ml). The mixture was heated under reflux (12 hr) and when unreacted Na had been destroyed with MeOH, was poured into ice–water (450 ml). The mixture was acidified (HCl) and extracted with $CHCl_3$. The extract was washed, dried and evaporated leaving a yellow solid (9·15 g) which was crystallized from MeOH–$CHCl_3$ to give *7-methoxycarbonyl-4',4'',5',5''-tetramethoxy-1,2,3,4-dibenzocyclohepta-1,3-diene-6-one* (XII), m.p. 202 205°, ν_{max} (CH_2Cl_2) 1745 (ester CO) and 1725 cm^{-1} (7-ring ketone). (Found: C, 65·0; H, 6·0 $C_{21}H_{22}O_7$ requires: C, 65·3, H, 5·7%)

4',4'',5',5''-Tetramethoxy-1,2,3,4-dibenzocyclohepta-1,3-diene-6-one (XIII) The β-ketoester XII (3·05 g) was heated under reflux with n-BuOH (250 ml) and conc HCl (190 ml) for 5 hr. The solvents were removed under reduced press. and the solid residue was boiled with MeOH. The ketone XIII (1·62 g) remained undissolved and was crystallized from EtOH dioxan, m.p. 252–256°, ν_{max} (CH_2Cl_2) 1720 cm^{-1} (7-ring ketone) (Found C. 69·5; H. 5·9 Calc for $C_{19}H_{20}O_5$: C. 69·5; H. 6·1%) Matarasso-Tchiroukhine[13] reports m.p. 259.

The oxime XIV crystallized from EtOH as needles, m.p. 186 187·5°, ν_{max} (CH_2Cl_2) 3595 cm^{-1} (O–H). (Found: C, 66·7; H, 6·4; N, 4·3. Calc. for $C_{19}H_{21}NO_5$: C, 66·5; H, 6·2; N, 4·1%). Matarasso-Tchiroukhine[13] reports m.p. 189.

Beckmann rearrangement. The oxime XIV (1·0 g) in benzene (40 ml) was shaken with PCl_5 (1·49 g) for 1 hr. Water was added, and the mixture yielded to $CHCl_3$ an oil (1·05 g) which was chromatographed in benzene on alumina (Brockmann activity V; 20 g). Elution with benzene gave *2-chloromethyl-2'-cyanomethyl-4,4',5,5'-tetramethoxybiphenyl* VIII (489 mg), which was crystallized from heptane benzene, m.p. 159–160°, ν_{max} (CH_2Cl_2) 2255 cm^{-1} (nitrile). (Found: C, 62·8; H, 5·5; Cl, 9·8; N, 4·0. $C_{19}H_{20}ClNO_4$ requires: C, 63·1; H, 5·4; Cl, 9·8; N, 3·9%). Elution with $CHCl_3$–benzene (4:6 v/v) gave *4' 4'',5',5''-tetramethoxy-1,2,3,4-dibenzo-6-azacycloocta-1,3-diene-7-one* XVIII (120 mg) which was crystallized from benzene, m.p. 110 112°, ν_{max} (CH_2Cl_2) 3425 (N H) and 1680 cm^{-1} (8-ring amide). (Found: C, 66·4; H, 6·0; N, 4·2. $C_{19}H_{21}NO_5$ requires: C, 66·5; H, 6·2; N, 4·1%).

Wolff Kishner (Huang Minlon) reduction. The ketone XIII (400 mg) was added to a soln of KOH (2·24 g) and $N_2H_4 \cdot H_2O$ (4·0 ml) in diethylene glycol (10 ml) at 150°. After 90 min at this temp, the soln was cooled and poured into water (50 ml). After 16 hr at room temp a solid separated (201 mg) which was crystallized from heptane–benzene to give *4',4'',5',5''-tetramethoxy-1,2,3,4-dibenzo-cyclohepta-1,3-diene* (XV), m.p. 153·5 155°. (Found C, 72·4; H, 6·7. $C_{19}H_{22}O_4$ requires. C, 72·6, H, 7·05%).

Reduction with lithium aluminium hydride The ketone XIII (530 mg) in THF (40 ml) was heated under reflux with LAH (218 mg) for 16 hr. When unreacted LAH had been destroyed with EtOAc, dilute H_2SO_4 was added, and the mixture was extracted with $CHCl_3$, yielding *4',4'',5',5''-tetramethoxy-1,2,3,4-dibenzocyclohepta-1,3-diene-6-ol* XVI (516 mg) which crystallized from EtOH, m.p. 181·5 183·5°, ν_{max} (CH_2Cl_2) 3615 cm^{-1} (O H). (Found C. 69·3; H, 6·8. $C_{19}H_{22}O_5$ requires: C, 69·1; H, 6·7%)

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