Molecular Structures, Electronic Spectra, and Aromaticity of 1,6- and 1,8-Dioxa Analogues of Pyrene and Benzo[a]pyrene. Semiempirical Molecular Orbital Calculations

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The molecular structures of [1]benzopyrano[6,5,4-*def*][1]benzopyran, [2]benzopyrano[7,8,1-*def*]-1-benzopyran, 1-benzopyrano[6,5,4-*mna*]xanthene, and 2-benzopyrano[7,8,1-*mna*]xanthene have been optimized by using the PM3 semiemperical MO method. These calculated molecules have been shown to be planar. Their aromaticity has been investigated by use of the HOMA index. The molecules are found to be less aromatic than the corresponding parent hydrocarbons, pyrene and benzo[a]pyrene. The CNDO/S MO method has been used to interpret the experimental uv-vis spectroscopic data. The results of the PM3, CNDO/S and HOMA-index calculations are in good agreement with the experimental data.

Introduction.

Recently, Buisson and Demerseman [1-3] have first succeeded in preparing the unsubstituted dioxa analogues of pyrene and benzo[a]pyrene: [1]benzopyrano[6,5,4-*def*][1]benzopyran (1,6-dioxapyrene, **1**), [2]benzopyrano[7,8,1-*def*]-1-benzopyran (1,8-dioxapyrene, **2**), 1-benzopyrano[6,5,4-*mna*]xanthene (1,6-dioxabenzo[a]pyrene, **3**). They have accomplished spectroscopic studies of **1-3**. On the basis of the ^{1}H and ^{13}C nmr spectra of **1-3**, Platzer, Buisson and Demerseman [2-4] have discussed the aromaticity of these molecules. The X-ray structural analysis of **1** [5] has shown that the geometric structure of **1** is fairly different from that of pyrene. The electronic spectra of **1-3** also have been reported [2,3]. However, no interpretation of the electronic spectra has been reported nor has structural data on **2** and **3** been provided. This lack of information led us to examine the molecular structures and electronic spectra of **1-3** by the use of semiempirical MO methods. We also examined the 1,8-isomer of **3**, 2-benzopyrano[7,8,1-*mna*]xanthene (**4**), which has not yet been synthesized. Furthermore, we investigated the aromaticity of **1-4** by using the HOMA index.

Computational Methods.

The calculations reported were obtained by the MOPAC 93 Program [6]. Full geometry optimizations were performed by using the PM3 method [7,8]. No symmetry constraints were imposed. The ground-state structure was minimized until a gradient norm of less than 0.01 kcal mol^{-1} Å^{-1} was achieved. The optimized structures were also checked by frequency calculations to confirm that they are minimal. To calculate the electronic spectrum, the CNDO/S method [9-11] was used. One hundred single excitations were considered. All calculations in this work were carried out with the use of the Silicon graphics (SGI), IRIS INDIGO/ELAN and IBM, RS/6000 model 590.

Results and Discussion.

Calculated Structure.

The calculated skeletal C-C and C-O bond lengths of **1-4** are summarized in Figure 1. These molecules are found to be planar: **1** belongs to C_{2h}, **2** to C_{2v}, and **3** and **4** to C_s.

The results show that **1** has the localization of a double-like C-C bond adjacent to a C-O bond. The C-O bond lengths are 1.370 and 1.389 Å, which indicates the bonds to be like single bonds because a single C-O bond is estimated to be 1.395 or 1.410 Å from the bond-order bond-length relationship [12,13]. These structual features agree with the experimental data shown in Figure 1. The presence of C-C bonds with double bond character and single C-O bonds disrupts the delocalization of π-electrons. Similar features are seen in **2**: there are two double bond-like C-C bonds and the four single bond-like C-O bonds. On the other hand, **3** has a benzene-like region and one C-C bond has double bond-like character adjacent to a C-O bond that does not connect to the benzene-like region. Molecule **4** has a similar structure. These structural features influence the aromaticity of compound **1-4**. We then considered the aromaticity of these molecules.

Aromaticity.

The concept of aromaticity is considered one of the most important concepts for the understanding of heterocyclic chemistry [14]. During the last decade, the concept of heteroaromaticity has been fully discussed; the most recent review has been reported by Simkin, Minkin and Glukhovtsev [14]. These authors concluded that although there were no general parameters to give a quantitative scale of aromaticity, geometrical criteria may be used to evaluate quantitative variation of aromaticity. Among them, the HOMA index proposed by Krygowski [15-17] has been successfully used in describing the aromatic character of various π systems: alternant and nonalternant hydrocarbons [15], fullerenes [15], five- and six-membered heterocycles [16] and aza analogues of benzenoid hydrocarbons [17].

Therefore, we use the HOMA index presently in examining the aromatic character of **1-4**.

The HOMA index reads [15,16]:

$$HOMA = 1 - EN - GEO. \qquad (1)$$

In equation (1), $GEO = (\alpha/n)\Sigma(R_{av}/\text{Å} - R_i\text{Å})^2$, and

$$EN = \begin{cases} \alpha(1.388 - R_{av}/\text{Å})^2, \text{ for } R_{av}/\text{Å} > 1.388 \\ -\alpha(1.388 - R_{av}/\text{Å})^2, \text{ for } R_{av}/\text{Å} < 1.388, \end{cases}$$

where $\alpha = 257.7$, and n is the number of skeletal bonds. The GEO term indicates the degree of bond alternation, whereas the EN term indicates the loss of stability, related to the resonance energy [18]. These terms are measures of the dearomatization [15-18].

Table 1 lists the aromaticity indices, HOMA, EN, and GEO of **1-4** as well as their parent hydrocarbons, pyrene and benzo[a]pyrene. When calculating their indices, we used the molecular geometries given with the PM3 calculations.

In Table 1 it is shown that **1** and **2** are less aromatic than pyrene. The dearomatization in **1** and **2** is due mainly to the GEO term; the EN term is less important. Similar results are seen in **3** and **4**. The HOMA values of both the molecules are smaller than that of benzo[a]pyrene. These results agree with the nmr data given by Buisson and Demerseman's group [1-4].

Table 1
Aromaticity Indices (HOMA, EN, and GEO) for **1-4**

Molecule	HOMA	EN	GEO
pyrene	0.741	0.083	0.176
1	0.322	0.232	0.446
	(0.221) [a]	(0.125)	(0.654)
2	0.323	0.232	0.445
benzo[a]pyrene	0.714	0.093	0.193
3	0.456	0.202	0.341
4	0.458	0.202	0.340

[a] The values for the observed structure, see reference [5].

It turns out that in these molecules the substitution of carbon atoms by oxygen atoms reduces the aromaticity of their parent hydrocarbons, pyrene and benzo[a]pyrene. This is in contrast to the results for the substitution by nitrogen atoms. Cyrański and Krygowski [17] have shown that aza analogues of benzenoid hydrocarbons are usually more aromatic than their parent hydrocarbons. That is, the introduction of nitrogen atoms increases the aromaticity of parent hydrocarbons.

The HOMA index has been used also for examining the aromaticity of individual rings in conjugated molecules [15-17]. The aromaticity indices HOMA and its components EN and GEO for individual rings of **1-4** are summa-

rized in Figure 2. For comparison the results for pyrene and benzo[a]pyrene are also given.

In **1** and **2**, the rings with an oxygen atom have smaller values for the HOMA indices than the corresponding pyrene rings. In contrast, the neighboring C-C rings have larger HOMA indices than the corresponding pyrene rings. Similar results are found for **3** and **4**: the O-substituted rings exhibit smaller HOMA indices wheras the neighboring C-C rings show larger HOMA indices. In the 1-substituted ring, the decrease in aromaticity is due mainly to the EN term. In the 6- or 8-substituted rings, both EN and GEO terms contribute to the decrease in aromaticity to a similar extent.

Cyrański and Krygowski [17] have found that in aza analogues of benzenoid hydrocarbons, an increase in aromatic character appears not only in the ring which contains nitrogen atoms but also in the closest neighboring rings. In **1-4**, however, the aromaticity of the O-substituted rings decreases whereas that of the neighboring C-C rings increases.

Electronic Spectra.

To discuss the excited states of **1-4**, we carried out CNDO/S calculations. When calculating the electronic spectra, we used the molecular structures obtained by the PM3 method (Figure 1). In Tables 2-5 are presented the calculated transition energies and intensities for comparison with available experimental data [2,3]. The calculated spectra are in good agreement with the observed spectra. The observed absorption peaks can be adequately accounted for by using the calculated singlet transitions. In **1**, the lowest absorption band observed is located at the energy region of about 3 eV. It can be assigned to two transitions of B_u symmetry. The next lowest absorption band is located at 5.51 eV and can be assigned to the transition of B_u symmetry. For **2**, the lowest absorption peak (2.62 eV) observed corresponds to the transition of B_2 symmetry. The strong peak observed at 5.66 eV can be assigned to the A_1 transition. The calculations suggest that the lowest absorption band observed for **3** is composed of the three transitions of A' symmetry.

Table 2
Calculated Singlet Transition Energies (ΔE) and Intensities (f) for **1**

transition symmetry	ΔE/ev	theoretical f		experimental [a] ΔE/eV (log ε)
A_g	2.95	forbidden	$(\pi \to \pi^*)$	
B_u	3.04	0.1432	$(\pi \to \pi^*)$	2.97 (3.75), 3.14 (3.75)
B_u	3.33	0.3832	$(\pi \to \pi^*)$	3.44 (4.03)
B_u	4.22	0.1492	$(\pi \to \pi^*)$	
A_g	4.85	forbidden	$(\pi \to \pi^*)$	
A_g	5.11	forbidden	$(\pi \to \pi^*)$	
A_g	5.24	forbidden	$(\pi \to \pi^*)$	
B_u	5.31	0.3418	$(\pi \to \pi^*)$	5.51 (4.59)
B_u	5.58	0.5461	$(\pi \to \pi^*)$	

[a] Reference [2].

Table 3

Calculated Singlet Transition Energies (ΔE) and Intensities (f) for **2**

transition symmetry	theoretical $\Delta E/eV$	f		experimental [a] $\Delta E/eV$ (log ε)
B_2	2.87	0.1549	$(\pi \rightarrow \pi^*)$	2.62 (3.57)
A_1	3.07	0.0915	$(\pi \rightarrow \pi^*)$	2.82 (3.76),
				3.02 (3.90),
				3.20 (3.79)
B_2	3.42	0.2553	$(\pi \rightarrow \pi^*)$	3.60 (3.71),
				3.73 (3.69)
A_1	4.12	0.1475	$(\pi \rightarrow \pi^*)$	
A_1	4.93	0.0440	$(\pi \rightarrow \pi^*)$	
A_1	5.23	0.2119	$(\pi \rightarrow \pi^*)$	
B_2	5.23	0.0033	$(\pi \rightarrow \pi^*)$	
B_2	5.38	0.1714	$(\pi \rightarrow \pi^*)$	
A_1	5.42	0.1923	$(\pi \rightarrow \pi^*)$	
B_2	5.57	0.0829	$(\pi \rightarrow \pi^*)$	
A_1	5.68	0.6450	$(\pi \rightarrow \pi^*)$	5.66 (4.62)

[a] Reference [2].

Table 4

Calculated Singlet Transition Energies (ΔE) and Intensities (f) for **3**

transition symmetry	theoretical $\Delta E/eV$	f		experimental [a] $\Delta E/eV$ (log ε)
A'	3.08	0.0067	$(\pi \rightarrow \pi^*)$	2.85 (3.47)
A'	3.12	0.2986	$(\pi \rightarrow \pi^*)$	3.05 (4.03)
A'	3.32	0.3858	$(\pi \rightarrow \pi^*)$	3.25 (4.14)
A'	4.04	0.0105	$(\pi \rightarrow \pi^*)$	
A'	4.19	0.1124	$(\pi \rightarrow \pi^*)$	
A'	4.84	0.0278	$(\pi \rightarrow \pi^*)$	
A'	4.98	0.0330	$(\pi \rightarrow \pi^*)$	
A'	5.07	0.2318	$(\pi \rightarrow \pi^*)$	
A'	5.18	0.0508	$(\pi \rightarrow \pi^*)$	
A'	5.33	0.3908	$(\pi \rightarrow \pi^*)$	
A'	5.40	0.1793	$(\pi \rightarrow \pi^*)$	
A'	5.60	0.3121	$(\pi \rightarrow \pi^*)$	5.53 (4.72)
A'	5.68	0.0768	$(\pi \rightarrow \pi^*)$	
A'	5.75	0.5986	$(\pi \rightarrow \pi^*)$	
A'	5.85	0.0820	$(\pi \rightarrow \pi^*)$	
A"	5.85	0.0000	$(n \rightarrow \pi^*)$	
A'	5.89	0.8116	$(\pi \rightarrow \pi^*)$	5.99 (4.74)
A'	6.08	0.5511	$(\pi \rightarrow \pi^*)$	

[a] Reference [3].

Table 5

Calculated Singlet Transition Energies (ΔE) and Intensities (f) for **4**

transition symmetry	theoretical $\Delta E/eV$	f	
A'	2.94	0.3002	$(\pi \rightarrow \pi^*)$
A'	3.17	0.1175	$(\pi \rightarrow \pi^*)$
A'	3.46	0.2492	$(\pi \rightarrow \pi^*)$
A'	4.02	0.0157	$(\pi \rightarrow \pi^*)$
A'	4.11	0.0899	$(\pi \rightarrow \pi^*)$
A'	4.86	0.1411	$(\pi \rightarrow \pi^*)$
A'	4.99	0.1993	$(\pi \rightarrow \pi^*)$
A'	5.10	0.0062	$(\pi \rightarrow \pi^*)$
A'	5.15	0.0682	$(\pi \rightarrow \pi^*)$
A'	5.29	0.3284	$(\pi \rightarrow \pi^*)$
A'	5.43	0.4379	$(\pi \rightarrow \pi^*)$

Table 5 (continued)

transition symmetry	theoretical DE/eV	f	
A'	5.54	0.3827	$(\pi \rightarrow \pi^*)$
A'	5.61	0.0250	$(\pi \rightarrow \pi^*)$
A'	5.73	0.4419	$(\pi \rightarrow \pi^*)$
A"	5.80	0.0000	$(n \rightarrow \pi^*)$
A'	5.86	0.0729	$(\pi \rightarrow \pi^*)$
A"	5.89	0.0000	$(n \rightarrow \pi^*)$
A'	6.00	0.3456	$(\pi \rightarrow \pi^*)$
A'	6.11	0.3653	$(\pi \rightarrow \pi^*)$

Figure 1. Predicted skeletal-bond lengths of **1-4** (Å); the values in parentheses are the observed bond lengths.

In this way, the observed absorption peaks of **1-3** can be interpreted by the theoretical transition energies. For **4**, there are no experimental data for comparison with the theoretical values at present. In this molecule, however, the lowest absorption band is predicted to be located at about 3 eV and composed of the three A' transitions.

Conclusion.

The geometrical structures, aromaticity and electronic spectra of **1-4** have been investigated by the use of semi-empirical PM3 and CNDO/S methods and the HOMA index. The results are compared with experimental structural data and the observed electronic spectra. The PM3
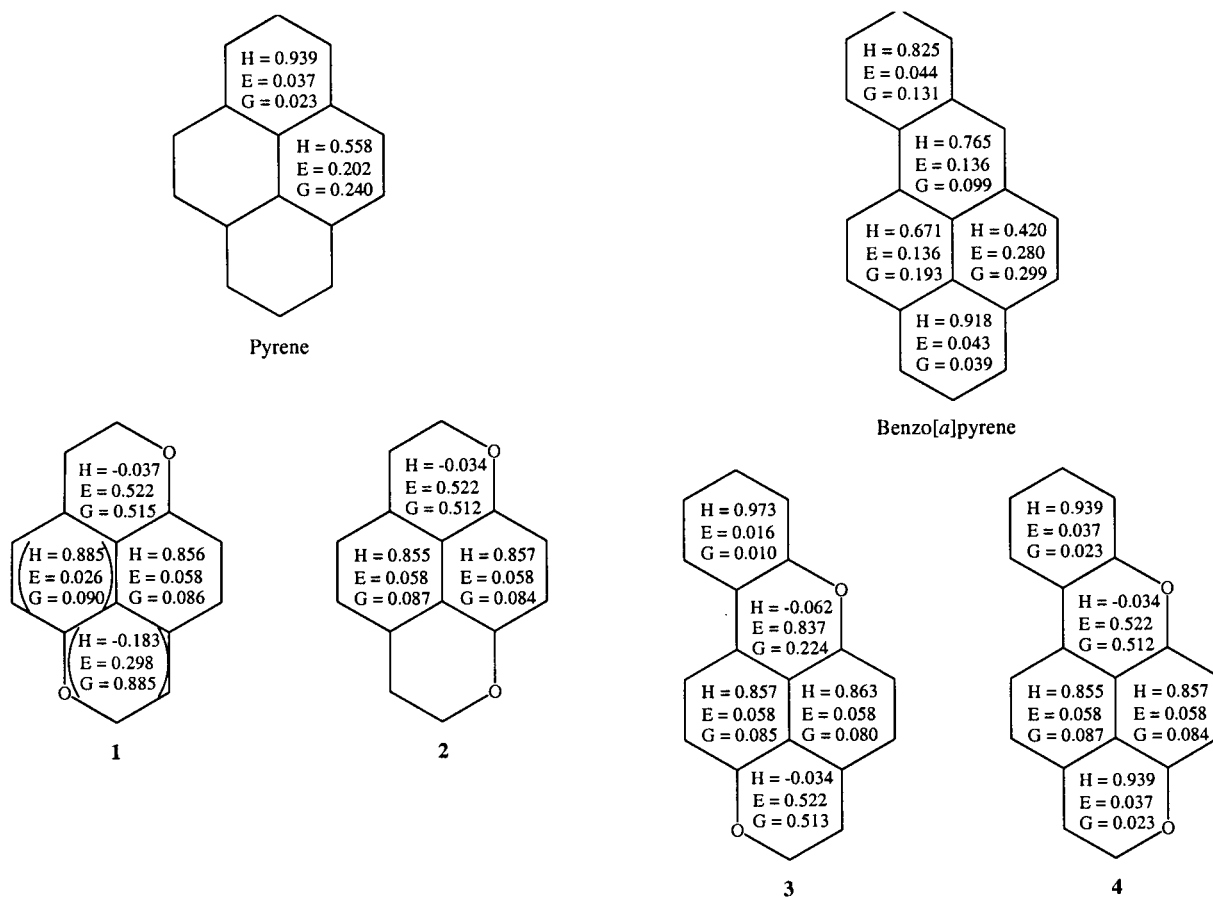
Figure 2. HOMA (H), EN (E), and GEO (G) indices of the individual rings of 1-4, pyrene, and benzo[a]pyrene; the values in parentheses are those of the observed structure.

calculations show that ring systems **1-4** have planar structures. The observed electronic spectra of **1-3** have been satisfactorily interpreted by use of the results of the CNDO/S calculations.

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