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π-Electron Distribution in Benz[*a*]indeno[1,2,3-*cd*]azulene and the Corresponding Azepinium Ion

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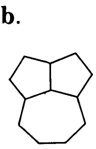
(Received December 21, 1983)

Synopsis. The π-electron density distribution in benz[*a*]indeno[1,2,3-*cd*]azulene and the corresponding azepinium ion has been calculated by the PPP MO method. The effects of the hetero atom and the benzo annellation on the π-electron density and bond order of the cyclopent[*cd*]azulene are discussed.

Since Hafner *et al.* synthesized the dimetyl derivatives of cyclopent[*cd*]azulene (**1**) and cyclohept[*cd*]azulene (**2**) (Hafner's hydrocarbon),[1] their electronic structures have attracted the interest of many organic and theoretical chemists.[2,3] Parent molecules **1** and **2** were treated by the self-consistent field molecular orbital theory on π-conjugated systems developed by Pariser, Parr, and Pople.[4] The essence of these theoretical calculations[5] is summarized as follows. Thermodynamically, **1** is more stable than **2** as shown by their Dewar's resonance energy of 0.018 and 0.016$|\beta|$, respectively. However there is higher olefinic character in the 5-membered rings of **1**, and therefore **1** should be kinetically less stable of the two.

Some more derivatives of **1** and **2** were synthesized, and in 1969 and 1970 crystallographic studies on 5,7-dimethyl-2-phenylcyclopentazulene[6] and 3,5,8,10-tetramethylcycloheptazulene[7] showed almost planar structure of these molecules. More recently we found a facile access to the dibenzo derivative (**1b**) of **1** *via* the photorearrangement of 1-alkoxytriptycenes.[8] The corresponding azepinium salt (**3b**) was also obtained by the hydride abstraction reaction of the similar photoproduct of 1-azatriptycene.[9]

Since the benzoannellation is so located as to block the reactive olefinic bonds in **1**, **1b** proved to be a very stable compound. These experimental work encouraged us to study the electronic structure of **1b** and **3b**.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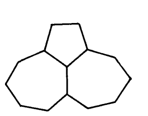
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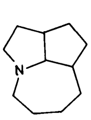

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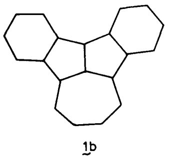
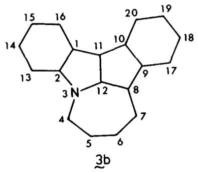

1b



3b

Method and Parameters

The self-consistent-field method used here is the Pariser-Parr-Pople method within the zero-differential-overlap approximation. The matrix elements of the closed shell Hartree-Fock operator are written as follows,

$$F_{rr} = -\mathrm{I}_r + \frac{1}{2}q_r\gamma_{rr} + \sum_{s\neq r}(q_s-1)\gamma_{rs},$$

$$F_{rs} = \beta_{rs} - \frac{1}{2}p_{rs}\gamma_{rs},$$

where q_r and p_{rs} are π-electron density and bond order, respectively, and I_r is the ionization potential of atom r in its valence state, and γ_{rr} is one-center repulsion integral which is estimated as the difference between valence state ionization energy and electron affinity.

As the resonance integral, β_{rs}, a constant value was used for neighboring atoms, and for non-neighboring atoms β_{rs} was assumed to be zero. The two-center repulsion integral, γ_{rs}, was calculated by the Mataga-Nishimoto formula[10] using the standard geometries.

The parameters used in this calculation are shown in Table 1, with the Hückel parameters h and k in $\alpha_N = \alpha_C + h\beta_{CC}$, and $\beta_{CN} = k\beta_{CC}$ for initial guess.[11] These vaules were determined in reference to the DasGupta's work on nonbenzenoid hydrocarbons[5] and the study of methyleneammonium ion by Brown.[12]

The molecules discussed here are all assumed to have planar geometries, with all the carbon–carbon and carbon–nitrogen bonds being 1.39 Å and 1.36 Å, respectively. The bond angles of the cyclopent[*cd*]azulene moiety are close to those of the crystal structure[6] of related compounds and collected in Table 2. The bond angles of the annulated benzene rings are assumed to be equal to 120°.

Calculations were carried out on a Hitachi M-200H computer, using "SCF-CI-PI-MO Program with PPP Approximation" programmed by Mueller-Westrhoff and filed in the program library of the Computer Center of Institute for Molecular Science.

Table 1. Parameters used in the calculations

$I_C = 11.16$ ev	$I_N = 14.16$ ev
$\gamma_{CC} = 11.134$ ev	$\gamma_{NN} = 12.82$ ev
$\beta_{CC} = -1.7901$ ev	$\beta_{CN} = -2.57$ ev
$h = 2.0$	$k = 1.0$

Table 2. Bond angles in molecules **1**, **1b**, **3**, and **3b** employed for the PPP calculations[a]

Bond angle	$\phi/°$	Bond angle	$\phi/°$
1 and **1b**		C_{12}-C_{11}-C_1	106.0
C_1-C_2-C_3	109.6	C_{11}-C_1-C_2	108.2
C_2-C_3-C_{12}	105.2	C_{11}-C_{12}-C_8	111.0
C_3-C_{12}-C_{11}	111.0	C_{12}-C_8-C_9	105.2
C_{12}-C_{11}-C_1	106.0	C_8-C_9-C_{10}	109.6
C_{11}-C_1-C_2	108.2	C_9-C_{10}-C_{11}	108.2
C_3-C_4-C_5	125.8	C_{10}-C_{11}-C_{12}	106.0
C_4-C_5-C_6	131.2	N_3-C_4-C_5	132.6
C_7-C_8-C_{12}	124.0	C_4-C_5-C_6	126.9
3 and **3b**		C_5-C_6-C_7	131.2
C_1-C_2-C_3	108.0	C_6-C_7-C_8	125.8
C_2-N_3-C_{12}	108.5	C_7-C_8-C_{12}	124.0
N_3-C_{12}-C_{11}	109.3	C_{12}-N_3-C_4	119.8

a) Numbering scheme is given for **3b**.

Results and Discussion

In Table 3 are given the calculated π-electron densities and π-bond orders of cyclopent[*cd*]azulene (**1**) and its dibenzo derivative (**1b**) together with their azepinium derivatives (**3** and **3b**). The present results for cyclopent[*cd*]azulene agree with those of the previous calculations,2,3,5,6) confirming the validity of our parametrization. Although the π-electron density is somewhat sensitive to choice of parameters,5) the data in Table 3 indicate some trends which do not depend on the parameters. Firstly, we note that the charge density at the positive nitrogen center (position 3) is more effectively neutralized in **3b** than in **3**. As a result, π-electron densities are slightly reduced not only at the neighboring carbons (position 2, 4, 12) but also the remote carbon atoms (position 6, 8, 10). Secondly, the π-electron density on the benzene rings is little influenced by the change of atoms at position 3. For a third, when the dibenzo derivatives are compared with the parent compounds, it is noted that the extent of the separation of charge densities is smaller in the dibenzo derivatives. Thus **1b** and **3b** are expected to be less polar and therefore less reactive than the corresponding parent compounds.

An operational test for the validity of the calculated charge distributions is provided by the ^{1}H NMR data for **1b** and **3b**. Plots of the chemical shifts of the nonbenzenoid hydrogens 4—7 *vs.* the calculated π-electron densities gave a line as shown in Fig. 1. The slope is close to the well-known 10 ppm/π-electron. The reason why the proton at position 5 of **3** deviated from the line is not clear for the moment.

Turning now to π-bond orders (Table 3), we note that the bond alternation in the 7-membered ring is more evident in the dibenzo derivatives than in their parent compounds in which the bond orders in the 7-membered rings are more uniform and suggest the reasonably high aromatic character. Whereas the 3–12 and 8–12 bonds, which are shared by two rings of different type, have a single bond character with bond order 0.38—0.44, the 11–12 bond between the same ring types has an aromatic character with bond order 0.68—0.69 in the dibenzo derivatives. Bonds 1–2 and 9—10 on the 5-membered rings of **1** and **3** have very high bond order 0.73—0.77 which is supported by the short bond length (1.359 and 1.386 Å) found in the crystal structure of the related compounds.6) The benzo annellation reduced the latter bond orders to 0.55—0.57 by sharing the bonds as a part of the benzene ring. Whereas the double bond character of these bonds is reduced, the bond alternation in the rest of the molecules is found to be enhanced by the benzo annellation in these systems. The trend is interpreted in terms of an increased contribution of canonical structure A over B and B′ which require the quinonoid structure of one of the benzene rings. In the aza-analogs, the extent of the bond alternation is somewhat enlarged as compared to the hydrocarbons.

Table 3. π-Electron densities and bond orders of cyclopentazulenes

Carbon atom	π-Electron densities 1	1b	3	3b	Bond	π-Bond orders 1	1b	3	3b
1	0.937	0.971	0.949	0.977	1–2	0.771	0.568	0.733	0.550
2	1.110	1.057	1.066	1.018	1–11	0.474	0.413	0.490	0.424
3	0.922	0.933	1.142	1.151	2–3	0.488	0.406	0.528	0.453
4	0.944	0.956	0.840	0.840	3–12	0.423	0.408	0.452	0.441
5	0.965	0.968	0.987	0.991	3–4	0.621	0.686	0.617	0.675
6	0.965	0.968	0.931	0.930	4–5	0.658	0.591	0.618	0.546
7	0.944	0.956	0.956	0.969	5–6	0.646	0.704	0.670	0.729
8	0.922	0.933	0.889	0.898	6–7	0.658	0.591	0.637	0.568
9	1.110	1.057	1.120	1.063	7–8	0.621	0.686	0.641	0.705
10	0.937	0.971	0.909	0.958	8–9	0.488	0.406	0.479	0.401
11	1.124	1.118	1.129	1.120	8–12	0.423	0.408	0.389	0.376
12	1.119	1.069	1.082	1.032	9–10	0.771	0.568	0.774	0.565
13		0.993		0.998	10–11	0.474	0.413	0.458	0.403
14		1.025		1.026	11–12	0.637	0.687	0.636	0.684
15		0.993		1.000	2–13		0.594		0.570
16		1.013		1.015	13–14		0.701		0.709
17		0.993		0.998	14–15		0.624		0.618
18		1.025		1.026	15–16		0.702		0.704
19		0.993		0.986	1–16		0.595		0.593
20		1.013		1.013	9–17		0.594		0.599
					17–18		0.701		0.696
					18–19		0.624		0.628
					19–20		0.702		0.696
					10–20		0.595		0.601

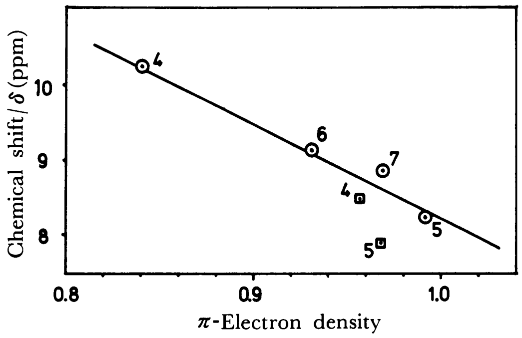
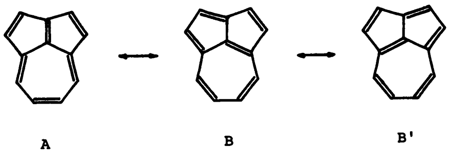


Fig. 1. Plots of chemical shifts of the non-benzenoid hydrogens *vs.* the calculated π-electron densities. ☐: Hydrocarbon **1b**, ⊙: azepinium salt **3b**.



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