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Layered Compounds. LXI.[1] Carbon-13 NMR Study of [*n*]-, [*n.n*]-, and Multilayered [2.2]Paracyclophanes

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The carbon resonances of several [*n*]paracyclophanes (n=8—12) were assigned with the aid of partially deuterated derivatives. The ^{13}C NMR spectra of the title paracyclophanes were examined from viewpoints of the steric compression effect and the ring-current effect. Although the compression effect is a dominant factor for carbon resonances of closely stacked paracyclophanes, the ring-current effect was evidently observed in the spectra of [10]paracyclophane–[10](9,10)anthracenophane pair, [3.3]paracyclophane, and multilayered [2.2]paracyclophanes.

It is well known that ^{1}H NMR spectra of a variety of cyclophanes are characterized by extraordinary upfield shifts due mainly to the ring-current effect of the benzenoid rings. Multilayered paracyclophanes composed of closely stacked benzenes were reported as suitable models for evaluating systematically such an effect.[2] On the other hand, it is difficult to evaluate the ring-current effect on ^{13}C NMR spectra because the range of carbon chemical shifts is much greater than that of proton chemical shifts and thereby carbon shieldings are often sensitive to other effects.[3] Especially in rigid or crowded systems there was observed the steric compression as a dominant effect which often obscured the ring-current effect. Recently, a small extent of the ring-current effect was reported on the resonances of the middle methylene carbons of [12]-paracyclophane **5**.[4] The conclusion is, however, somewhat questionable because their assignment of methylene carbons remained equivocal. In order to investigate the anisotropic effect of a benzene ring on ^{13}C NMR in detail, we measured ^{13}C NMR spectra of [*n*]paracyclophanes **1**—**6**[5] and a dibenzo derivative, *viz.*, [10](9,10)anthracenophane **7**[6] as well as [*n.n*]-paracyclophanes **8**—**16**[7,8] and multilayered [2.2]-paracyclophanes **17**—**20**,[8] some of whose geometries are well confirmed by X-ray crystallography.

Experimental

All the samples were prepared as described in the previous papers.[5–8] The ^{13}C NMR measurements were made on deuteriochloroform solutions (concentration 0.2—0.5 M) using TMS as an internal standard. The spectra of most of the cyclophanes were recorded at 25.05 MHz on a JEOL FX-100 spectrometer equipped with a Fourier transform system, JEC-980B computer, ^{2}H field frequency lock, and noise-modulated proton-decoupling system. The observed free-induction decay after a 45° pulse width of 6 μs was sampled in 8192 data points with a spectrum width of 5000 Hz and a repetition time of 3 s (digital resolution 1.25 Hz). The spectra of [10](9,10)anthracenophane **7** and alkylbenzenes, **21** and **22**, were run on a Varian XL-100-15FT spectrometer (25.2 MHz), ^{1}H noise decoupling, 0.2 M CDCl$_3$, TMS as an internal standard, $\delta \pm 0.1$ ppm.

[11]Paracyclophane **4**. Catalytic hydrogenation of [11]-paracyclopha-3,5-diyne[19] (500 mg) by the usual method (5% Pd–C in MeOH) gave [11]paracyclophane **4** as a colorless liquid (427 mg, 82.4%), bp 168—178 °C (bath)/9 mmHg 1 mmHg=133.322Pa. Found: C, 88.40; H, 11.54%; M$^+$, 230. Calcd for $C_{17}H_{26}$: C, 88.62; H, 11.38%; MW 230.

Deuteration of [n]*Paracyclophadiynes.* Catalytic deuteration of [*n*]paracyclophadiynes[9] was performed by treatment of the substrate with 5% Pd–C and MeOD (Merck D-content >99%) at 40—60 °C for 1.5 h in an atmosphere of deuterium, which was evolved by addition of aluminium to *ca.* 2M D_2SO_4 prepared from concd D_2SO_4 (96—98%, Merck, D-content >99%) and D_2O (Merck, D-content>99.75%). Distillation of the crude product gave deuterated [*n*]paracyclophanes (n=10—12), **23**—**26**, in 84—93 wt% yield, bp 135—180 °C (bath)/4—5 mmHg. Deuterium-content and -distribution in these products were determined by mass spectrometry. Relative intensity ratios of the parent peaks due to isotopic species and of the base peaks due to *p*-xylene fragment showed that 79—85% of the products consisted of [*n*]paracyclophane-d_7—d_{11}, and isotopic species substituted by more than two deuterium atoms at the two benzyl methylenes were contained by 4—9% in the products.

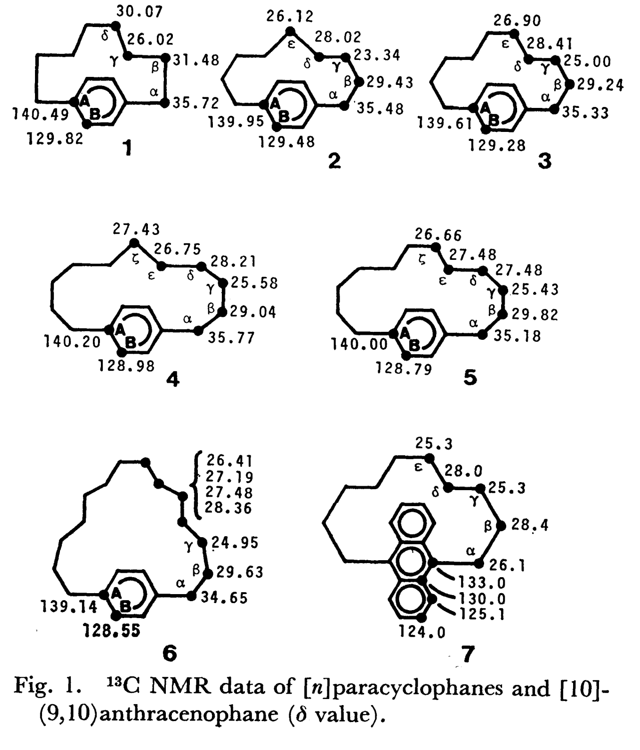

Fig. 1. ^{13}C NMR data of [*n*]paracyclophanes and [10]-(9,10)anthracenophane (δ value).

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Results

All the ^{13}C NMR data are summarized in Figs. 1, 2, and 3. The ^{13}C signals were assigned by means of ^{1}H off-resonance and selective decoupling techniques. Comparisons of signal intensities and chemical shifts were also helpful to assign a group of similarly constructed compounds. The resonances of alkyl derivatives of the cyclophanes were assigned by considering the substituent effect on the data observed for non-substituted, parent cyclophanes. Additional shift parameters for dimethyl substitution can be evaluated by comparing the carbon resonances of **21** and **22** (Fig. 3).

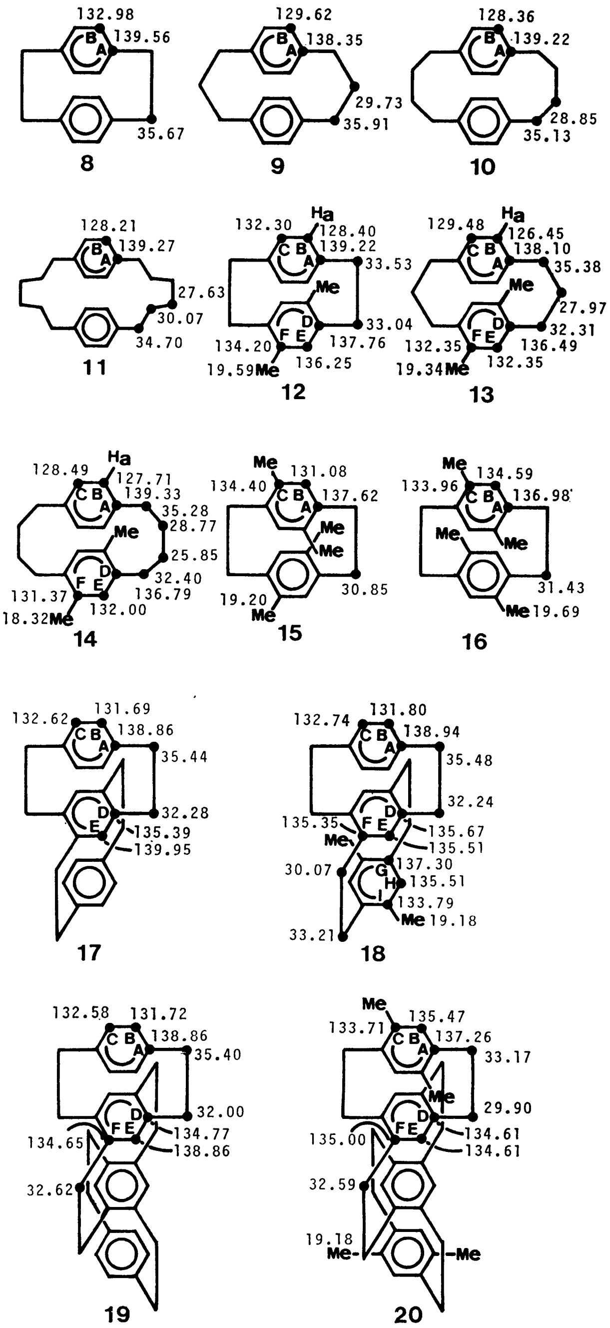

Fig. 2. ^{13}C NMR data of [*n.n*]paracyclophanes and multilayered paracyclophanes (δ value).

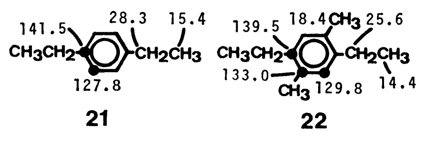

Fig. 3. ^{13}C NMR data of alkylbenzenes (δ value).

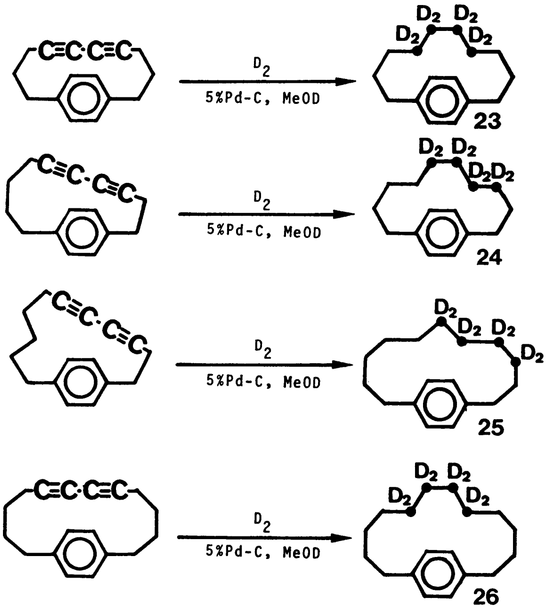

Fig. 4. Catalytic deuteration of [*n*]paracyclophadiynes.

The assignment for medium-sized [*n*]paracyclophanes has been not so easy because of closely positioned signals of the polymethylene carbons. This difficulty was overcome, for example, by deuterium substitution of the four middle methylene groups as seen in catalytic deuteration of a few [*n*]paracyclodiynes (Fig. 4).[9] [10]Paracyclophane **3** shows five signals of the methylene carbons, of which two signals at lower field, δ 35.33 and 29.24, are easily assigned to the α and β methylene carbons, respectively. Of the remaining three signals the two at δ 26.90 and 28.41 disappear in the spectrum of deuterated [10]paracyclophane **23**. For its isomeric deuterated [10]paracyclophane **24**, on the other hand, only one signal (δ 26.90) disappears and other two signals (δ 25.00 and 28.41) decrease to one-half of the initial intensities. Consequently, the three signals at δ 25.00, 28.41, and 26.90 are explicitly assigned to γ, δ, and ε methylene carbons, respectively.

TABLE 1. ^{1}H NMR DATA OF THE METHYLENE PROTONS OF [*n*]PARACYCLOPHANES (100 MHz, δ value)[b]

	α	β	γ	δ	ε	ζ
[8]PC[a] **1**	2.64	1.43	0.87	0.19		
[9]PC **2**	2.59	1.42	0.96	0.33	0.59	
[10]PC **3**	2.60	1.54	1.07	0.48	0.69	
[11]PC **4**	2.55	1.55	1.18	0.79		0.68
[12]PC **5**	2.60	1.57	1.06	1.00		0.78

a) PC: paracyclophane. b) The spectra were recorded in $CDCl_3$ at ambient temperature on a JEOL FX-100 spectrometer equipped with a FT system and JEC-980B computer, using TMS as an internal standard.

The deuterium substitution of [*n*]paracyclophanes concomitantly enabled the signal assignment of methylene protons, which has not been clear so far. The data are given in Table 1. The middle methylene protons of the smallest cycle, [8]paracyclophane **1**, are situated just above the benzene ring according to X-ray analysis[10] and thereby resonate at a higher field than the other methylene protons owing to the magnetic anisotropy. On the other hand, the chemical shifts of the middle methylene protons are not the case for [9]- and [10]paracyclophanes **2** and **3**. As shown in Table 1, our assignment for **2** and **3** is the order of proton resonance: α, β, γ, ε, δ with the δ proton at highest field, which is distinct from the orders by Waugh and Fessenden:[11] α, β, δ, γ, ε and by Agarwal *et al.*:[12] α, β, γ, δ, ε. In addition, the present assignment emphasizes that the central methylene protons may not always appear at the highest field.

Discussion

[*n*]Paracyclophanes have a unique structure, in which a polymethylene chain is bridged at para-positions of the benzene ring and placed above the ring, and the benzene ring is bent into a boat shape as the length of the bridging chain shortens.[13] Therefore, the middle methylene groups are essentially shielded by the ring-current of the benzene and appear at higher fields as seen in Table 1. Levin and Roberts reported that in the ^{13}C NMR spectrum of [12]paracyclophane **5** the high-field resonances of the methylene carbons are attributed to the ring-current effect of the benzene ring.[4] However, noteworthy is that γ carbon signals appear in the highest fields for all the present [*n*]paracyclophanes. This upfield shift of γ carbons seems to be independent of the shielding effect of the benzene ring since the γ methylenes are presumably located in positions insusceptible to the effect, according to the ^{1}H NMR data in Table 1.

In the ^{13}C spectrum of [8]paracyclophane **1**, the methylene carbons reveal considerable deshieldings and no explicit dependence of the ring-current effect which is responsible for striking upfield shift of δ methylene protons in the ^{1}H spectrum. This can be explained by a direct carbon-carbon compression in the strained, small cyclic compound since the ring-current effect likely is concealed by the steric effect. For somewhat less strained compound or [9]paracyclophane **2**, however, the middle methylene carbon resonates at a relatively higher field, suggesting the ring-current effect.[18] Clear-cut evidence for the ring-current effect on ^{13}C shielding is given by comparison of two further less strained decamethylene compounds, [10]paracyclophane **3** and [10](9,10)anthracenophane **7**. In the latter compound, the two fused benzo groups do not affect steric environment of the middle methylene carbons. Accordingly, a marked upfield shift of the carbon resonances of **7** relative to **3** is ascribed to the larger ring-current effect of the anthracene ring than that of the benzene ring.[14]

[n.n]*Paracyclophanes and Methyl Derivatives.* The two benzenes of [*n.n*]paracyclophanes are, as $n<6$, stacked in parallel and brought close to each other with decreasing number of *n*. In [2.2]- and [3.3]paracyclophanes, the ring-to-ring distances are within the van der Waals contact, 3.4 Å, according to crystallographic analyses.[15] Therefore, the aryl carbons of both paracyclophanes are undoubtedly compressed by π-π repulsive interaction as described by Sato and coworker.[16] In order to pursue such a compression effect, the aryl carbon resonances of **8** were compared with those of strainless cyclophanes, [6.6]paracyclophane **11** and [14]paracyclophane **6**. A marked downfield shift was observed for the protonated carbon C_B, while no difference for the bridgehead carbon C_A. This downfield shift is comprehended with much easier polarization based on the π-π compression.

As one would expect, the protonated carbon C_B of [3.3]paracyclophane **9** exhibits a similar but smaller downfield shift reflecting its own less compression. On the other hand, the bridgehead C_A signal of **9** appears at a higher field by a little less than 1 ppm compared to those of **11** and **6**. This upfield shift is probably responsible for the ring-current effect of the faced benzene. In the case of [2.2]paracyclophane **8**, the chemical shifts of both aromatic carbons are explained by concealing the ring-current with strong compression effect.

The ^{13}C shifts of [4.4]- and [6.6]paracyclophanes **10** and **11** are almost the same as that of [14]paracyclophane **6**, indicating that the two benzenes in **10** and **11** are too apart from each other to interact sterically and magnetically.

Methyl substitution of [2.2]paracyclophane **12** gives a large perturbation on the shieldings not only for aryl carbons of the methyl-attached ring, but also for aryl carbons of the faced ring. The aryl carbon C_B pseudo-geminal to the methyl substituent is subjected to no deshielding effect compared to the corresponding carbon resonances of **6** and **11**, whereas the pseudo-ortho carbon C_C reveals a marked deshielding. This can be understood by depression of the polarization along the C_B–Ha bond due to strong compression of the methyl group on the proton Ha, since the compression was provided by ^{1}H chemical shifts.[2] Similar phenomena were observed for the pseudo-gem protonated carbons of other methyl derivatives, C_B of **15**, C_E of **18**, and C_E of **20**.

Dimethyl[3.3]paracyclophane **13** also shows the shielding of the protonated carbon C_B pseudo-geminal to the methyl group besides the bridgehead carbons C_A and C_D. Compared with the difference in C_B resonances of **8** and **12**, such a considerable upfield shift of C_B of less strained **13** indicates that the contribution of the ring-current effect on ^{13}C resonance becomes relatively larger in the [3.3]phane system than in the [2.2]phane system, while the compression effect becomes relatively lower. In the case of dimethyl[4.4]paracyclophane **14**, pseudo-gem C_B signal is shifted slightly upfield, although there are no longer steric and magnetic transannular effects in the parent cyclophane **10**. It is probably due to a weak compression effect of the bulky methyl group on the Ha proton.

Such a steric contribution by a methyl group is also supported by progressive downfield shift of methyl carbon resonances as the methylene number of [*n.n*]-paracyclophanes decreases, that is, the ring-to-ring distance between two benzene rings shortens. A marked downfield shift of methyl carbon resonance due to the methyl-methyl compression is observed for centrosymmetric isomer **16** of tetramethyl[2.2]paracyclophane.

Triple- and Quadruple-layered [2.2]Paracyclophanes. The π-π compression also exerts pronounced effect on ^{13}C spectra of multilayered [2.2]paracyclophanes **17**—**20**. Thus, aryl carbons of all the outer benzene rings reveal the same extent of downfield shifts as those of double-layered series. The non-equivalence of protonated aromatic carbons C_B and C_C of **17**—**19** is caused by depressed C_B–H polarization due to the compression with the bridge methylene group, which is smaller than the compression with a methyl group.

It is noticeable that triple-layered [2.2]paracyclophane **17** provides a novel example of the double compression effect. The signal of aryl carbon C_E of **17** is shifted to a lower field by 7.95 ppm than the corresponding carbon resonance of a reference compound, **14**. This downfield shift is about twice as large as the difference value (4.25 ppm) between **12** and **14**, indicating an additivity of the steric compression contribution on carbon resonances.

Triple- and quadruple-layered [2.2]paracyclophanes may permit a straightforward evaluation of the anisotropic contribution arising from additional third and fourth benzene rings which are stacked on double-layered [2.2]paracyclophane, providing that the steric contribution can be eliminated from the total effect by choice of a suitable reference compound. The outer benzene rings of **17** and **19** have a geometry very similar to the double-layered homolog as revealed by the X-ray analyses.17) Accordingly, a small upfield shift observed for the bridgehead carbon signal of the outer benzene of triple-layered cyclophanes **17** and **18** is considered to be due to the third benzene (C_A of **17** *vs.* C_A of **12**, −0.36 ppm; C_A of **18** *vs.* C_A of **12**, −0.28 ppm; C_G of **18** *vs.* C_A of **15**, −0.32 ppm), being close to an average shielding value (−0.22 ppm) seen in ^{1}H NMR data.2) However, the shielding effect (*ca.* −0.05 ppm) of the fourth benzene was observed to be negligible by comparing the bridgehead carbon resonances of outer benzenes of both quadruple-layered cyclophanes, **19** and **20**, and triple-layered cyclophanes, **17** and **18**.

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