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

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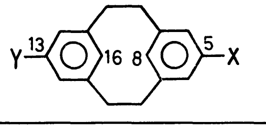
Synopsis. The substituent effects on the chemical shifts and CNDO/2 total electron densities of the facing aryl carbons, C-8 and C-16, in [2.2]metacyclophanes are reported.

In the course of ^{13}C NMR and electron density studies of [2.2]cyclophanes, we found that there is neither detectable transmission of spin information$^{1)}$ nor detectable charge transfer *via* a transannular route in the ground electronic state.$^{2)}$ Furthermore, we explained$^{3)}$ the known paramagnetic proximity effect on aryl carbon resonances in [2.2]cyclophanes$^{4)}$ by assuming a local decrease in the excitation energy term of the paramagnetic shielding expression by Karplus and Pople.

In the present work, we have studied the relationships between the chemical shifts (δ) and the total electron densities (q^t) of the facing inner aryl carbons, C-8 and C-16, in the nine [2.2]metacyclophanes, **1**—**9**, shown in Table 1. This study has been undertaken mainly in an attempt to explain the recent results by Atobe and Sato$^{5)}$ that in substituted [2.2]metacyclophanes the resonance of C-8 (or C-16) moves downfield with an increase in the Hammett σ_p constant of a substituent at the 13 (or 5)-position, respectively.

Table 1 gives the excess total electron densities (Δq^t: $4-q^t$) on C-8 and C-16 in **1**—**9** together with the δ values observed in CDCl$_3$. The q^t values were calculated using the CNDO/2-MO method.$^{6)}$ In these calculations,$^{7)}$ the geometry of each substituted cyclophane was assumed to be the same as that of the parent hydrocarbon, **1**,$^{8)}$ but with the hydrogen replaced by a substituent. As for the substituents, X and Y, the standard geometry parameters$^{9)}$ were used.

Table 1. Chemical shifts and excess total electron densities of C-8 and C-16 in the cyclophanes



Compound	X	Y	C-8 $\delta(\Delta q^t \times 10^3)$	C-16 $\delta(\Delta q^t \times 10^3)$
1	H	H	136.3$^{a)}$ (−22)	136.3(−22)
2	F	H	132.6$^{b)}$ (−44)	136.2(−22)
3	NO$_2$	H	142.1$^{c)}$ (+1)	136.9(−25)
4	CH$_3$O	CH$_3$	130.0$^{d)}$ (−53)	133.6(−32)
5	CH$_3$	CH$_3$	133.9$^{a)}$ (−32)	133.9(−32)
6	CN	CH$_3$	140.6$^{d)}$ (−17)	134.2(−34)
7	NO$_2$	CH$_3$	142.3$^{d)}$ (+1)	134.4(−36)
8	CH$_3$O	CH$_3$O	129.3$^{d)}$ (−52)	129.3(−52)
9	NO$_2$	CH$_3$O	141.9$^{d)}$ (+2)	130.0(−56)

a) Data taken from Ref. 4. b) From Ref. 3. c) From Ref. 2. d) From Ref. 5.

The δ and the Δq^t values in Table 1 bear a fairly good linear relationship, as Fig. 1 shows. It should be noticed that X (or Y) has small, but significant, effects for both values of C-16 (or C-8), respectively. These effects can be confirmed by inspecting the data for the following groups of compounds, each having either X or Y as a fixed substituent (A) and the other as an unfixed one (B): **1**—**3** (H as A), **4**—**7** (CH$_3$ as A), **4**, **8**, and **9** (CH$_3$O as A), and **3**, **7**, and **9** (NO$_2$ as A).

For example, in the group of **4**—**7** having a methyl as Y (= A), an electron-withdrawing X (= B) causes a decrease in Δq^t (increase in q^t) and an increase in δ (downfield shift of the resonance) for C-16. In the other groups, the same can be found. From this result it is evident that, in spite of the increase in q^t, the resonance of C-16 is shifted downfield. A possible explanation for this downfield shift may be obtained by assuming that the introduction of the electron-withdrawing X causes a decrease in the diamagnetic anisotropy effect of the X-bearing ring, resulting from the decreased electron density, and a local decrease in the electronic excitation energy$^{10)}$ by a transannular interaction between C-8 and C-16.$^{3)}$

The above results give additional support to our previous proposal$^{3)}$ that the known paramagnetic proximity effect in [2.2]cyclophanes is not due to a decrease in electron density.

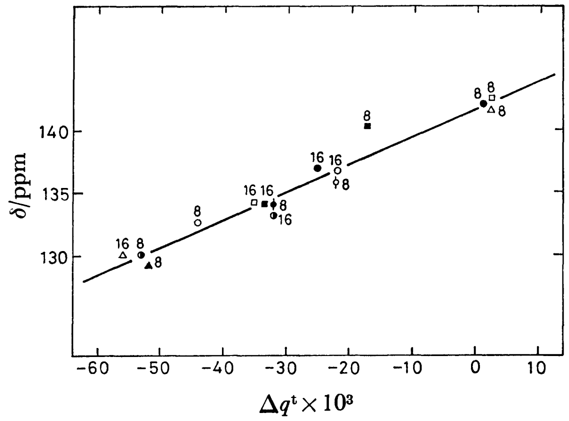


Fig. 1. Plots of δ *vs.* Δq^t for C-8 and C-16 of Compounds **1**—**9**.
⦶: **1**, ○: **2**, ●: **3**, ◑: **4**, ⬤: **5**, ■: **6**, □: **7**, ▲: **8**, △: **9**. The least-squares relationship: $\delta = 229\ \Delta q^t + 141.9$ (correlation coefficient: 0.978; standard deviation: 0.86).

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