

Novel bonding structure of some nonalternant polycyclic systems

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Abstract - Spectroscopic evidence suggests that a highly amphoteric hydrocarbon, 8,16-diisopropyl-*s*-indaceno[1,2,3-*cd*:5,6,7-*c'd'*]diphenylene exhibits the unique switching between diatropism and paratropism accompanied by its oxidation levels. London-McWeeny ring current calculations suggest a rationale for the abnormal $^1\text{H-NMR}$ phenomena of the series of redox states of this molecule. The bonding structure of 2-triphenylmethyl-dicyclohept[*cd,g*]indene is a bond shift equilibrium between two Kekulé structures of unknown dicyclohept[*a,d*]benzene perturbed by an external double bond.

INTRODUCTION

We have been investigating many aspects of the properties of nonalternant hydrocarbons for more than twenty years. During the course of these studies, it occurred to us that the molecular orbital characteristics of these nonalternant systems might be used to construct various organic molecules having intriguing properties..

Initially we were interested in the electronic feature of phenalenyl, an odd alternant hydrocarbon. Let us consider the molecular orbital of phenalenyl which comprises the cation (1^+) the radical (1^\bullet), and the anion (1^-). Simple Hückel molecular orbital theory predicts that the phenalenyl system has a nonbonding and six bonding molecular orbitals with the energies indicated in Figure 1. The phenalenyl cation (1^+) possesses twelve π -electrons which exactly fill pairwise the six bonding molecular orbitals. The extra one and two π -electrons of the radical (1^\bullet) and the anion (1^-) occupy the nonbonding molecular orbital. It means that all three entities should have the same magnitude of π -electron energy (ref. 1).

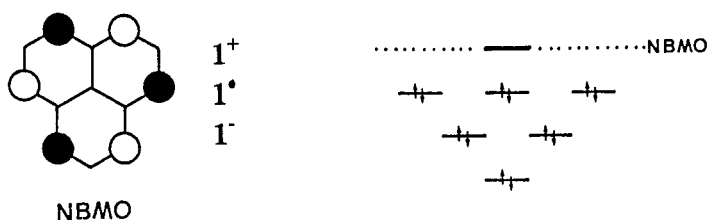
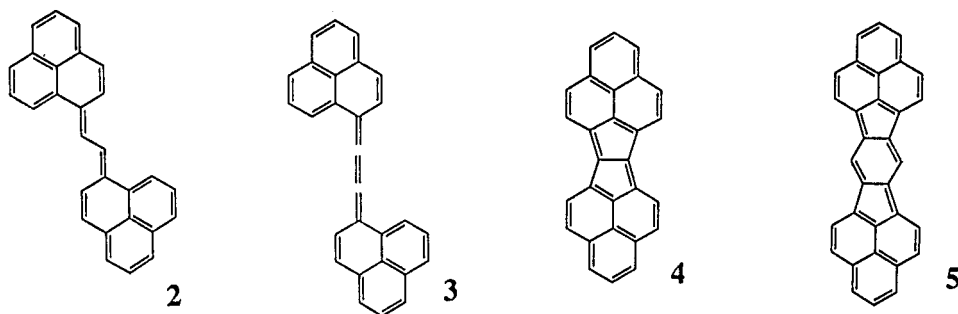


Fig. 1. Nonbonding molecular orbital of phenalenyl (1) and the electronic configuration of the phenalenyl cation (1^+).

Therefore, the odd alternant hydrocarbon phenalenyl radical (1^\bullet) appears to be a potential candidate to build up highly amphoteric hydrocarbons. However, a serious disadvantage of the open-shell phenalenyl radical is its lack of kinetic stability, since it is known to dimerize in solution even at low temperature. In order to construct closed-shell amphoteric redox hydrocarbons based on the phenalenyl system, we have designed and synthesized 1,2-bis(phenalen-1-ylidene)ethane (2) (ref. 2) and ethene (3) (ref. 3) in which both two-stage anodic oxidation and cathodic reduction steps are observed. A reasonable way to enhance the amphotericity of a certain pericondensed polycyclic hydrocarbon is that the aromatic stabilization in the

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neutral closed-shell state of a molecule should be minimized while the phenalenyl stabilization in the redox states of the molecule should be maintained. Along this line, pentaceno[1,2,3-*cd*:4,5,6-*c'd'*]diphenylene (4) has been synthesized (ref. 4). As would be expected, 4 exhibits the highest amphotericity among the hydrocarbons reported so far.

s-INDACENO[1,2,3-*cd*:5,6,7-*c'd'*]DIPHENYLENE SYSTEM

In addition to the aforementioned hydrocarbons, *s*-indaceno[1,2,3-*cd*:5,6,7-*c'd'*]diphenylene (5) is also expected to be a highly amphoteric hydrocarbon, since the neutral state of 5 will be destabilized by the unfavorable electronic contribution of a nonaromatic *s*-indacene moiety and the redox states 5^{2+} , 5^+ , 5^{\cdot} , and 5^{2-} will be substantially stabilized by the formation not only of two terminal phenalenyl moieties but also of a central benzene structure with loss of the *s*-indacene conjugation in its expected redox behavior as depicted in Figure 2.

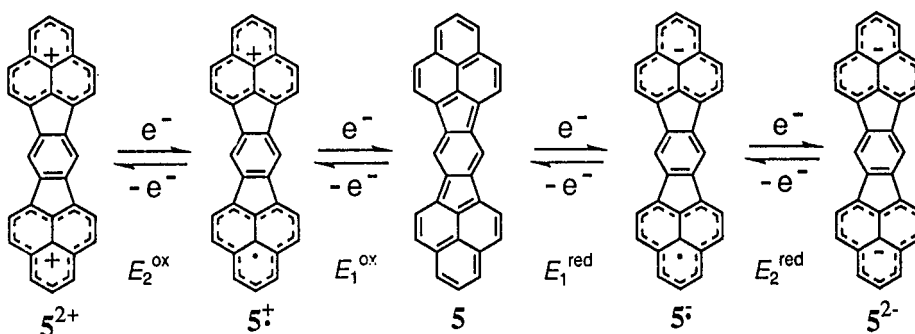
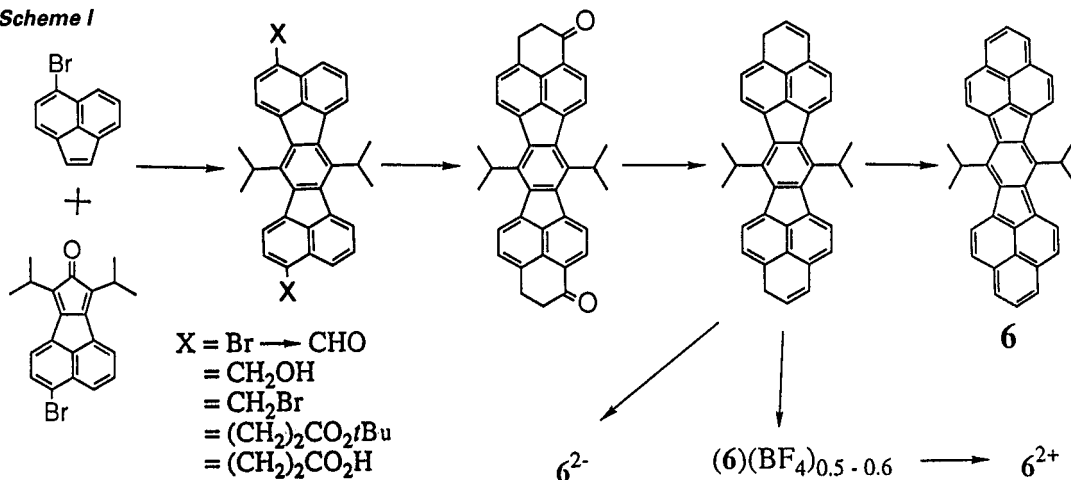


Fig. 2. Expected redox behavior for 5

Our synthesis of an alkyl derivative of 5, 8,16-diisopropyl-*s*-indaceno[1,2,3-*cd*:5,6,7-*c'd'*]diphenylene (6), is outlined in Scheme I (ref. 5).

Scheme I



Diels-Alder reaction of 5-bromoacenaphthylene (ref. 6) and 3-bromo-7,9-diisopropylcyclopent-[a]acenaphthylene-1,2-dione (ref. 7) followed by decarbonylation and aromatization with *p*-chloranil afforded an isomeric mixture of the 3,10- and 3,11-dibromo compounds. The formation of two isomeric dibromides at this stage was not of long-range consequence, since they converged to a single symmetrical product in the final step. Conversion of the dibromide to the bis(bromomethyl) derivative was accomplished by the usual method, which was converted into the bispropionic acid by the Schlessinger two-carbon elongation procedure (ref. 8). Friedel-Crafts cyclization of the bispropionic acid gave the non-cyclic diketone, which was transformed into the dihydro-6 through a reduction-dehydration sequence. Dehydrogenation of dihydro-6 with *p*-chloranil in benzene afforded the final product 6 as a green crystalline solid.

The electrochemical behavior of 6 was examined by cyclic voltammetry, and exhibited two reversible reduction waves at $E_1^{\text{red}} = -0.48$ V and $E_2^{\text{red}} = -1.07$ V and two irreversible oxidation waves at $E_1^{\text{ox}} = 0.62$ V and $E_2^{\text{ox}} = 0.84$ V vs. SCE. If we adopt the numerical sum of oxidation and reduction potentials [$E^{\text{sum}} = E^{\text{ox}} + (-E^{\text{red}})$] as an experimental measure to evaluate the amphotericity of a molecule, 6 is considered to be a highly amphoteric hydrocarbon (ref. 9).

Unexpectedly, hydride abstraction of the dihydro-6 with excess trityl tetrafluoroborate afforded, instead of the expected mono- or di-cation salts, a radical cation salt with non-stoichiometric composition (6)(BF₄)_{0.5-0.6} in 74% yield, which on dissolution in conc. D₂SO₄ yielded the dication (6²⁺) as a dark blue solution. On the other hand, the dianion (6²⁻) could be generated when dihydro-6 was treated with potassium mirror under vacuum at -78 °C for a week, as a bluish purple solution.

The ¹H-NMR chemical shifts for the three redox states, 6²⁺, 6, and 6²⁻, are compared in Table 1 (ref. 10). The most striking feature is that, despite the shielding caused by the two negative charges, the isopropyl protons (both CH₃ and CH) as well as the protons at the 1-, 7-, 9-, and 15-positions of 6²⁻ surprisingly resonated at lower magnetic field than those of the corresponding protons in the dication 6²⁺. Nevertheless, the chemical shifts of the remaining ring protons (H-2, -3, and -4) of 6²⁻ are comparable to those of the neutral

Table 1. Comparison of ¹H-NMR chemical shifts for 6²⁺, 6, and 6²⁻

proton	6 ²⁺ (a)	6(b)	6 ²⁻ (c)
CH ₃	1.47	1.49,1.50	2.09
CH	3.40	3.67	5.45
H-1,7,9,15	7.60	7.11,7.20	8.39
H-2,6,10,14	8.22	6.99,7.01	6.95
H-3,5,11,13	8.25	7.09	7.01
H-4,12	7.50	6.95	7.14

(a) Measured in D₂SO₄ at 60 °C. (b) Measured in CS₂ + acetone -d₆ (4:1) at -80 °C. (c) Measured in THF - d₈ at 0 °C.

species 6. This clearly suggests the operation and dominance of a diamagnetic ring current in the dianion 6²⁻ which possesses a conjugated periphery of 30π electrons consisting of an aromatic system weakly perturbed by two inner ethylenic double bonds (ref. 11). In contrast, the dication 6²⁺, a two-electron oxidation state of the neutral 6, exhibited paratropism despite having 4n+2 π-electrons both in the whole molecule (30π) and in the periphery (26π).

London-McWeeny ring current calculations (ref. 12) performed on the parent ring systems, 5²⁺, 5, and 5²⁻ together with the nodal properties of the HOMOs of these species suggest a rationale for the abnormal ¹H-NMR phenomena of the series of redox states of the present molecule 6. It is clear from Figure 3 that the parent dianion 5²⁻ will sustain pronounced diamagnetic ring current mainly along the periphery of the molecule. The nodal plane of the HOMO of 5²⁻ exists along the long symmetry axis of the molecule, hence the atomic orbital coefficients reside only along the periphery of 5²⁻. Furthermore, the nodal property of the central part of HOMO of 5²⁻ is exactly the same as that of *s*-indacene dianion which is known to exhibit substantial diamagnetic ring current both in theory and in practice (ref. 13).

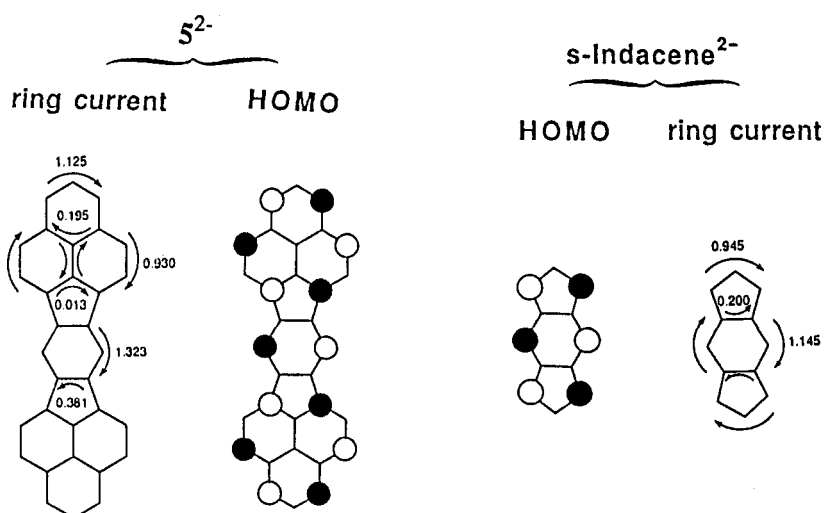


Fig. 3. Calculated ring currents and HOMOs for 5^{2-} and *s*-indacene dianion. Clockwise and counterclockwise arrows denote diamagnetic and paramagnetic ring currents, respectively. Diamagnetic ring current for benzene (1.0000) was taken as standard.

Unlike the dianion 5^{2-} , the dication 5^{2+} shows strong and weak paratropism at the central *s*-indacene and the terminal six-membered rings, respectively (Figure 4). In the HOMO of the dication 5^{2+} , the nodal property of *s*-indacene moiety possesses the same symmetry with that of the HOMO of neutral *s*-indacene itself which is known to show paratropism to some extent (ref. 14).

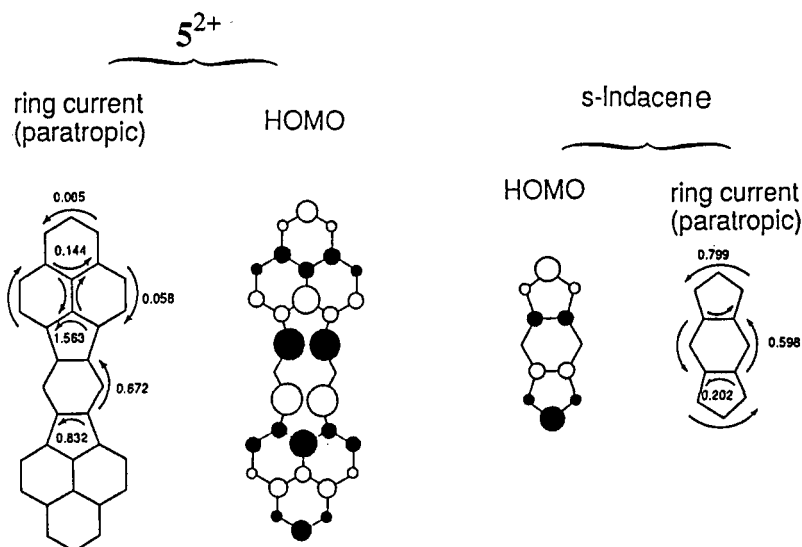
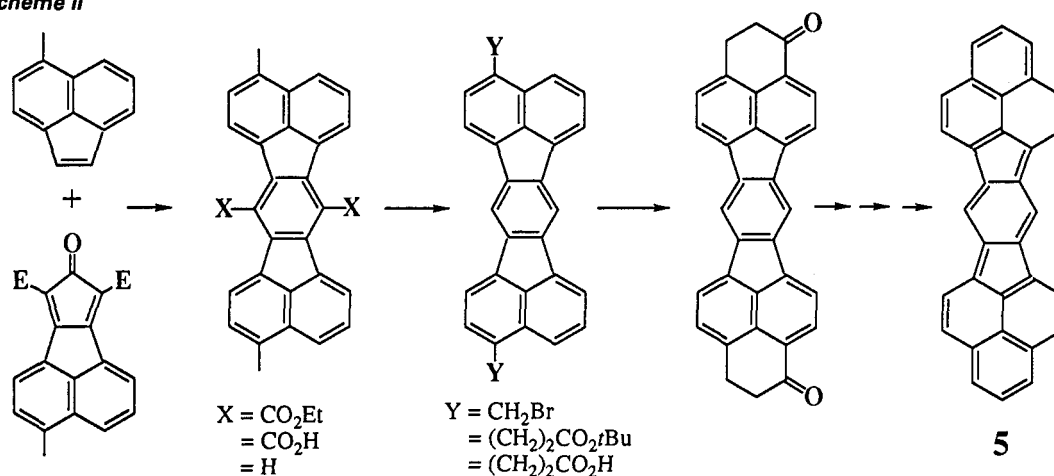


Fig. 4. Calculated ring currents and HOMOs for 5^{2+} and *s*-indacene.

These results provide the first example of the switching between diatropism (for 6^{2-}) and paratropism (for 6^{2+}) accompanied by changes in the oxidation levels.

In order to gain further insight into this unusual behavior of **6**, we aimed at synthesis of unsubstituted parent hydrocarbon **5**. The synthetic scheme for **5** is essentially the same with that for **6** starting from 5-methylacenaphthylene and diethyl 3-methyl-8-oxocyclopent[*a*]acenaphthylene-7,9-dicarboxylate as shown in Scheme II (ref. 15). Although the parent hydrocarbon **5** could be obtained as dark green solid, extremely low solubility of this compound makes it impossible to examine the physical properties of **5** in detail.

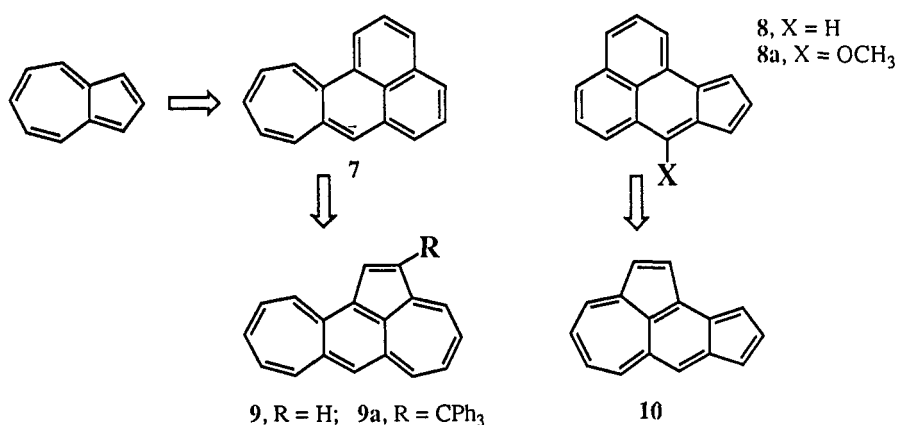
Scheme II



DICYCLOHEPT[*cd,g*]INDENE SYSTEM

Two nonalternant hydrocarbons, cyclohepta[*a*]phenalene (**7**) and cyclopenta[*a*]phenalene (**8**), formally derived from azulene by replacing one of its two rings by phenalene conjugation, are known as Reid's hydrocarbons (ref. 16). Based on the Hückel MO treatment, molecules **7** and **8** were characterized to have a high-energy HOMO (+0.1055 β) and a low-energy LUMO (-0.1154 β), respectively.

Therefore, **7** is predicted to be highly electron donating whereas **8** is predicted to be highly electron accepting. Our recent synthesis of **7** (ref. 17) and a methoxy derivative of **8** (ref. 18) has upheld this prediction.

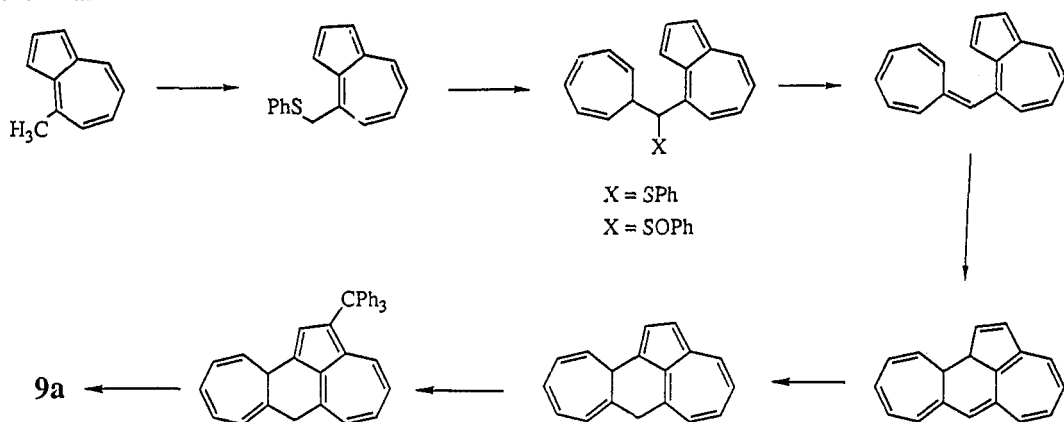


As an extension of this molecular design, we are interested in the molecules, dicyclopent[*cd,g*]indene (**9**) and cyclohept[*cd*]as-indacene (**10**), which contain cyclohept[*cd*]indene conjugation instead of the phenalene system in **7** and **8**. Dicyclopent[*cd,g*]indene (**9**), an isomer of **7**, is a new class of compound in the series, since **9** is formally composed of two prototype nonalternant systems, azulene and heptafulvene chromophores.

Our synthesis of a triphenylmethyl derivative **9a**, black needles, mp 200 °C (decomp.), involves a unique 14 π electrocyclic reaction for the construction of the desired ring skeleton and is briefly shown in Scheme III (ref. 19).

The redox properties of **9a** were examined by cyclic voltammetry and exhibited two oxidation waves at 0.43 and 1.10 V as well as a reduction wave at -1.18 V. As expected from its high Hückel HOMO level (0.1778 β), the first oxidation potential of **9a** is close to that of **7** ($E^{\text{ox}} = 0.39$ V). Furthermore, the reduction potential of **9a** is explicitly more positive than that of **8a** ($E^{\text{red}} = -1.27$ V) suggesting that **9a** is an amphoteric hydrocarbon ($E^{\text{sum}} = 0.61$ V) to an appreciable extent.

Scheme III



The $^1\text{H-NMR}$ parameters of **9a** are summarized in Figure 5 from which some interesting bonding features emerged. As far as the chemical shifts ($\delta = 5.56\text{--}6.30$) and the coupling constants ($J_{\text{vic}} = 8.9\text{--}11.7$ Hz) of the ring-a are concerned, these are quite similar to those of 8-phenyl- and 8,8-diphenylheptafulvenes (ref. 20). However, the chemical shifts of the hydrogens attached to the ring-c and -d, which constitute formally an azulene chromophore, are substantially higher than those of azulene itself. This means that the bonding structure of **9a** cannot be explained as a simple composite of azulene and heptafulvene (model-A). An alternative bonding structure is anticipated to be either a composite of sesquifulvalene and hexatriene (model-B) or that of cyclohept[e]indene and butadiene (model-C).

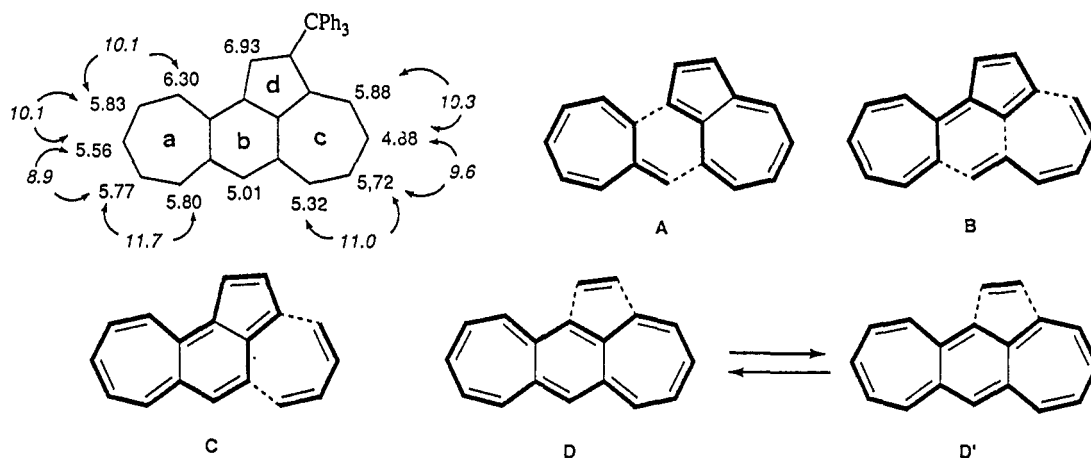


Fig. 5. $^1\text{H-NMR}$ parameters and possible bonding structure for **9a**.

However, these models are also inadequate for the real structure of **9a**, since the seven-membered ring hydrogens of sesquifulvalene ($\delta = 6.20\text{--}7.05$) (ref. 21) and 2,3-dicyano-4-phenylcyclohept[e]indene ($\delta = 7.85\text{--}9.50$) (ref. 22) resonate at substantially lower field than those of the ring-a hydrogens of **9a**. A most likely possibility would be a bond shift equilibrium between two Kekulé structures of unknown dicyclohepta[*a,d*]benzene (ref. 23), which should sustain a paramagnetic ring current associated with its peripheral 16π electrons, perturbed by an external ethylenic double bond (model D ↔ D')

The molecular design, synthesis, and physical properties of some novel nonalternant hydrocarbons described in this survey reveal many unexpected chemical and physical behaviors. Although many studies, such as detailed solid state properties of the radical cation salt (**6**)(BF_4) $_{0.5-0.6}$, isolation of the dication salt of 6^{2+} , X-ray crystallographic determination of **6** and **9a**, attempt to freeze the non-degenerate π -bond shift of **9a** and so on, have to be carried out, our findings may serve to understand the intricate mode of cyclic conjugations.

Acknowledgement With pleasure I would like to express my appreciation to my able coworkers, Dr. K. Nakasuji, Dr. Y. Sugihara, Dr. K.-U. Klabunde, S. Sasaki, J. Saito, who developed this chemistry. Our work was supported by Grant-in-Aid for Scientific Research on Priority Areas from the Ministry of Education, Science and Culture, Japan.

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