A ^{13}C NMR and CNDO/2 Calculation Study of the Transannular Interaction in [2.2]Cyclophanes[1]

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The relationships between the aryl carbon chemical shifts and the CNDO/2 electron densities for several [2.2]cyclophanes are reported. Plots of the chemical shifts against the excess total electron densities indicate additional downfield shifts of 6—9 ppm on the average for those aryl carbons that are in close proximity to other aryl carbons. A plot of the ^{13}C shielding constant, calculated using the Karplus-Pople theory, against the chemical shift shows a downfield shift of a similar magnitude for the proximate carbons relative to the others. It is found that this difference can be essentially eliminated simply by adjusting the ΔE parameter in the Karplus-Pople equation from 10.0 eV to 9.7 eV for the proximate carbon atoms.

Although the transannular interactions in [2.2]-cyclophanes of electronically excited states have been thoroughly investigated, the interactions in the ground electronic states are still not well understood. In their photoelectron spectral study of the [2.2]para- and [2.2]-metacyclophanes, **7** and **10**, Boschi and Schmidt[2] suggested that the interaction in **7** takes place between all the facing aryl carbons, whereas in **10** it is confined to C(8) and C(16), which are in the closest proximity to each other. In the ground state, however, no such interaction could be detected by means of ^{13}C NMR spectroscopy.[3] Recent ^{13}C NMR results for **7** and **10**[4] have indicated that the interacting carbons, especially C(8) and C(16) in **10**, are noticeably deshielded compared with open-chain models. Similar deshieldings were observed for other facing unsaturated carbons whose p-orbital axes were nearly colinear.[4-6]

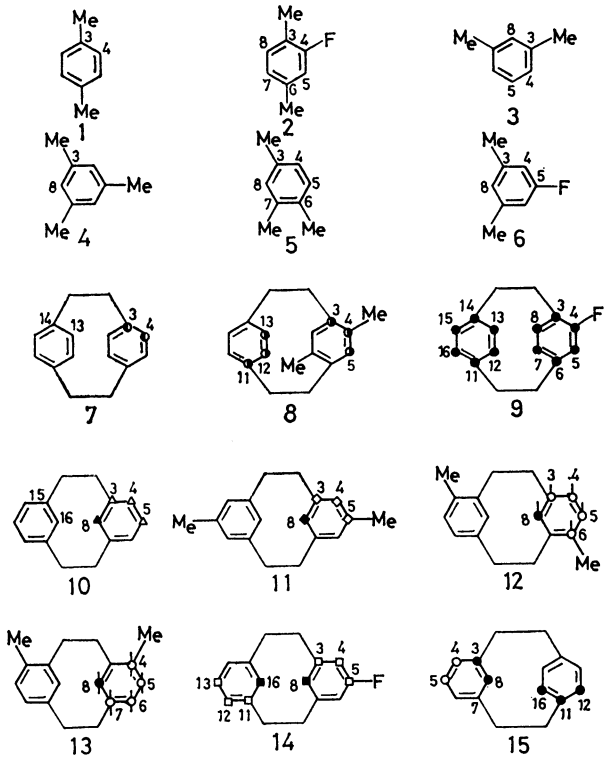

Fig. 1. The reference and [2.2]cyclophane compounds examined. The positions in **1**—**6** are numbered so as to correspond to those in **7**—**15**.

In an attempt to explain these observations we have first investigated the relationships between the aryl carbon chemical shifts and the CNDO/2 electron densities in the nine [2.2]cyclophanes, **7**—**15**, shown in Fig. 1, and in six monocyclic reference compounds, **1**—**6**. Then we have compared the observed chemical shifts with the shielding constants calculated using the Karplus-Pople theory.[7]

Calculation

The theoretical ^{13}C shielding for an atom, σ, was calculated in terms of the Karplus-Pople theory[7] using:

$$\sigma = \sigma_d + \sigma_p, \quad (1)$$

but the local diamagnetic term, σ_d, was estimated using:[8]

$$\sigma_d = 4.45Zq^t, \quad (2)$$

where Z is the effective nuclear charge estimated according to Slater's rules and q^t is the total electron density on the atom. The electron densities and bond orders used in these calculations were those estimated by the CNDO/2-Molecular Orbital method.[9] In the MO calculations for all the cyclophanes, the geometry parameters of the parent unsubstituted compounds[10] were used in defining the input geometries, but the standard geometry parameters[11] were used for the methyl and fluorine substituents in the methyl- and fluorocyclophanes, **8**, **9**, and **11**—**14**, and for all the monocyclic compounds.

All the computations were performed on a HITAC-8800/8700 computer at the Computer Centre of the University of Tokyo.

Results and Discussion

Table 1 gives the excess π- and total electron densities, Δq^π and Δq^t, as calculated by the CNDO/2 approximation,[9] together with the observed and calculated aryl carbon chemical shifts, δ and σ from Eq. 1 using 10.0 eV[12] as ΔE for all compounds.

In Models **1**—**6**, the δ value was found to bear a better linear relationship with the Δq^t than with the Δq^π value. The least-squares graph of the correlation ($r^{**}=0.972$) is drawn in Figs. 2—4, together with similar plots for the cyclophanes. The line ($s^{**}=153$) is very

** r: correlation coefficient; s: slope of the line.

Table 1. ^{13}C Chemical shifts and excess total electron densities

Compd	Carbon[h]	$\delta(^{13}C)$[a] ppm	$\Delta q^{\pi}\times 10^3$	$\Delta q^{t}\times 10^3$	$-\sigma_p$ ppm	$-\sigma$ ppm
1[b]	(3)	134.5	12	38	273.4	215.9
	(4)	129.1	−11	6	260.0	202.2
2[c]	(3)	121.5	−27	−11	—	—
	(4)	161.0	16	225	—	—
	(5)	115.7	−44	−51	—	—
	(6)	137.5	31	58	—	—
	(7)	124.6	−34	−13	—	—
	(8)	131.2	7	24	—	—
3[b]	(3)	137.5	34	50	275.1	217.7
	(4)	126.4	−34	−7	258.3	200.4
	(5)	128.3	19	24	258.4	200.5
	(8)	130.1	−42	−13	261.6	204.0
4[b]	(3)	137.6	42	52	275.6	218.2
	(8)	127.4	−55	−22	257.3	199.3
5[b]	(3)	135.2	14	42	274.2	216.0
	(4)	126.7	−21	−3	258.9	201.0
	(5)	129.8	−10	9	260.6	202.8
	(6)	133.4	6	24	272.3	214.7
	(7)	136.3	7	36	276.8	219.3
	(8)	130.5	−30	−9	258.9	201.0
6[c]	(3)	140.2	54	70	—	—
	(4)	113.0	−79	−65	—	—
	(5)	163.2	47	245	—	—
	(8)	125.7	−67	−33	—	—
7[d]	(3)	139.4	31	29	274.9	217.3
	(4)	132.8	−22	−10	259.7	201.8
8[e]	(3)	137.7	21	26	—	—
	(4)	134.5	−7	24	—	—
	(5)	131.2	−36	−18	—	—
	(11)	139.2	31	26	—	—
	(12)	128.4	−22	−8	—	—
	(13)	132.4	−22	−7	—	—
9[f]	(3)	125.8	−12	−23	—	—
	(4)	161.1	12	218	—	—
	(5)	122.2	−70	−68	—	—
	(6)	142.8	49	51	—	—
	(7)	128.0	−46	−29	—	—
	(8)	135.4	0	10	—	—
	(11)	138.8	26	27	—	—
	(12)	132.9	−21	−11	—	—
	(13)	129.2	−22	−11	—	—
	(14)	139.7	29	29	—	—
	(15)	132.5	−20	−12	—	—
	(16)	133.5	−20	−11	—	—
10[d]	(3)	138.6	42	39	281.8	224.3
	(4)	125.1	−47	−30	259.6	201.5
	(5)	128.6	9	2	264.0	206.0
	(8)	136.3	−33	−22	258.1	200.1
11[d]	(3)	138.7	53	46	—	—
	(4)	125.7	−72	−48	—	—
	(5)	137.8	39	45	—	—
	(8)	133.9	−48	−32	—	—
12[d]	(3)	136.2	29	31	—	—
	(4)	125.3	−36	−25	—	—
	(5)	130.0	−16	−16	—	—
	(6)	132.3	−17	13	—	—
	(8)	136.6	−2	−16	—	—
13[d]	(4)	132.5	−17	13	—	—
	(5)	130.0	−15	−15	—	—
	(6)	125.1	−36	−25	—	—
	(7)	136.4	30	32	—	—
	(8)	136.6	−22	−16	—	—
14[c]	(3)	141.0	65	63	—	—
	(4)	112.0	−100	−89	—	—
	(5)	163.0	43	232	—	—
	(8)	132.6	−61	−44	—	—
	(11)	138.6	41	40	—	—
	(12)	125.5	−46	−30	—	—
	(13)	128.6	9	1	—	—
	(16)	136.2	−46	−22	—	—
15[g]	(3)	140.6	53	48	278.4	220.9
	(4)	124.7	−48	−32	259.1	201.0
	(5)	126.8	21	11	264.1	206.3
	(8)	133.0	−56	−38	258.6	200.4
	(11)	138.5	31	16	272.6	214.9
	(12)	129.7	−26	−38	255.5	197.3
	(16)	128.2	−22	−35	254.0	195.9

a) Downfield from internal TMS (all data in $CDCl_3$). b) δ taken from J. B. Stothers, "Carbon-13 NMR Spectroscopy," Academic Press, New York (1972), p. 95. c) Obtained in this work (Ref. 15). d) Taken from Ref. 4. e) Taken from H. Horita, H. Takemitsu, T. Otsubo, Y. Sakata, S. Misumi, M. Mishima, and Y. Tsuno, Abstract presented at the 32 nd Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1975. f) δ taken from T. Takemura and N. Mori, *Chem. Lett.*, **1978**, 857. g) Taken from Ref. 1. h) Numbering as in Fig. 1.

close to that ($s=160$) shown by Bloor and Breen[12] for monosubstituted benzenes. Also, the correlation graph obtained between the σ and δ values of **1**, **3**, **4**, and **5** is shown in Fig. 5.

Figures 2—4 show plots of the δ against the Δq^{t} values for the **7**—**9**, **10**—**14**, and **15** cyclophanes respectively. It should be noticed in any of the figures that the aryl carbons proximate to each other show a linear relationship different from that for the remote or non-interacting carbons, as will be discussed further below (see Table 2).

In Fig. 2, the plots for all the facing carbons of the paracyclophanes lie roughly on the same correlation line,

Table 2. The least-squares linear relationships between δ and Δq^{t} for Compounds **1**—**15**

$$\delta = a\Delta q^{t} + b$$

Compd	a[a]	b[a]	r[b]
1—**6**	153	128.0	0.972
7—**9**	(138)	(133.4)	(0.951)
10—**14**	153 (153)	130.4 (139.4)	0.980 (0.980)
15	(113)	(135.9)	(0.953)

a) The values in parentheses are those for the proximate carbons. b) Correlation coefficient.

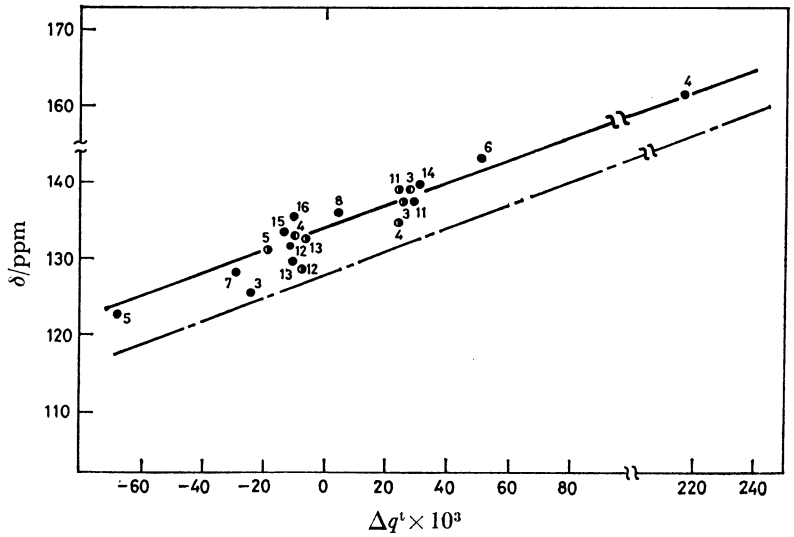

Fig. 2. Plots of δ *vs.* Δq^t for [2.2]paracyclophanes **7**—**9**. Numbering and designations as in Fig. 1. Reference line for **1**—**6**: — - —.

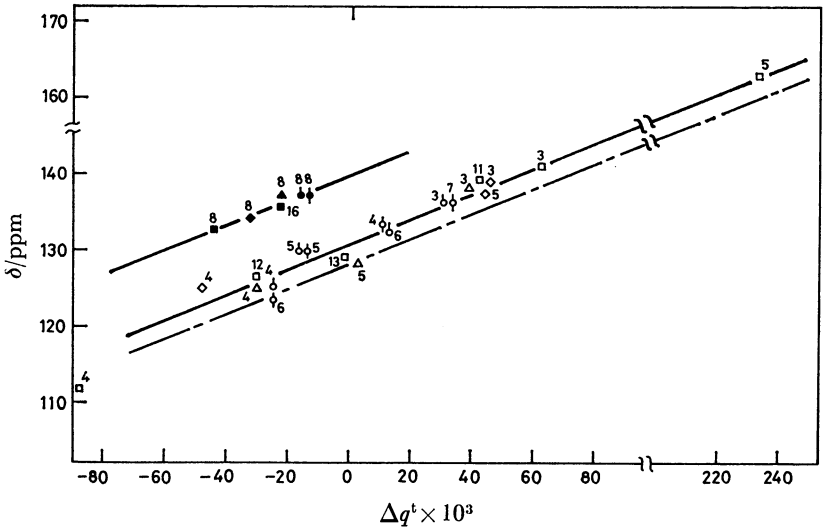

Fig. 3. Plots of δ *vs.* Δq^t for metacyclophanes **10**—**14**. Numbering and designations as in Fig. 1. Reference line for **1**—**6**: — - —.

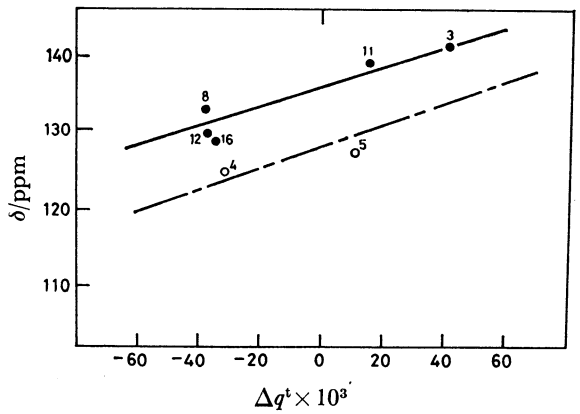

Fig. 4. Plots of δ *vs.* Δq^t for metaparacyclophane **15**. Numbering and designations as in Fig. 1. Reference line for **1**—**6**: — - —.

which is *ca.* 6 ppm upward (or downfield) from the line for the reference monocycles. Figure 3 indicates that the inner, C(8) and C(16), and the outer carbons, C(3)—C(5), of the metacyclophanes are distinguished by two separate linear relationships. The least-squares lines are parallel and are 9.0 ppm apart. The lower line for the outer carbons is only 2 ppm away from the reference line. This slight discrepancy between the latter two is unimportant, if one considers the approximate nature of the theory used to calculate the electron densities and the fact that the observed data are uncorrected for the ring current and other anisotropic shielding effects. Figure 4 shows that, in metaparacyclophane **15**, the plots for the outer carbons, C(4) and C(5), of the meta ring fall on the reference line, whereas those for the rest of the aryl carbons are on a separate line which is *ca.* 8 ppm away from the reference. From these results it may be concluded that the proximate carbons

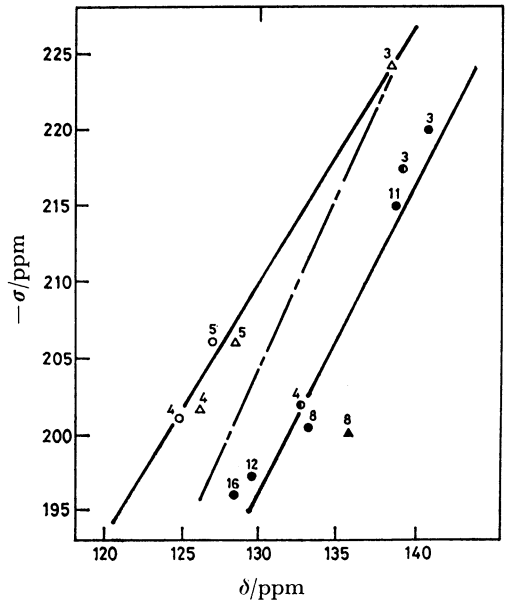

Fig. 5. Plots of σ *vs.* δ for [2.2]cyclophanes **7**, **10**, and **15**, using 10.0 eV as ΔE for all carbons. Numbering and designations as in Fig. 1. Reference line for **1**, **3**, **4**, and **5**: — — —

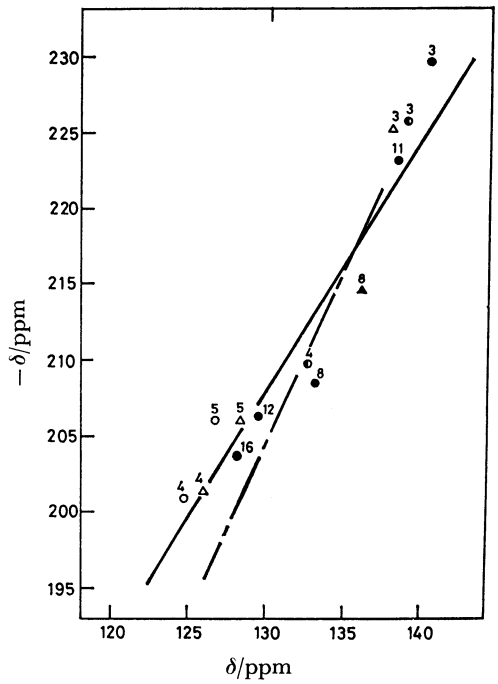

Fig. 6. The effect of using decreased ΔE for the proximate carbons, 9.5 eV for C(8) of **10** and 9.7 eV for all the others.

are shifted downfield compared with the remote carbons with the same total electron densities. The magnitude of the downfield shifts varies with the type of the cyclophane series within the range of *ca.* 6—9 ppm. This is probably attributable to decreases in the excitation energy term, ΔE, of the paramagnetic shielding expression, σ_p, as will be interpreted below.

Figure 5 shows plots of the σ values predicted from Eq. 1, using 10.0 eV as ΔE, against the δ values for the **7**, **10**, and **15** cyclophanes. Apparently, there are two different linear relationships, which are characteristic of the proximate and the remote carbons. The least-squares lines are nearly parallel, with a space of *ca.* 10 ppm between; both are in poor agreement with the reference line. Exactly, the use of the ΔE value of 10.0 eV leads to an estimation of the chemical shifts for the proximate carbons 8—12 ppm smaller than those for the remote carbons, except for the inner C(8) of **10** and **15**, which are underestimated by 20 and 14 ppm respectively (similar results were obtained by using 8.0 eV as the ΔE). The magnitude of the underestimation is seemingly correlated with the interatomic distance between the interacting carbons and the relative orientation of the p-orbitals concerned, as Table 3 shows. A possible explanation for the underestimation can be obtained by assuming decreases in ΔE caused by a transannular interaction.[13] Such decreases in the meta- and metaparacyclophanes must be highly local (Karplus and Pople[7b] suggest the possibility of localized excitations). For example, a decrease in the ΔE from 10.0 to 9.7 eV changes the σ value for C(3) of **7** from −217.3 to −225.8 ppm. The graph of Fig. 6 shows the effect of using the ΔE of 9.7 eV for all the proximate carbons except for C(8) of **10**, for which 9.5 eV is used. All the points now lie roughly on the same line, which is closer to the reference than in Fig. 5. The assumption of the local decreases in ΔE can also explain the downfield-shift trend of the proximate carbon resonances shown in Figs. 2—4, because a decrease in ΔE should cause a downfield shift. Recent studies of smaller molecules[14] indicate that the correlation between theory and experiment for ^{13}C chemical shifts is improved by using different excitation energies for individual carbons in calculating their chemical shifts.

Table 3. Underestimated chemical shifts, $\Delta\sigma$ and interatomic distances, l, for the proximate carbons

Compd	Centers	l/Å	$\Delta\sigma$/ppm[a]
7	C(3)–C(14)	2.77[10c]	8
	C(4)–C(13)	3.09	12
10	C(8)–C(16)	2.69[10a]	20
	C(3)–C(15)	3.02	0
15	C(8)–C(12)	3.1[10b]	14 for C(8)
	C(8)–C(11)	3.0	12 for C(12)
	C(7)–C(11)	2.7	10 for C(11)
			9 for C(7)

a) Predicted chemical shift difference of the proximate from the remote carbon.

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15) The ^{13}C and ^{1}H FT NMR spectra of Compounds **2**, **6**, and **14** were measured in 0.2—0.3 mol dm^{-1} solutions in $CDCl_3$, using a JEOL-PFT-100/JNM-PS-100 spectrometer operating at 25 and 100 MHz respectively, in the Fourier transform mode, as has previously been described.[3] The ^{13}C chemical shifts were assigned by means of selective decouplings using the ^{1}H data and by taking account of the J_{C-F} coupling pattern.[16]

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