

Fig. 1. $^1\text{H-NMR}$ spectra of compounds (6), (7), and (8); all in 10% solution in C_6H_6 ; 100 MHz; 25 $^\circ\text{C}$; internal standard TMS = 10 τ .

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[5] On kinetically controlled addition of H^- to pentadienyl- $\text{Fe}(\text{CO})_3$ compounds there are formed, not only the diene-, but also 1,3,4,5- η -pentadienyl- $\text{Fe}(\text{CO})_3$ systems [2]. The product ratio is greatly influenced by ring-conformation effects [R. Aumann, unpublished work].

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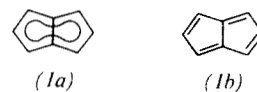
[13] Small amounts of deuterium are incorporated at ring positions 3 and 5 due to 1,5-hydrogen shifts on the metal side of the ring ligand. This could be demonstrated convincingly also by "inverse labeling", using a compound (6), in which all hydrogen atoms except H^1 pseudoequatorial are substituted by deuterium as starting material for rearrangement studies (R. Aumann, unpublished results).

1,3,5-Tri-*tert*-Butylpentalene. A Stabilized Planar 8π -Electron System^[**]

By Klaus Hafner and Hans Ulrich Süss^[*]

Dedicated to Professor Fritz Kröhnke on the occasion of his 70th birthday

The question of the nature of bonding in pentalene (1) has motivated numerous experimental and theoretical studies during the past 50 years^[1] and frequently led to a great deal of controversy^[2]. Whereas "aromatic" properties were initially postulated for (1), recent quantum mechanical calculations predict for a delocalized pentalene according to a D_{2h} structure (1a) resonance destabilization by



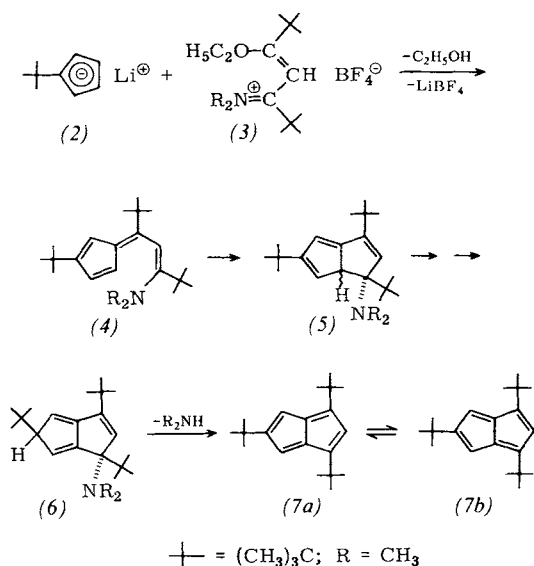
about 6 kcal/mol relative to a polyolefin structure of C_{2h} symmetry (1b)^[3,4]. The hydrocarbon (1) should accordingly be characterized by high reactivity and low thermal stability. This is confirmed by the latest experimental results: attempts to prepare (1) and its 2-methyl, 1,3-dimethyl, and 1,3-di-*tert*-butyl derivatives exclusively yielded the dimerization products^[5]. On photolysis at -196°C ^[5] some of these yield the highly thermolabile monomers (detected by UV spectroscopy). Similar observations were made by *de Mayo et al.*^[6] on attempted preparation of 1-methylpentalene, whose existence could likewise only be deduced from UV and IR spectra owing to its unusually pronounced tendency to undergo dimerization even at temperatures below -100°C .

NMR spectroscopic studies of a simple pentalene were expected to provide information about the bonding character of this cyclooctatetraene perturbed by a central σ bond and thus to afford a solution of the "pentalene problem". This required a derivative of (1) whose dimerization is hindered by steric effects only. This requirement is fulfilled by 1,3,5-tri-*tert*-butylpentalene (7).

The synthesis of (7) was readily accomplished by reaction of lithium *tert*-butylcyclopentadienide (2) with the ketimmonium salt (3)^[7] in ether/methylene chloride (2:1) at 0°C (15 h). The reaction mixture is then rapidly worked up at 0°C and the product mixture chromatographed on Al_2O_3 (activity 3, basic) at -75°C with *n*-pentane. Com-

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Compound (7) is isolated in about 10% yield^[9] as deep-blue crystals (scales) of m. p. 59°C (low temperature MS (at -100°C): $M^+ = 270$ ^[10]). The crystals are stable for several hours at room temperature in the absence of air, while a low concentration *n*-hexane solution of the compound is stable for several days under N_2 . Dimer formation has not yet been observed.

By analogy with the preparation of 2-methyl- and 1,3-dimethylpentalene^[5], (2) and (3) probably first yield the fulvene (4) which undergoes electrocyclic reaction to give (5). Subsequent double 1,5-H shifts lead to the 1,5-dihydropentalene (6) which suffers 1,4-elimination of dimethylamine to furnish (7).

The UV spectrum of (7) [(in *n*-hexane at 20°C): $\lambda_{\text{max}} = 211$ ($\log \epsilon = 4.27$), 280 (3.34), 333 (3.50), and 598 nm (1.81)] is in good agreement with calculated^[4] values for the electronic spectrum of (1) and resembles those of mono- and dimethylpentalenes^[5,6] as well as those of hexaphenylpentalene^[11], 1,3-bis(dimethylamino)pentalene^[12], and 1,4-diamino-2,5-dicyano-3,6-dimethylpentalene^[13].

The pentalene structure (7) is proved by the NMR spectra, which provide additional information about the bonding

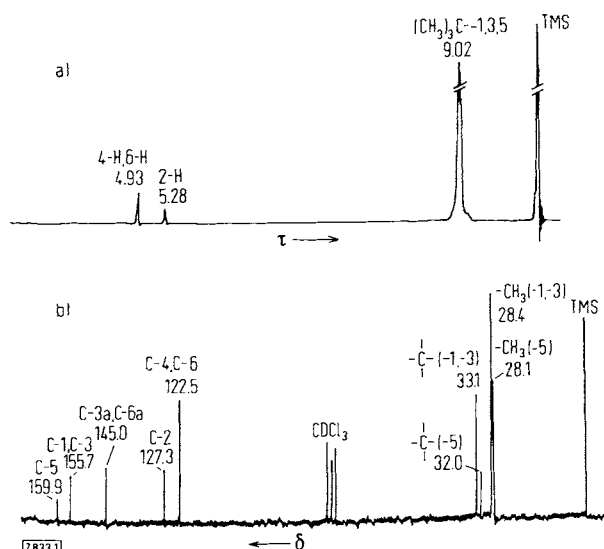


Fig. 1. a) 60-MHz ^1H -NMR spectrum of (7) in CCl_4 at -27°C with TMS as internal standard. b) ^1H -broad band decoupled ^{13}C -NMR spectrum of (7) in CDCl_3 at -50°C with TMS as internal standard.

character of the 8π -electron system. The 60-MHz ^1H -NMR spectrum of (7) (Fig. 1a) shows two singlets of intensity 2:1 for the three ring protons, while the absorptions of the *tert*-butyl protons coincide to give just one signal. The ^{13}C -NMR spectrum of (7) (Fig. 1b)^[14] contains five signals in the sp^2 C range for the ring system. This assignment was deduced from the off-resonance spectrum, the known influence of *tert*-butyl groups on neighboring sp^2 C atoms, as well as the relative intensities of the signals of C-1/C-3, C-5, C-3a/C-6a on the one hand and of C-2, C-4/C-6 on the other. In contrast to the 60-MHz ^1H -NMR spectrum, the ^{13}C -NMR spectrum permits recognition of the different *tert*-butyl groups.

The ring proton signals of (7) are shifted upfield compared to those of heptalene ($\tau = 4.2$ and 4.9)^[15], cyclooctatetraene ($\tau = 4.31$)^[16], and particularly those of fulvene ($\tau = 3.9$)^[17] and 1,2-dihydropentalene ($\tau = 3.29$ – 4.18)^[18]. The same observation is made on comparison with the signals of the outer protons of [16]annulene ($\tau = 4.67$)^[19] and of 1,7-methano[12]annulene ($\tau = 4.2$ – 4.6)^[20], both of which exhibit a paramagnetic ring current.

Accordingly, a paramagnetic ring current is probably operative in (7) too, the compound thus possessing "antiaromatic" character. The presence of only five signals in the ^{13}C -NMR spectrum for the eight ring C atoms of (7) rules out the existence of a localized bond system depicted by one of the Kekulé structures (7a) and (7b). However, our present experimental results do not permit a decision whether the π -electron system of (7) is delocalized in the same way as (1a) or is undergoing rapid oscillation between the Kekulé structures (7a) and (7b).

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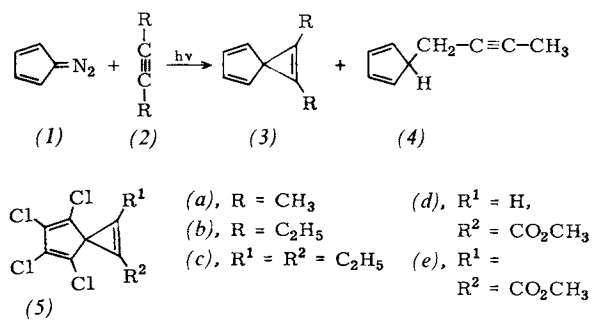
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Definite Proof of Spiroconjugation in [1.2]Spirenes^[**]

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Linkage of conjugated segments of polyenes (ribbons^[1]) via a formally sp³-hybridized C atom should lead to a spirene exhibiting an interaction designated as spiroconjugation^[2]. HMO^[2] and CNDO/2 calculations^[3] on [1.2]spirene^[**] predict stabilization of the HOMO by interaction between the π ribbons while the energy of the LUMO remains largely unaffected^[2,3]. This should result in a hypsochromic shift of the longest wavelength UV band compared with that of the partially hydrogenated system (7).

However, both electronic and steric substituent effects can perturb the system and mask the spiroconjugation. Thus the spirene (5c) provides no unequivocal evidence for spiroconjugation^[2], whereas (5d) and (5e) exhibit a marked hypsochromic shift in the UV spectrum^[4]. These differing results prompted us to synthesize the alkyl-substituted [1.2]spirenes (3a) and (3b) in order to substantially eliminate substituent effects.



Compounds (3a) and (3b) were prepared by irradiating diazocyclopentadiene (1) in 2-butyne (2a) or 3-hexyne (2b) with long wave UV light ($\lambda > 360$ nm) until evolution of nitrogen had ceased (cf. ref. [5]). (3a) and (3b) are pale yellow oils (yield 47 and 35% respectively) which decompose on attempted gas chromatography but could be purified by chromatography and vacuum microdistillation at room temperature.

The structure follows from the spectra. IR: (3a): 1938; (3b): 1925 cm⁻¹ (cyclopropene stretching mode); NMR: (3a): $\tau = 3.8-4.0$ (m) and 3.3-3.5 (m) (cyclopentadiene

H), 7.86 ppm (s) (CH₃) (2:2:6); (3b): $\tau = 3.3-3.5$ (m) and 3.7-3.9 (m) (cyclopentadiene H), 7.53 (q) (³J = 7.5 Hz) (CH₂) and 8.95 ppm (t) (CH₃) (2:2:4:6); mass spectrum: (3b): *m/e* = 146 (M⁺); UV, see Table 1. Further structural proof comes from the Diels-Alder adducts of (3a) and (3b) to tetracyanoethylene and to 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (cyclopropene band at 1860 to 1880 cm⁻¹).

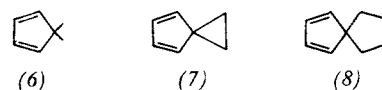


Table 1. UV data for [1.2]spirenes (3a) and (3b) and the 5,5-disubstituted cyclopentadienes (6)–(8).

Cpd.	Solvent	λ_{max} [nm]	ϵ
(3a)	methanol	239	1300
(3b)	methanol	241	2450
	isooctane	242	2900
(6)	ethanol	250	2880
(7)	ethanol	257	2690
(8)	ethanol	254	2750

The possibility of spiroconjugation was examined by comparison of the UV spectra of (3a) and (3b) with those of (6)–(8) which cannot show spiroconjugation. The theoretically predicted hypsochromic shift^[2,3] of the longest wavelength absorption band is indeed observed on comparison of (3a) and (3b) with (8). It amounts to 12–15 nm, i.e. 5–6 kcal/mol.

While the UV spectra of spirotetraenes may be compared with those of the corresponding saturated hydrocarbons^[6,7], the method runs into difficulties with (3a), (3b), and (7). The p orbitals (Walsh model) of the cyclopropene single bonds can enter into pseudoconjugation via the sp²-hybridized spiro-C atom with the π electrons of the five-membered ring^[8]. In (3a) and (3b) a hypsochromic shift becomes operative due to spiroconjugation and a bathochromic shift due to pseudoconjugation. Comparison of (7) and (8) shows that the latter effect should result in a bathochromic shift of the order of 3 nm. In reality the stabilization of (3a) and (3b) will therefore be greater than 5–6 kcal/mol. Spiroconjugation can thus be regarded as established in [1.2]spirenes. Photoelectron spectroscopic studies are currently in progress.

1,2-Diethylspiro[2.4]hepta-1,4,6-triene (3b):

A solution of (1) (4.0 g, 43.5 mmol) in (2b) (150 ml) was irradiated, after 15 minutes' purging with N₂, with a Philips HPK 125 W lamp (GW_v filter) for 4 h at 0°C. (60–70% of the calculated amount of N₂ was liberated.) Unreacted (2b) was then removed *in vacuo* and the blackish brown residue rapidly chromatographed over silica gel (150 g) with CH₂Cl₂. Chromatography with CCl₄ under the same conditions afforded (3b) as a pale yellowish oil. Prior to spectroscopy (3b) was distilled in a microapparatus at room temperature.

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