SYNTHESIS AND PHYSICAL PROPERTIES OF 6,12-DIARYLAZULENO[1,2-b]AZULENES

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The structure of a minor dimer (<u>2a</u>) of 1-arylcycloheptatrienylidenethylene was determined by X-ray crystallography. Dehydration of <u>2a</u> and <u>2b</u> gave novel non-benzenoid aromatics---6,12-diarylazuleno[1,2-b]azulenes (<u>3a</u> and <u>3b</u>), whose electronic and NMR spectral properties were reported.

Recently we reported the generation of 1-cycloheptatrienylidene-2-phenylethylene  $(\underline{1})$  and its interesting dimerization reactions giving three different types of dimers.<sup>1</sup> While the structures of the two major dimers have been clarified,<sup>1</sup> that of the third one  $(\underline{2})$  could not be determined because of the small amounts of material available<sup>2</sup> (e. g.,  $\underline{2a}$ , mp 221°, and  $\underline{2b}$ , mp 215°, were obtained only in 1.7 and 2.8% yields, respectively).<sup>3</sup> The structure of the minor dimer 2a was determined by X-ray crystallography.

Crystals of  $\underline{2a}$  are triclinic: space group belongs to  $P_{\overline{1}}$ : cell constants are as follows; a=11.180 (1), b=9.953 (1), c=10.014 (1) Å,  $\alpha$ =100.13 (2),  $\beta$ =103.36 (2),  $\gamma$ =91.00 (1)°, and Z=2. The structure was solved by the direct method using a total of 3911 independent reflections and the final R value was 0.08. The structure of  $\underline{2a}$  is not symmetrical: two phenyl groups are in trans configuration to each other; two protons at C<sub>6</sub> and C<sub>6a</sub> are in cis and those of C<sub>12</sub> and C<sub>12a</sub> are trans relation. All double bonds are conjugated except with two phenyl groups. This is in agreement with the fact that  $\underline{2a}$  has absorption maximum at long wave length regions.<sup>3</sup> Cycloheptatriene moieties are in a boat form which is in good accordance with other cycloheptatriene systems.<sup>4</sup> The structure of  $\underline{2b}$  was deduced from its spectral properties by comparison with those of  $\underline{2a}$ .<sup>3,5</sup>





Fig. 1 A computer generated perspective drawing of molecule 2a

Bromination of 2a and 2b resulted in brominationdehydrobromination to afford 6,12-diarvlazuleno[1,2-b]azulenes (3a, mp 260°, and 3b, mp >280°, in 56 and 53% yields, respectively). Their physical properties are as following. 3a [electronic spectrum:  $\lambda_{max}^{cyclohexane}$ , nm  $(\log \epsilon); 210 (4.45), 229$ (4.37), 254 (4.44), 344 (4.76 sh), 357 (5.11), 409 (3.75), 430 (3.87), 457 (4.02)486 (4.05), 570 (2.34 sh), 915 (2.41), 1050 (2.49), and 1253 PMR spectrum: (2.34).

 $\delta$  (ppm in CDCl<sub>3</sub>, 100 MHz); 6.8-7.0 (H<sub>2.4.8.10</sub>, m), 7.2-7.7 (phenyl's H and H<sub>3.9</sub>, m), 8.18 (H<sub>1,7</sub>, d, J<sub>1,2</sub>=11.0 Hz), and 8.42 (H<sub>5,11</sub>, d, J<sub>4,5</sub>=8.5 Hz)]. <u>3b</u> [ $\lambda_{max}^{cyclohexane}$ , nm (log  $\varepsilon$ ); 259 (4.47), 340 (4.66), 364 (5.10), 410 (3.74), 435 (3.78), 461 (3.90), 580 (2.37 sh), 840 (2.26 sh), 920 (2.32), 1055 (2.38), and 1242 (2.22). & (ppm in CDC1<sub>3</sub>, 200 MHz); 6.8-7.2 ( $H_{2,4,8,10}$ , m), 7.4-7.9 (phenyl's H and  $H_{3,9}$ , m), 8.20 ( $H_{1,7}$ , d,  $J_{1,2}$ -10.7 Hz), and 8.45  $(H_{5,11}, d, J_{4,5}=8.9 \text{ Hz})]$ . The electronic spectrum of <u>3a</u> is shown in Fig 3; the shape of the spectrum is resemble with those of azulenes except the longest absorption bands shifted to near-infrared regions. In the PMR spectra, differences in chemical shifts between H<sub>17</sub> (8.18 ppm for  $\underline{3a}$ , and 8.20 ppm for  $\underline{3b}$ ) and  $H_{5,11}$  (8.42 ppm for  $\underline{3a}$ , and 8.45 ppm for  $\underline{3b}$ ) were rationalized by the following explanation. Investigation of the Dreiding models of 3 indicates that H, and H<sub>2</sub> are received big anisotropy effect from the aryl groups, but H<sub>5</sub> and H<sub>11</sub> are not. The coupling constants between  $H_1$  and  $H_2$  (also  $H_7$  and  $H_8$ ) (J=8.5 Hz for <u>3a</u>, and 8.9 Hz for <u>3b</u>), and those between  $H_A$  and  $H_5$  ( $H_{10}$  and  $H_{11}$ ) (J=11.0 Hz for <u>3a</u>, and 10.7 Hz for 3b) are different, indicating bond length alternations in seven-membered moieties of azuleno-[1,2-b]azulene system. The degree of bond length alternations of 3 is nearly the same as that of 1,2-benzoazulene.<sup>b</sup>

The azulenoazulenes (<u>3a</u> and <u>3b</u>) are novel non-benzenoid aromatics and the first example of azuleno[1,2-b]azulene compound. As analogous compounds of <u>3</u>, 5-cyanoazuleno[1,2-f]azulene

have been reported by Jutz and his coworkers.<sup>7</sup> Hess and Schaad have predicted the resonance energy and stability of azuleno[1,2-b]azulene system, and shown that this system possesses fairly large resonance energy per double bond.<sup>8</sup> Toyoda calculated molecular diagram and singlet transitions of azuleno[1,2-b]azulene as shown in Fig. 2 and 3, and in the Table.<sup>9</sup>

Table : Singlet transitions of azuleno[1,2-b]azulene<sup>9</sup>



Fig. 3 Electronic spectrum of <u>3a</u> (curve), and singlet transitions of azuleno[1,2-b]azulene shown in Table (solid lines are Bu and dotted lines are Ag symmetry)<sup>9</sup>

Each absorption bands of their electronic spectra are in good accordance with those of theoretical predictions.<sup>9</sup> Toyoda's results also indicate that this system possesses bond length alternations which are agreeable with the conclusion by the PMR spectra of 3. The azuleno[1,2-b]azulenes might show some different properties with those of azulenes, because azuelene does not show such bond length alternations. Actually we could not observe any emmision spectra from S<sub>2</sub> state of 3.

## References and Notes

- 1. T. Toda, N. Shimazaki, and T. Mukai, Chemistry Letters, 1979, 171.
- 2. The p-bromophenyl derivative <u>2b</u> was prepared from l-(p-bromophenyl)-2-(2,4,6-cyclohepta-trien-l-yl)acetylene by a procedure analogous to the preparation of <u>2a</u>.<sup>1</sup> Correct elemental analyses were obtained for all new compounds reported in this paper.
- $\frac{2a}{max}$  [  $\lambda_{max}^{cyclohexane}$ , nm (log  $\epsilon$ ); 246 (4.53), 303 (3.78), and 403 Spectral data of 2. 3.  $\delta$  (ppm in CDCl<sub>3</sub>, 200 MHz); 3.28 (H<sub>12a</sub>, m, J<sub>12,12a</sub>=4.0, J<sub>1,12a</sub>=3.5, and (4,35).  $J_{2,12a}=2.0$  Hz), 3.72 (H<sub>6a</sub>, m,  $J_{6,6a}=9.2$ ,  $J_{6a,7}=4.2$ ,  $J_{6a,8}=2.0$ , and  $J_{6a,11}=1.5$  Hz), 4.12  $(H_{12}, dd, J_{6,12}=2.1 Hz), 4.58 (H_7, dd, J_{7,8}=10.2 Hz), 4.75 (H_6, dd), 5.59 (H_{11}, dd, J_{1,8}=10.2 Hz), 4.75 (H_6, dd), 5.59 (H_{11}, dd, J_{1,8}=10.2 Hz), 4.75 (H_{11}, dd, J_{11}, dd), 4.75 (H_{11}, dd), 4.75 (H_{11}, dd), 4.75 (H$  $J_{10,11}$ =5.8 Hz), 5.67 (H<sub>5</sub>, d,  $J_{4.5}$ =6.9 Hz), 5.68 (H<sub>1</sub>, dd,  $J_{1.2}$ =9.8 Hz), 5.83 (H<sub>8</sub>, m,  $J_{8,9}=5.1$  Hz), 6.07 (H<sub>2</sub>, ddd,  $J_{2,3}=5.8$  Hz), 6.20 (H<sub>3</sub> and H<sub>9</sub>, dd,  $J_{3,4}=J_{9,10}=11.4$  Hz), 6.23 (H<sub>4</sub> and H<sub>10</sub>, dd), and 7.13-7.32 (phenyl's H, m)].  $2b \begin{bmatrix} \lambda cyclohexane \\ max \end{bmatrix}$  $(\log \ \varepsilon)$ ; 223 (4.57), 232 (4.56), 246 (4.51), 305 (3.75), and 400 (4.23). б (ppm in  $CDC1_3$ , 90 MHz); 3.20 (H<sub>12a</sub>, m), 3.70 (H<sub>6a</sub>, m), 4.05 (H<sub>12</sub>, m), 4.53 (H<sub>7</sub>, dd, J<sub>7 8</sub>=10.0 and  $J_{6a,7}^{=4.0 \text{ Hz}}$ , 4.65 (H<sub>6</sub>, dd,  $J_{6,6a}^{=9.0 \text{ and }} J_{6,12}^{=2.0 \text{ Hz}}$ ), 5.45-6.40 (6H, m), 6.97 (2H, d, J=8.5 Hz), 7.15 (2H, d, J=8.5 Hz), 7.45 (2H, d, J=8.5 Hz), and 7.46 (2H, d, J=8.5 Hz)7.
- 4. R. E. Davis and A. Tulinsky, J. Am. Chem. Soc., <u>88</u>, 4583 (1966).
- 5. Details of the dimerization mechanisms of 1 will be published in near future.
- 6. D. J. Bertelli and P. Crews, Tetrahedron, 26, 4717 (1970).
- 7. C. Jutz, H. G. Peuker, and W. Kosbahn, Synthesis, 1976, 673.
- 8. B. A. Hess and L. J. Schaad, J. Org. Chem., 36, 3418 (1971).
- 9. Private communication from Dr. A. Toyoda (Yamagata University). The data shown in thi paper were calculated by PPP variable bond length SCF MO and quoted by permission and courtesy of Dr. Toyoda. We are very much indebted to Dr. Toyoda for the information before publication.

(Received in Japan 18 June 1980)