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SPIRANS—XII

SPIROPARACYCLOPHÁNES

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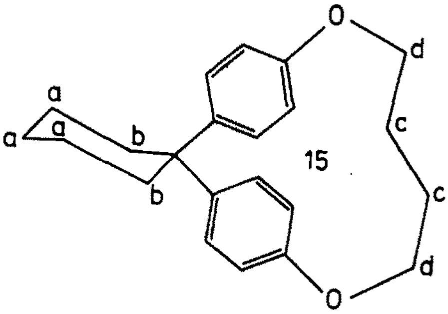
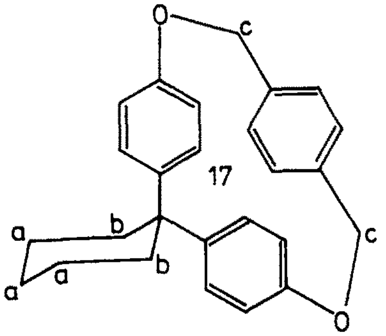
Abstract—A synthesis of three new spiran systems, each containing one heterocyclic ring with 15, 17 to 28 ring atoms, is described. The structures 1 and 3 may be regarded as the spiran and its moiety. The comparison of their absorption spectra in UV reveals the small degree of hyperchromism and a lack of bathochromic shift for spiroparacyclophane 1 which possesses two bent benzene rings. The last effect is probably caused by conjugation of the n-electrons of the O atoms with the π electrons of benzene rings.

We have been able to prepare new spiran systems, containing large rings of 15, 17 or 28 members, by condensing the Na-salt of 1,1-di(p-hydroxyphenyl) cyclohexane with 1,4-dibromobutane, ω,ω'-dibromo-p-xylene or 1,3-dibromopropane respectively These condensations were carried out in sealed tubes, the first and third at 160° for 200 hr and the second at 180° for 250 hr.

Compounds, **1**, **2** and **3**, were the reaction products:



1



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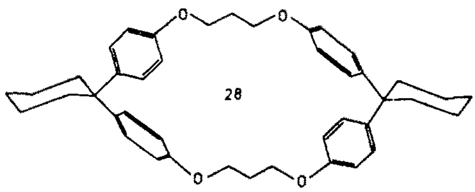

3

The structures assigned to the obtained spirans has been supported by the results of elemental analysis, measurement of UV and IR absorption curves, as well as by NMR spectrum.

The comparison of the UV absorption curves of compounds **1** and **3** was very useful since **1** possesses one methylene group more than the moiety of **3**, thus one can regard **3** (bispiran) as a dimer of **1** (monospiran). UV Absorption curves of such pairs, as far as we have found in previous investigations[1,2] are of the same shape and show the same maxima, but with different extinction coefficients. Since spirans **1** and **3** can also be regarded as compounds of paracyclophane character (therefore we have named them spiroparacyclophanes) we have analyzed their absorption curves as detailed in Cram's studies[3]

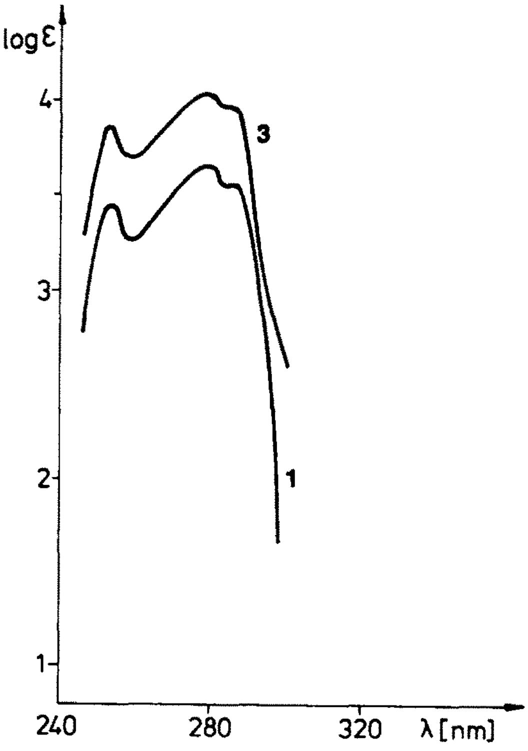

Fig. 1. UV spectra of compound **1** and **3**.

in order to find the bathochromic shift for spiran **1**, which possesses bent benzene rings.

UV absorption curves of spirans **1** and **3** possess identical shape as well as identical maxima of absorption, however the ratio of the extinction coefficients at λ_{max} are 1:2·49; 1:2·47; 1:2·53. The small degree of hyperchromism is probably caused by π electron interactions of benzene rings orthogonally situated in compound **3**.[4] The bathochromic shift has been found in strained carbocyclic paracyclophanes by Cram.[3] In our system which contains O atoms we observe no bathochromic shift, this is probably because the n electrons of the O atoms are conjugated with the π electrons of the benzene rings.

The absorption curve for spiran **2**, differs from the others in extinction values, but shows maxima at nearly the same wave-length.

Dreiding's stereo-models for spirans **1** and **2** indicate the presence of bent benzene rings. On the other hand spiran **3** may be represented by two major conformations having differently positioned benzene rings. The dominant form of these two conformations contains two pairs of opposing benzene rings which are perpendicular to each other, i.e. one pair lies in the same plane, whilst the benzene rings of the other pair are in parallel planes. The less dominant form has the benzene rings of opposing pairs in parallel planes.

The IR absorption curves exhibited by the spirans contained bands which confirmed the assumed structures.

The NMR spectra for compounds **1** and **2** were also measured. It was not possible to determine the NMR spectrum for spiran **3** owing to insolubility of this compound in the majority of organic solvents, and even in conc. H_2SO_4.

The NMR spectrum of spiran **1** shows a singlet at δ = 1·53 for "a" protons of the cyclohexane ring, a singlet at δ = 1·93 for "c" protons of a methylene group or "b" protons of cyclohexane ring, a singlet at δ = 2·23 for "b" protons or "c" protons, a singlet at δ = 4 for "d" protons and a multiplet at δ = 6·8–7·49 for aromatic protons in the ratio 6:4:4:4:8.

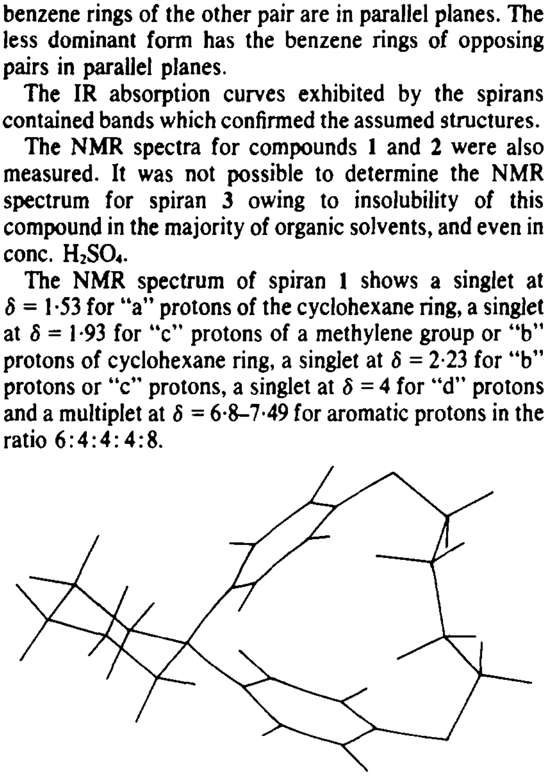

Fig. 2. The dominant conformation of spiran 1.

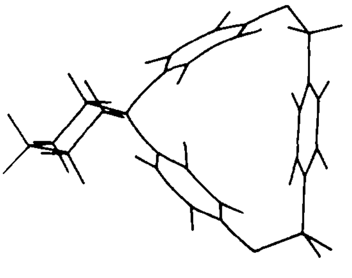

Fig. 3. The dominant conformation of spiran 2.

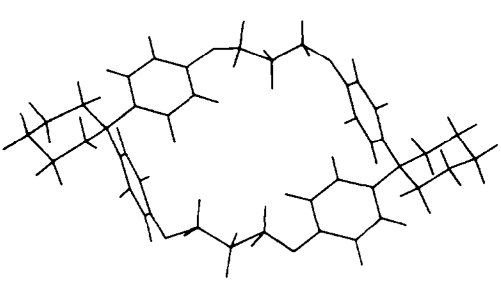

Fig. 4. The dominant conformation of spiran 3.

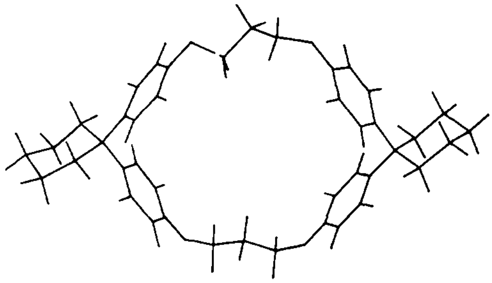

Fig. 5. The possible conformation of spiran 3.

The NMR spectrum of spiran **2** shows a singlet at δ = 1·55 for "a" protons of the cyclohexane ring, a singlet at δ = 2·27 for "b" protons of the cyclohexane ring, a singlet at δ = 5·1 for methylene protons "c" and a multiplet at δ = 6·73–7·68 for aromatic protons. The ratio of peak areas is 6:4:3, 5:12.

Mass spectra for all compounds showed the peaks for the molecular ions, as well as other peaks for heavier ions which indicated aglomeration.

EXPERIMENTAL

The IR spectrum was measured using a Zeiss UR-10 instrument in KBr and the UV spectrum with a spectrophotometer Unicam SP-1800 in tetrachloroethane. The NMR spectrum was measured using a Jeol at 100 MHz in CD_2Cl_2 for **1** and in $CDCl_3$ for **2**. The reference material was TMS. The elemental analysis was made using the milligram and submilligram method.

Spiro(cyclohexane - 1,2′ - (7,12) - *dioxatricyclo*(11.2.2.2^{3,6}) - ***nonadeca***(3,5,13,15,16,18) ***hexaene***) (**1**). Na (0·85 g; 0·04 g.at.) was added to cellosolve in a thick glass tube. The suspension of sodium-cellosolvat was heated with 1,1-di(*p*-hydroxyphenyl)-cyclohexane[5] (5 g; 0·019 mole) on a water bath for 1 hr, 1,4-dibromobutane (4·03 g; 0·019 mole) was then added and the tube sealed. The sealed tube was then heated at 160° for 200 hr. Evaporation of the solvent under vacuum left a residue which was washed several times with hot 5% NaOH aq and then with water. The crude product was purified chromatographically on an Al_2O_3 column (the eluent was CH_2Cl_2), recrystallized from methylene chloride, washed with ether and dried under high vacuum, m.p. 124° (Kofler block), yield 0·04 g (0·7%); IR (KBr): 828(s), 1248(s), 1458(m), 1514(s), 1609(m), 3045 (w) cm^{-1}; UV: λ_{max} 252 nm (log ϵ = 3·4314), 278 nm (log ϵ = 3·6721), 285 nm (log ϵ = 3·5798); (Found: C, 81·58; H, 8·42. $C_{22}H_{26}O_2$ requires: C, 81·95; H, 8·13%).

Spiro(cyclohexane - 1,2′ - (7,14) - *dioxatetracyclo* - (13.2.2.2^{3,6}2^{9,12}) *tricosane*(3,5,9,11,15,17,18,20,22) - ***nonaene***) (**2**). Na (2·6 g; 0·113 g.at) was added to 120 ml cellosolve in a thick glass tube, 1,1-di(*p*-hydroxyphenyl) cyclohexane (15 g; 0·056 mole) and *ωω′* - dibromo - *p* - xylene (14·8 g; 0·056 mole) were then added. The tube was evacuated, sealed and heated at 180° for 250 hr. In the course of the reaction a colourless ppt was formed which, after the opening the tube, was filtered off, washed with water, as well as with EtOH. The product was very difficult to dissolve in all organic solvents. It was purified chromatographically on an Al_2O_3 column by using anisole as the eluent and by recrystallisation from *p*-xylene and then from pyridine, m.p. 169° Kofler block), yield 3·2 g (16%); IR (KBr): 826(s), 1243(m), 1457(m), 1514(s), 1608(m), 3044(w) cm^{-1}; UV: λ_{max} 250 nm (log $\epsilon = 3{\cdot}8451$), 278 nm (log $\epsilon = 3{\cdot}6972$), 285 nm (log $\epsilon = 3{\cdot}6021$); (Found: C, 83·95; H, 6·92. $C_{26}H_{26}O_2$ requires: C, 84·28; H, 7·08%).

Dispiro(*cyclohexane* - 1,2′ - (7,11,21,25) *tetraoxapentacyclo* ($24.2.2.2^{3,6}.2^{12,15}.2^{17,20}$) *hexatriaconta* (3,5,12,14,17,19,26,28, - 29,31,35) - *dodecaene* - 16′,1″ - *cyclohexane*) (**3**). Na (0·85 g; 0·04 g.at.) was added to cellosolve in a thick glass tube. To the sodium-cellosolvat 1,1-di(*p*-hydroxyphenyl)-cyclohexane (5 g; 0·019 mole) was introduced and the whole heated for 1 hr. Then 1,3-dibromopropane (3·72 g; 0·019 mole) was added, the tube sealed, and heated at 160° for 200 hr. After opening the tube the solvent was removed under reduced pressure on a water bath and the product washed with a hot 5% NaOH aq and then with water. The crude product was purified chromatographically on an alumina column at 170° (the eluent was diphenyl oxide). The collected soln, which was at room temp. was colloidal. After centrifugation of this colloidal solution the product was filtered off, washed with MeOH and water, and then dried under high vacuum, m.p. 218° (Kofler block), yield 0·07 g (1·2%); IR (KBr): 829(s), 1248(s), 1452(m), 1515(s), 1610(m), 3048(w) cm^{-1}; UV: λ_{max} 252 nm (log $\epsilon = 3{\cdot}8261$), 278 nm (log $\epsilon = 4{\cdot}0645$), 285 nm (log $\epsilon = 3{\cdot}9823$); (Found: C, 81·70; H, 7·55. $C_{42}H_{48}O_4$ requires: C, 81·78; H, 7·84%).

REFERENCES

[1] S. Smoliński and G. Kinyua, *Tetrahedron* **27**, 265 (1971).
[2] S. Smoliński and I. Deja, *Ibid.* **27**, 1409 (1971).
[3] D. J. Cram, N. L. Allinger and H. Steinberg, *J. Am. Chem. Soc.* **76**, 6132 (1954); **80**, 3094,3109,3115 (1958).
[4] S. Smoliński, *et al.*, *Spirans* **XIII**, in press.
[5] J. Niederl, *J. Am. Chem. Soc.* **61**, 347 (1939).