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Spirans. XXII.[1] Spiroconjugation in Heteraspirans Studied by UV and ^{13}C NMR Spectra

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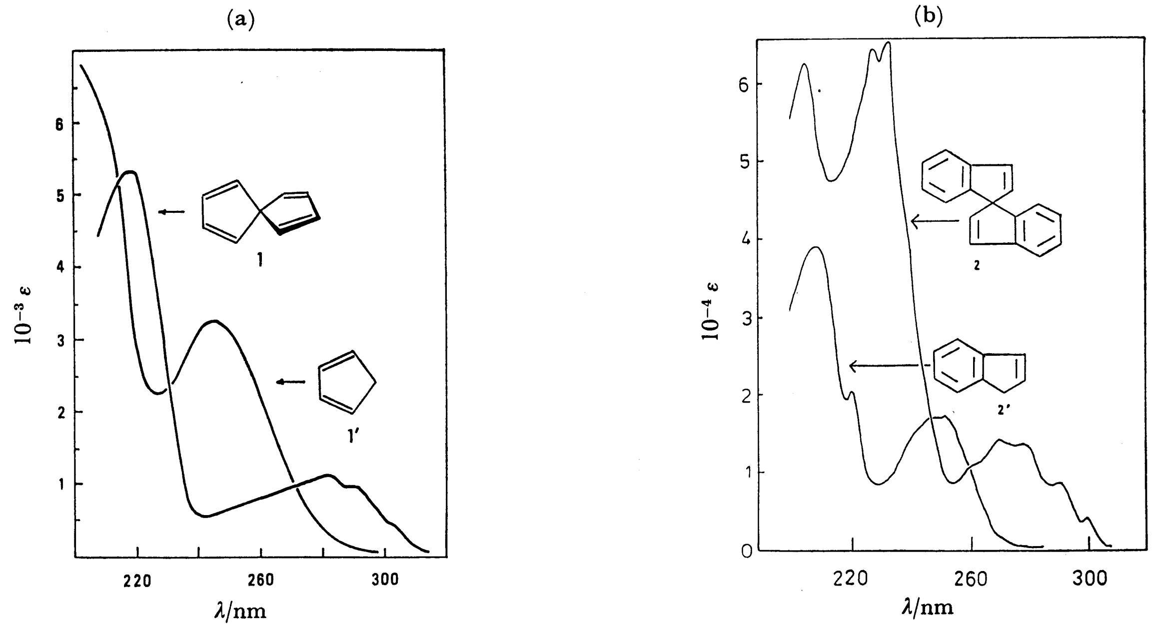
UV and ^{13}C NMR spectra of spirocyclic orthocarbonates, a spirobi(benzodithiepin) and a spirobi(naphthopyran) have been measured and compared with those of the "half compounds" to see the spiroconjugation effect. Whereas batho- and hyperchromic shifts are usually brought about by spiroconjugation, hypso- and hypochromic effects have been observed for 2,2′-spirobi[1,3-benzodioxole]. Through-bond interaction similar to the mechanism for the anomeric effect is considered to be operative in attenuating the electron release from the orthocarbonate moiety to the benzene chromophore. The downfield shifts of 20—25 and *ca.* 40 ppm were noted for the spirocarbons of the conformationally flexible and rigid orthocarbonates, respectively, as compared to the corresponding methylene carbons of the half compounds. The largest paramagnetic shift of 66.3 ppm is observed for the orthothiocarbonate and attributed to the presence of the low-lying d-orbitals due to through-space interaction of the four sulfur atoms.

Stimulated by the concept of spiroconjugation put forward by Simmons and Fukunaga,[2] and by Hoffmann *et al.*,[3] a number of theoretical[4] and experimental works[5] have since been carried out to delineate the extent and the mechanism of such conjugative effects. UV absorption and photoelectron spectroscopy have proved to be most instrumental in studying spiroconjugation. In the well-known case of spiro[4.4]nona-1,3,6,8-tetraene (**1**), the effect of spiroconjugation can be shown by comparing the UV spectra of the spiran and its half moiety, cyclopentadiene (**1′**). A large bathochromic shift (35 nm) of the long-wavelength band of the spiran is observed.[5b] The He(I) photoelectron spectra of spirocompounds have revealed that the splitting pattern in the low-energy region provides a measure of splitting of occupied MO's due to spiroconjugation. The spiro-splitting amounts to 1.23, 0.57, and 0.3 eV for **1**, 3,3′-spirobi[3*H*-indene] (**2**) and 9,9′-spirobi[9*H*-fluorene] (**3**), respectively,[6] showing that spiroconjugation is weakened by increasing benzoannelation which enhances the number of mesomeric structures of the "half compound."

In the present work, we would like to report the UV and ^{13}C NMR spectral data for spirocyclic orthocarbonates **4**—**6**, a spirobibenzodithiepin **7**, spirobinaphthopyran **8**, related spiran **9**, and their half compounds **4′**—**9′** to see the effect of spiroconjugation. Because of high electronegativity and consequent contraction of the 2p orbitals of the oxygen atoms, we expect a rather low through-space oxygen lone pair interaction. In such a case other mechanisms can be important. Conformational flexibility and/or rigidity may also affect the conjugation.

Results and Discussion

UV Spectra. Typical absorption spectra are given in Fig. 1. The data for the absorption maxima



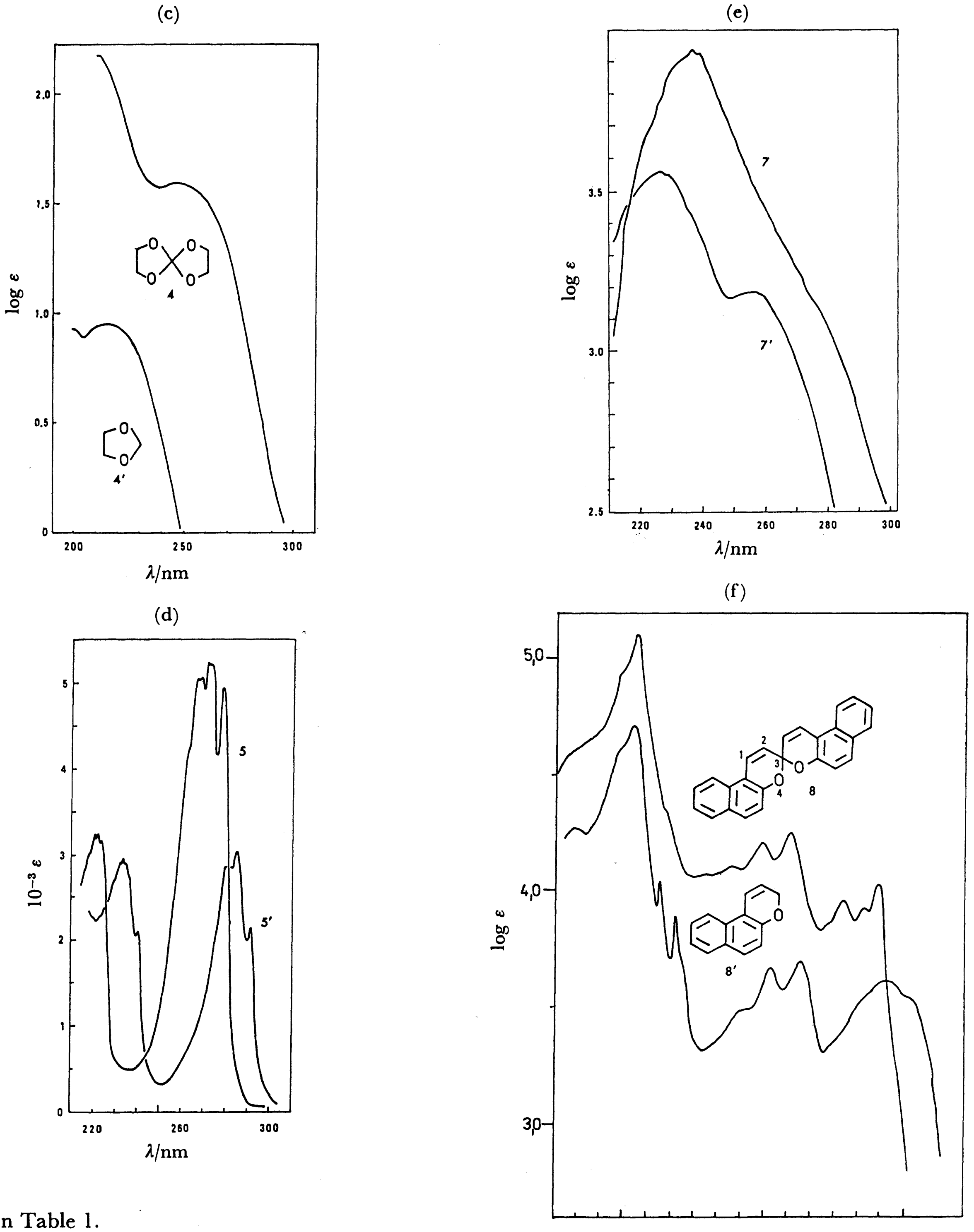


Fig. 1. UV absorption spectra of heteraspirans and their half compounds.

are listed in Table 1.

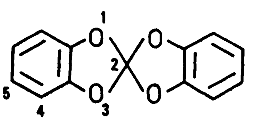
Spiroconjugation between two chromophores leads to extended conjugation. In other words, MO levels of each chromophore interact to split in energy and to make excitation of electrons more feasible. As a result, bathochromic shift of the UV absorption takes place. This is illustrated by the absorptions of **1** and **2**. There appears to be no exception to this rule for spiroconjugation through carbon 2pπ orbitals. Whereas **4** and **4'** are not the π-system and it is not clearly defined whether the excited state pertinent to the UV absorption should be n→σ* or the Rydberg state,⁷⁾ they show the spectral pattern similar to those of **1** and **1'** with the exception that the long-wavelength band in **4** has greater intensity than the corresponding band in **4'**. The difference in absorption maxima ($\Delta\lambda=32$ nm≈0.75 eV) approximates the spiro-splitting of 0.55 eV obtained by PE spectroscopy.⁸⁾

2,2'-Spirobi[1,3-benzodioxole] (**5**) provides an excep-

TABLE 1. UV ABSORPTION DATA FOR HETERASPIRANS AND THEIR HALF COMPOUNDS IN HEXANE

Compound	λ_{max}/nm (log ε)
4	247(1.60)[a]
4′	215(0.95)
5	221(3.51), 273(3.72)
5′	233(3.47), 285(3.49)
6	222(1.14), 247(1.24)
6′	213($\bar{1}$.38), 254($\bar{1}$.03)
7	229(3.64), 292(2.36)[b,c]
7′	217(3.29), 274(2.45)[c]
8	215(4.58), 244(5.10), 311(4.25), 348(4.03)
8′	219(4.26), 243(4.70), 315(3.70), 350(3.60)
9	218($\bar{1}$.71), 251($\bar{1}$.65)

a) 254 (3.57) in ethanol.[5b] b) Shoulder. c) In dioxane.



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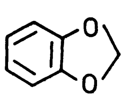

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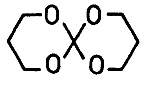

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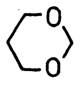

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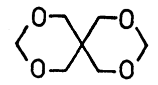

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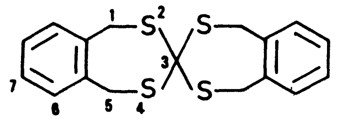

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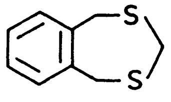
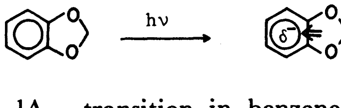
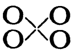
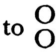


(7′)

tion. We have encountered for the first time an example in which hypso- and hypochromic effects are observed in the spiroconjugative system relative to the half moiety. The phenomenon is most reasonably explained in terms of inhibition by spiroconjugation of the local charge-transfer absorption from the oxygen lone pair to the benzene ring.



The $^1B_{2u} \leftarrow {}^1A_{1g}$ transition in benzene is forbidden and is observed only because of vibrational interaction. In the case of substituted compounds, the corresponding band is no longer strictly forbidden. When two oxygen atoms are introduced to the ring, the inductive effect affects the ground and excited states about equally and in the same direction. However, the lone pair of electrons on the two oxygen atoms interact with the π-electrons of the benzene ring to give a total of ten electrons on the eight center system. As a consequence of this delocalization, the energy of the highest occupied orbitals rich in the lone pair character is raised and the lowest unoccupied orbitals are affected only to a minor extent. The low-intensity band at 260 nm as well as the 203 nm high-intensity band is shifted to the red. The red shift is greater for the substituent in which the lone pair participation is enhanced by some electron release effect. This is exactly what is observed as we go from anisole (λ_{max}=217 (log ε 3.81) and 269 nm (log ε 3.17) in methanol) to 1,3-benzodioxole (**5′**) (see Table 1). On the other hand, the larger the electronegativity which is directly related to the ionization potential, the more difficult it is to remove an electron. The migration of charge distorts the symmetry responsible for the forbiddenness of the $^1B_{2u} \leftarrow {}^1A_{1g}$ transition of benzene and removes some of the forbiddenness. The absorption intensifies. The greater the migration of charge, the greater the intensification.

With the above generalization of the benzenoid absorption in mind, the observed hypo- and hypsochromic effects for **5** are concluded to be due to the diminution of the ease of electron release from the  moiety as compared to . The interpretation is supported by the observed PE spectral data for **5** and **5′**.[9] We note that the HOMO of **5** which is rich in the lone pair orbitals is stabilized relative to that of **5′** by 0.27 eV. There are at least two *a priori* mechanisms possible for the spiroconjugative interaction in orthocarbonates. One is through-space interaction which usually leads to repulsion of the non-bonding orbitals or reduction of ionization potential of the oxygen lone pair,[10] the trend which is not compatible with our observation (see Fig. 2). Second is through-bond interaction in which polar C–O bonds take part.[9] Since a pair of the C–O bonds in one half of the molecule are in the plane perpendicular to the other half in **5**, the skeleton with D_{2d} symmetry is quite adequate for the through-bond interaction. If the lone pair orbitals interact with the high-lying C–O bonding orbital, destabilization of the former would take place. The effect is similar to the through-space lone pair-lone pair interaction. It is the interaction of the lone pair orbitals

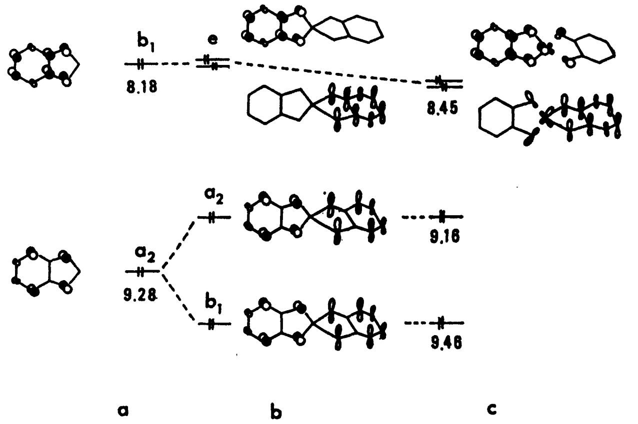
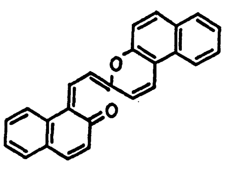


Fig. 2. Schematic correlation diagram for the higher occupied orbitals of **5** and **5′**. Stage (a): b_1 and a_2 orbitals of **5′** with C_{2v} symmetry obtained by mixing of the symmetric and antisymmetric combinations of the lone pair orbitals of 1,3-dioxolane with the HOMO's of benzene. Stage (b): the MO with a_2 symmetry of **5′** (and not the b_1 MO) splits into a_2 and b_1 orbitals as a result of through-space interaction in **5** (D_{2d} symmetry). Stage (c): through-bond interaction with the C–O σ* orbitals of the other half of the 1,3-benzodioxole moiety stabilizes the e orbital (no such effect for a_2 and b_1 orbitals). The numbers are from ionization potential values in the literature.

with the low-lying C–O anti-bonding orbitals which should be responsible for the stabilization of the HOMO of **5** with e symmetry relative to the b_1 orbital of **5′**, and for the observed hypo- and hypsochromic effects in the UV absorptions of **5** and **5′**.

The interaction of the lone pair of electrons with the anti-bonding orbital of the neighboring polar bonds is exactly what is currently adopted for the origin of the anomeric effect in carbohydrate chemistry.[11] The interpretation is also supported by a rather short C_{spiro}–O bond length of 1.38 Å in **5** as compared to the normal value of 1.43 Å.[12]

A pair of 3,3′-spirobi[3*H*-naphtho[2,1-*b*]pyran] (**8**) and 3*H*-naphtho[2,1-*b*]pyran (**8′**) provide an intermediate case where hypsochromic shift is observed only for the long-wavelength band. Through-bond interaction between the carbon 2pπ orbitals and the C–O anti-bonding orbitals would make the C–O single bond weaker and vulnerable to cleavage on heating.[13] As a result, compound **8** shows characteristic thermochromism attributable to reversible formation of **10**.



(10)

The spectrum of **7** somewhat resembles that of 1,5,7,11-tetrathiaspiro[5.5]undecane[14] in both bathochromic shift and hyperchromic effect as compared to the half compound. The transition giving rise to the absorption at 274 and 292 nm is considered to arise from an excitation of a non-bonding electron of a sulfur atom to a molecular orbital formed by overlap of d-orbitals on the four sulfur atoms. Let us take the d_{z^2} atomic orbitals, for example, as forming such a molecular orbital. These combine to give a pair of bonding and anti-bonding levels. The former splits further into two levels b_2 and a_1 after spiroconjugative interaction of one ring with another (see Fig. 3). Thus the bathochromic shift can be taken as a measure of the splitting due to spiroconjugation. The splitting amounts to 0.28 eV for **7** and 0.37 eV for the tetrathiaspiroundecane.[14]

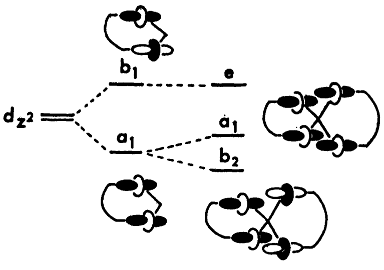


Fig. 3. Splitting of the vacant MO's due to through-space interaction of the d_{z^2} atomic orbitals of four sulfur atoms in orthothiocarbonates. Note that, in contrast to p orbitals where less stable a_2 orbitals are split by spiroconjugation, splitting of more stable a_1 orbitals in the C_{2v} moiety takes place for a combination of d_{z^2} orbitals.

^{13}C NMR Spectra. The proton-noise-decoupled ^{13}C NMR spectra were obtained at 20.1 and/or 25.0 MHz and the data are collected in Table 2. The signal due to the spirocarbons is among the most difficult to measure by the pulsed FT technique owing to their slow spin-lattice relaxation. Spin-lattice relaxation of ^{13}C nuclei in typical organic molecules is practically dominated by dipolar interaction with the near-by proton spins within the molecule. The spirocarbon of **5** which is four bonds apart from the nearest hydrogens thus resisted our effort to detect the signal under the standard pulsed FT measurement conditions of the pulse repetition time as long as 15 s. The difficulty was not overcome by addition of a few mg of a typical relaxation reagent such as $Cr(acac)_2$. The signal was finally obtained by adding a trace of cupper nitrate trihydrate in an acetone solution.[15] In Table 2 are also given differences in chemical shifts on going from the half compounds to the corresponding spiro compounds. The minus sign indicates the upfield shift of the latter signals relative to the former.

Examination of the data in Table 2 shows several trends. First of all, downfield shift of the spirocarbons is most conspicuous. The size of this shifts is 20—40 ppm for orthocarbonates **4**—**6** and ethyl orthocarbonate (**11**), 6—53 ppm for the spirocarbons attached to four carbon atoms, and 66 ppm for orthothiocarbonate **7**. Secondly, the spirocarbon chemical shifts for the orthocarbonates fall in two regions: 20—25 ppm for the conformationally flexible compounds and *ca.* 40 ppm for the rigid tetraoxaspiro[4.4] systems. For a third, upfield shifts up to 5 ppm are observed for the non-spirocarbons attached to oxygens on going from the reference to spiro compounds.

Chemical shifts of ^{13}C nuclei have been shown to be governed by local paramagnetic screening which arises from contributions of higher electronic states to the description of the ground state in the magnetic field. The screening increases as the mean inverse cube of the radius of the 2p orbitals on the carbon atom increases or effective excitation energy of the electron at the carbon decreases.[16] The observed downfield shifts of the central carbons as we go from the acetal (bonded to two oxygens) to the orthocarbonate (bonded to four oxygens) are ascribed to contraction of the radius of the carbon 2p orbitals by bonding to the increased number of the electronegative oxygen atoms. The larger paramagnetic shift in rigid **4** and **5** may be interpreted in terms of two effects; the synergic σ-bond polarization towards oxygen and the steric γ-effect. As described in the discussion of the UV spectra, the lone pair of electrons are donated to the adjacent σ* orbitals of the C–O bonds. Synergic to this flow of electrons from oxygen to carbon, the C–O bonding orbital, *i.e.*, σ-bonds will tend to polarize more towards oxygen atoms. As a result, contraction of the radius of the spirocarbon 2p orbitals may take place to effect stronger paramagnetic screening of the central spirocarbons. The effect is more pronounced in conformationally rigid **4** and **5** where the lone pair orbitals of the oxygens on one ring and the σ* orbitals of the C–O bonds on the other ring are

TABLE 2. ^{13}C NMR CHEMICAL SHIFTS (δ VALUES) OF HETERASPIRANS AND RELATED COMPOUNDS

Compound	C-1	C-2	C-3	C-4	C-5	Others
1	150.5	151.0			77.0	
1′	132.8	132.2			41.6	
Δ	17.7	18.8			35.4	
3						90.2[a] 148.8[b] 141.8[c]
3′						36.8 143.2 141.7
Δ						53.3 5.6 0.1
Ph_4C						65.3[d]
Ph_2CH_2						42.0
Δ						23.3
9		94.5		70.5	33.7	
6′		94.5		67.1	27.1	
Δ		0		3.4	6.6	
4		135.3		65.0		
4′		95.3		64.8		
Δ		40.0		0.2		
5		139.6		108.8	123.2	143.5[e]
5′		100.7		108.8	121.8	147.5
Δ		38.9		0	1.4	−4.0
6		114.1		62.1	23.9	
6′		94.5		67.1	27.1	
Δ		19.6		−5.0	−3.2	
11	58.5	14.9				119.9[d]
11′[h]	63.2	15.3				95.1
Δ	−4.7	−0.4				24.8
8			96.0			113.4[f] 149.3[c]
8′			65.3			115.5 130.2
Δ			30.7			−2.1 19.1
7	36.2		104.1			138.9[g]
7′	36.3		37.8			138.6
Δ	−0.1		66.3			0.3

a) C-9. b) C-9a. c) C-4a. d) The central carbon. e) C-3a. f) C-10b. g) C-5a. h) Diethoxymethane.

better aligned. Secondly and perhaps less importantly, there is an additional γ-carbon atom gauche to the spirocarbons introduced as we go from **6′** to **6**. As a result, the stereospecific γ-effect will operate to move the signal due to the spirocarbon somewhat upfield.[17] The same effect may also be operative in the conformationally flexible **11**.

One of the largest downfield shifts ever observed for the spirocarbon is 66.3 ppm in 1,1′,5,5′-tetrahydro-3,3′-spirobi[2,4-benzodithiepin] (**7**). As discussed in the section of its UV absorption, the low-lying d-orbitals are presumably contributing to the low-energy excited states for the 2p electrons of the spirocarbon to be mixed with the ground state.

Dowinfield shift of 53.3 ppm on going from fluorene to **3** may be compared with the shift difference of 23.3 ppm between diphenylmethane and tetraphenylmethane. Here again diminution of effective excitation energy of the carbon 2p electrons is considered to be responsible for the larger paramagnetic screening.

In conclusion, spiroconjugation in heteraspirans is reflected in their characteristic UV and ^{13}C NMR spectra. The spectral changes due to the spiroconjugation in these compounds are often different from those of spirohydrocarbons and are interpreted mainly in terms of the through-bond $n \rightarrow \sigma^*$ interaction.

Experimental

Materials. The previously described procedures were employed to prepare 2,2′-spirobi[1,3-dioxolane](**4**),[18] 2,2′-spirobi[1,3-benzodioxole](**5**),[19] 2,2′-spirobi[1,3-dioxane] (**6**),[20] (**6**),[20] 1,1′,5,5′-tetrahydro-3,3′-spirobi[2,4-benzodithiepin] (**7**),[21] 1,5-dihydro-2,4-benzodithiepin (**7′**),[22] 3,3′-spirobi[3*H*-naphtho[2,1-*b*]pyran] (**8**),[23] 3*H*-naphtho[2,1-*b*]pyran (**8′**),[24] and 5,5′-spirobi[1,3-dioxane] (**9**).[25] Purity of the samples for spectral studies was confirmed by their ^{1}H NMR spectra and VPC.

Spectra. The UV absorption spectra were taken from hexane solutions, unless otherwise stated, at 25 °C with a UNICAM SP-1800 and a Cary 17 spectrophotometer. Compounds **7** and **7′** were measured in dioxane and their absorption maxima were obtained by resolving the observed curve by using the program BANDF run on a Cyber 72 computer.

^{13}C NMR spectra were recorded on a JEOL FX-100 spectrometer operating at 25 MHz in the pulsed FT mode. A radiofrequency pulse of width 6 μs (45°) was generally employed with the repetition time of *ca.* 10 s. For Fourier transformation, 8 K spectral data points were available for spectral width 4000 Hz. Samples were *ca.* 10% solutions in $CDCl_3$ unless otherwise stated. Only a few mg samples of **7** and **8** were soluble in $CDCl_3$. The chemical shift due to the spirocarbon of **5** was obtained for the solution of 10 mg of **5** and 1 mg of $Cu(NO_3)_2 \cdot 3H_2O$ in 0.35 ml of acetone-d_6 with TMS as an internal standard.

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