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NMR and CD Spectral Features of Thiaheterohelicenes. Effect of Intramolecular Overlap of Aromatic Rings

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NMR and CD spectral features of a series of thiaheterohelicenes containing alternant thiophene and benzene rings were examined as associated with their helical structures. The terminal ring protons of the thiaheterohelicenes reflected the characteristics of intramolecular overlap of aromatic rings in ^{1}H NMR spectra. With the progression of the helix a sudden chemical shift of the β proton in the end thiophene ring to the higher field occurred, in contrast to carbohelicenes in which the drift of the upfield shift of the corresponding terminal ring proton was gradually suppressed. The CD spectra of thiaheterohelicenes were quite different from those of carbohelicenes. The intensities of the α and β absorption bands weakened with the progressive annelation, whereas the intensity of the p absorption band gradually increased, accompanied by a successive increase in the anisotropy factor of the band. These facts suggest that the structures of thiaheterohelicenes differ from those of carbohelicenes in having a peculiar distortion of the helix.

It has been of interest in helicene chemistry that helicenes are powerful inherently-dissymmetric chromophores of themselves, and that they possess the possibility of interactions between overlapping aromatic rings owing to their helically shaped structures. Chiroptical properties,[1,2] NMR[3] and ESR[4,5] spectral features, and X-ray analyses[6–8] of helicenes have been widely studied, together with molecular orbital calculations.[9,10] However, these investigations have so far been limited to [9] rings, especially in the field of heterohelicenes, presumably because of difficulties in preparations and purifications of the compounds with multi-rings; thus the properties of helicenes higher than [9] rings have remained uncertain. We found high performance liquid chromatography (HPLC) very useful for purifications and optical resolutions of thiaheterohelicenes annelated with alternant thiophene and benzene rings.[11,12] The pure racemic and enantiomeric thiaheterohelicenes obtained by applying this method to the final stages of preparations enabled us to perform the present work.

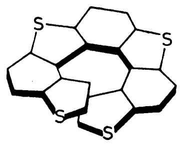
We describe here the characteristics of ^{1}H NMR and circular dichroism (CD) spectra of thiaheterohelicenes ([7] to [15]), compare them with those of carbohelicenes, and discuss the effect of intramolecular overlap of aromatic rings.

Experimental

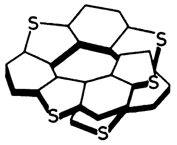
The preparations[11] and the optical resolutions[12] of thiaheterohelicenes studied have been reported in previous papers. ^{1}H NMR spectra (in $CDCl_3$) were recorded on a JEOL PFT-100 spectrometer operating at 100 MHz in the Fourier transform mode. CD spectra (in $CHCl_3$) were measured on a JASCO J-20A automatic recording spectropolarimeter at 23 °C with concentrations of 8.5×10^{-6}—6.0×10^{-5} mol dm^{-3}; the concentration was 4.25×10^{-4} mol dm^{-3} for the measurement of the α band of [13]thiaheterohelicene.

Results and Discussion

^{1}H NMR Spectral Features. In the previous communication we have assigned the ^{1}H NMR spectra of thiaheterohelicenes studied here, except for that of [15] homolog, where some ambiguity remained because of the partial overlapping of the peaks.[11] Among the protons in this series of compounds the chemical shifts of two protons in the terminal thiophene rings, giving AB or AX type quartet peaks, reflected most characteristically the effect of intramolecular overlap of the aromatic rings. Figure 1 demonstrates the changes in the chemical shifts of the terminal ring protons in the thiaheterohelicene series (A and B protons) against the number of rings, along with the changes in the carbohelicene series (X and Y protons).[13] To clarify the degree of helical turns, the abscissa indicates also the internal angles of the molecules, which were assessed by allocating 45° for a thiophene and 60° for a benzene ring.[2]



[7]



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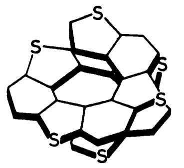

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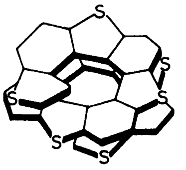

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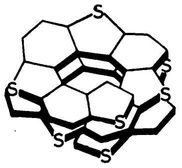

[15]

The chemical shifts of both A proton in [5]thiaheterohelicene and X proton in [4]carbohelicene likewise appeared in the lower field owing to the mutual van der Waals compressions between the continuous hydrogens.[3,14] When an overlap between the terminal rings occurs (internal angle is more than 360°), large upfield shifts of the protons appeared in both series. Molecular models suggest that A proton is located approximately above the center of the adjacent faced ring and B proton is located in the vicinity outside the helix, whereas X proton lies in the vicinity of the axis of the helix and Y proton lies above the faced ring. These situations are supported by the fact that A and Y

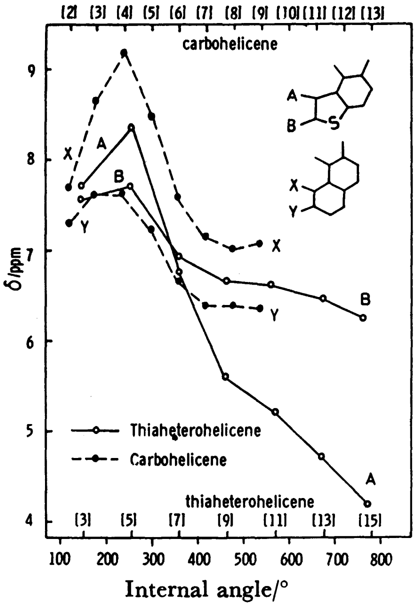

Fig. 1. Influence of the progressive overlap of aromatic rings on the chemical shifts of the terminal ring protons in thiaheterohelicenes and carbohelicenes. The data for carbohelicenes were quoted from the literature.[3]

protons shifted to higher fields than B and X protons, as a consequence of the stronger diamagnetic shielding by the ring current of the faced rings.

In the carbohelicene series the drifts of upfield shifts of both X and Y protons seem almost to converge with an increase of helical turns, indicating that the diamagnetic shielding effect might become constant at the higher homologs. This is substantiated by X-ray analyses which show that the pitch of the inner helix of carbohelicenes has not varied so much with an increase of number of benzene rings ([7], [10], and [11]-carbohelicene: 3.17, 3.22, and 3.22 Å, respectively).[6] In the thiaheterohelicene series this trend holds approximately for B proton, but not for A proton, the behavior of the latter in the chemical shifts making the thiaheterohelicenes very peculiar. A few reports on the syntheses of carbohelicenes up to [14] rings have been published;[15] nevertheless, to our regret, no NMR data of the carbohelicenes are available for comparing the trends of chemical shifts.

The extents of upfield shifts by the ring current remained in the range of 0.6—1.0 ppm for X and Y and B protons; these values may be compared with those for naphthalene ([2]carbohelicene) and benzo[1,2-*b* : 4,3-*b*′]dithiophene ([3]thiaheterohelicene), which possess no diamagnetic shielding effect. On the other hand, the upfield shift of A proton went up far beyond this range; 2.1 ppm in [9]thiaheterohelicene and 3.5 ppm in [15]. It is rare that an aromatic ring proton shifts as high as about 4 ppm(δ); this is only found for those of metacyclophanes which have a great constraint in a molecule.[16] The trend of A proton shifts may imply that the proton comes closer to the adjacent faced ring with the progression of the helix, since their relative position does not alter, as molecular models suggest. In this case the degree of diamagnetic shielding may be mainly determined by the distance between the proton and the aromatic ring. In order to shorten the distance we can not make the pitches of the thiaheterohelicene helices become smaller with the progressive annelation, because this does not occur in the case of carbohelicenes, as mentioned above.

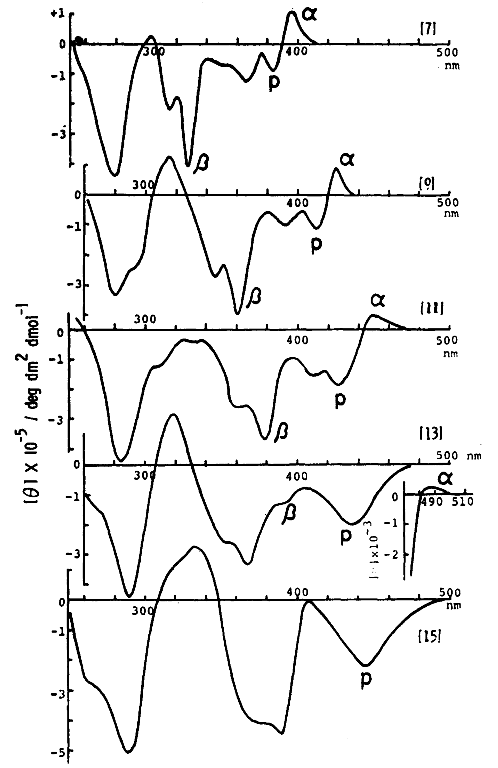

Fig. 2. CD spectra of (*M*)-(−)-thiaheterohelicenes in $CHCl_3$.

The significant structural difference between thiaheterohelicenes and carbohelicenes lies in the presence of bulky sulfur atoms. The sulfur atoms in the upper and lower decks of the molecules are relatively close to each other (refer to the Figure). The repulsive forces between the sulfur atoms may keep them as far away from each other as possible and thus bring about distortion of the molecules. This distortion compels the A proton to come closer to the faced ring. With an increase of the number of rings an accumulation of the distortions caused by the repulsions between some pairs of sulfur atoms in a molecule makes the distance smaller and smaller, resulting in the more and more upfield shift of A proton.

CD Spectral Features. In order to study the chiroptical properties of helicenes, precise optical resolutions are needed. We reported the resolutions by HPLC fitted with a silica-gel column containing a chiral charge transfer complexing agent, 2-(2,4,5,7-tetranitro-9-fluorenylideneaminooxy)propionic acid, which functions as a selector.[12] The preparative HPLC was somewhat tedious, but ensured the complete separations between enantiomers. Though CD spectra of some helicene congeners have been described, few changes of the spectra have been discussed from the standpoint of the progression of the helix.

Figure 2 shows the CD spectra of (*M*)-(−)-enantiomers of [7] to [15]thiaheterohelicenes. CD absorption

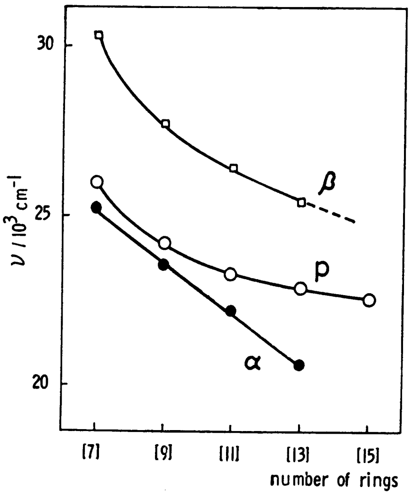

Fig. 3. Changes in transition energies of α, p, and β absorption bands of thiaheterohelicenes.

bands of thiaheterohelicenes are resolved well in comparison with those of carbohelicenes, and there is a clear difference between the spectra.[17] Band assignments to α, p, and β absorptions according to the Clar's nomenclature were tentatively made by the comparison with their UV spectra and by the supposition that the more the extension of the conjugated systems, the longer the wavelength light they absorb. The transition energies of the three longest wavelength absorptions thus assigned are illustrated in Fig. 3 for each thiaheterohelicene. The energies for p and β absorptions appear nearly to converge, but not that for α absorption which is anticipated to have the same tendency in homologs higher than [13]. It is interesting, though the reason is not clear as yet, that the convergency of the energies becomes faster in the order of p>β>α, which is contrary to that of the case in polynuclear aromatic hydrocarbons.[18]

As seen in Fig. 2, each band became successively broader, showing some variation of its intensity with an increase of the number of rings. The broadening of the bands may be ascribable to the increasing overcrowding of the molecules. The intensity of p band was gradually enhanced as the number of rings increases, while those of α and β bands were gradually diminished and finally could not be discerned in the [15] homolog. Wavelength at absorption maxima and molecular ellipticity(θ) of the three bands, together with molecular absorption coefficient(ε) and anisotropy factor(g) of p band, are tabulated in Table 1. Apparent ε values of p band decreased from [7] to [15]thiaheterohelicenes, but the absolute values of [θ], in contrast, increased, leading the absolute values of g to become greater.

As the absorption for p band is due to the transition polarized mainly along the molecular axis,[17] the increment of the intensity may be explicable in terms of the enhanced transition moments caused by an increase of helical turns along the axis. The trend of g factors may reflect the cumulatively increasing distortions with the progression of the helix, as noted in the NMR study. It turns out that the extent of molecular dissymmetry of the present thiaheterohelicene is enhanced as the number of rings increases. On the other hand, as the absorptions for α and β bands are due to the transitions polarized along the perpendicular (C_2 axis) to the molecular axis,[17] the intensities of these bands are not expected to vary significantly with the progressive annelation because molecular diameters along the C_2 axis on a molecular plane are almost the same for each thiaheterohelicene studied. In addition, the increasing overcrowding of the series of molecules may bring about the gradually broadening of the two absorption peaks, resulting in the weak intensity which makes them unobservable in [15]thiaheterohelicene.

In consequence, the configurations of thiaheterohelicenes studied are anticipated to differ considerably from those of carbohelicenes owing to the existence of bulky sulfur atoms. However, we inferred the difference on the basis of the properties only in solutions, and X-ray crystallographic analysis on the compounds may reveal such interesting results.

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TABLE 1. THREE LONGEST WAVELENGTH ABSORPTIONS (α, p, AND β) OF (M)-(−)-THIAHETEROHELICENES IN $CHCl_3$

Figures in parentheses are wavelengths (nm) at absorption maximum.

	α	β	p		
	[θ]×10^{-4} / deg dm^2 dmol^{-1}	[θ]×10^{-4} / deg dm^2 dmol^{-1}	[θ]×10^{-4} / deg dm^2 dmol^{-1}	ε×10^{-3} / mol^{-1} dm^3 cm^{-1}	g×10^3
[7]	11.2 (397)	−44.4 (330)	−9.6 (385)	19.0 (389)	−1.5
[9]	10.0 (426)	−39.7 (361)	−11.5 (413)	15.1 (424)	−2.3
[11]	5.8 (450)	−35.0 (379)	−18.0 (429)	8.1 (430)	−6.8
[13]	3.1×10^{-2} (485)	−12.6 (394)	−20.0 (437)	7.2 (434)	−8.4
[15]	—	—	−22.8 (443)	6.0 (440)	−11.5

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