The Ultraviolet Absorption Spectra of 2,2′-Biphenyls with Bridges containing Ether, Sulphide, and Sulphone Groups

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The u.v. spectra have been measured for a series of 2,2′-bridged biphenyls, with ether, sulphide, or sulphone groups at both ends of a bridge containing up to five methylene groups. The spectra indicate that the dihedral angles between the planes of the phenyl rings are determined not only by the length and rigidity of the bridging group but also by the nature of the functional groups at the ends of the bridge. The tendency to maintain the phenyl rings of the biphenyl system antiplanar increases in the order ether < methylene < sulphide < sulphone. The characteristic biphenyl band is present in the spectra of all the ethers. However, the repulsive forces between the sulphone groups inhibit biphenyl conjugation and are probably sufficient to produce a preference for a transoid conformation when the bridge contains four or five methylene groups.

THE stereochemistry of 2,2′-bridged biphenyls has been investigated previously using u.v. and n.m.r. spectroscopy.[1-3] A wide range of biphenyls with single and double three-membered bridges, and incorporating various heteroatoms in the centre of the bridge, have been studied.[2,3] More recently the 2,2′-bridged biphenyl (1) has been prepared; this is the first singly bridged dithiabiphenyl to be investigated spectroscopically.[4,5]

The present study is of three series of 2,2′-biphenyl heterocycles (2)—(4) in which the heteroatoms are directly attached to two positions *ortho* to the coannular bonds of the biphenyl system. Eleven different bridging groups Y, having one to five members, provide a wide range of dihedral angles between the planes of the phenyl rings in the three series of heterocycles. The spectra of these compounds have been compared with the spectra of the unbridged biphenyl derivatives (5)—(7).

The disulphides and diethers were prepared from the disodium salt of the dithiol (6; X = H) and the diphenol (7; X = H) respectively, and the αω-dihalide of the bridging group Y.[6] The disulphones were obtained by oxidation of the disulphides with hydrogen peroxide in acetic acid.[6] The heterocyclic compounds were shown to be monomeric by mass spectral and solution vapour pressure measurements.[6]

The u.v. spectra of the sulphones show two well defined bands; methyl phenyl sulphone (8; X = Me) has an intense primary (p) band at 217 nm and a structured secondary (α) band at 264 nm. The overall variation in $\lambda_{max.}$ of the p band in the sulphone series of biphenyl compounds is little more than 5 nm compared with 18 nm for the α band. The biphenyl disulphones which possess an extended bridge *e.g.* (2; $Y = [CH_2]_n$; $n > 1$) or no bridge, *i.e.* (5), exhibit a p band at shorter wavelength (207—208 nm) than the alkyl phenyl sulphones.[7] This shift reflects the presence of an out-of-plane aryl substituent in the phenyl sulphone

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[1] W. E. Truce and D. D. Emrick, *J. Amer. Chem. Soc.*, 1956, **78**, 6130.

[2] K. Mislow, S. Hyden, and H. Schaefer, *J. Amer. Chem. Soc.*, 1962, **84**, 1449.

[3] K. Mislow, M. A. W. Glass, H. B. Hopps, E. Simon, and G. H. Wahl, *J. Amer. Chem. Soc.*, 1964, **86**, 1710.

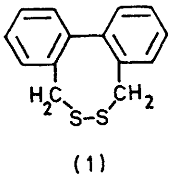
[4] A. Lüttringhaus, U. Hess, and H. J. Rosenbaum, *Z. Naturforsch.*, 1967, **22b**, 1296.

[5] A. Lüttringhaus and H. J. Rosenbaum, *Monatsh.*, 1967, **98**, 1232.

[6] D. W. Allen, P. N. Braunton, and I. T. Millar, *Chem. and Ind.*, 1969, 522; D. W. Allen, P. N. Braunton, I. T. Millar, and J. C. Tebby, *J. Chem. Soc. (C)*, 1971, 3454.

[7] E. A. Fehnel and M. Carmack, *J. Amer. Chem. Soc.*, 1949, **71**, 231; 1950, **72**, 1292.

chromophore of the biphenyl compounds. When the length of the bridge is reduced to a single methylene group, conjugation between the rings increases and the p band undergoes a small bathochromic shift of *ca.* 5 nm.



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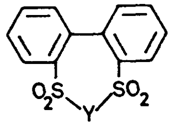

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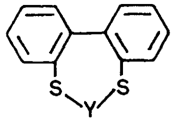

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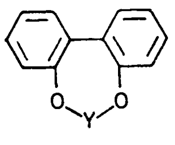

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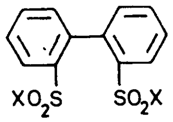

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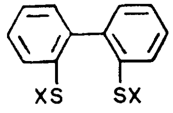

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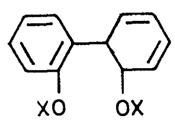

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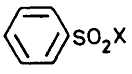

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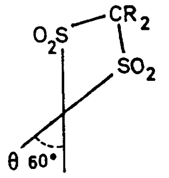

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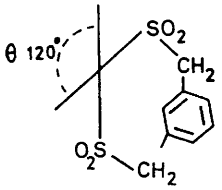

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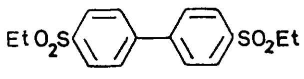


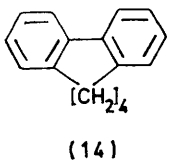
(11)

$PhS{\cdot}CH_2{\cdot}O{\cdot}CH_2{\cdot}SPh$

(12)

$PhO{\cdot}CH_2{\cdot}O{\cdot}CH_2{\cdot}OPh$

(13)



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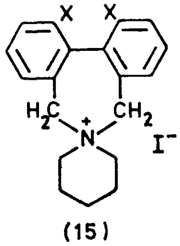

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The structured secondary (α) band of the sulphones shows a more uniform behaviour than the p bands with change in molecular structure (see Table 1). The α band, which is centred at 254 nm in the spectrum of benzene, increases in intensity and is moved successively to longer wavelengths on substitution. A sulphone group [as in (8; X = Me)] produces a 10 nm shift and a non-planar *ortho*-phenyl group [as in (5; X = Me)] increases $\lambda_{max.}$ by a further 7 nm (see Figure 1 and Table 1).

Because the conjugation between the sulphone group and the phenyl ring is stereo-independent,[7] the spectra of the biphenyl disulphones is governed mainly by the dihedral angle θ between the phenyl rings. The unbridged disulphones all have similar spectra, which

TABLE 1

U.v. spectra of sulphones in 95% ethanol *

	Biphenyl band †		Secondary benzenoid band	
Compound	$\lambda_{max.}$/nm	$10^{-3}\,\varepsilon$	$\lambda_{max.}$/nm	$10^{-3}\,\varepsilon$
Benzene			254	0·2
(8; X = Me)			264	1·05
(5; X = Me)			271	3·5
(5; X = Et)			271	3·5
(5; X = $PhCH_2$)			271·5	2·8
(2a; Y = $[CH_2]_2{\cdot}O{\cdot}[CH_2]_2$)	240i	6·00	282	4·1
(2b; Y = $[CH_2]_5$)	238i	6·00	281·5	5·0
(2c; Y = $[CH_2]_4$)			280·5	4·2
(2d; Y = $CH_2{\cdot}O{\cdot}CH_2$)			272	4·0
(2e; Y = $[CH_2]_3$)			271	3·5
[2f; Y = $CH_2{\cdot}C_6H_4{\cdot}CH_2$(*o*)]			273	4·0
(2g; Y = $[CH_2]_2$)	240i	5·35	272	4·6
[2h; Y = $CH_2{\cdot}C_6H_4{\cdot}CH_2$(*m*)]			287·5	4·7
(2i; Y = CH_2)	245	4·8	288·5	6·0
(2j; Y = CHPh)	245i	14·0	289	6·6
(2k; Y = Me_2C)	246·5	5·3	289·5	6·8
(11)	265	27·0		

* i Denotes an inflection and s a shoulder. † At 249 nm (ε 18,000) for biphenyl itself.

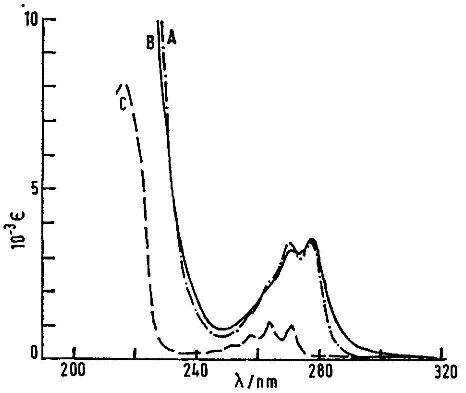

FIGURE 1 U.v. spectra of sulphones in 95% ethanol; A, (2e; Y = $[CH_2]_3$); B, (5; X = Me); C, (8; X = Me)

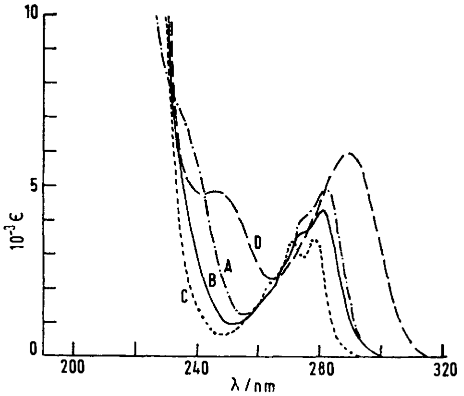

FIGURE 2 U.v. spectra of bridged biphenyl disulphones in 95% ethanol, A, (2b; Y = $[CH_2]_5$); B, (2c; Y = $[CH_2]_4$); C, (2e; Y = $[CH_2]_3$); D, (2i; Y = CH_2)

are characterised by a structured α band at *ca.* 271 nm. This, and the absence of the characteristic biphenyl band which is discussed in the next paragraph, suggest that the phenyl rings are roughly perpendicular to one another. In the sulphones (2h)—(2k) the α band is intensified with loss of fine structure and is shifted to *ca.* 288 nm, which indicates that there is increased conjugation between the phenyl rings.* Dreiding models suggest that the methylene-bridged compounds are locked in a cisoid conformation with θ *ca.* 60° [see (9)], whereas the rigid *m*-xylylene bridged compound has a transoid conformation with θ near to 120° [see (10)], both compounds having similar deviations from planarity. The dimethylene-bridged compound has a dihedral angle of *ca.* 80° and shows a reduction in the structured nature of the α band even though the rings must be nearly perpendicular to each other. Models indicate that the three-atom bridges in (2d) and (2e) and the *o*-phenylenedimethylene bridge in (2f) allow cisoid conformations up to a dihedral angle of *ca.* 90°. However the bulky sulphone groups force the rings to their maximum dihedral angle, producing spectra similar to those of the unbridged compounds (see Figure 1). Still longer bridges cause a gradual loss of the structure of the α band, consistent with an increase in dihedral angle beyond 90° and a preference for transoid conformations (see Figure 2). Variation in the structured nature of the α band was first observed in the spectra of 2- (and 2,6-di-) methylbiphenyls.[8]

Bands which are attributed to the biphenyl chromophore appear as inflections at *ca.* 240—245 nm in the spectra of the sulphones (2a, b, g, and j). The bands are clearly defined only in the spectra of the smallest bridged biphenyl sulphones (2i) and (2k) (see Figure 2). The bands occur at $\lambda_{max.}$ 245 nm (ε *ca.* 5000), *i.e.* at a similar wavelength but of lower intensity than in the case of biphenyl itself [$\lambda_{max.}$ 249 nm (ε 18,000)]. Although this is in accord with the recognised decrease in intensity with relatively little change in wavelength, caused by small twists in the biphenyl system,[9] it is possible that conjugation to the sulphone groups partly compensates for a hyposochromic shift. In these compounds the electric vectors of the biphenyl and phenyl sulphone chromophores of (2i) and (2k) approach right angles and separate bands are observed. On the other hand the corresponding electric vectors of the 4,4′-biphenyl disulphone (11) are parallel and a single very intense band is observed at 265 nm (ε 27,000).

The u.v. spectra of both the ether and sulphide compounds are made more complex by the variation in *p* orbital overlap of the heteroatom's lone pair of electrons and the phenyl group. The effect of the overlap is most noticeable on the secondary bands.

The spectra of the unbridged biphenyl disulphides and those which have an extended bridge, *e.g.* (3; Y = $[CH_2]_n$; $n > 2$), possess an intense primary band at a similar wavelength to that of thioanisole (*ca.* 205 nm). For the shorter bridged compounds, *i.e.* (3i)—(3k) and also (3h), improved conjugation between the biphenyl rings produces a small bathochromic shift. In contrast the intense p band of the biphenyl diethers at *ca.* 210 nm undergoes little change of wavelength with shortening of the bridge.

TABLE 2

U.v. spectra of sulphides in 95% ethanol *

	Biphenyl band *		Phenyl sulphide band	
Compound	λ/max. nm	10^{-3} ε	λ/max. nm	10^{-3} ε
Thioanisole			254	9·5
(6; X = Me)	239i	13·3	255	13·0
(6; X = Et)	240i	12·0	259	10·5
(6; X = Pr^i)	243i	12·0	264	9·3
(6; X = $PhCH_2$)			260i	10·0
(3a; Y = $[CH_2]_2\cdot O\cdot[CH_2]_2$]	240i	8·0	270	7·8
(3b; Y = $[CH_2]_5$)	242s	10·0	271	8·7
(3c; Y = $[CH_2]_4$)	238i	6·7	272	5·5
(3d; Y = $CH_2\cdot O\cdot CH_2$)			250	4·8
(3e; Y = $[CH_2]_3$)			266	5·0
[3f; Y = $CH_2C_6H_4CH_2$(*o*)]			276	4·2
(3g; Y = $[CH_2]_2$)			267	2·0
[3h; Y = $CH_2\cdot C_6H_4\cdot CH_2$(*m*)]	248i	10·0	274	4·2
(3i; Y = CH_2)	243i	11·0	258s	8·0
			275i	4·2
(3j; Y = CHPh)			260s	8·5
			278i	4·7
(3k; Y = Me_2C)	243i	9·7	256s	8·0
			275i	4·0
(12)			247	15·0

* See notes to Table 1.

The intense band of thioanisole at 254 nm undergoes a small bathochromic shift when an *ortho*-aryl group is introduced, *e.g.* the unbridged biphenyl disulphide (6; X = Me). There is also a reduction in intensity if one takes into account the presence of two phenyl sulphide chromophores, which indicates that steric effects are already reducing conjugation between the benzenoid ring and the lone pair of electrons on the sulphur atom. Replacement of X = Me in compound (6) by Et or Pr^i causes further bathochromic shifts and decreases in intensity of this band (see Figure 3 and Table 2). A dramatic bathochromic shift occurs when the two sulphur atoms are connected by a polymethylene bridge, and even with the most flexible bridges [(3a) and (3b)] the '254 nm' band is shifted to its longest wavelength at *ca.* 270 nm. The intensity of the band drops a step further and continues to fall as the length of the chain is reduced. It reaches its minimum intensity for compound (3g), which has a two-membered polymethylene chain. The intensities are probably affected mostly by the degree of conjugation between the aryl ring and the sulphide group.

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* We agree with a referee that this may be interpreted in terms of an interchange of the relative energies of the biphenyl and benzenoid bands. However we do not think that this makes it necessary to reassign the bands because the appearance of a band due to the biphenyl chromophore and the intensifying of the benzenoid band occurs simultaneously. The spectra of the ethers and sulphides are further complicated by variation of the conjugation to the heteroatom.

[8] G. H. Beaven in 'Steric Effects in Conjugated Systems,' ed. G. W. Gray, Butterworths, London, 1958, ch. 3.

[9] H. H. Jaffé and M. Orchin, 'Theory and Applications of Ultraviolet Spectroscopy,' Wiley, New York, 1962, p. 384.

The position of the band does not behave so regularly. After the initial large bathochromic shift caused by the bridge the band moves back to shorter wavelengths for the compounds with two- and three-membered chains. Models indicate that in these compounds the two aryl rings are almost perpendicular, which suggest that the original large bathochromic shift to *ca.* 270 nm may be connected with an increase in the biphenyl conjugation in comparison with the unbridged disulphides. Conjugation of the phenyl ring with the sulphide groups is expected to become important again for the smallest bridged compounds (3i)—(3k). The spectra of these compounds do contain a moderately intense band at *ca.* 258 nm (ε 8000) but the presence of an additional band at 275 nm (ε 4000) complicates the interpretation.

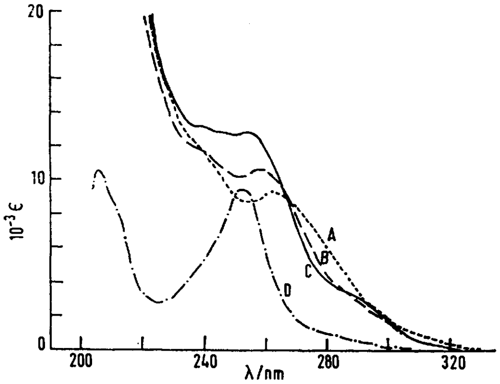

FIGURE 3 U.v. spectra of sulphides in 95% ethanol, A, (6; X = Pr^i); B, (6; X = Et); C, (6; X = Me); D, PhSMe

In contrast, the secondary band of anisole ($\lambda_{max.}$ 271·5 nm) undergoes a fairly large bathochromic shift (8·5 nm) on introducing a second aryl group, *e.g.* (7; X = Me or Et). There is complete loss of the structure of the band and the intensity is doubled (if the presence of two chromophores is allowed for). Increased conjugation may not be the main cause of the shift since the *ortho* orientation of the substituent would inhibit lone-pair conjugation. Further, the spectra of the sulphones in which the phenyl rings are anti-planar show similar bathochromic shifts. The increased absorption may arise from dipole effects or spectroscopic coupling with the additional aryl ring. Of course, when the rings are approaching planarity [*e.g.* (4h)] the increased conjugation produces further bathochromic shifts. The longest-bridged diethers (4a) and (4b) show very similar spectra to the unbridged diethers (see Figure 5), in contrast with the behaviour shown by the disulphides. The situation is analogous to that observed for the alkyl phenyl sulphides and ethers, which will be discussed in a future paper. The difference is attributed to a greater resistance to twisting about the O–phenyl bond in the ethers than about the S–phenyl bond in their sulphur analogues.

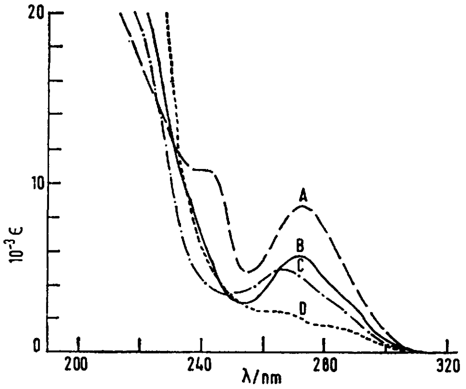

FIGURE 4 U.v. spectra of bridged biphenyl disulphides in 95% ethanol, A, (3b; Y = $[CH_2]_5$); B, (3c; Y = $[CH_2]_4$); C, (3e; Y = $[CH_2]_3$); D, (3g; Y = $[CH_2]_2$)

TABLE 3

U.v. spectra of ethers in 95% ethanol *

Compound	Biphenyl band * $\lambda_{max.}$ nm	Biphenyl band * $10^{-3}\varepsilon$	Secondary benzenoid band $\lambda_{max.}$/nm	Secondary benzenoid band $10^{-3}\varepsilon$
Anisole			271·5	1·48
(7; X = Me)	242s	6·5	280·5	6·0
(7; X = Et)	242s	6·5	282	6·1
(4a; Y = $[CH_2]_2\cdot O\cdot[CH_2]_2$)	244s	7·0	282	5·7
(4b; Y = $[CH_2]_5$)	245	7·3	282·5	6·0
(4c; Y = $[CH_2]_4$)	244	10·0	283	5·7
(4d; Y = $CH_2\cdot O\cdot CH_2$)	237·5	9·25	272·5	2·75
(4e; Y = $[CH_2]_3$)	241	8·0	279	4·0
[4f; Y = $CH_2\cdot C_6H_4\cdot CH_2$(*o*)]	244s	9·0	282	5·1
(4g; Y = $[CH_2]_2$)	241	11·25	271	2·5
(4h; Y = CH_2)	254	12·25	302	4·0
(13)			268	2·35

* See notes to Table 1.

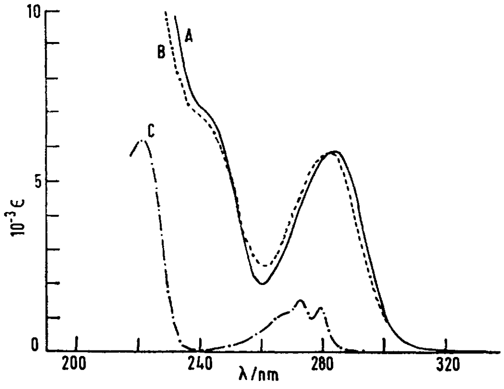

FIGURE 5 U.v. spectra of ethers in 95% ethanol, A, (4b; Y = $[CH_2]_5$); B, (7; X = Et); C, PhOMe

Although changes in the secondary bands are fairly uniform, an exception occurs in each series when the bridge contains an oxygen atom β to the aryl hetero-atom. The β-ether linkage in compounds (4d) and (3d) produces a blue shift and a reduction in intensity relative to that of the corresponding methylene-bridged compounds *i.e.* (4e) and (3e), respectively. The model compounds (12) and (13) show the same changes. We attribute this change to inductive withdrawal of electrons by the central oxygen atom.

The intensity and definition of the biphenyl conjugation band (249 nm in biphenyl) varies markedly in the three series. It appears in the spectra of all the ethers which we have studied and in most of the sulphides, but, as has already been mentioned, only in the spectra of the sulphones with the long or the short bridges. The band is absent from the spectra of biphenyl disulphides whose bridges are of sufficient length to maintain the biphenyl rings approximately perpendicular to each other, *i.e.* (3d)—(3g), and is at its maximum wavelength and intensity in the shortest bridged biphenyl diether (4h).

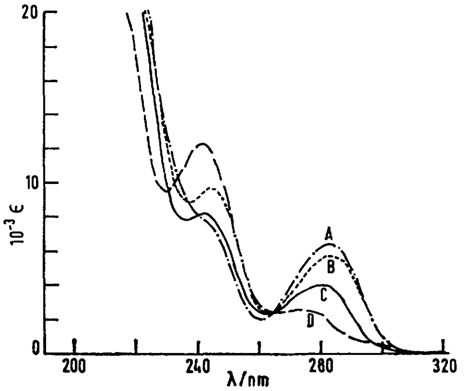

FIGURE 6 U.v. spectra of bridged biphenyl diethers in 95% ethanol, A, (4b; $Y = [CH_2]_5$); B, (4c; $Y = [CH_2]_4$); C, (4e; $Y = [CH_2]_3$); D, (4g; $Y = [CH_2]_2$)

The wavelength and intensity of the conjugation band cannot be used directly to estimate the dihedral angle between the phenyl rings of the biphenyl system without taking into account the bathochromic effect of the 2,2′-oxygen or -sulphur atoms. When this latter effect is at a minimum, *i.e.* for (4g) as indicated by the low intensity of the secondary band, the biphenyl conjugation band is still at longer wavelength (241 nm) and with a higher intensity (ε 11,250) than in the corresponding tetramethylene compound (14) $\lambda_{max.}$ 235 nm (ε 9680).[10] This indicates that the oxygen atom presents a lower barrier to rotation, which is in accord with the small steric effect of the 6- and 6′-methoxy-groups in the azepine (15; X = OMe) compared with the methyl analogue (15; X = Me).[10] We conclude that the effect of the terminal groups of the bridge in tending to maintain the biphenyl rings antiplanar increases in the order ether < methylene < sulphide < sulphone.

U.v. spectra were determined with a Unicam SP 800 spectrophotometer.

[1/678 *Received, May 3rd*, 1971]

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[10] D. M. Hall, *Progr. in Stereochem.*, 1969, **4**, 21.