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CMR CHEMICAL SHIFTS AND TOTAL CHARGE DENSITIES OF [2.2]CYCLOPHANES. THE EFFECT OF TRANSANNULAR π-π INTERACTION

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The chemical shifts for the transannularly π-π interacted and the non-interacted aryl carbons in three [2.2]cyclophanes bear linear relationships to the total charge densities. The interacted carbons are shifted downfield by ca. 7 ppm compared with the non-interacted ones, when the total charge densities are the same.

[2.2]Cyclophanes are distinguished by abnormal physical and chemical properties. Several qualitative explanations have been given for the origin of the abnormality: π-electron repulsion between the benzene rings,[1,2] hyperconjugation with the bridging C-C bonds,[3] nonplanarity of the benzene rings,[4] and transannular π-π interaction between the benzene rings.[5] Boschi and Schmidt[5] suggested from the ionization energies and transannular π-π resonance integrals of [2.2]metacyclophane, <u>1</u>, and [2.2]paracyclophane, <u>3</u>, that transannular π-π interaction may take place between C-8 and C-16 in <u>1</u> and between C-3 and C-14 and between C-4 and C-13 in <u>3</u>. Sato and Takemura[2] found unusually large ^{13}C chemical shifts for spatially adjacent aryl carbons in <u>1</u> and <u>3</u> and in [2.2]metaparacyclophane, <u>2</u>, and attributed this to π-electron repulsion between the carbons in consideration of the correlation between electron density and ^{13}C chemical shift (δ) found in planar aromatic systems.[6,7]

In order to investigate whether a similar correlation is practically possible in <u>1</u>-<u>3</u>, we have calculated the π-, σ- and total charge densities (D_π's, calculated using 2pz orbital only, D_σ's and Dt's) by the CNDO/2 method[8] using the geometrical data from X-ray analyses.[9] The Dt's thus calculated are given in Fig. 1. A fairly good linear relationship was obtained between δ[10] and Dt or D_π (Fig. 2, showing a

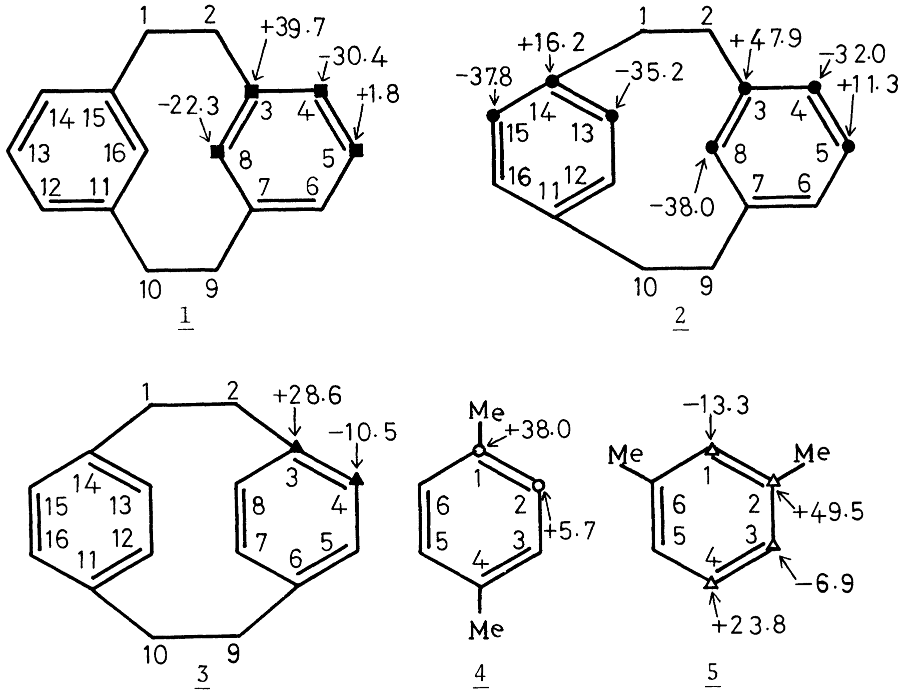

Fig. 1. Total charge densities (Dt×10^3) for [2.2]cyclophanes (1-3) and xylenes (4,5)

plot of δ vs. Dt), but not between δ and Dσ (Fig. 3). In Fig. 2, the transannularly π-π interacted and the non-interacted carbons in 1 and 3[5] lie roughly on parallel, lower and upper straight-lines separated by ca. 7 ppm. The non-interacted aryl carbons in planar models, 4 and 5, lie on the upper line. Judging from this relationship, in 2 only C-4 and C-5, which lie on the upper line, may be non-interacted and the other carbons, positioned on the lower line, may be π-π interacted. This may be expected from the geometry,[9] in which C-4 and C-5 are most remote from the p-bridged benzene ring. Although the reason for the 7 ppm deshielding for the π-π interacted carbons is not clear, this would, at least in part, be attributed to a decrease of the effective excitation energy (ΔE)[12] in the paramagnetic term (σ_p),[13] since the UV absorption maxima $\lambda_{max}(^1A_{1g} \rightarrow B_{2u})$ of compounds 1-3 are bathochromically shifted by 10-20 nm from those of their open-chain analogs.[4,14] A further work on this problem is under way.

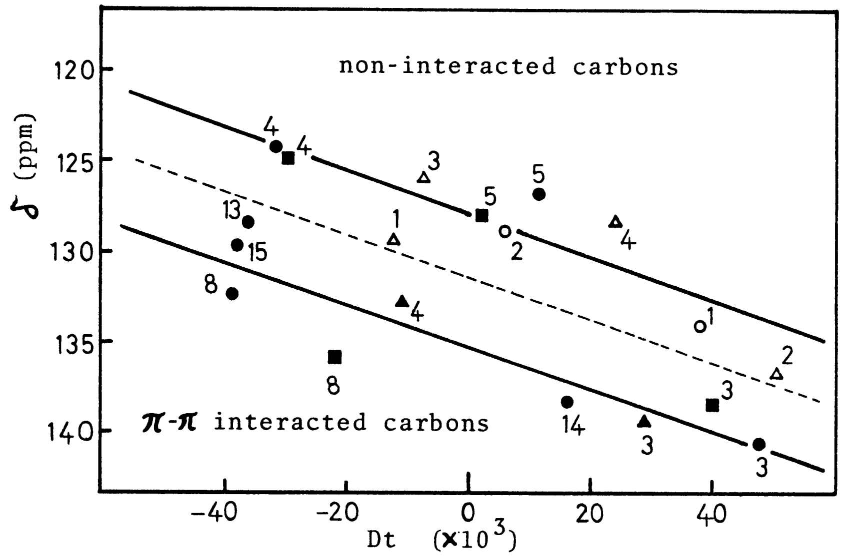

Fig. 2. A plot of ^{13}C chemical shift (δ) vs. total charge density (Dt): ■, 1; ●, 2; ▲, 3; △, m-xylene; ○, p-xylene.

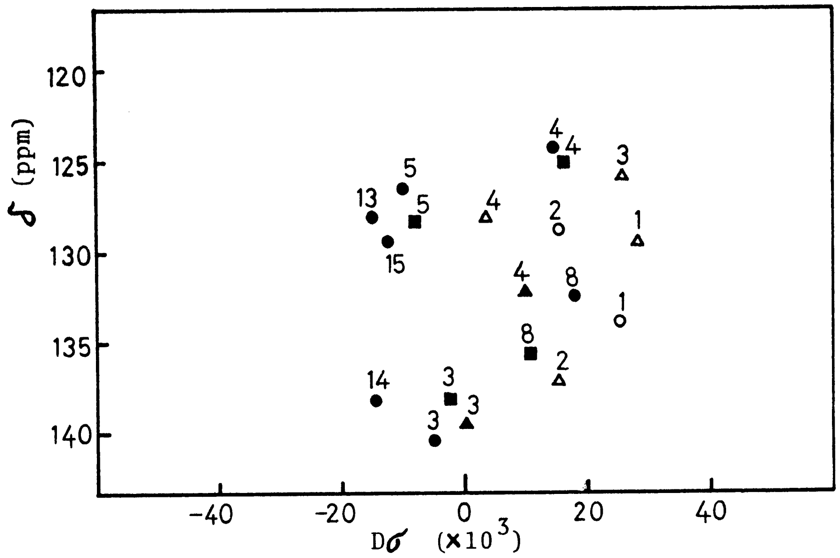

Fig. 3. A plot of ^{13}C chemical shift (δ) vs. σ-charge density (Dσ): ■, 1; ●, 2; ▲, 3; △, m-xylene; ○, p-xylene.

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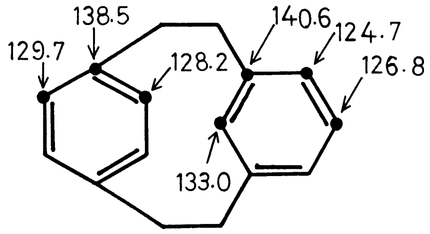
10) The δ's of 1 and 3 were taken from Ref. 2 and those of 4 and 5, from Ref. 11. The full assignment for 2 was made by means of the selective decoupling technique based on its FT-PMR spectrum (for protonated aryl carbons) and by comparison with the data of its 8-substituted derivatives (for non-protonated carbons). The results are given in the right Figure. The CMR and PMR spectra of 2 were recorded using a JEOL-PFT 100 spectrometer operating at 25 and 100 MHz, respectively, on samples dissolved in $CDCl_3$. Chemical shifts are given in ppm downfield from TMS.



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