

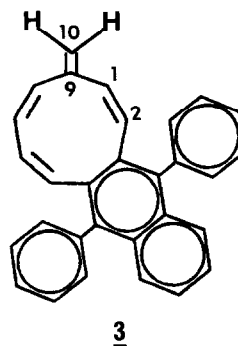
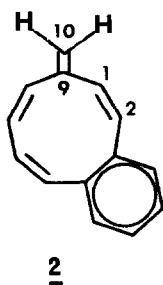
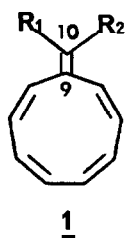
THE MONOBENZO AND MONONAPHTHO NONAFULVENE FRAMES

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The synthesis and spectroscopic characterization of two thermally stable, all-hydrocarbon, nonafulvenes, 2 and 3, are described.

Fulvene and its higher  $\pi$  homologs are members of a uniquely structured family of cross conjugated molecules where the type and degree of "cross"  $\pi$  interaction is heavily controlled by the basic " $4n + 2$ " rule of aromaticity. Nonafulvene, the nine membered analog of parent fulvene, is a particularly interesting member of this family insofar as its basic all-cis array of  $\pi$  centers is well known to represent the size limit beyond which "static" planarity within a  $\pi$  monocycle becomes skeletally inaccessible.

The few available nonafulvenes incorporating an unsubstituted ring, i.e., 1a, 1b<sup>2</sup> and 1c<sup>3</sup> are known to undergo  $\pi 6s$  electrocyclization to the corresponding cis-dihydroindenenes with relative rates which are clearly indicative of increased stability due to enhanced availability of the desired " $4n + 2$ "  $\pi$ -excessive ( $10\pi$ ) ring component. Since proper monobenzenoid fusion to the nonafulvene skeleton ought to effectively prevent electrocyclization under conditions of only minimal electronic perturbation we have prepared and studied the monobenzo derivative 2 and its sterically congested mononaphtho relative 3.<sup>4</sup>



**a** ;  $R_1 = R_2 = H$

**b** ;  $R_1 = R_2 = N(Me)_2$

**c** ;  $R_1 = Me, R_2 = OSi(Me)_3$

Nonafulvenes 2 and 3 were prepared in 88% and 66% yield respectively upon exposure of the corresponding ketones<sup>5</sup> to lithium triphenylphosphinemethylene in ether at ambient temperature. Purification was effected by column chromatography ( $Al_2O_3$ ,  $-15^\circ C$ ) and the pure samples were

characterized by entirely consistent spectroscopic data; **2** [colorless oil; IR (neat):  $1575\text{ cm}^{-1}$  (exomethylene); UV (hexane):  $255\text{ nm}$  ( $\epsilon$  7800); H-NMR (80 MHz;  $\text{CDCl}_3$ ):  $\delta_{\text{TMS}}$  4.96 (2H, s,  $\text{H}^{1^0}$ ), 5.45 (1H, dd,  $J = 12.5, 3.0\text{ Hz}$ ), 5.80 (1H, d,  $J = 12.5\text{ Hz}$ ), 6.05 (1H, dd,  $J = 12.0, 3.0\text{ Hz}$ ), 6.35 (2H, s,  $\text{H}^1 + \text{H}^2$ ), 6.40 (1H, d,  $J = 12.0\text{ Hz}$ ), 6.9-7.2 (4H, m, "aromatic");  $^{13}\text{C}$ -NMR (20 MHz; THF- $d_6$ ; H-coupled):  $\delta_{\text{TMS}}$  120.43 (t,  $J = 158, \text{C}^{1^0}$ ), 125-136 (m), 143.5 (s,  $\text{C}^9$ ); MS (70 eV): m/e 180 ( $\text{M}^+$ , 59%), 165 (100%)] and **3** [yellow crystals; IR(KBr):  $1568\text{ cm}^{-1}$  (exomethylene; UV (hexane):  $297\text{ nm}$  ( $\epsilon$  17,700);  $^1\text{H}$ -NMR (80 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{TMS}}$  4.75 (1H, s,  $\text{H}^{1^0}$ ), 5.00 (1H, s,  $\text{H}^{1^0'}$ ), 5.55 (1H, dd,  $J = 12.5, 2.5\text{ Hz}$ ), 5.90 (1H, dd,  $J = 11.10, 5.0\text{ Hz}$ ), 5.95 (1H, d,  $J = 12.5\text{ Hz}$ ), 6.25 (2H, s,  $\text{H}^1 + \text{H}^2$ ), 6.25 (1H, d,  $J = 11.0\text{ Hz}$ ), 7.1-7.7 (14H, "aromatic");  $^{13}\text{C}$ -NMR (80 MHz, THF- $d_6$ , H-coupled):  $\delta_{\text{TMS}}$  119.76 (t,  $J = 156, \text{C}^{1^0}$ ), 121-139 (m), 144.59 (s,  $\text{C}^9$ ); MS (70 eV): m/e 382 ( $\text{M}^+$ , 100%)]].

Particularly revealing in the spectroscopic characterization of **2** and **3** is the presence, in each case of the key  $\text{C}=\text{CH}_2$  function as established by the appearance in the "sp<sup>2</sup>" region of the H-coupled  $^{13}\text{C}$ -NMR spectra of (i) a triplet ( $\text{C}^{1^0}$ ) and (ii) a low field singlet ( $\text{C}^9$ ). On the other hand, **2** and **3** exhibit fundamentally different  $^1\text{H}$ -NMR patterns for the pair of geminal protons bound to  $\text{C}^{1^0}$  which appear as a 2H singlet in **2** and as two well separated (0.25 ppm) singlets in **3**. For obvious reasons, this difference is best ascribable to the differing conformational mobilities of the two nine-membered moieties with that of **2** being, as expected, more flexible than that of **3**.<sup>6</sup>

With regards to "chemical" stability it may be worth noting that whereas **2** and **3** are quite inert to prolonged exposure to acetic acid (ambient temperature) they readily decompose in the presence of trifluoroacetic acid.

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#### References and Notes

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- (6) The conformational rigidity of the nine-membered frame, of **3** is clearly deducible from the  $^1\text{H}$ -NMR spectrum in which the methylene protons give rise to two distinct 1H signals separated by 21.5 Hz. As expected, the separation of signals decreases with increasing temperature (19 Hz at  $142^\circ\text{C}$ ) although the thermal instability of the molecule precludes the observation of coalescence. The conformational mobility of **2** is clearly evident from the  $^1\text{H}$ -NMR spectrum determined at ambient temperature in which the two methylene protons give rise to a single 2H signal and the fact that equally weighed signal separation (1H each) occurs upon cooling; 5.2 Hz at  $-100^\circ\text{C}$ .

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