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# NAPHTHO[1,8-ab:4,5-a'b']DIAZULENE, THE FIRST NONALTERNANT ISOMER OF DIBENZOPYRENE

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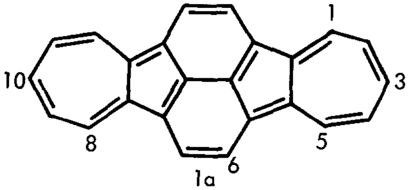
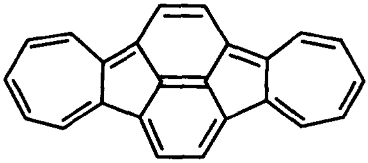
Abstract The title compound was synthesized by the transannular reaction of [2.2](1,3)azulenophane and subsequent dehydrogenation. It exhibits characteristic electronic absorption bands extended to near IR region (~1400 nm) and its PMR spectrum indicates the presence of large ring current. MO calculations suggest no bond alternation in the entire π system.

Naphtho[1,8-ab:4,5-a'b']diazulene (1) is one of the totally unknown nonalternant isomers of dibenzopyrene and is predicted to be aromatic by the Craig rule$^{1)}$. Since two basic structures, the 2,2'-biazulene with two extra double bonds (1a) and the peripheral [22]annulene with a central double bond (1b), can be written, it is of considerable interest to find the evidences to define the main resonance contributor of this novel aromatic polycycle. Furthermore, if the latter (1b) is indeed the predominant contributor, the compound would provide us with an opportunity to evaluate the perturbation by a central double bond to the 22π system and compare with other similar ring systems$^{2)}$. We describe herein the synthesis and some physical properties as well as the result of MO calculations of 1.

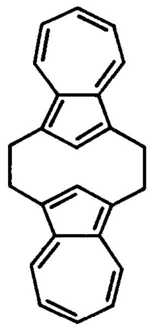


1a

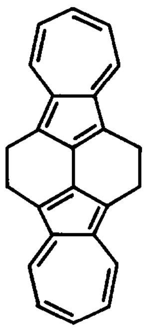


1b

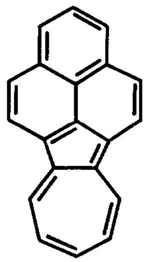
The synthesis was performed starting from [2.2](1,3)azulenophane (2)$^{3)}$ in a similar way reported for pyrene$^{4)}$ and azuleno[1,2,3-cd]phenalene (4)$^{5)}$. When irradiated or treated with iodine in dichloromethane, 2 yielded the corresponding 2,2'-biazulene derivative 3 in 48% and 85% yield, respectively. 3: green needles, m.p. 231°C (decomp.); m/e 306 ($M^+$, 100%), 302 (57), 290 (39), 289 (39), 153 (35); $\delta_{CDCl_3}$ 3.52 (8H, s), 6.90 (4H, t, J=10), 7.32 (2H, t, J=10), 8.04 (4H, d, J=10). All absorption bands in the electronic spectrum of 3 ($\lambda_{max}^{CH_2Cl_2}$ (log ε) 255 nm (4.24), 331 (4.81), 345 (4.87), 402 (3.90), 424 (4.45), 452 (4.89), 586 (2.96), 633 (2.98) (Cf. Fig. 1)) exhibited bathochromic shift



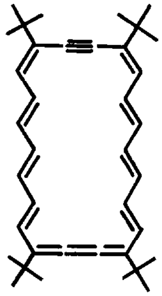
**2**



**3**



**4**



**5**

compared with those of 2,2'-biazulene[6], suggesting that **3** takes a more coplanar conformation than the latter due to two ethano bridges. The biazulene **3** was stirred overnight with chloranil in benzene to give quantitatively the desired **1**, dark violet leaflets, m.p. 223-226° (benzene-cyclohexane); m/e 302 ($M^+$, 100%), 300 (18), 298 (7), 276 (24), 274 (13), 250 (2).

The PMR spectrum of **1** in dioxane-$d_8$[7] shows a 4H doublet at $\delta$=9.17 ppm (J=10.0 Hz, H-1, 5, 8, 12), a 2H triplet at 7.92 (J=10.0, H-3, 10), a 4H triplet at 7.42 (J=10.0, H-2, 4, 9, 11) and a 4H singlet at 8.38 (H-6, 7, 13, 14). The chemical shift values of all protons are quite similar to those of the corresponding protons of **4**[5], and azulene protons appear in ca 1 ppm lower field than those of **3**, suggesting the presence of considerable diamagnetic ring current in the periphery of the molecule.

The shorter wave-length region of electronic spectrum of **1** (Fig. 1), consisting of two intense absorptions and a weak one, is similar to the [22]annulene **5**[8], rather than to **3**. However, the absorption extends to ~1400 nm unlike either **3** or **5**. These absorptions may also suggest a large contribution of the perturbed [22]-annulene structure (**1b**).

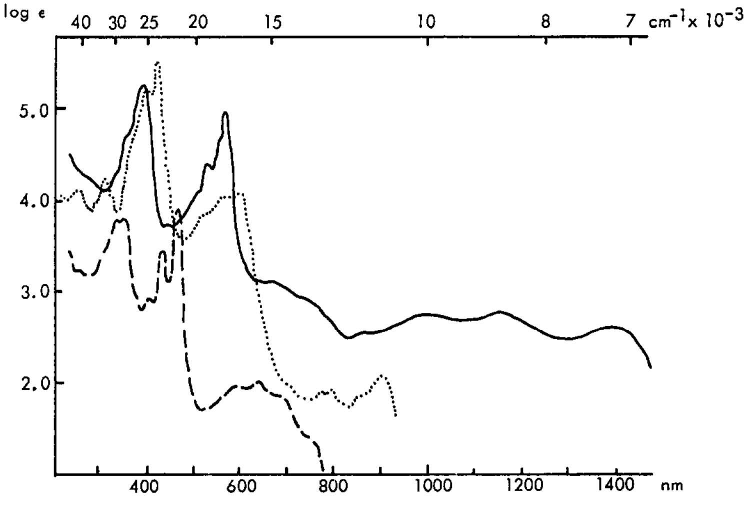
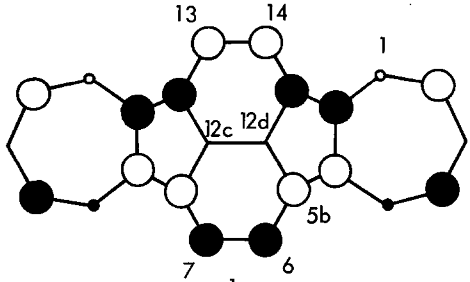
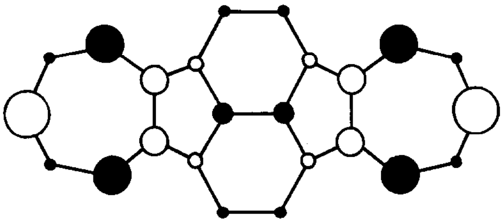


Fig. 1 Electronic spectra of **1** (——), **3** [(– – –), log ε -1] and **5** (······)

In order to correlate this unusual electronic absorption with molecular geometry, the semi-empirical SCF LCAO-π-MO calculations were carried out, using the variable bond length method (method A) developed by Nakajima[9]. The results, the bond alternation in the final (optimized) structure and the electronic transitions, are listed in the Table. The optimized geometry obtained by this method indicates bond alternation mainly in etheno bridges and the electronic transition in the longest wave-length shorter than the observed one.



1c



1d

The calculation was also carried out for a model with no bond alternation in etheno bridge using PPP-CI (fixed bond length) method (method B) on the following considerations. According to the perturbation theory, the elongation of the bond $C_6$-$C_7$ and $C_{13}$-$C_{14}$ and the shortening of $C_{5b}$-$C_6$ and its equivalents would increase the orbital energy of HOMO (1c) but not of LUMO (1d) and result in the bathochromic shift of the absorption in the longest wave-length. The results are also shown in the Table[10].

Table. Final (optimized) structures and electronic transitions of 1 calculated by SCF LCAO-π-MO methods

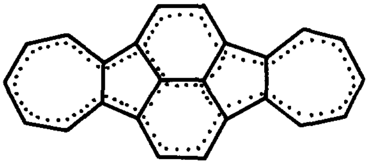
| Symmetry in initial structures | Method*1 | Optimized structures | Predicted transitions (nm)*2 |
|---|---|---|---|
| $C_2h$ | A | 1a*3 | 979, 521, 340 |
| $C_2v$ (two types) | A | | |
| $D_2h$ | A | | |
| $D_2h$[10] | B | 1e | 1283, 563, 346 |

*1 Method A and Method B: See text.

*2 The observed absorption maxima are at 1397, 553, 383 nm.

*3 $R_{6,7}$=1.369 Å $R_{5b,6}$=1.435 Å $R_{12c-12d}$=1.426 Å. Other bond lengths are very close to those of azulene[11].

As is clear from the Table, the completely delocalized structure (**1e**) gives rise to all electronic transition closer to the observed value. Therefore the structure of **1** should be best represented by **1e**. Further studies including X-ray analysis are in progress.



**1e**

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## References and Footnotes

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