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[7],[9],[11],[13], AND [15]HETEROHELICENES ANNELATED WITH ALTERNANT THIOPHENE AND BENZENE RINGS. SYNTHESES AND NMR STUDIES

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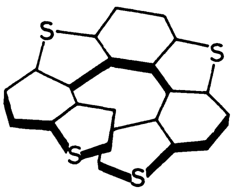
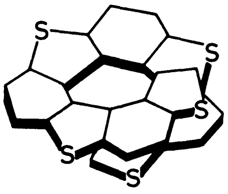
Syntheses of the title heterohelicenes are described and their NMR spectra showed the conspicuous phenomena reflecting the overlapping of aromatic rings.

Many efforts have been focused to synthesize higher helicene series, since a particular interest has been directed to how an extension of the helix brings about a change of their helical structure as well as their spectral, chiroptical, and physical properties$^{1)}$. As yet, the extension has been limited to [14] rings in carbohelicene series$^{2)}$, and [11] in heterohelicene$^{3)}$. We report herein the first syntheses of [13] and [15]heterohelicene containing alternant thiophene nucleus and their NMR spectral features in comparison with those of [7], [9], and [11] homologs.

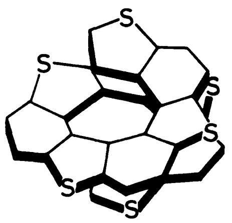
The syntheses of [13] and [15]heterohelicenes were capable by utilizing the photocyclization of precursor olefins or diolefins, which has been well established in the syntheses of the lower homologs$^{3)}$. Among them [15]heterohelicene is of



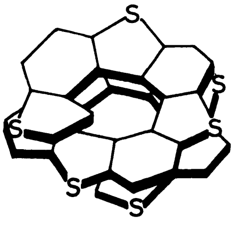
[7]



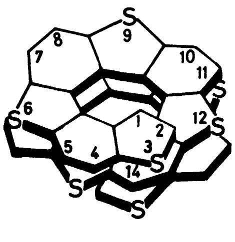
[9]



[11]



[13]



[15]

Table 1. Syntheses of Heterohelicenes

Heterohelicene	Precursor	Yield(%)	M^+(m/e)
[7]	[3]-CH=CH-[3]	50	403
	Th-CH=CH-[3]-CH=CH-Th	32	403
[9]	[5]-CH=CH-[3]	38	508
[11]	[3]-CH=CH-[3]-CH=CH-[3]	8	614
[13]	[7]-CH=CH-[5]	17	720
[15]	[5]-CH=CH-[3]-CH=CH-[5]	5	826

[3] and Th represent benzo[1,2-b:4,3-b']dithiophene and 2-thienyl respectively. [3]-, [5]-,and [7]- denote 2-substituted [3], [5], and [7] respectively, -[3]-, 2,7-disubstituted [3].

particular interest since this is the first member in the congeners with a three-layered structure. The precursor olefins or diolefins were prepared by the Wittig reactions from the corresponding aldehydes and phosphonium salts according to the usual procedures. Table 1 summarizes the syntheses of heterohelicenes on the use of the precursors specified. High performance liquid chromatography (HPLC) was used for the final stage of purifications of the products to give the yields shown in the Table. Mass spectroscopic analyses for the purified products by means of the field-desorptive ionization all gave the molecular peak(M^+) of the target heterohelicene as shown in the last column in the Table. Note that double

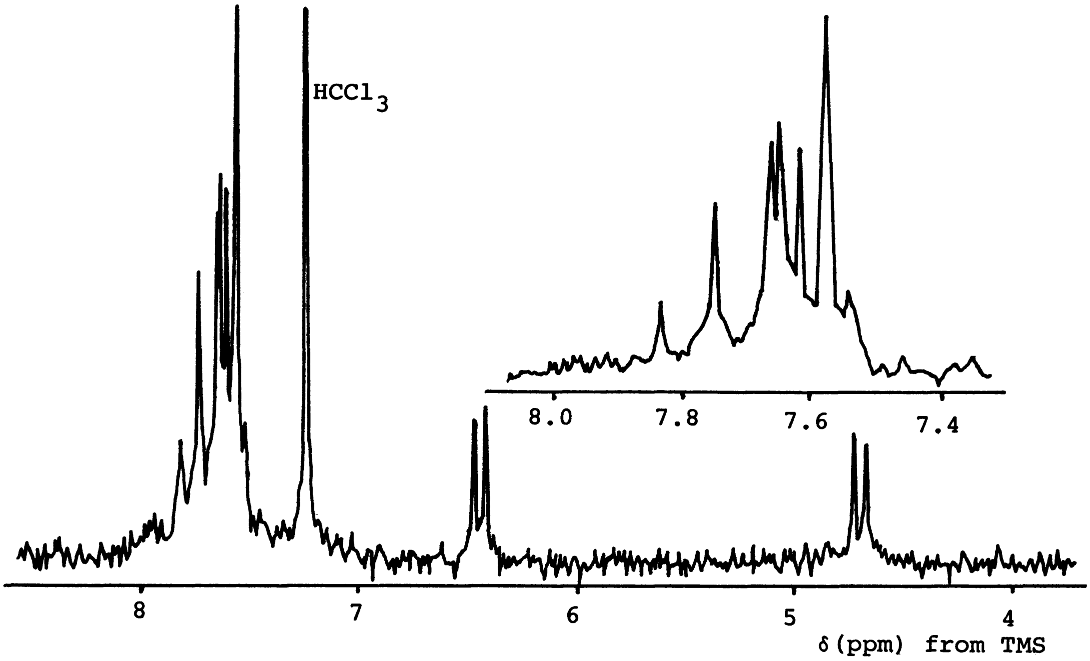


Fig. 1. 100 MHz NMR Spectrum of [13]Heterohelicene in $CDCl_3$

Table 2. ^{1}H NMR Chemical Shifts(δ, ppm) of Heterohelicenes in $CDCl_3$ with TMS as an Internal Standard

Position	1	2	4, 5	7, 8	10, 11	13
[3]	7.70	7.55	7.81	——	——	——
[5]	8.36	7.71	7.86, 8.02	——	——	——
[7]	6.75	6.91	8.02	8.00	——	——
[9]	5.60	6.65	7.47, 7.49	8.18	——	——
[11]	5.21	6.62	7.52, 7.54	7.60	8.13	——
[13]	4.71	6.45	7.66, 7.67	7.58	7.59, 7.79	——
[15]	4.20	6.23	7.4–8.0 multiplet*			7.00

* not assigned

photocyclizations of diolefins, which have been recommended to be useful for the preparations of higher carbohelicenes[2)], afford the products in lower yield in this case.

The insulation of benzene rings by a thiophene ring immediately results in a simplified NMR spectrum, as is evident from inspection of a 100 MHz spectrum of [13]heterohelicene(Fig.1). All signals are well resolved; AX quartet peaks in the higher field are due to the protons in the terminal thiophenes, two peaks close each other at 7.66 and 7.67 ppm(δ) to 4- and 5-(19- and 20-)positioned protons, singlet peak at 7.58 ppm to 7- and 8-(16- and 17-)positioned protons, and the residual signals composing AB quartet to the protons on the 10 and 11(13 and 14) positions. In the case of [15]heterohelicene the AX quartet signals of the protons attached to the end thiophene rings exhibited a pronounced upfield shift. The singlet peak in the higher field, 7.0 ppm, was easily assigned to the central benzene protons(13 and 14 positions) of the molecule, reflecting an increase in shielding caused by the upper and lower thiophene rings of the three decks (refer to Figure). Multiplet signals in the range of 7.4 to 8.0 ppm, which are due to the residual benzene protons, have not been assigned as yet.

Chemical shifts of the heterohelicenes studied are gathered in Table 2. Assignments to each proton in [3] to [7]heterohelicenes are unambiguously determined by deuteration and the comparison of the spectra of higher heterohelicenes with those of lower homologs gave the reasonable assignments to each proton in the higher homologs. More noticeable is that a large upfield shift of the terminal thiophene protons(1 and 2 positions) appears as soon as an overlap between the terminal rings occurs, and amplifies its tendency with the progression of a helix. It is very interesting that the shift of the 1-positioned proton in [15]heterohelicene against benzodithiophene([3]), which possesses no diamagnetic shielding effect, goes up to 3.5 ppm, whereas the shifts of the benzene protons remain relatively small(~0.5 ppm).

HPLC was not only useful to purify the racemic heterohelicene but also very powerful to separate the enantiomers. Fig. 2 shows the CD spectrum of (P)-(+)-[13]heterohelicene$^{4)}$ which was isolated by HPLC fitted with a chiral column$^{5)}$. Obvious bands assigned to α, p, β, and β' absorption$^{6)}$, by which the electronic structure of heterohelicene is to be characterized$^{7)}$, appear ensueing some vicissitude of the intensities in comparison with the spectra of the lower homologs. A trend in variations of the absorption intensities with the progression of helical turns may be an interesting subject on the electronic structure of the multilayered heterohelicenes and may be discussed elsewhere.

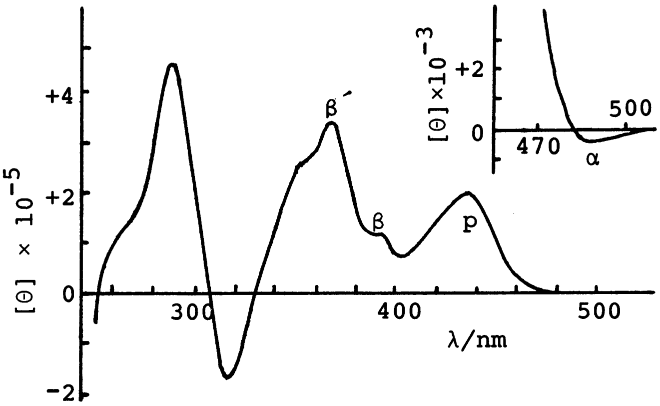


Fig. 2. CD Spectrum of (P)-(+)-[13]-Heterohelicene in CHCl$_3$

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References and Notes

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4) A CD spectrum of chiral [15]heterohelicene could not be quantitatively measured as yet because of its small amount of isolation. Optical rotation of (P)-(+)-[13]heterohelicene showed $[\alpha]^{23}_{500}$ 8170°, the largest value in the chiral homologs we have measured.
5) We used a 30 cm silica-gel column linked with 11% (S)-(+)-2-(2,4,5,7-tetranitro-9-fluorenylideneaminooxy)propionic acid as a selector, as shown in the literatures; F.Mikes, G.Boshart, and E.Gil-Av, Chem. Commun., 1976, 99. F.Mikes, G.Boshart, and E.Gil-Av, J.Chromatogr., 122, 205(1976). F.Mikes and G.Boshart, J.Chromatogr., 149, 455(1978).
6) According to the Clar's nomenclature
7) M.B.Groen and H.Wynberg, J. Am. Chem. Soc., 93, 2968(1971).

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