Carbon-13 Nuclear Magnetic Resonance Spectra of Strained Molecules. Diamagnetic and Paramagnetic Shifts of Sterically Compressed Carbon Resonances in [2,2]Metacyclophanes

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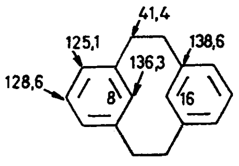
Summary Carbon-13 nuclear magnetic resonance spectra of [2,2]metacyclophanes show two types of steric compression shifts (van der Waals shifts) operating in an opposite direction: a large diamagnetic shift of bridging methylene carbon resonances due to an *ortho*-alkyl group and an anomalous paramagnetic shift of the inner aryl carbon resonances caused by direct carbon–carbon compression.

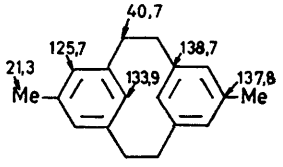
Steric compression effects in ^1H n.m.r. spectra result in marked downfield shifts, which are a valuable tool in stereochemical problems. In ^{13}C n.m.r. spectra steric compression has been observed to cause a diamagnetic shift in cyclohexanes,[1,2] vicinally substituted alkyl benzenes,[2] and certain polycondensed aromatic compounds.[3]

We have found, in contrast, a paramagnetic shift for sterically compressed carbon resonances, in the [2,2]-metacyclophanes (**1**)—(**8**)† together with a large diamagnetic shift. Chemical shifts for (**1**), as shown, were assigned by intensity consideration and off-resonance continuous wave decoupling. The *J* (^{13}C–H) values for C-4, C-5, and C-8 were 154, 158, and 160 Hz respectively. Incremental changes for aryl carbon chemical shifts upon alkylation agreed fairly well with those calculated from Woolfenden's additivity parameters.[4] With the dimethyl derivative (**2**), for example, the observed and calculated values agree to within 0·2 p.p.m.

Two anomalous shifts were noticed. When an alkyl group is introduced *ortho* to the bridge, the benzyl methylene carbon signals showed a large upfield shift attributable to the usual steric compression effects.[1–3] The upfield shift from (**1**), Δ (MCP), is *ca.* 5—6 p.p.m. regardless of the alkyl group but is 11·5 p.p.m. for (**8**) where an additional strain is imposed by an inner methyl group (Table). In comparison, the methylene shift due to an *ortho*-methyl group in the acyclic models, (**9**) and (**10**), is only 3·6 p.p.m. The value for (**3**) calculated from Grant and Cheney's equation[2] is *ca.* 2·2 p.p.m. Unlike flexible acyclic models an equatorial methylene hydrogen in rigid [2,2] metacyclophanes lies almost in the benzene plane and severe interaction results between the *ortho*-substituents.



(1)



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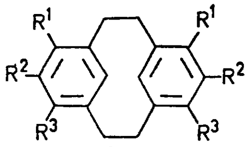
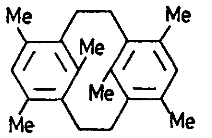
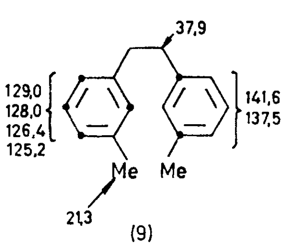


	R^1	R^2	R^3
(3)	Me	H	H
(4)	Me	H	Me
(5)	Me	Me	Me
(6)	Et	H	Et
(7)	Pr^i	H	Pr^i



(8)



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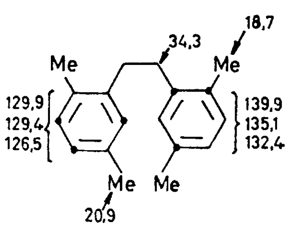

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† The preparation of new materials will be reported elsewhere. Proton-decoupled spectra were recorded by pulse Fourier transform using a Varian XL-100 spectrometer on samples dissolved in $CDCl_3$. Chemical shifts are given in p.p.m. downfield from Me_4Si.

Comparison of the downfield shift for the inner aryl carbon resonances (C-8, C-16) with the corresponding shifts for acyclic models is interesting. There is a downfield shift of at least 7·3 p.p.m. for (**1**) compared with the lowest CH signal for (**9**). The difference between (**3**) and (**10**) is > 6·7 p.p.m. Shift comparisons with related methylbenzenes, Δ(ArH) [*e.g.* (**1**) *vs.* *m*-xylene], are shown in the Table.

TABLE. Carbon-13 chemical shifts (relative to Me$_4$Si) and van der Waal's shifts

Compound	C-1,2 (C-9,10)	Δ(MCP) /p.p.m.	C-8,16	Δ(ArH) /p.p.m.[a]
(**1**)	41·4	0·0	136·3	+6·2
(**2**)	40·7	−0·7	133·9	+6·5
(**3**)	35·4 (40·7)	−6·0 (−0·7)	136·6	+6·1
(**4**)	34·9	−6·5	136·9	+5·7
(**5**)	36·2	−5·2	134·8	+3·3
(**6**)	35·5	−5·9	137·7	
(**7**)	35·6	−5·8	137·3	
(**8**)	29·9	−11·5	141·9	+7·4

[a] The chemical shift difference between C-8 and C-16 of metacyclophanes and the corresponding carbon in alkyl-benzene models: data from ref. 4.

The downfield shift for C-8 and C-16 is in the opposite direction to that expected from the usual steric effects. Comparison of J(^{13}C–H) values for C-8 and C-16 with that for C-4 shows that C-8 has slightly more *s* character but perturbation due to hybridization appears to be small.‡ Roberts *et al.*[5] found that ring-current effects on carbon-13 shifts in [12]paracyclophane were relatively small, the maximum contribution being only 0·7 p.p.m., and again the shift is in the opposite direction. According to Grant and Cheney's model,[2] the Van der Waals interaction involves compression of hydrogen along the C–H axis. In [2,2]metacyclophane, however, direct interference between two inner aryl carbon atoms can occur owing to their proximity (*ca.* 2·7 Å).

We attribute the primary cause of the downfield shift to a decrease in π-electron density on C-8 and C-16 as the results of transannular repulsion.§ In contrast to the localized electronic structure in [2,2]metacyclophanes, the paracyclophanes have a delocalized π-electron system. In accordance, [2,2]paracyclophane has less unusual chemical shifts; 35·7 (CH$_2$), 132·8 (protonated Ar-C), and 139·4 (quarternary Ar-C). An upfield shift of the inner methyl (15·6 p.p.m.) compared with the outer methyl group (19·1 p.p.m.) in (**8**) may be ascribed to ring-current and steric compression effects.

(*Received*, *2nd November* 1973; *Com.* 1507.)

‡ Alternatively, variation in J (^{13}C–H) may be associated with an energy term rather than the hybridization term.

§ Perturbation to the σ-electron system is possible but it would be less important than the perturbation of the π-electron system. Recently, E. Langer and H. Lehner (*Tetrahedron*, 1973, **29**, 375) gave evidence which indicated the absence of transannular π–π interaction based on comparison of dissociation constants for bis-tricarbonylchromium complexes. Our results give more direct evidence for their conclusion.

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[3] T. D. Algar, D. M. Grant, and E. G. Paul, *J. Amer. Chem. Soc.*, 1966, **88**, 5397.
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