SPIRANS-XIII

UV-ABSORPTION OF SOME SPIRANS

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Abstract-UV absorption spectra of some spirans and their "half-compounds" have been obtained and their comparison has allowed the dominating conformation to be defined for respective spirans.

In our investigations concerning UV measurements of the spiran system and its "half-compounds" the helical conformation is suspected to be dominant for spiran systems showing hypochromism. The absorption curves for both compounds have the same shape and the relationship of extinction coefficients at λ_{max} were as follows 1:1.35 or 1:1.38.

The spirans whose dominant conformation is known as bihelical showed hyperchromism, i.e. the relationship of extinction coefficients for both curves of the same shape at $\lambda_{\text{max}} = 232$ nm was 1:2.85, 248 nm 1:2.48, 284 nm 1:2.14 for spiran VI²⁺ measured in CH₂Cl₂ and at $\lambda_{max} = 237$ nm was 1:2.09, 299 nm 1:2.29, 330 nm 1:3.16 for spiran VIII' measured in CH₂Cl₂. The appearance of hyperchromism has been explained as an effect of conformational transmission.³

Finally it has been shown that UV absorption curves of the compound that is not a "half-compound" of a respective spiran, but possesses the same chromophores as the spiran, crosses the UV curve of the spiran.²⁵

It has been decided that at present the above studies should include some other kinds of geometries and other spiran systems. For this purpose the UV absorption spectra of fluorene and 9,9-spirobifluorene have been compared. As it is generally known the last spiran has both halves orthogonal to each other. In Fig. 1 the absorption curve of 9,9'-spirobifluorene, obtained according to Clarkson and Gomberg,⁶ has the same shape as the absorption curve of fluorene, with however, one exception, which is that the absorption curve of the spiran shows a batochromic shift of the UV spectra of about 8 nm. The relationship of extinction coefficients of these two derivatives is for $\lambda_{\text{max}} = 265-275$ nm 1:1.15, $\lambda_{\text{max}} =$ 289-297 nm 1:1.55, and $\lambda_{max} = 300-308$ nm 1:1.95. This low value of the extinction coefficient relationship for λ_{max} and the batochromic shift is considered to be caused by spiroconjugation, i.e. the mutual overlapping of the aromatic π -orbitals "through-space".

In turn it was decided that out of a number of the lately prepared spirans containing S atoms one should chose such a spiran that has both halves of the dominating orthogonal conformation, but in which the transmission of mutual influences would take place "though-bond". Thus out of this number of spirans, spiran 1 was selected since it was also possible to obtain its "half-compound" 2.

Fig. 1. UV spectra (in chloroform) of fluorene and 9,9'-spirobifluorene

Orthogonal geometry has been ascribed to compound 1 assuming that the dominant conformation for compound 2 is the chair-conformation similar as for unsaturated 7-member ring systems investigated by Friebolin et al.⁸

The UV spectra for compounds 1 and 2 (Fig. 2) show the existence of only a small degree of hyperchromism, $\lambda_{max}^{\text{CH,Cl}}$, 256 nm (1 g ϵ = 4.24) to $\lambda_{max}^{\text{CH,Cl}}$, 252 nm (1 g ϵ = 3.88) $1:2.29.$

The result of comparing the UV absorption spectra for spiran V, obtained earlier,' its "half-compound" 3 and the dimer of 3, i.e. compound 4, was a surprise.

The relationship of extinction coefficients for spiran V and compound 3 indicates a high degree of hyperchromism. Both curves are of the same shape and the lack of

^{*}In paper' on Fig. 1 there is no sign 2x on the absorption curve of the monomer. Now the cited relationship ϵ_3/ϵ_H has been obtained from many repeated measurements.

Fig. 2. UV absorption spectra (in chloroform) of compounds 1 and 2.

Fig. 3. UV absorption curves (in chloroform) of spiran V, compound 3 and dimer 4.

a bathochromic shift is noted, the relationship of the extinction coefficients is for $\lambda_{max} = 248$ nm 1:4.37, $\lambda_{max} =$ 274 nm 1:2.57, $\lambda_{max} = 313$ nm 1:3.31, $\lambda_{max} = 326$ nm $1:3.89$. In order to explain such a high ratio of the extinction coefficients one should assume a skew conformation for both 7-membered spiran rings according to the assumptions of Archer, Claret and Heyman.¹⁰ However the geometry of biskew conformation in the same spiran can be represented both by the orthogonal structure, as far as the placement of the chromophores is concerned, or by the coplanar structure. Since the orthogonal conformation of the spiran is associated with only low hyperchromism it is considered that the investigated spiran is a biskew structure of spirocoplanar geometry in the dominant conformation (Fig. 4).

In Fig. 3 one can see that the UV absorption curve of dimer 4 has an analogous shape to the UV absorption curve for spiran V crossing the spiran curve twice and yet,

Fig. 4. Stereomodels of the dominant conformation of spiran V showing spiroplanar arrangement in both halves.

having a greater extinction coefficient than the analogous spiran V. We consider that in compound 4 the dominant conformation has the naphthalene rings lying in the same plane: this arrangement is called "all lateral". A similar situation is seen in Fig. 4 of the paper "Spirans-VII".²

The next problem was the undertaking of further investigations into spirans showing hypochromism, for this purpose the following compounds were synthesised.

Among these derivatives A, B,¹¹ C, D,¹² have been described in the literature. As it can be seen the UV absorption spectra of derivatives A, B,' (Fig. 5), measured in methylene chloride, have analogous curves, show the same $\lambda_{\text{max}}^{\text{CH,Cl}} = 232 \text{ nm}$, with the extinction coefficient relationship 1:1.44 for the pair, spiran "half-compound" and 1:1.43 for the pair, dimer-monomer. As can be seen spiran 5 and dimer B show hypochromism of the same order and so the dominant conformation of both compounds will be the helical structure with the heterocyclic rings being in the skew conformation.

UV absorption for the pair, monomer A and dimer B, have also been measured in ethyl alcohol with an extinction coefficient relationship at $\lambda_{\text{max}} = 207 \text{ nm} 1:1.29$ and $\lambda_{\text{max}} = 227 \text{ nm}$ 1:1.40. On the other hand in *n*-hexane the extinction coefficient relationship of the pair.

Fig. 5. Absorption UV spectra of compounds A, B and 5 in chloroform.

Fig. 6. Dominant conformation of spiran 5.

monomer A and dimer B, at $\lambda_{\text{max}} = 204$ nm is 1:1.39. It is concluded that the dominating conformation for dimer B is as shown in Fig. 7.

Derivatives 6 and C also show UV absorption curves of the same shape and the same $\lambda_{max} = 232$ nm when measured in methylene chloride. The extinction coefficient

Fig. 7. Dominant conformation of dimer B.

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Vid - $24.7.1.1$ $V(\neg \neg)$ Fig. 8. UV absorption curves of spiran 6 and compound C in CH:CI:.

 $220 - 240 - 260 - 31$: m) Fig. 9. UV absorption curves (in $CH₂Cl₂$) of spiran 7 and

Fig. IO. Stereomodels of spirans 6 and 7

Fig. 11. UV absorption curves (in CHCI,, CH₂CI,, cyclohexane) of compound 8 and 9.

relationship at λ_{max} is 1:1.86 and consequently the spiran **shows low hypochromism (Fig. g).**

On the other hand the extinction coefficient relationship for compound pair 7 and D is respectively I: **1.42 and** 1 : **IS2 and indicates the dominating helical conformation of spiran (Fig. 9).**

A review of the models according to Dreiding has been made for establishing the symmetry class in order to explain the phenomenon of considerable hypochromism in compound 7 and low hypochromism in compound 6. It appears that in the case of compound 7 of symmetry C, the transition moments of the n-electrons working along the helix are very likely parallel, while the direction of the transition moments of n-electrons of the same sulphur atoms of compound 6 of symmetry c₂ are not parallel (Fig. **IO).**

An attempt to establish the dominating conformation of spiran 8. for which spiran 9 was going to be the "half-compound" was the next problem to be tackled.

The phenomenon of hypochromism has been observed in solutions of CHCl₁, CH₂Cl₂ and cyclohexane. At $\lambda_{\text{max}}^{\text{CH}}$ **241-242 nm** I: **1.16, A_. 277-219 nm** I : 1.40. **at Azy.':** 239 nm 1:1.46, λ_{max} 278-280 nm 1:1.50 and at $\lambda_{\text{max}}^{\text{cylobetator}}$ **227-228 nm** I : I. **19. A,, 272-278 nm** I : I **.38.**

The review of the models according to Dreiding has been made in order to explain the appearance of the hypochromic effect. It has shown that the structure

represented in Fig. 12 can be ascribed to the spiran with the assumption that for both halves of the spiran the skew configuration is dominant.

In this structure one can differentiate three pairs of benzene rings which are located on the helix and one pair

Fig. 12. Stereomodels of spiran 8

Fig. 13. UV absorption curves of spirans 10 (CHCl₃) 11,12 (CH₃Cl₃) and the corresponding spirans of symmetrical **constitution and their "half-compounds".**

located in parallel relationship to each other. This differentiation enables the requirement of Tinoco to be fulfilled for the derivatives showing hypochromism." Thus it can be seen that the hihelical structures'.' not having parallel benzene rings show low hyperchromism and that helical structures with parallely located rings show hypochromism, " in agreement with the postulates of Tinoco.

In order to check that using spiran 9 instead of the "half-compound" is correct three mono-spirans of the following structures were synthesised:

absorption curve has been compared with the absorption curve of E" previously shown.

It can be seen that the introduction of the two extra cyclohexane- rings into system F has practically no effect on the basic spectrum.

EXPERIMENTAL

The m.ps of the compounds were made on a Boetius block and corrected. IR spectra were recorded using a **Zeiss** UR-10 **spectrometer. UV absorption spectra were measured usmg IWO** different spectrophotometers: for compound 2 a Hilger H-700.308

Scheme 5

The UV absorption spectra of the monospirans have been measured and compared with the respectiv **constitutionally symmetrical spiran described earlier'.*." and with their "half-compounds". It is shown in Fig. 13 that using spirans IO. 11 and I2 as "half-compounds" is fully justified since their absorption curves are identical to that obtained for constitutionally symmetrical spirans.**

Their $\lg \epsilon$ at λ_{max} is also slightly different from the respective $\lg \epsilon$ of the "half-compounds".

Finally the tetra-spiran has been synthesised whose

and for remaining compounds an Unicam SP-1800. SMR spectra were obtained using a Tesla BS 487 apparatus at 80 MHz for the **compounds 5.6.7. IO and 12. for compounds 9 and** I I **wrth a Jcol apparatus at IOOMHz. for sample** I **with a bran apparatus at 6OMHr usmg TMS as a standard and sampk in CDCI,. and** sample 2 also with the last apparatus but with HDMS as a **standard. Mass spectra were measured at 7OeV on a I.KB 9OM S apparalus.**

Grnrral *pmcrdun*

3.3. Spirobi(8. methyl. (f) - benzo - 1.5 dithiepen. 6) (1). 0.9 g

Fig. 14. UV absorption curves (in Tetrachloroethane) of spiran 13 and E.

 $(0.04 g.$ at.) of Na were introduced to 15 ml of cellosolve in a thickwalled tube. After the reaction was completed $3.3 g$ (0.02 m) of 3.4-dimercaptotoluene were added followed by 3.8 g (0.01 m) of lctrabromoncopcntanc. The sealed tube was then heated for 100 hr at 150°. After evaporation of the solvent, unconverted tetrabromoneopentane was removed by steam distillation. The residue was dissolved in benzene and purified chromatographically on an Al₂O₁ column. The crude product was then sublimated

and colourless plates from benzene or EtOH were obtained, m.p. 208-209°. (0.31 g 3.9% of theoretical yield). IR(KBr): 600-700 KS-0 810.820. 860. 3040 (C-H arom). 2910. 2950cm ' (C-H aliph): LVtCH,CI,): Allog r) = 256nm (4.24); NMRtCDCI,): 2.3 ppm (s. 6H, -CH₃), 3.1 (s, 8H, -CH₃), 6.9-7.6 (m, 6H, arom), C,H& (376.6). Found C, 60.22; H, 5.55; S. 33.73. Requires: C. 60.59; H, 5.35; S, 34.05. MS m/e 376.

In the same manner compounds Z-13 were obtained.

Table 2. IR, UV, NMR and MS data of compounds 1-13

| | IR(KBr) | | UV | | | NMR | | | |
|-----------------|---|---|---------------------------------|--------------------------|----------------------|------------------------|-------------------------|---|-----------|
| Compound No. | Frequency (cm') | Kind of excitation | Solvent | λ_{max} (nm) | log e | Solvent | δ (ppm) | Proton type | мs m/c |
| \mathbf{I} | $600 - 700$ 810, 820, 3040 2910, 2950 | $C-S-C$ $C-H(\text{arom})$ C-H(aliph) | CH ₂ CI ₂ | 256 | | 4.24 CDCI, | 2.3 3.1 $6,9-7,6$ | $s.6H, -CH$ $s.8H, -CH, -$ m.6H, arom. | 376 |
| \overline{c} | 600-700 810, 820, 3050 2910, 2950 | $C-S-C$ $C-H(\text{arom})$ $C-H(\alpha$ liph) | CH ₂ CI ₂ | 252 | | 3.88 CCL | 2.2 ₁ | s.3H, -CH, $2.0 - 2.4$ m.2H, $-CH2$ - $2.6 - 2.8$ m.4H, $-\text{CH}_2 - \text{S}-$ 6.6-7.4 m.3H, arom. | 196 |
| 3 | 1170, 1260 1360 950, 1040, 3050 C-H(arom) | $C - 0 - C$ $C-H(bend)$ | CHCI, | 248 274 313 | 3.72 3.11 | 3.83 CDCl, | | 1.9-2.4 $q.2H$, $-\frac{C}{H}$, $-\frac{C}{H}$ $J = 5 Hz$ $4.0 - 4.3$ t.4H, $-0 - CH$,-, $J = 5 Hz$ | 200 |
| | 1460, 2950 | C-H(aliph) | | 326 | 3.15 | | | 7.1-7.7 m.6H, arom. | |
| 4 | 1180, 1260 | $C - O - C$ | сись | 248 | | 4.60 CDCl, | | 1.6–1.9 q.4H, $-CH_{2}$ -, J SHz | 400 |
| | 850, 960, 3070 2850, 2950 | $C-H({\rm arom})$ $C-H(aliph)$ | | 274 313 | 4.15 3.60 | | | $4.1 - 4.5$ t.8H, $-0 - CH$,- J SHz | |
| | | | | 326 | 3.78 | | | 6.9-7.6 m.12H, arom. | |
| \$. | 678 812 1417, 2909, 2944C-H(aliph) | $C-S-C$ C⊣C | CH ₂ CI ₂ | 232 | | 3.01 CDCI, | 2.78 2.90 | $s.8H^{\bullet}a^{\prime}$, $-(H,-S)$ $S.8H^{\bullet}$, $-S-CH_2$ | 252 |
| 6 | 703 820, 832 1417, 2855, 2905C-H(aliph) | $C-S-C$ C-C | CH ₂ CI ₂ | 232 | | 3.00 CDCI, | $2.71 -$ | $1.0 - 2.2$ m.16H $^{\circ}$ c $2.4 - 2.6$ m.4H'a" <u>s.4H ኮ</u> $2.7-3.2$ q.4H ⁻¹ b [*] , J = 15 Hz | 360 |
| 7 | 697 812, 830 1410, 2858, 2930C-H(aliph) | $C-S-C$ $C-C$ | CH ₂ CI ₂ | 232 | | 3.08 CDCI, | | $1.2 - 2.3$ m.16H'c" 2.3–2.9 $q.8H^{\dagger}b^{\dagger}$, J = 15 Hz $2.9 - 3.2$ m.4H"a" | 360 |
| 8 | 1231, 1267 2855, 2940 1583, 3022, 3065C-H(arom) | $C - O - C$ $C-H(\text{aliph})$ | CH ₂ CI ₂ | 278 272 233 227 | 3.70 4.06 4.20 | 3.75 CDCI, | 3.96 4.24 | s , $4H_1 - CH_2 -$ s.8H. $-CH2-O-$ 6.7-7.3 m.16H, arom. | 464 |
| 9 | 1258, 1268 2850, 2928 1500, 3034, 3064C-H(arom) | $C - D - C$ $C-H(aliph)$ | CH,Cl, | 233 280 | 3.89 3.57 | CDCI, | 1.59 4.01 | s.10H, $-CH_{2}$ - $s.6H, -CH, -O-$ 6.8-7.3 m.8H, arom. | 308 |
| 10 | 1257, 1270 2858, 2929 1478, 3030, 3060C-H(arom) | $C - 0 - C$ C-H(aliph) | CHCI, | 249 330 | 4.45 | 3.33 CDCl ₃ | 1.43 3.95 | s.10H, $-CH_{2}$ - s .4H, $-CH$, $-O-$ $7.1 - 7.6$ m.6H, arom. | 268 |
| $\mathbf{11}$ | 1246, 1270 2860, 2934 1503, 3028, 3069C-H(arom) | $C - O - C$ $C-H(\text{aliph})$ | CH_2Cl_2 | 232 247 285 | 4.47 4.35 4.03 | CDCI, | | 1.1-1.6 \cdot s.10H, \cdot CH ₂ - $3.9 - 4.4$ s.4H, $-CH_2 - O -$ 6.9-7.4 m.8H, arom. | 294 |
| 12 | 1265, 1279 2862, 2930, | $(-0)-$ C-H(aliph) | CH ₂ CI ₂ | 238 304 | 4.85 3.98 | CDCI, | | $0.9-1.6$ s.10H, $-CH$. $3.8-4.5$ AB-quartet $J = 12$ Hz, $4H$ | 394 |
| | 1593, 3060 | $C-H({\rm arom})$ | | 355 | 3.88 | | | 7.0-8.0 m.12H, arom. | |
| 13 | 1245, 1266 2860, 2940 1611, 3042, 3061C-H(arom) | $-0-$ C-H(aliph) | $C2H4Cl4$ | 251 278 287 | 3.90 3.81 3.65 | | | | 753 |

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