

## ANNELATED NONAFULVENES<sup>1</sup>

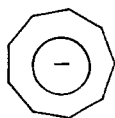
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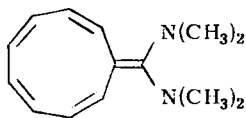
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Cyclononatetraenyl anion (I) was prepared in 1963 and proved to be a stable aromatic  $10-\pi$  electron system.<sup>2</sup> The corresponding bis-(N-dimethylamino)-nonafulvene (II) was found to be unstable at room temperature.<sup>3</sup> We wish to report the preparation and properties of nonafulvenes<sup>4,5</sup> derived from the dibenzo derivative III of cyclononatetraene (DBCNT) for which we have developed recently<sup>6</sup> a convenient synthesis.

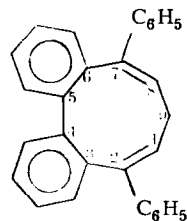
Treatment of 2,7-diphenyl-3,4:5,6-dibenzocyclononatetraene (III) in diethyl ether- $d_{10}$  with n-butyl lithium at room temperature in vacuo gave a deep red-violet solution. The freshly prepared anion showed nmr<sup>7</sup> signals at  $\delta=7.50-7.33$  (20 H, m), 3.76 ppm (2H, t,  $J=8.0$  Hz), which slowly changed; the triplet at 3.76 ppm disappeared and a new aromatic multiplet emerged, and all protons appeared at 6.00-8.00 ppm. The analogous phenomenon was observed recently in the corresponding non-phenylated anion.<sup>8</sup> We submit that the freshly prepared anion is a pentadienyl anion which undergoes a transformation to the delocalized and therefore probably planar anion IV. Quenching of the latter with  $D_2O$  gave the 9-monodeuterated derivative of III in 50% yield ( $H_1, H_8$  appear at  $\delta=6.0$  ppm, 2H, d). Successive deuterations yielded the 9,9'-dideuterated derivative of III ( $H_1, H_8$  appear at  $\delta=6.0$  ppm, 2H, s). The reaction of the anion derived from III with the complex derived from DMF and  $(CH_3)_2SO_4$ <sup>9</sup> (in ether at 0°)



I



II



III



What is the contribution of the dipolar resonance form VI to the ground state of these fulvenes and what is the degree of their aromaticity? In all the fulvenes studied the vinylic ring protons are shifted approx. 40-50 Hz to lower field and merge with the aromatic protons. Neither of the nonafulvenes Va and Vb, exhibits a significant shift of their dimethylamino protons upon addition of  $\text{Eu(DPM)}_3$  even at a molar ratio of 1 : 1. It should be noted that also in the nmr spectra of N-dimethylamino-pentafulvene no shift of the dimethylamino protons has been observed upon the addition of up to 1 : 1 molar ratios of  $\text{Eu(DPM)}_3$ .<sup>12</sup> This fact can be interpreted in terms of reduced electron density at the nitrogen atoms of Va and Vb which would indicate a high dipolar character of Va and Vb in the ground state. The electronic spectra of the fulvenes Va-e show a high intensity band in the region of 340-400 nm thus resembling the pentafulvene series.<sup>13</sup> The solvent dependence of the absorption of the long-wave band in the uv spectra also resembles that of dipolar systems.<sup>14</sup> Hafner<sup>3</sup> assigns the long-wave absorption at 403 nm to the nonafulvene II. This absorption as well as the chemical shift of the ring protons of II ( $\delta = 7.1-7.7$ ) are in accord with our results thus indicating that the annelation did not affect diversely the "nonafulvene character". Most significant are the dipole moments of the nonafulvenes reported here.<sup>15</sup> The dipole moments of Va and Vb are 2.7 and 2.8 Debye respectively; these dipole moments are lower than those of the corresponding simple pentafulvenes.<sup>16</sup>

These results together with the nmr and uv data indicate that the dipolar structure (VI) contributes to the ground state of the annelated nonafulvenes. However, this contribution cannot be assessed quantitatively at this moment. We hope that X-ray studies and theoretical calculations will shed light upon this problem.

#### References

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(b) E. A. LaLancette and R. E. Benson, J. Am. Chem. Soc., 85, 2853 (1963); 87, 1941 (1965).
3. K. Hafner and H. Tappe, Angew. Chem. internat. edit., 8, 593 (1969). K. Hafner, Proc. Third Jerusalem Symposium on "Aromaticity, Pseudoaromaticity and Antiaromaticity", p. 256 (1971).

4. While this work was in progress Garratt has reported the first nona-heptafulvalene.<sup>5</sup> We have also prepared a number of fulvalenes which will be reported soon.
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7. Nmr spectra were recorded on a Varian HA-100 spectrometer at 100 MHz, tetramethylsilane served as an internal reference.
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10. All new compounds gave satisfactory elementary analysis, Ir and mass spectra.
11. The temperature-dependence of the nmr spectra is being studied and will be reported in the full account of this work.
12. S. Rozen and A. Gazit, unpublished results from this laboratory.
13. The long-wave band of the simple pentafulvene derivatives analogous to V are:  
6-Dimethylamino  $\lambda_{\max}^{C_8H_{14}}$  316 nm (lg  $\epsilon$  4.49); 6-para-dimethylaminophenyl  $\lambda_{\max}^{C_7H_{18}}$  342 nm (lg  $\epsilon$  4.52), 385-400<sup>S</sup>; 6-phenyl  $\lambda_{\max}^{C_7H_{18}} \sim 300$ ; 6-para-anisyl  $\lambda_{\max}^{C_7H_{18}}$  337 nm (lg  $\epsilon$  4.39), 385-400<sup>S</sup>. P. Yates in Advances in Alicyclic Chemistry, Vol. 2, H. Hart and G. J. Karabatsos editors, Academic Press, 1968, pp. 105-107.
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15. In benzene, 30°, heterodyne beat method, I. F. Halverstadt and W. K. Kumler, J. Am. Chem. Soc., 64, 2988 (1942).
16. The dipole moments of the corresponding pentafulvalenes are: 6-dimethylaminofulvene-4.48 D;<sup>17</sup> 6-(para-dimethylaminophenyl)fulvene-3.65D.<sup>18</sup>
17. K. Hafner, K. H. Voepel, G. Ploss and C. Koenig, Ann., 661, 52 (1963).
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