816. *Steric Effects in 2,2′-Bridged Biphenyls with a Heterocyclic Bridging Ring. Part III.*[1] *The Ultraviolet Absorption Spectra of some Dihydrodibenzazepinium Compounds.*

By Shakti R. Ahmed and D. Muriel Hall.

The four 4′,1″-dihalogeno-2,7-dihydro-3,4:5,6-dibenzazepinium-1-spiro-1‴-piperidinium bromides (I) have been prepared and their ultraviolet absorption spectra determined. Some conjugation between the two benzene rings is evident, even in the di-iodo-compound, indicating that the steric effect of the halogen atoms is less in these compounds than it is in the 2,2′-dihalogenobiphenyls.

The ultraviolet absorption spectra of 2,2′-bridged biphenyls with a saturated homocyclic or heterocyclic seven-membered ring show a large measure of conjugation between the two aromatic rings.[2,3,4] The study of the effect of *ortho*-substituents on the spectra of such compounds has been limited to the substituents methoxyl [2] (where the large mesomeric effect may complicate assessment of a purely steric effect), methyl,[5] and chloro; [6] in the case of the chloro-compounds strongly auxochromic *p*-chlorine atoms were also present, masking some of the finer points of the *ortho*-effect.

In order to extend this range the *oo*′-dihalogenodihydrodibenzazepinium-spiro-piperidinium bromides (I; X = F, Cl, Br, I) were selected for study. Not all the halogens show the strongly perturbing spectral effects of, for example, methoxyl, and the series has the

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[1] Part II, *J.*, 1959, 3383.

[2] Beaven, Hall, Lesslie, and Turner, *J.*, 1952, 854; see also Cohen, Cook, and Roe, *J.*, 1940, 194; Huang, Tarbell, and Arnstein, *J. Amer. Chem. Soc.*, 1948, **70**, 4181; Horowitz, Ullyot, E. C. Horning, M. G. Horning, Koo, Fish, Parker, and Walker, *ibid.*, 1950, **72**, 4330; Rapoport, Williams, and Cisney, *ibid.*, 1951, **73**, 1414; Rapoport, Allen, and Cisney, *ibid.*, 1955, **77**, 670.

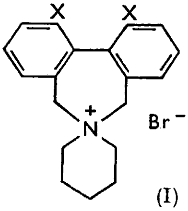
[3] Beaven, Bird, Hall, Johnson, Ladbury, Lesslie, and Turner, *J.*, 1955, 2708.

[4] Beaven and Johnson, *J.*, 1957, 651.

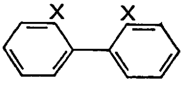
[5] Wittig and Zimmermann, *Chem. Ber.*, 1953, **86**, 629.

[6] Hall and Minhaj, *J.*, 1957, 4584.

added advantage that a similar study of 2,2′-dihalogenobiphenyls (II; X = F, Cl, Br, I) has already been made.[7]



(I)



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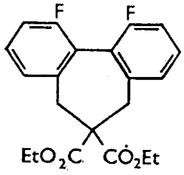

(III)

The azepinium compounds were synthesised by standard methods and isolated and purified as the quaternary iodides, which are less soluble than the bromides and are not solvated. They were reconverted into the bromides for spectroscopic study since the iodide ion absorbs strongly in the 210—250 mμ region. All the bromides crystallised with two molecules of water and were extremely soluble in water.

In the spectrum (Fig. 1 and Table) of the 4′,1″-dichloro-bromide (I; X = Cl) some loss in conjugation in comparison with the unsubstituted compound (I; X = H) is apparent, indicated by a lower intensity of the conjugation band rather than by any significant shift to shorter wavelengths. At the same time the increase in wavelength of the short-wave band has led to some filling up of the minimum between it and the conjugation band.

In the dibromo-compound both these effects are more pronounced, with the result that the conjugation band is no longer clearly separated from the short-wave band but appears as a conspicuous inflection at 246 mμ.

The spectrum of the di-iodo-compound is complicated by the intense absorption of the iodophenyl partial chromophore. Beaven and Hall [7] correlated the band at 230 mμ (ε 19,700) in 2,2′-di-iodobiphenyl with the band at 228—233 mμ (ε 13,300) in iodobenzene.[8] In the azepinium compound there is a very broad band at rather longer wavelength; it seems reasonable to attribute this to overlapping of the iodophenyl band by the residual conjugation band, leading to a slight maximum at 235 mμ (ε 18,200) (where iodophenyl absorption predominates) and a marked inflection at *ca.* 254 mμ (ε 13,000) (where the conjugation band falls off steeply). (As Fig. 1 shows, the precise positions of these features have little significance.) The absorption is much higher in the region 240—260 mμ (ε 17,300—9300) than in the same region in 2,2′-di-iodobiphenyl (ε 12,000—2200) (where conjugation is considered to be absent), suggesting strongly that appreciable conjugation is still present in the di-iodo-azepinium bromide.

The three compounds (I; X = Cl, Br, I) thus form a series showing increasing steric hindrance with increase in size of the halogen atom. The spectrum (Fig. 2) of the difluoro-compound (I; X = F) is at first sight anomalous since it shows a considerable short-wave shift of the conjugation band. However, introduction of fluorine into an aromatic compound sometimes causes a hypsochromic shift in the spectrum [9] and, for biphenyls, Beaven and Hall [7] found that 4-fluoro-, 4,4′-difluoro-, and 4,4′-difluoro-3,3′-dimethyl-biphenyl all absorb at shorter wavelengths than biphenyl itself, whereas the normal effect of *para*-substitution is a marked bathochromic shift; thus 4,4′-difluorobiphenyl has $\lambda_{max.}$ 245 mμ (ε 15,000) whereas 4,4′-dichlorobiphenyl [6] has $\lambda_{max.}$ 259 mμ (ε 25,200).

The difluoro-azepinium bromide shows some reduction in intensity of the conjugation band but less than the dichloro-compound does. In this respect it falls into place in the series of halogeno-compounds. It seems probable that part of the short-wave shift of *ca.* 6 mμ is attributable to the hypsochromic effect of fluorine substitution rather than to a pronounced steric effect; possibly some of the (greater) blue shift observed by Beaven

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[7] Beaven and Hall, *J.*, 1956, 4637.

[8] American Petroleum Institute, Research Project No. 44, Ultraviolet Spectral Data, Serial no. 308.

[9] Burawoy and Thompson, *J.*, 1956, 4314.

and Hall [7] in the spectrum of 2,2′-difluorobiphenyl is also due to the specific electronic character of fluorine rather than to its size.

We have also examined the spectrum (Fig. 2) of a difluoro-compound (III) with a homocyclic bridging ring and find that the effect of the fluorine atoms on both wavelength and intensity of absorption closely parallels their effect in the heterocyclic compound. The long-wave absorption in the two difluoro-compounds reflects the strong absorption of fluorobenzene ($\varepsilon_{max.}$ 1060) in this region compared with that of the other halogenobenzenes.[10] Where the absorption of the fluorophenyl partial chromophore is superimposed on the already high long-wave absorption of the heterocyclic system, a very intense band results.

Ultraviolet absorption spectra.

	Short-wave band		Minimum		Conjugation band		Minimum		Long-wave features	
Compound	$\lambda_{max.}$	ε	$\lambda_{min.}$	ε	$\lambda_{max.}$	ε	$\lambda_{min.}$	ε	$\lambda_{max.}$	ε
(I; X = H) [a] (in H_2O)	—	—	224	4500	248	15,000	—	—	(*ca.* 281·5)	2250
									(*ca.* 272)	4750
(I; X = F)	(*ca.* 208)	42,000	229	8250	243·5	12,600	257	2900	282	8340
					241	12,600			275	8900
(I); X = Cl)	219	43,000	238	9000	247	10,000	264·5	2300	(285)	2350
									277	3750
(I; X = Br)	221	35,100	—	—	(246)	8850	266·5	2050	(286)	1900
									277·5	3000
(I; X = I)	(*ca.* 212)	23,000	234	18,000	(254)	13,000	277·5	3140	282	3250
	235	18,200							281	3240
Me 3,4:5,6-dibenzocyclohepta-3,5-diene-1-carboxylate [b]	207·5	42,500	227·5	5700	248·5	15,500	—	—	(*ca.* 274)	1700
(III)	(*ca.* 208)	36,300	224·5	6230	244	13,100	262	3840	(*ca.* 277)	4250
					241·5	13,000			271·5	4950

Solvent, 96% ethanol, except for (I; X = H); wavelengths in mμ; values in parentheses denote inflections.

[a] Beaven, Hall, Lesslie, and Turner, *J.*, 1952, 854. [b] Beaven, Bird, Hall, Johnson, Ladbury, Lesslie, and Turner, *J.*, 1955, 2708.

FIG. 1. FIG. 2.

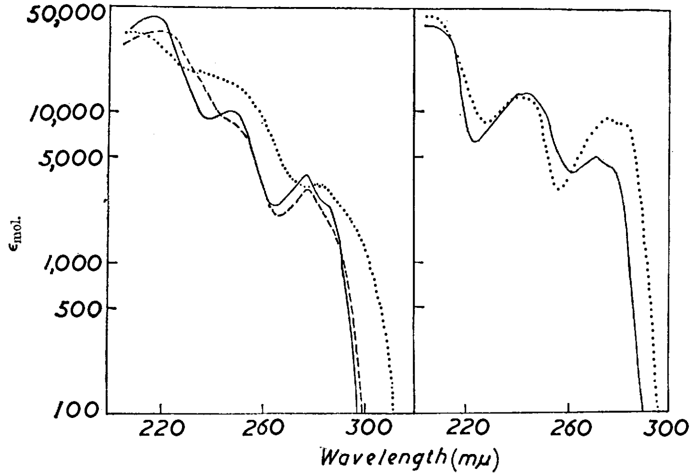

FIG. 1. *Ultraviolet absorption spectra, in* 96% *ethanol, of* 4′,1″-*dichloro-* (——), 4′,1″-*dibromo-* (— — —), *and* 4′,1″-*di-iodo*-2,7-*dihydro*-3,4:5,6-*dibenzazepinium*-1-*spiro*-1‴-*piperidinium bromide* (. . . .).

FIG. 2. *Ultraviolet absorption spectra, in* 96% *ethanol, of* 4′,1″-*difluoro*-2,7-*dihydro*-3,4:5,6-*dibenzazepinium*-1-*spiro*-1‴-*piperidinium bromide* (. . . .) *and ethyl* 4′,1″-*difluoro*-3,4:5,6-*dibenzocyclohepta*-3,5-*diene*-1,1-*dicarboxylate* (——).

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[10] Ref. 8. Serial nos. 296, 300, 304, 308.

The results for these five bridged compounds are of interest in connection with the conformations of bridged and non-bridged biphenyls. The 2,2'-dihalogenobiphenyls have a "*cis*"-conformation;[11,12,13] experimental and calculated values of θ (the angle between the planes of the benzene rings) have been discussed earlier.[7] Except for the difluoro-compound, θ is almost certainly of the order of 75° or more; spectroscopically, only the difluoro-compound shows a distinct conjugation band and steric inhibition of conjugation appears to be complete with the di-iodo-compound. In the dihydrodibenzazepinium-spiro-piperidinium bromides, however, a strainless conformation for the heterocyclic rings gives a value[6] (calculated) of 47° for θ. The halogen atoms can only be accommodated in the *ortho*-positions, without great distortion of the bridging ring, if they approach one another much more closely than is normal for non-bonded atoms.

In a non-bridged biphenyl steric strain caused by the introduction of large *ortho*-substituents can most readily be eased by increase in θ; in the bridged compounds the strain is presumably distributed between (*a*) compression of the substituents (equivalent to decrease in the van der Waals radius), (*b*) out-of-plane bending of the substituents (an effect known to occur fairly readily with halogens; cf. *o*-dichlorobenzene[14] and 2,2'-di-iodobiphenyl-5,5'-dicarboxylic acid[15]), and (*c*) increase in θ with corresponding distortion of the seven-membered ring. As a result two *o*-chlorine atoms can be accommodated so that the compound still gives a distinct conjugation band and even with two *o*-iodine atoms θ does not become large enough for all conjugation to be obliterated.

The difluoro-ester (III) was converted into the corresponding monocarboxylic acid with a view to optical resolution. So far, all attempts have failed, although the optical stability of 4',1''-difluoro-2,7-dihydro-1-methyl-3,4:5,6-dibenzazepine[16] makes it rather unlikely that the failure is due to configurational instability in the acid.

EXPERIMENTAL

Ultraviolet absorption spectra were measured on a Unicam S.P. 500 spectrophotometer.

4',1''-Difluoro-2,7-dihydro-3,4:5,6-dibenzazepinium-1-spiro-1'''-piperidinium Bromide.—A solution of the corresponding iodide[16] in aqueous alcohol was shaken for ½ hr. with an excess of freshly prepared silver bromide. Silver halides were filtered off and the filtrate, which was iodide-free, was evaporated to dryness under reduced pressure. The residual *bromide*, crystallised thrice from ethanol–ethyl acetate, had m. p. 234—235° (Found: C, 55·2; H, 6·1; Br, 19·8; N, 3·4. $C_{19}H_{20}BrF_2N,2H_2O$ requires C, 54·8; H, 5·8; Br, 19·2; N, 3·4%).

4',1''-Dichloro-2,7-dihydro-3,4:5,6-dibenzazepinium-1-spiro-1'''-piperidinium Bromide—2,2'-Dichloro-6,6'-dimethylbiphenyl[17] was obtained by a Sandmeyer reaction on 2,2'-diamino-6,6'-dimethylbiphenyl[18] [the (−)- and the (±)-form have been similarly prepared by Mislow[19]]. It was brominated in carbon tetrachloride solution with *N*-bromosuccinimide in the presence of benzoyl peroxide; the resulting dibromo-compound * (an oil) was dissolved in dry benzene and treated with piperidine without further purification. The resulting quaternary compound was isolated as the *iodide*, which crystallised from very dilute alcohol as needles, m. p. 283—284° (decomp.) (Found: C, 49·3; H, 4·6; Cl + I, 43·2; N, 3·25. $C_{19}H_{20}Cl_2IN$ requires C, 49·6; H, 4·4; Cl + I, 43·0; N, 3·0%). The *bromide* was prepared from it as described for the difluoro-compound and crystallised from ethanol–ethyl acetate with m. p. 287—288° (decomp.) (Found: C, 50·5; H, 5·4; Cl + Br, 32·9; N, 3·5. $C_{19}H_{20}BrCl_2N,2H_2O$ requires C, 50·8;

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* McGinn *et al.*[19] obtained the (+)-dibromo-compound from the corresponding diol as a solid, m. p. 70—71°.

[11] Bastiansen, *Acta Chem. Scand.*, 1949, **3**, 408; 1950, **4**, 926.
[12] Bastiansen and Smedvik, *Acta Chem. Scand.*, 1954, **8**, 1593.
[13] Littlejohn and Smith, *J.*, 1954, 2552.
[14] Bastiansen and Hassel, *Acta Chem. Scand.*, 1947, **1**, 489.
[15] Rieger and Westheimer, *J. Amer. Chem. Soc.*, 1950, **72**, 19.
[16] Ahmed and Hall, *J.*, 1958, 3043.
[17] Cf. Angeletti, Atti X Congr. Internaz. Chim., 1938, Vol. III, p. 26.
[18] Kenner and Stubbings, *J.*, 1921, **119**, 593.
[19] McGinn, Lazarus, Siegel, Ricci, and Mislow, *J. Amer. Chem. Soc.*, 1958, **80**, 476.

H, 5·4; Cl + Br, 33·6; N, 3·1%). Fitts, Siegel, and Mislow [20] obtained the (−)-bromide in an unsolvated form.

4′,1″-Dibromo-2,7-dihydro-3,4:5,6-dibenzazepinium-1-spiro-1‴-piperidinium Bromide.—2,2′-Dibromo-6,6′-dimethylbiphenyl, isolated by steam-distillation, was obtained in 24% yield from the diamino-compound (cf. Bell and Dinsmore [21]). It was brominated by *N*-bromosuccinimide, and the product was treated with piperidine. The quaternary *iodide* crystallised from aqueous alcohol in needles, m. p. 304—305° (decomp.) (Found: C, 42·1; H, 3·7; Br + I, 51·85; N, 2·3. $C_{19}H_{20}Br_2IN$ requires C, 41·6; H, 3·7; Br + I, 52·2; N, 2·55%). The *bromide*, crystallised from ethanol–ethyl acetate, had m. p. 272—273° (decomp.) (Found: C, 42·3; H, 4·8; Br, 44·5. $C_{19}H_{20}Br_3N,2H_2O$ requires C, 42·4; H, 4·5; Br, 44·55%).

2,7-Dihydro-4′,1″-di-iodo-3,4:5,6-dibenzazepinium-1-spiro-1‴-piperidinium Bromide.—2,2′-Di-iodo-6,6′-dimethylbiphenyl [22] was brominated by *N*-bromosuccinimide, and the product was treated with piperidine. The quaternary *iodide* crystallised from aqueous alcohol and had m. p. 315—317° (decomp.) (Found: C, 35·3; H, 3·1; I, 59·2; N, 2·4. $C_{19}H_{20}I_3N$ requires C, 35·5; H, 3·1; I, 59·2; N, 2·2%). The *bromide* had m. p. 300—301° (decomp.) (from ethanol–ethyl acetate) (Found: C, 36·5; H, 3·7; Br + I, 52·2. $C_{19}H_{20}BrI_2N,2H_2O$ requires C, 36·1; H, 3·8; Br + I, 52·8%).

Diethyl 4′,1″-Difluoro-3,4:5,6-dibenzocyclohepta-3,5-diene-1,1-dicarboxylate.—2,2′-Bisbromomethyl-6,6′-difluorobiphenyl [16] (from 8·7 g. of difluorobitolyl) in ether was added to a solution of sodiomalonic ester (made from 1·84 g. of sodium and 6·4 g. of diethyl malonate) with stirring, and the mixture was heated under reflux for 1 hr. Most of the ether was distilled off and heating continued for another hr. Alcohol was distilled off and water was added to the residue. Solid *ester* separated and recrystallised from ethanol, giving 4·5 g. (30%), m. p. 140—144°. After two more crystallisations the m. p. was 146—147° (Found: C, 67·5; H, 5·6. $C_{21}H_{20}F_2O_4$ requires C, 67·4; H, 5·4%).

4′,1″-Difluoro-3,4:5,6-dibenzocyclohepta-3,5-diene-1-carboxylic Acid.—The above ester was hydrolysed with alcoholic potassium hydroxide to the *dicarboxylic acid*, m. p. 206—207° (decomp.) (from aqueous ethanol) (Found: C, 63·8; H, 4·0. $C_{17}H_{12}F_2O_4$ requires C, 64·15; H, 3·8%). This was heated in a bath kept at 220°, giving the *monocarboxylic acid*, m. p. 193° (from aqueous alcohol) (Found: C, 69·8; H, 4·7. $C_{16}H_{12}F_2O_2$ requires C, 70·1; H, 4·4%).

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

[21] Bell and Dinsmore, *J.*, 1950, 3691; see also Angeletti and Migliardi, *Gazzetta*, 1935, **65**, 819.

[22] Angeletti, *Gazzetta*, 1933, **63**, 145; Bell, *J.*, 1934, 835; Lothrop, *J. Amer. Chem. Soc.*, 1942, **64**, 1698.