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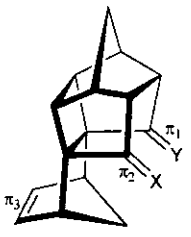
A NMR Chemical Shift Analysis on Two Nonconjugated Tri-π-Systems

Tahsin J. Chow*[a,c] (周大新), Kuo-Pin Chu[b] (朱國平),
Shou-Shun Liu[c] (劉守舜) and Ching-Yang Liu[b] (劉清陽)
[a]*Institute of Chemistry, Academia Sinica, Nankang, Taipei, Taiwan, R.O.C.*
[b]*Department of Applied Chemistry, Chinese Culture University, Taipei, Taiwan, R.O.C.*
[c]*Department of Chemistry, National Taiwan University, Taipei, Taiwan, R.O.C.*

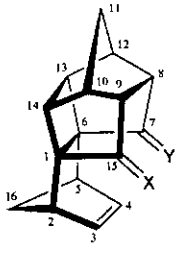
Electronic interactions in two nonconjugated tri-π systems are analyzed in terms of ^{13}C NMR chemical shifts. Comparisons of chemical shift values (Δδ) among di-methylenes, di-ketones and methylene-ketones support the presence of electron delocalization among the three π moieties.

INTRODUCTION

Orbital interactions among nonconjugated π bonds in polycyclic systems are of current interest. Recent progress indicates that the σ-bonding structure of polycyclic molecules has a significant influence on the energy of the π-bonds.[1-3] There are three basic types of transannular interactions operating in a molecule, i.e. field effect and orbital interactions either through space (OITS) or through bonds (OITB). It has been reported that the chemical shifts in ^{13}C NMR spectra can be used as a sensitive probe to detect these interactions.[4] The theory is based on the change of electron density while orbitals are mixing with each other. This concept has been applied successfully in many cases, and the results generally agree with the calculated electron densities on the corresponding atoms.[5] In this report, the triene systems **1-4** are examined in order to analyze the interactions among three nonconjugated π systems on different geometries. Compounds **2** and **4** are diastereomers of **1** and **3**, respectively. It is expected that OITB among the isomeric pairs would be similar to each other, however, OITS as well as field effects among them may be noticeably different.



1 a: X = Y = CH_2
b: X = CH_2; Y = O
c: X = Y = O



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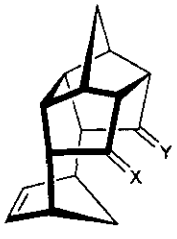

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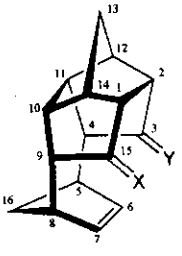

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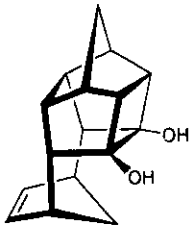

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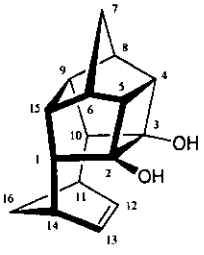

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RESULTS AND DISCUSSION

Compounds **1c** and **2c** are prepared according to published procedures.[6] Methylenation of **1c** and **2c** by a titanium reagent with different reactivities gave the corresponding dimethylene compounds **1a**, **2a** and the methylene-ketones **1b**, **2b** separately in ca. 60% yields.[7] The NMR spectra of both dimethylenes and diketones show the presence of a two-fold symmetry. Diketones **3c** and **4c** are prepared by reductive ring-opening reactions from **1c** and **2c** according to a published procedure.[8] Treatment of **3c** and **4c** with titanium methylenation reagent gave trienes **3a** and **4a** (ca. 20% yield), along with significant quantities (ca. 60% yield) of

Dedicated to Professor Kung-Tsung Wang on the occasion of his 70th birthday.

Table 1. NMR ^{13}C Chemical Shifts (δ in ppm) for sp^2 Hybridized Carbon Atoms of **1** and **2**, and Their Calculated Electron Densities (*me*)

		1a	**1b**	**1c**	Δ^a	**2a**	**2b**	**2c**	Δ^a
C=	δ	155.1	151.1	---	-4.0	154.0	149.9	---	-4.1
	me	-83	-115	---	-32	-80	-112	---	-32
$=CH_2$	δ	99.6	102.0	---	2.4	101.9	104.3	---	2.4
	me	-156	-130	---	26	-154	-128	---	26
C=O	δ	---	218.4	213.6	-4.8	---	216.4	211.8	-4.6
	me	---	318	299	-19	---	322	303	-19

[a] Positive $\Delta\delta$ values indicate downfield shifts, whereas negative ones indicate upfield shifts.

diols **5** and **6**, which were formed through pinacol-type reductive couplings.[8]

The high polarity of carbonyl groups is known to induce a significant field effect on nearby π orbitals. The effect is evidenced on a comparison of ^{13}C NMR chemical shifts between the methylene groups $C=CH_2$ of **1a** and **1b**.[5a] The quaternary carbon of **1b** shows an upfield shift ($\Delta\delta$ = -4.0 ppm, Table 1) with respect to that of **1a**, indicating an increase of electron density, whilst the terminal carbons show an opposite effect ($\Delta\delta$ = +2.4 ppm). The difference on chemical shifts agrees with the change of electron densities calculated by semiempirical model PM3.[9] As shown in Table 1, the differences between **1a** and **1b** is -32 m*e* on the quaternary carbons and +26 m*e* on the terminal ones.

Similar amounts of changes both on chemical shifts and on electron densities are observed for the corresponding groups of **2a** and **2b**. The quaternary carbon of **2b** shows an upfield shift ($\Delta\delta$ = -4.1 ppm) with respect to that of **2a**, whilst the terminal ones show an opposite effect ($\Delta\delta$ = +2.4 ppm). The polarity effect between the two carbonyl groups of **1c** and **2c** is also evident by comparisons with those of **1b** and **2b**, respectively. The upfield shifts, i.e., $\Delta\delta$ = -4.8 ppm for **1c** and -4.6 ppm for **2c** (Table 1) comply well with estimated values of electron densities (Δ = -19 m*e*) in both cases.

In a previous study on homohypostrophene derivatives (analogous to the top half of **1**), it was concluded that the two nearby double bonds interact with each other effectively both through-bond and through-space.[10] As a result, the energies of HOMO and SOMO split, which correspond to ($\pi_1 + \pi_2$) and ($\pi_1 - \pi_2$). The presence of the third CH=CH bond (π_3) in **1-4** further perturbs the configuration of energy levels. Results done by semiempirical model PM3 showed that π_3 interacts heavily with the symmetrical combinations ($\pi_1 + \pi_2$), but has virtually no interaction with ($\pi_1 - \pi_2$) as restricted by the rule of symmetry. Drawings for the three highest occupied MOs of **4a** are shown in Fig. 1.[9] The energy of ($\pi_1 + \pi_2 + \pi_3$) (HOMO-1) is higher than that of ($\pi_1 - \pi_2$) (HOMO-2), which can be explained by a substantial mixing of σ-bondings with the former. From the geometry

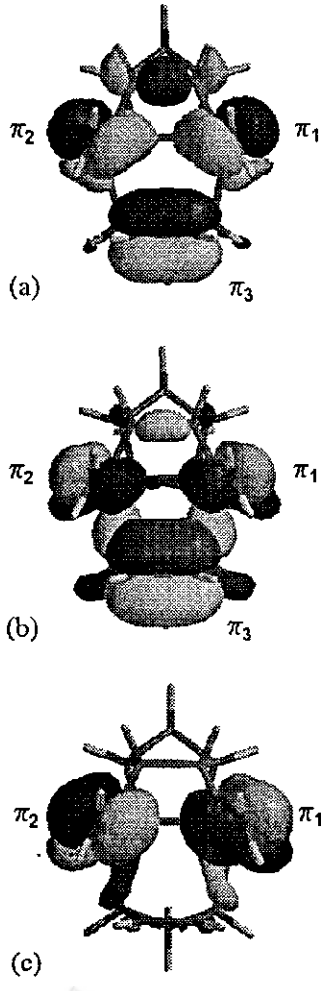

Fig. 1. The HOMO (a), HOMO-1 (b), and HOMO-2 (c) of **4a** calculated by PM3 implanted in SPARTAN.[9] Different shades indicate the phases of corresponding atomic orbitals.

Table 2. Comparison Among ^{13}C NMR Chemical Shifts (δ in ppm) for sp^2 Hybridized Carbon Atoms of *syn* and *anti* Isomers of Dimethylenes and Diketones

		1a	2a	Δ[a]	3a	4a	Δ[a]
C=	δ	155.1	154.0	-1.1	157.6	156.3	-1.3
$=CH_2$	δ	99.6	101.9	2.3	107.8	109.4	1.6
		1c	**2c**	**Δ[a]**	**3c**	**4c**	**Δ[a]**
C=O	δ	213.6	211.8	-1.8	219.0	216.4	-2.6

[a] Footnote as shown in Table 1.

shown in the drawings (Fig. 1), it seems that the amount of direct overlapping (through-space) among the three π orbitals should be relatively weak. Most of the interactions are most likely transmitted through σ bonds that connect the π moieties. Although OITB in **1** and **3** are expected to be the same as those of **2** and **4**, OITS in the latter may be stronger than that in the former. The difference of interactions caused by geometrical changes between **1** and **2** as well as that between **3** and **4** are therefore of interest. Comparisons of their ^{13}C chemical shifts are listed in Table 2.

In a comparison among the methylene groups of **1a** and **2a**, the quaternary carbons of **2a** move toward upfield (Δδ = -1.1 ppm) with respect to those of **1a** (Table 2), while the terminal ones move toward an opposite direction (Δδ = +2.3 ppm). A similar trend is observed when the methylene group of **4a** is compared with that of **3a**. The carbonyl carbons of **2c** and **4c** also show upfield shifts compared with those of **1c** (Δδ = -1.8 ppm) and **3c** (Δδ = -2.6 ppm). Though the magnitudes of Δδ values are relatively small, the trends are consistent within the two pairs of compounds, i.e., **1** and **2** as well as **3** and **4**. These data seem to indicate that the interactions between π_1 and π_2 are more pronounced in the case where π_3 is oriented *syn* to the former, i.e., in **2** and **4**. However, whether such mild differences are derived solely from OITS is not yet conclusive. A more thorough analysis with the aids of photoelectron spectra is under current investigation.

SUMMARY

We have found that the changing pattern of ^{13}C NMR chemical shifts for the double bonds of **1-4** is consistent with the prediction that π_1 and π_2 interact considerably with each other, whereas the *syn* or *anti* geometry of π_3 shows a rather mild influence on the chemical shifts of π_1 and π_2.

EXPERIMENTAL

Preparation of Titanium Reagents for Methylenation

To a round bottom flask containing freshly distilled THF (50 mL) was added activated zinc powder (5.5 g), CH_2Cl_2 (2.02 mL) and $TiCl_4$ (3.1 mL) at 0 °C under a nitrogen atmosphere. The mixture was stirred for 3 d at 0 °C, then stored at -5 °C. The resulting heterogenous dark brown liquid contains grayish precipitates, which need to be fully shaken before use (reagent A). A less reactive reagent (reagent B) was prepared through a similar process, except a CH_2Cl_2 solution of $TiCl_4$ (1.0 M, 3.1 mL) was used instead of pure liquid. Reagent A was used in the reactions of bismethylenation of diketones, whilst reagent B was used for monomethylenation.

7,15-Dimethyleneheptacyclo[7.5.1.1^{2,5}.0^{1,6}.0^{6,13}.0^{8,12}.0^{10,14}]hexadec-3-ene (*anti* and *syn* isomers 1a and 2a)

To a round bottom flask containing freshly distilled THF (4.0 mL) was added diketone **1c** (100 mg, 0.42 mmol) and titanium reagent A (4.0 mL) under nitrogen. The mixture was stirred with a magnetic bar at room temperature for 8 h. It was quenched by the addition of distilled water and was extracted with ether. The ether layers were combined, washed with saturated $NaHCO_3$, dried over anhydrous $MgSO_4$, and filtered. The filtrate was concentrated *in vacuo*, and was purified by silica gel column chromatography. Triene **1a** was collected in 57% yield (55 mg, 0.24 mmol) as a light yellowish solid: ^1H NMR ($CDCl_3$) δ 1.38 (d, J = 11 Hz, 1H), 1.58 (AB pattern, 2H), 1.70 (d, J = 11 Hz, 1H), 2.08 (m, 2H), 2.36 (m, 2H), 2.72 (m, 2H), 2.82 (m, 2H), 4.45 (d, J = 1 Hz, 2H), 4.62 (d, J = 1 Hz, 2H), 6.40 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 38.42, 43.23, 43.50, 46.36, 50.25, 53.14, 59.57, 99.55, 136.99, 155.14. Compound **2a** was obtained through a similar procedure. Physical data of **2a**: mp 119-121 °C; IR (KBr) ν 3080, 3057, 2954, 1569, 1453 cm^{-1};

^{1}H NMR ($CDCl_3$) δ 1.49 (d, J = 11 Hz, 1H), 1.61 (d, J = 9 Hz, 1H), 1.76 (d, J = 11 Hz, 1H), 1.99 (d, J = 9 Hz, 1H), 2.32 (m, 2H), 2.45 (m, 2H), 2.67 (m, 2H), 2.82 (m, 2H), 4.37 (d, J = 1 Hz, 2H), 4.61 (d, J = 1 Hz, 2H), 6.17 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 38.51, 43.53, 44.41, 47.12, 47.39, 52.74, 59.22, 101.88, 134.79, 153.94. MS (EI, 70 eV) *m/z* (rel intensity) 234 (M^+, 100%). HRMS Calcd for $C_{18}H_{18}$: 234.1408; found 234.1406.

7-Methyleneheptacyclo[7.5.1.1^{2,5}.0^{1,6}.0^{6,13}.0^{8,12}.0^{10,14}]-hexadec-3-en-15-one (*anti* and *syn* isomers 1b and 2b)

To a round bottom flask containing freshly distilled THF (4.0 mL) was added diketone **1c** (100 mg, 0.42 mmol) and titanium reagent B (4.0 mL) under nitrogen. The mixture was stirred with a magnetic bar at room temperature for 8 h. It was quenched by the addition of distilled water and was extracted with ether. The ether layers were combined, washed with saturated $NaHCO_3$, dried over anhydrous $MgSO_4$, and filtered. The filtrate was concentrated *in vacuo*, and was purified by silica gel column chromatography. Dienone **1b** was collected in 60% yield (64 mg, 0.26 mmol) as a white solid: mp 73-75 °C; IR ($CDCl_3$) ν 1735 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.54-1.65 (m, 3H), 1.85 (d, J = 11 Hz, 1H), 2.16 (m, 1H), 2.41-2.48 (m, 2H), 2.60 (m, 1H), 2.68 (m, 1H), 2.87 (m, 2H), 3.07 (m, 1H), 4.60 (s, 1H), 4.76 (s, 1H), 6.40 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 37.88, 40.26, 41.38, 43.23 (2C), 44.44, 47.53, 50.58, 55.00, 55.43, 61.44, 62.02, 102.00, 136.87 (2C), 151.10, 218.38; MS (EI, 70 eV) *m/z* (rel intensity) 236 (M^+, 76%), 221 (5), 207 (7), 193 (14), 178 (17), 171 (100). Compound **2b** was obtained through a similar procedure. Physical data of **2b**: mp 132-134 °C; IR (KBr) ν 3067, 2965, 1734, 1666 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.57 (d, J = 9 Hz, 1H), 1.69 (d, J = 11 Hz, 1H), 1.87 (m, 2H), 2.31-2.38 (m, 2H), 2.62 (m, 2H), 2.72 (m, 1H), 2.76 (m, 1H), 2.83 (m, 1H), 2.93 (dm, J = 10 Hz, 1H), 4.46 (s, 1H), 4.67 (s, 1H), 6.13 (m, 1H), 6.23 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 38.72, 39.98, 41.78, 43.63 (2C), 45.42, 46.58, 48.18, 53.94, 54.93, 61.00, 62.55, 104.03, 134.53, 134.99, 150.05, 215.09; MS (EI, 70 eV) *m/z* (rel intensity) 236 (M^+, 100%). Anal. Calcd for $C_{17}H_{16}O$: C, 86.40; H, 6.82. Found: C, 86.38; H, 6.84.

3,15-Dimethylenehexacyclo[7.5.1.1^{5,8}.0^{2,12}.0^{4,11}.0^{10,14}]-hexadec-6-ene (*anti* and *syn* isomers 3a and 4a) and Heptacyclo[7.5.1.1^{11,14}.0^{2,5}.0^{3,10}.0^{4,8}.0^{6,15}]hexadecan-12-en-2,3-diol (*anti* and *syn* isomers 5 and 6)

Using the same procedure as for the preparation of **1a**, both compounds **3a** and **5** are obtained from **3c**. Yield of **3a** was 29%: ^{1}H NMR ($CDCl_3$) δ 1.30-1.60 (m, 4H), 2.09 (m, 4H), 2.64 (m, 2H), 2.70-2.81 (m, 2H), 2.98 (m, 2H), 4.68 (m, 2H), 4.97 (m, 2H), 5.98 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 33.64, 42.06, 46.64, 48.12, 51.46, 53.18, 53.43, 107.79, 135.48, 157.62. Yield of **5** was 56%: white solid, mp 135-138 °C; ^{1}H NMR ($CDCl_3$) δ 1.12 (d, J = 11 Hz, 1H), 1.38-1.49 (m, 2H), 1.61 (br, 2H, -OH), 1.91 (d, J = 11 Hz, 1H), 2.09 (s, 2H), 2.20 (s, 2H), 2.26-2.32 (m, 4H), 2.59-2.62 (m, 2H), 6.13 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 36.61, 37.76, 39.01, 42.68, 44.53, 46.17, 51.24, 84.86, 137.55. Following the same procedure as for the preparation of **1a**, both compounds **4a** and **6** are obtained from **4c**. Yield of **4a** was 19%: IR ($CDCl_3$) ν 3071, 2930, 2854, 1729, 1650 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.53 (d, J = 11 Hz, 1H), 1.67 (d, J = 11 Hz, 1H), 1.82 (m, 2H), 2.14 (m, 2H), 2.48 (m, 2H), 2.55 (m, 2H), 2.85 (m, 2H), 3.15 (m, 2H), 4.51 (t, J = 1 Hz, 2H), 4.90 (d, J = 3 Hz, 2H), 5.94 (d, J = 1 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 34.87, 39.92, 40.29, 48.76, 49.65, 51.39, 54.35, 109.40, 135.16, 156.26. Yield of **6** was 62%: white solid, mp 155-157 °C; IR ($CDCl_3$) ν 3436, 3251, 2946, 2866 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.21 (d, J = 11 Hz, 1H), 1.61 (m, 2H), 1.72 (d, J = 11 Hz, 1H), 2.25 (m, 4H), 2.31 (m, 2H), 2.37 (m, 2H), 2.58 (m, 2H), 6.15 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 37.94, 40.40, 41.98, 43.43, 46.08, 48.32, 51.17, 82.90, 136.02; MS (EI, 70 eV) *m/z* (rel intensity) 242 (M^+, 39%), 176 (25), 110 (100); Anal. Calcd for $C_{16}H_{18}O_2$: C, 79.31; H, 7.49. Found: C, 78.91; H, 7.29.

Hexacyclo[7.5.1.1^{5,8}.0^{2,12}.0^{4,11}.0^{10,14}]hexadec-6-en-3,15-dione (*anti* and *syn* isomers 3c and 4c)

To a round bottom flask was added **1c** (108 mg, 0.45 mmol), acetic acid (5.4 mL) and zinc powder (200 mg). The mixture was stirred magnetically at room temperature for 8 h. It was poured onto ice water, and the aqueous mixture was extracted several times with CH_2Cl_2. The combined organic solution was washed with 0.1 M NaOH, followed by saturated $NaHCO_3$. It was dried over anhydrous $MgSO_4$, and filtered. The filtrate was concentrated *in vacuo*, and purified by silica gel column chromatography. Endione **3c** was collected in 68% yield (73 mg, 0.30 mmol) as a white solid: mp 167-169 °C; IR ($CDCl_3$) ν 2958, 1743 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.53-1.59 (m, 1H), 1.69 (d, J = 11 Hz, 1H), 1.82-1.90 (m, 2H), 2.47 (s, 2H), 2.55-2.60 (m, 4H), 2.82-2.91 (m, 4H), 6.03 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 34.38, 35.45, 39.67, 43.45, 45.73, 54.42, 57.01, 136.23, 218.99; MS (EI, 70 eV) *m/z* (rel intensity) 240 (M^+, 100%), 212 (12), 175 (26), 158 (28), 146 (35), 118 (94). Anal. Calcd for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71. Found: C, 79.46; H, 6.53. A similar procedure was used for the preparation of **4c** from **2c**. Yield of **4c** was 81%: mp 130-132 °C; IR ($CDCl_3$) ν 1746 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.77-1.83 (m, 3H), 1.98 (d, J = 12 Hz, 1H), 2.54-2.57 (m, 4H), 2.82-2.94 (m, 6H), 6.16 (s,

2H); ^{13}C NMR (CDCl$_3$) δ 35.85, 38.97, 39.31, 46.78, 47.23, 54.61, 57.09, 134.73, 216.43; MS (EI, 70 eV) *m/z* (rel intensity) 241 (M^++1, 100%), 223 (13), 213 (10), 145 (18); Anal. Calcd for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71. Found: C, 79.92; H, 6.62.

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Key Words

NMR chemical shift; Through-bond and through-space interactions.

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