

1017. *The Kinetics and Mechanisms of Aromatic Halogen Substitution. Part XIX.*¹ *Products and Rates of Chlorination of Bridged Biphenyls.*

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The rates and products of chlorination of 1,2:3,4-dibenzocyclohepta-1,3-diene (I; R = H), of its 5-methyl derivative (I; R = Me) and of *trans*-6,7-dimethyl-1,2:3,4-dibenzocyclo-octa-1,3-diene (II; R = Me), have been examined. Despite the considerable steric inhibition of conjugation between the aryl groups in all these compounds, the orientation of substitution is still dominated by the aryl group rather than by the alkyl side-chain. The results are discussed in relation to those for the chlorination of other bridged biphenyls, and for related reactions. It is concluded that the angle between the planes of the aryl groups in biphenyl and its non-planar bridged derivatives is nearer to coplanarity in the transition state than in the initial state; and that the rate of chlorination of fluorene is enhanced by a special structural factor, probably to be identified with ring-strain.

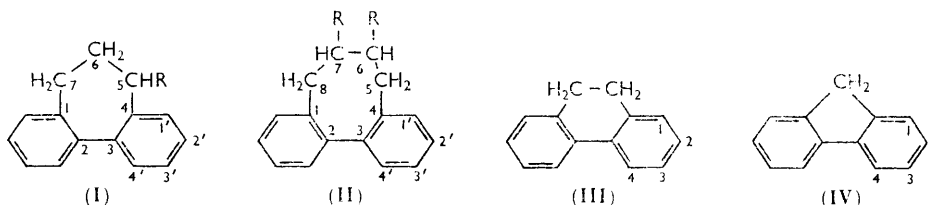
WE² reported the rate of chlorination of 5-methyl-1,2:3,4-dibenzocyclohepta-1,3-diene* (I; R = Me), together with those of 9,10-dihydrophenanthrene (III) and fluorene (IV),

* In discussing the bridged biphenyls referred to in this Paper, it is convenient to use the numbering indicated in structures (I)—(IV).

¹ Part XVIII, de la Mare, Dusouqui, Tillett, and Zeltner, preceding Paper.

² de la Mare, Hall, Harris, and Hassan, *Chem. and Ind.*, 1958, 1086.

in support of the view that steric inhibition of resonance, by altering the angle between the planes of the aryl groups, can modify the reactivity to attack by electrophils. We have since reported more detailed studies of 9,10-dihydrophenanthrene and of fluorene.³



We now give evidence relating to 1,2:3,4-dibenzocyclohepta-1,3-diene and its 5-methyl derivative (I; R = H, Me), and to 6,7-dimethyl-1,2:3,4-dibenzocyclo-octa-1,3-diene (II; R = Me). These measurements allow a full comparative discussion of the data already given.

EXPERIMENTAL

Some materials and methods have been described in earlier Parts. 1,2:3,4-Dibenzocyclohepta-1,3-diene was prepared *via* 6-imino-1,2:3,4-dibenzocycloheptadiene-5-carboxylic acid, obtained as described by Kenner and Turner.⁴ This was decarboxylated and hydrolysed to 1,2:3,4-dibenzocycloheptadiene-6-one, which was reduced to the hydrocarbon, m. p. 54.5–55° (lit.,⁵ 54.5–55°). 2'-Chloro-1,2:3,4-dibenzocyclohepta-1,3-diene was prepared similarly from 2-nitrophenanthraquinone, m. p. 257° (lit.,⁶ 258–260°) the main product of nitration of phenanthraquinone; we thank Dr. T. M. Poole and Miss B. Prakobsantisukh for this. It was oxidised by refluxing for 3 hr. with potassium dichromate in dilute sulphuric acid. The product, 4-nitrobiphenyl-2,2'-dicarboxylic acid, after crystallisation from aqueous ethanol, had m. p. 215° (lit.,⁷ 215.5–216°). This material (7 g.) was added during 10 min. to a boiling solution of stannous chloride (20 g.) in concentrated hydrochloric acid (50 ml.). The resulting solution was boiled for 20 min. and allowed to cool. Tin salts were precipitated by the addition of water and sodium hydroxide (10%) and filtered off. The filtrate was boiled down to 100 ml. and acidified (conc. HCl; 10 ml.). The resulting solution of the amine was diazotised with 5% sodium nitrite at 0–5°, then treated with cuprous chloride as usual. 4-Chlorobiphenyl-2,2'-dicarboxylic acid, a yellowish-white precipitate, was filtered off, washed with water, and crystallised from dilute ethanol; it had m. p. 239° (lit.,⁸ 240°) (Found: C, 60.4; H, 3.2; Cl, 13.0; O, 23.2. Calc. for C₁₄H₉ClO₄: C, 60.8; H, 3.3; Cl, 12.8; O, 23.1%). Esterification by heating (5 g.) for 4 hr. under reflux with methanol (50 ml.) and sulphuric acid (2.8 ml.) gave *dimethyl 4-chlorobiphenyl-2,2'-dicarboxylate* which, extracted with ether and crystallised from a little ether, had m. p. 104° (Found: C, 63.4; H, 4.3. C₁₆H₁₃ClO₄ requires C, 63.5; H, 4.2%). The ester (2.5 g.) in dry ether (100 ml.) was added during 10 min. to lithium aluminium hydride (0.5 g.) in dry ether (50 ml.). The mixture was refluxed for 15 min. and allowed to cool. Water and dilute sulphuric acid were added. The ethereal layer was washed (aq. NaHCO₃) and dried (MgSO₄). Evaporation of the solvent gave an orange oil which was then boiled for 20 min. in 48–50% hydrogen bromide in water (50 ml.). The product was extracted with ether and chromatographed on a column of silica gel in light petroleum (b. p. 40–60°). 4-Chloro-2,2'-di(bromomethyl)biphenyl, a colourless oil which crystallised on treatment with ligroin, had m. p. 109–110.5°. It was still impure (Found: C, 42.7; H, 2.7; labile Br, by treatment with AgNO₃, 40.5. C₁₄H₁₁Br₂Cl requires C, 44.9; H, 3.0; Br, 42.8%). It was, however, possible to convert it into the dinitrile by adding it (1.7 g.) to a hot solution of potassium cyanide (0.65 g.) in water (1.5 ml.) and ethanol (5 ml.). The mixture was refluxed for 30 min., cooled, and extracted with ether. The product was then cyclised in ethanol (7 ml.) to which was added a 5% solution of sodium in ethanol (0.2 ml.). The mixture was refluxed

³ Beaven, de la Mare, Johnson, and Klassen, *J.*, 1962, 988; de la Mare, Johnson, and Lomas, *J.*, 1963, 5973.

⁴ Kenner and Turner, *J.*, 1911, 99, 2101.

⁵ Rapoport and Williams, *J. Amer. Chem. Soc.*, 1949, 71, 1774.

⁶ Schmidt and Spoun, *Ber.*, 1922, 55, 1194.

⁷ Moore and Huntress, *J. Amer. Chem. Soc.*, 1927, 49, 1324.

⁸ Schmidt and Sauer, *Ber.*, 1911, 44, 3251.

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for 2 hr. in a current of hydrogen and then was cooled in ice. Recrystallisation from ethanol gave 2'-chloro-5(or 7)-cyano-6-iminodibenzocyclohepta-1,3-diene, m. p. 208—209° (Found: C, 72.3; H, 4.2. C₁₆H₁₁ClN₂ requires C, 72.5; H, 4.0%). A further crop of less pure material, m. p. 195—197°, was obtained by evaporation of the solvent and treatment of the residue with light petroleum. The iminonitrile (0.92 g.) was treated with sulphuric acid (6 ml.) for 2 hr. The solution was poured on ice; the product was filtered off and recrystallised from aqueous ethanol. There was obtained 2'-chloro-6-iminodibenzocyclohepta-1,3-diene-5(or 7)-carboxylic acid, m. p. 191—192° (decomp.) (Found: C, 67.6; H, 4.2; N, 4.4. C₁₆H₁₂ClNO₂ requires C, 67.7; H, 4.2; N, 4.8%). This (0.6 g.) was heated under reflux for 2 hr. with 88—90% phosphoric acid (18 ml.) and water (2.5 ml.). The mixture was cooled and poured on ice; 2'-chlorodibenzocyclohepta-1,3-diene-6-one was precipitated, chromatographed on alumina, and crystallised from light petroleum; m. p. 101—102.5° (Found: C, 74.1; H, 4.5. C₁₅H₁₁ClO requires C, 74.2; H, 4.6%). The ketone (0.55 g.) was added to a solution of potassium hydroxide (1.0 g.) and 99% hydrazine hydrate (2 ml.) in diethylene glycol (15 ml.). After the mixture had been refluxed for 90 min., its temperature was raised from 135 to 205° by distilling off water and some glycol. After 3 hr. at this temperature the solution was poured on ice, and the product was extracted into ether. The solvent was removed and the product, after chromatography on silica gel in light petroleum (b. p. 40—60°), was 2'-chloro-1,2:3,4-dibenzocyclohepta-1,3-diene, which was at least 90% pure, and was further purified by vapour-phase chromatography. It was a liquid (Found: C, 78.3; H, 5.6; Cl, 16.1. C₁₅H₁₃Cl requires C, 78.8; H, 5.7; Cl, 15.5%).

5-Methyl-1,2:3,4-dibenzocyclohepta-1,3-diene⁹ and 1,2:3,4-dibenzocyclo-octa-1,3-diene¹⁰ were much appreciated gifts from Dr. D. M. Hall of Bedford College, and Dr. R. D. Smith of the Massachusetts Institute of Technology, respectively.

For synthesis of a biphenyl bridged with a chain of four carbon atoms, ethyl 5,6:7,8-dibenzocyclo-octa-5,7-diene-2,2,3,3-tetracarboxylate was prepared by the method of Beaven *et al.*¹¹ Hydrolysis and decarboxylation of this material in alkaline ethylene glycol gave *trans*-5,6:7,8-dibenzocyclo-octa-5,7-diene-2,3-dicarboxylic acid, which with diazomethane gave its dimethyl ester, m. p. 127—128° after recrystallisation from ethanol (lit.,¹² 127—128°). This was reduced by heating it under reflux with lithium aluminium hydride in ether; the resulting diol had m. p. 151—152° after recrystallisation from benzene-light petroleum (b. p. 80—100°) (Found: C, 80.4; H, 7.5. C₁₈H₂₀O₂ requires C, 80.6; H, 7.5%). The diol was boiled with a solution (48%) of hydrogen bromide in water. From the resulting glass, the *bis-bromomethyl derivative* was isolated by chromatography on silica gel; it was eluted by benzene (75%)-light petroleum (b. p. 40—60°; 25%), and recrystallised from light petroleum (b. p. 40—60°); m. p. 101° (Found: C, 55.0; H, 4.7. C₁₈H₁₈Br₂ requires C, 54.8; H, 4.6%). This was then heated under reflux with a large excess of lithium aluminium hydride in tetrahydrofuran for 3 hr. Water and 2N-sulphuric acid were added and the organic product was extracted into ether and the extract dried (Na₂SO₄). After removal of ether, the oil was chromatographed on a column of silica gel; elution with light petroleum (b. p. 40—60°) gave the required *trans*-2,3-dimethyl-5,6:7,8-dibenzocyclo-octa-5,7-diene (II, R = Me; otherwise *trans*-6,7-dimethyl-1,2:3,4-dibenzocyclo-octa-1,3-diene; see footnote, p. 5317), m. p. 65—66° after recrystallisation from methanol (Found: C, 91.4; H, 8.6. C₁₈H₂₀ requires C, 91.5; H, 8.5%).

Its 2'-chloro-derivative was prepared similarly from 4-chloro-2,2'-di(bromomethyl)biphenyl. Insufficient material was available for purification of the intermediates, or for analysis of the final product. However, vapour-phase chromatography of this showed that the major component had a retention volume identical with that of the major product of chlorination of the parent hydrocarbon. The synthetic chloro-derivative was recovered after purification by vapour-phase chromatography; its ultraviolet spectrum was identical in form with that of the parent hydrocarbon, and its infrared spectrum was consistent with its being the main component of the chlorination of the parent hydrocarbon; in particular, both it and the product of chlorination of the parent hydrocarbon showed strong absorption in the C-Cl stretching region at 798 cm.⁻¹; the parent hydrocarbon showed no absorption at this frequency (see Table I).

⁹ Hall, Ladbury, Lesslie, and Turner, *J.*, 1956, 3475.

¹⁰ Cope and Smith, *J. Amer. Chem. Soc.*, 1956, **78**, 1012.

¹¹ Beaven, Bird, Hall, Johnson, Ladbury, Lesslie, and Turner, *J.*, 1955, 2708.

¹² Dvorken, Smyth, and Mislow, *J. Amer. Chem. Soc.*, 1958, **80**, 486.

TABLE I.

Infrared absorption bands (590—1600 cm^{-1}).

1,2:3,4-Dibenzocyclohepta-1,3-diene:			<i>trans</i> -6,7-Dimethyl-1,2:3,4-dibenzocyclo-octa-1,3-diene (in Nujol)
Unsubstituted	2'-Chloro	5-Methyl	
619w	633w	618w	599w
733sh	711w	695w	620w
	732w	730m	708w
749s	756s	746s	734sh
756sh			749s
777w	774m	778w	769m
819w	822m		
	844m	832w	
		862w	
		876w	
	879m	895w	
936w	938w	937w	944w
959w	960w	963w	978w
1006w	1007m	1009w	1005w
1013w	1020w	1031w	
1047w	1052w	1053w	1048w
1099w	1095m	1104w	1065w
	1121w		
1157w	1159w	1159w	1110m
1166w			1135w
1195w	1192m	1189w	1155w
	1236w	1222w	1174w
1262w	1260w	1258w	1258w
		1272w	
1307w	1300w	1305w	1279w
1348w	1337w	1353w	1370nj
1443w	1404m	1374w	
1451w	1447s	1447m	1449nj
1481w	1473s	1477m	
	1595m		

s = Strong; m = medium; w = weak; sh = shoulder; nj = Nujol bands.

The rate-measurements were made in anhydrous acetic acid, as described in earlier Papers.¹³ Results at 25° were as follows: 1,2:3,4-dibenzocyclohepta-1,3-diene (reactants *ca.* 0.01M) $k_2 = 0.058$ l. mole⁻¹ min.⁻¹; 5-methyl-1,2:3,4-dibenzocyclohepta-1,3-diene (reactants *ca.* 0.1M), $k_2 = 0.069$ l. mole⁻¹ min.⁻¹; 6,7-dimethyl-1,2:3,4-dibenzocyclo-octa-1,3-diene (reactants *ca.* 0.01M), $k_2 = 0.041$ l. mole⁻¹ min.⁻¹.

Products of Chlorination.—Vapour-phase chromatography of the product from the chlorination of 1,2:3,4-dibenzocyclohepta-1,3-diene (I; R = H) showed the presence of four components in the region expected for a monochloro-derivative, the ratios of peak areas being 17:10:11:62, and the retention volumes (V_R ; biphenyl = 1; 1,2:3,4-dibenzocyclohepta-1,3-diene = 3.6) being, respectively, 6.5, 8.05, 9.0, and 9.25. The component present in largest amount was identified by comparison with the synthetic material as 2'-chloro-1,2:3,4-dibenzocyclohepta-1,3-diene.

The pattern of chlorination of 5-methyl-1,2:3,4-dibenzocyclohepta-1,3-diene (I; R = Me) is consistent with the above. Seven components were detected by vapour-phase chromatography on a capillary column; a group of three, of low retention volume, in proportions 2.5:5.5:9.5, and a group of four of higher retention volume, in proportions (on the same scale) 5:33:11:34.5. Eight monochloro-substitution products are possible in this case, and presumably one has failed to be resolved. The retention volumes (V_R ; biphenyl = 1; 5-methyl-1,2:3,4-dibenzocyclohepta-1,3-diene = 4.8) were, respectively, 7.4, 8.25, 8.5, 10.4, 11.45, 11.8, and 12.2.

The ratio of hydrogen chloride produced to chlorine consumed was determined as usual for 1,2:3,4-dibenzocyclohepta-1,3-diene (0.84) and for 5-methyl-1,2:3,4-dibenzocyclohepta-1,3-diene (0.84).

Vapour-phase chromatography of the product from chlorination of 6,7-dimethyl-1,2:3,4-dibenzocyclo-octa-1,3-diene (II; R = Me) gave three peaks, representing components present

¹³ de la Mare and Robertson, *J.*, 1943, 279; de la Mare and Hassan, *J.*, 1958, 1519.

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in the ratio 6 : 5 : 18. The first of these was broad, and almost certainly contained two components. The relative retention volumes (V_R ; biphenyl = 1; 1,2:3,4-dibenzocyclo-octa-1,3-diene = 4.75; 6,7-dimethyl-1,2:3,4-dibenzocyclo-octa-1,3-diene = 7.0) were, respectively, 11.9, 13.8, and 16.5.

Spectra.—The infrared spectra were obtained by using a Grubb-Parsons D.B.2 grating spectrophotometer. In Table 1 are recorded the salient features of the new infrared spectra determined in the course of this work.

TABLE 2.

Ultraviolet spectral characteristics (solvent, light petroleum, b. p. 100—120°) of some bridged biphenyls and related compounds.

Compound	λ_{\min} (Å)	ϵ_{\min}	λ_{\max} (Å)	ϵ_{\max}	$\lambda_{\text{inf.}}$ (Å)	$\epsilon_{\text{inf.}}$
Biphenyl	2210	4400	2480	17,000	2920	60
4,4'-Dimethylbiphenyl	2260	4200	2550	21,000	ca. 2990	125
2-Methylbiphenyl	2240	7450	2365	10,250	ca. 2700	900
9,10-Dihydrophenanthrene	2365	2850	2635	18,000	2895	4950
			2995	4,750		
1,2:3,4-Dibenzocyclohepta-1,3-diene	2265	5200	2485	16,000	ca. 2760	1500
5-Methyl-1,2:3,4-dibenzocyclohepta-1,3-diene	2270	5850	2485	15,400	ca. 2760	1400
2'-Chloro-1,2:3,4-dibenzocyclohepta-1,3-diene	2285	5200	2525	19,600	ca. 2820	1600
1,2:3,4-Dibenzocyclo-octa-1,3-diene	2285	10,400	2360	12,100	2640	1050
					2730	590
6,7-Dimethyl-1,2:3,4-dibenzocyclo-octa-1,3-diene	2295	10,300	2385	12,600	2660	1200
					2750	660
2'-Chloro-6,7-dimethyl-1,2:3,4-dibenzocyclo-octa-1,3-diene	2305	ca. 10,000 *	2435	ca. 14,800 *	2725	2820

* The absolute extinction coefficients were determined only approximately because of the small amount available; the ratio, $\epsilon_{\max} : \epsilon_{\min} = 1.48$, was determined accurately.

Some ultraviolet spectra were recorded by using Hilger Uviscan and Unicam S.P. 700 recording spectrophotometers, and others with an S.P. 500 manual instrument. The main features of the new spectra are recorded in Table 2; data for some reference compounds¹⁴ are given also to facilitate comparison.

DISCUSSION

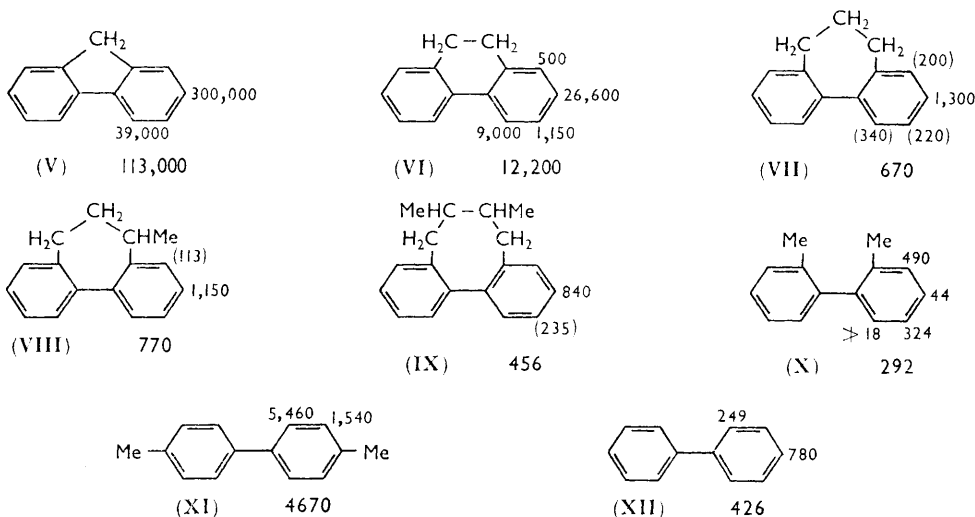
The only previous report of which we are aware describing an aromatic substitution in the 1,2:3,4-dibenzocyclohepta-1,3-diene system is that by Rapoport and Williams,⁵ who obtained from the parent hydrocarbon a nitro-derivative which was regarded as the 2'-isomer by analogy with the nitration of 9,10-dihydrophenanthrene.¹⁵ Assignment of configuration of nuclear substitution products on the basis solely of such a comparison, however, became less certain when it was shown that the reactivity of the 1,2:3,4-dibenzocyclohepta-1,3-diene system is considerably less than that of 9,10-dihydrophenanthrene.² The present study establishes that the main monochloro-derivative (62%) obtained by chlorination of 1,2:3,4-dibenzocyclohepta-1,3-diene with molecular chlorine in acetic acid is the 2'-chloro-derivative. Thus, despite the large angle between the planes of the benzene rings,¹¹ the mesomeric electron release from the aryl group is still large enough to determine the orientation of chlorination. It is reasonable, therefore, in view of the similarity generally observed between nitration and chlorination, to accept Rapoport and Williams's assignment of the structure of their nitro-derivative.

The other three nuclear-substituted 1'-, 3'-, and 4'-monochloro-1,2:3,4-dibenzocyclohepta-1,3-dienes were also detected in the product of chlorination by gas chromatography. Analogy with the related behaviour of the chloro-derivatives of 9,10-dihydrophenanthrene suggests an assignment: 1', 10%; 3', 11%; 4', 17%. These values are used in calculating the partial rate factors shown in structure (VII).

¹⁴ Beaven, Hall, Lesslie, and Turner, *J.*, 1952, 854; Everitt, Hall, and Turner, *J.*, 1956, 2286; Beaven and Johnson, *J.*, 1957, 651.

¹⁵ Krueger and Mosettig, *J. Org. Chem.*, 1938, 3, 340.

Products of addition account for some 16% of the chlorine consumed in reaction with 1,2:3,4-dibenzocyclohepta-1,3-diene. Most of the resulting material is probably a tetrachloride, and only small amounts of acetoxychlorides were detected. The tetrachlorides decompose on pyrolysis, to give in part dichloro-derivatives of the starting material.



Figures given beneath each formula relate to relative rate (PhH = 1).

Chlorination of 5-methyl-1,2:3,4-dibenzocyclohepta-1,3-diene proceeds at a rate similar to that of the parent compound. Vapour-phase chromatography on a capillary column resolved seven of the eight possible nuclear-substituted monochloro-derivatives. Partial rate factors are incompletely assigned in structure (VIII); they are in qualitative accordance with the corresponding values which we have attributed to the parent hydrocarbon (VII).

From the point of view of its expected reactivity with chlorine, we consider that 6,7-dimethyl-1,2:3,4-dibenzocyclo-octa-1,3-diene is an acceptable substitute for the less accessible 1,2:3,4-dibenzocyclo-octa-1,3-diene itself (of which only a very small sample was available), since the two methyl groups are too far away from the reactive centre to have a significant effect on the rate through a polar effect. Comparison of the ultraviolet spectra of the parent compound (II; R = H), its 6,7-dimethyl derivative (II; R = Me), and 1,2:3,4-dibenzocyclohepta-1,3-diene (Table 2), indicates, however, that the 6,7-dimethyl groups distort the geometry slightly towards planarity. From Suzuki's $\cos \theta - \lambda_{\max}$ relationship,¹⁶ which in the middle range of angles fits known molecular geometry better than later equations this distortion amounts to about 2°. By calculation, 1,2:3,4-dibenzocyclo-octa-1,3-diene has $\theta = 59^\circ$, and an angle $\theta = 57^\circ$ can therefore reasonably be attributed to its 6,7-dimethyl derivative. Its rate of chlorination is, as expected, somewhat less than that of the trimethylene-bridged compound, a result which accords with the somewhat diminished conjugation. The orientation of substitution is still, however, dominated by the aryl group, as we have shown by identifying the main product of chlorination as the 2'-derivative. The partial rate factor thus estimated is shown in structure (IX).

Comparison Between the Bridged Biphenyls.—We are now able to compare the chlorination of the bridged biphenyls, fluorene (IV, V), 9,10-dihydrophenanthrene (III, VI), 1,2:3,4-dibenzocyclohepta-1,3-diene (I, VII), and 6,7-dimethyl-1,2:3,4-dibenzocyclo-octa-1,3-diene (II, IX). Some of the relevant data from this and earlier Papers^{2,3,17} are set out in formulæ (V)—(XII) and in Table 3.

¹⁶ Suzuki, *Bull. Chem. Soc. Japan*, 1954, **27**, 597.

¹⁷ de la Mare, Hall, Harris, Hassan, Johnson, and Klassen, *J.*, 1962, 3784; de la Mare and Johnson, *J.*, 1963, 4076.

TABLE 3.

Chlorination of bridged biphenyls by molecular chlorine in acetic acid at 25°.

Compound	k_2 (l. mole ⁻¹ min. ⁻¹)	Rel. rate (PhH = 1)	HCl:Cl ₂	% <i>para</i> - substitution (a)	$f_o : f_p$ (b)	O:(2Cl) (c)
Fluorene	10.2	113,000	0.86	69	0.13	0.05
9,10-Dihydrophenanthrene	1.1	12,200	0.81	70	0.35	0.06
1,2:3,4-Dibenzocyclohepta- 1,3-diene	0.058	670	0.84	62	(0.15—0.26)	—
6,7-Dimethyl-1,2:3,4-dibenzo- cyclo-octa-1,3-diene	0.041	456	—	62	—	—
Biphenyl	0.038	426	0.825	62	0.32	0.04
2,2'-Dimethylbiphenyl	0.026	292	0.87	5	0.41	0.10

^a Substitution *para*- to the Ar-Ar link, determined by vapour-phase chromatography. ^b Partial rate factors for substitution *ortho*- and *para*- to the Ar-Ar link. ^c Atoms in crude product; upper limit. Blank determinations on biphenyl and fluorene indicate that these results should all probably be reduced by *ca.* 0.03.

In their qualitative features, the similarity is very striking. There is no evidence that any important steric effect on substitution *ortho*- to the Ar-Ar link is dependent on the angle between the planes of the rings. The proportion of reaction being diverted to addition is much the same in all cases. The range of reactivity covered by these compounds is, however, quite large (a rate-factor of 170). It seems very probable, as we suggested before,² that the most important feature determining this variation of reactivity is the conjugative power of the aryl group, and that this in turn is determined by the angle between the planes of the aryl groups in the transition state. The effect of this steric inhibition of resonance, progressively increasing from fluorene to 6,7-dimethyl-1,2:3,4-dibenzocyclo-octa-1,3-diene, is that substitution *meta* to the aryl group is negligible in fluorene, is detectable in 9,10-dihydrophenanthrene, and represents a still minor but substantial proportion in 1,2:3,4-dibenzocyclohepta-1,3-diene and in the 1,2:3,4-dibenzocyclo-octa-1,3-diene. It requires a still larger steric effect, as in 2,2'-dimethylbiphenyl (X) or in 2,2'-di-*t*-butylbiphenyl,¹⁷ to change the orientation sufficiently to make *ortho-para*-direction by the alkyl rather than by the aryl group dominant.

Transition-state Geometry in Bridged and Twisted Biphenyls.—It is generally considered¹⁸ that the energy, E , of conjugation between two aryl systems is related to the angle, θ , between their planes by the equation: *

$$E = E_0 \cos^2\theta$$

In attempting in the present case to relate reactivity with the angle between the planes of the aromatic rings, it is necessary to consider whether the partial rate factors estimated as we have done^{1,17} in this and other Papers are affected seriously by adduct-formation and decomposition. Certainly we have shown that interpretation of the amounts of minor components can be significantly influenced in this way;¹⁷ but it seems very unlikely that the comparisons of the partial rate factors for the components which make up the bulk of the product are affected to an extent which is significant for the present comparisons, especially as these are in terms of free energy of activation, and hence are converted to a logarithmic scale.

* Equations involving higher powers of $\cos \theta$ have been proposed on theoretical grounds,¹⁹ but are not adopted here because of related experimental evidence discussed by Wepster.²⁰ They also conform less well with our own results.

¹⁸ Pauling and Corey, *J. Amer. Chem. Soc.*, 1952, **74**, 3964; Dewar, *ibid.*, 1952, **74**, 3345; Fischer-Hjalmans, *Tetrahedron*, 1963, **19**, 2805.

¹⁹ Guy, *J. Chim. phys.*, 1949, **46**, 469; R. D. Brown, *J.*, 1952, 2229; Adrian, *J. Chem. Phys.*, 1958, **28**, 608.

²⁰ Wepster, in Klyne and de la Mare, "Progress in Stereochemistry 2," Butterworths, 1958, pp. 102, 122.

For a first approximation, therefore, we shall assume that our estimates of the partial rate factors for substitution *para* to the Ar-Ar bond in bridged biphenyls can be used as measures of energy of transition-state conjugation: the free-energy of activation for chlorination of a single position in benzene is reduced for a particular position (x) in a biaryl by an amount given by the equation $\Delta\Delta F = RT \ln f_x$, where f_x is the partial rate factor for chlorination in the x -position. We then treat fluorene as a planar biphenyl system with an alkyl substituent in both rings *ortho* to the ring-junction ($\theta = 0$; $f_2 = 300,000$). 9,10-Dihydrophenanthrene, 1,2:3,4-dibenzocyclohepta-1,3-diene, and 6,7-dimethyl-1,2:3,4-dibenzocyclo-octa-1,3-diene are then treated analogously, with, respectively, $\theta = 16^\circ$ ($f_2 = 26,600$); $\theta = 49^\circ$ ($f_2 = 1300$); and $\theta = 57^\circ$ ($f_2 = 840$). These angles are those derived from consideration of strainless models,²¹ the last being slightly corrected (see above); no doubt they would be modified in the transition state, but for the moment it is impossible to determine how much.

A further point of comparison can be added if we accept Suzuki's estimate¹⁶ from ultraviolet spectroscopy that in 2,2'-dimethylbiphenyl the angle θ is 70° ($f_4 = 44$).

A final point of reference would be provided if we had a biaryl with the two rings held at right angles, but with an alkyl bridge or alkyl groups in the *ortho*-positions (a "perpendicular 2,2'-dialkylbiphenyl"). From analysis of the rates of chlorination of substituted biphenyls, it appears that a *meta*-aryl group affects the rate of chlorination by a partial rate factor of 0.5—0.7, and this value does not seem to be much affected by the angle between the two rings.¹⁷ If for a perpendicular biphenyl only the inductive effect of the aryl group were operative (no conjugation), and if, as seems likely, the inductive effect is transmitted nearly equally to the *meta*- and *para*-positions, we can ascribe a factor of 0.5 to the influence of the constrained aryl group on the *para*-position. Taking Brown and Stock's value of $f_m^{\text{Me}} = 5$ for a *meta*-methyl group²² as applicable to alkyl bridges, we can reasonably assess the effects of the two substituents as together giving a partial rate factor of $0.5 \times 5 = 2.5$ ($\theta = 90^\circ$).

TABLE 4.

Angles (θ) between planes of aryl groups, partial rate factors (f) and derived quantities for chlorination *para* to the Ar-Ar link in bridged and 2-substituted biphenyls.

Compound	Position (x)	θ	$\cos^2 \theta$	f_x	$\Delta\Delta F = RT \ln f_x$ (kcal. mole ⁻¹)
Fluorene	2	0	1.00	300,000	7.6
9,10-Dihydrophenanthrene	2	16	0.92	26,600	6.1
1,2:3,4-Dibenzocyclohepta-1,3-diene	2'	49	0.43	1,300	4.3
6,7-Dimethyl-1,2:3,4-dibenzocyclo-octa-1,3-diene ...	2'	57	0.29	840	4.0
2,2'-Dimethylbiphenyl	4	70*	0.12	44	2.26
Hypothetical "perpendicular 2,2'-dialkylbiphenyl"	4	90	0.00	2.5 †	0.55 †

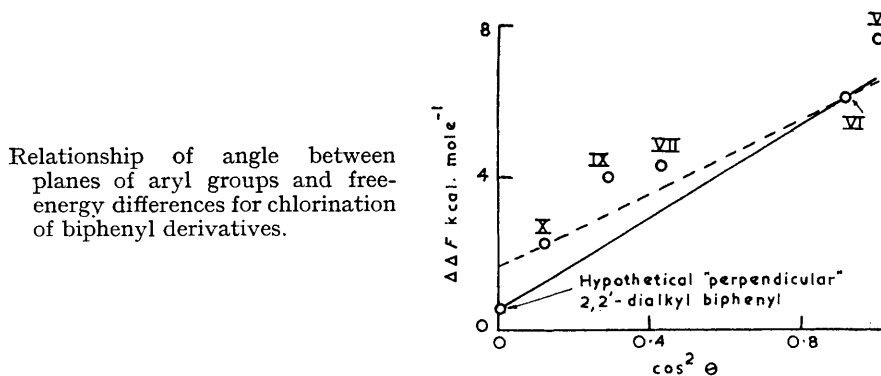
* Estimate from ultraviolet spectroscopy. † Calculated value; see text.

The results are summarised in Table 4, and plotted in the Figure. The reference point for $\theta = 90^\circ$ ($\cos^2\theta = 0$) can hardly be higher than the value which we have taken, for we ascribe only a very modest electron-withdrawing inductive ($-I$) effect to the phenyl substituent, together with a value for a *meta*-alkyl substituent which can hardly be too low by more than a very small factor.^{cf.22} A point very near the other end of the range is provided by 9,10-dihydrophenanthrene. Since this hydrocarbon (*a*) is unstrained, (*b*) has a bridging chain long enough to diminish substantially any inductive effect relayed through the bridge, and (*c*) is so nearly planar that the angle between the planes of the rings cannot be much modified in the transition state, the position of this point would seem to be the least dependent of all on the assumptions made in the treatment.

²¹ Beaven and Hall, *J.*, 1956, 4637; Hall and Minhaj, *J.*, 1957, 4584.

²² H. C. Brown and Stock, *J. Amer. Chem. Soc.*, 1957, 79, 5175.

On this basis, the full line represents accordance with the relationship $E = E_0 \cos^2 \theta$, and the positions of the points for the other compounds can be interpreted in terms of deviations from such agreement. The results indicate that 1,2:3,4-dibenzocyclohepta-1,3-diene, 6,7-dimethyl-1,2:3,4-dibenzocyclo-octa-1,3-diene, and 2,2'-dimethylbiphenyl are all chlorinated considerably more rapidly than would be expected on the basis of the angles between the planes of the rings. Since it is qualitatively to be expected that the electron-demand in the transition state for chlorination would in part be accommodated by a modification of the geometry of the system in the observed direction, we suggest that a substantial part of this unexpectedly large reactivity has its origin in a change towards planarity on going from the initial to the transition state. The two bridged compounds (Figure: VII, IX) are substantially more reactive than they should be even if 2,2'-dimethylbiphenyl (X; cf. broken line) is taken as a reference point instead of the hypothetical



“perpendicular 2,2'-dialkylbiphenyl” (full line). The change towards planarity in the transition state, if it is substantial for any of these compounds, is likely to be substantial for all of them. In treating the latter line as the basis of reference, we make the assumption that electron-release in chlorination is not much affected by “residual conjugation,”²³ to which we attribute here an effect similar only to that resulting from conjugative electron-release to the *meta*-position in biphenyl. Work is in progress, however, by which we hope to make a more satisfactory estimate of the importance of this factor.

The Reactivity of Fluorene.—Fluorene is markedly more reactive than biphenyl, and several factors contribute to this difference. The first is obvious, that fluorene can be considered as an arylalkyl-substituted biphenyl, and the arylalkyl group can be considered to be an electron-releasing substituent, with the power of activating the 2-position both inductively and hyperconjugatively (cf. XIII). The second is that fluorene is planar, whereas biphenyl is not; so conjugative effects between the two rings are enhanced in fluorene. Attention has been drawn by various groups^{24,25} to this feature. The investigation most closely related to our own work is that by Brown and Stock,²⁵ who analysed the reactivities of biphenyl, fluorene, and their derivatives. They attributed the difference in reactivity between biphenyl and fluorene essentially to these two factors.

Our own interpretation accepts, of course, that these two factors both contribute to the great reactivity of fluorene. Comparison with the other bridged biphenyl, and especially with 9,10-dihydrophenanthrene, suggests, however (see Figure), that fluorene is still more reactive than would be expected for a planar alkyl-bridged biphenyl by an

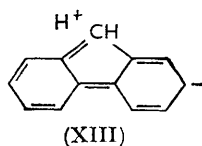
²³ Longuet-Higgins and Murrell, *Proc. Phys. Soc.*, 1955, *A*, **68**, 601; *J.*, 1955, 2552; Jaffé and Chalvet, *J. Amer. Chem. Soc.*, 1963, **85**, 1561.

²⁴ Berliner and Shieh, *J. Amer. Chem. Soc.*, 1957, **79**, 3849; cf. Berliner and Blommers, *ibid.*, 1951, **73**, 2479; Berliner, Newman, and Riaboff, *ibid.*, 1955, **77**, 478.

²⁵ Brown and Stock, *J. Amer. Chem. Soc.*, 1962, **84**, 1238; Stock and Brown, *ibid.*, p. 1242.

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amount which appears to involve a free-energy increment of about 1 kcal. mole⁻¹, and hence a rate-enhancement by a factor of at least 5.*



It seems unlikely that enhanced hyperconjugation²⁶ (structure XIII) can account for much of this rate-difference, since against it we need also to offset the inductive effect of the aryl group²⁷ acting through the methylene bridge, as well as the diminished conjugation arising from the non-linearity of fluorene.²⁸ We suggest that the structural factor most likely to provide a rationalisation of the extra rate-enhancement is distortion of the aromatic system by the methylene bridge. Such distortion, as revealed by *X*-ray crystallographic data,²⁸ is small insofar as the bond-lengths within the individual aryl groups are concerned. It may, however, be significant as far as reactivity is concerned, though it seems important to test the generality of this suggestion by study of other distorted aromatic systems.

The present view is in accordance with an earlier suggestion by Baker, Bott, and Eaborn,²⁹ who have pointed out that it may be unsafe to regard the methylene group in fluorene as having an effect similar to that of a *meta*-methyl group and an *ortho*-tolyl group combined additively in a substituted benzene. They draw attention to the possibility of enhanced hyperconjugation (XIII) in fluorene, but suggest that distortion of the aromatic system by the methylene bridge in fluorene might provide an extra factor contributing to the difference in reactivity between fluorene and biphenyl.

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* This value would be increased if any allowance had to be made for residual conjugation in "perpendicular biphenyl,"²³ or for distortion of 9,10-dihydrophenanthrene towards coplanarity in the transition state.

²⁶ de la Mare, *Tetrahedron*, 1959, **5**, 107; Baker, Eaborn, and Sperry, *J.*, 1962, 2382.

²⁷ Hartman and Robertson, *J.*, 1945, 891.

²⁸ G. M. Brown and Bortner, *Acta Cryst.*, 1954, **7**, 139; Burns and Iball, *Proc. Roy. Soc.*, 1955, **227A**, 200.

²⁹ Baker, Bott, and Eaborn, *J.*, 1963, 2136.