suggest caution in the use of rose bengal for photophysical experiments in view of the various structural isomers available to the molecule in differing environments. Each of these structural isomers may have different excited-state characteristics for they have obviously different spectra.

Rose bengal (**1**) was heated in DMF with 1.5 equiv of benzyl chloride as a model for the reaction with chloromethylated polystyrene/divinylbenzene. We demonstrate below that the benzyl ester **2** was produced (Scheme I). When repeated with 2.5 equiv of benzyl chloride in an attempt to convert both the carboxylate and the phenolate centers of **1** into an ester and an ether, respectively, the reaction led to the same deep purple product, **2**, which was insoluble in CH_2Cl_2. The absorption spectrum of **2** in MeOH had the same shape as that of **1** with a small red shift of the absorption maximum, and the IR of **2** was that of an ester (1730 cm^{-1}) (Table I, Figure 1). Elemental analysis indicated the incorporation of only one benzyl group in both experiments.

The reaction of benzyl chloride and rose bengal in acetone/water (50:50) afforded a bright orange-red product **3**, which was soluble in CH_2Cl_2, leading to a solution of the same color.[11] A solution of **3** in MeOH, however, had a distinctly different deep red color. The IR spectrum of **3** showed an OH stretch at 3410 cm^{-1} suggesting deprotonation of the phenolate function. The absorption spectrum in MeOH of both **2** and **3** was the same, whereas the spectrum of **3** in CH_2Cl_2 was totally different (Figure 1).

It has been reported repeatedly that the planes of the 2′-carboxyphenyl group and of the xanthene moiety of fluorescein dyes are perpendicular to one another and that the latter is largely responsible for the absorption characteristics of the molecule in the visible region.[7h,n,o,s] Therefore, it was concluded that upon a change of solvent from MeOH to CH_2Cl_2 a major change takes place in the xanthene portion of **3**. The benzyl ester of rose bengal has a protonated phenol group under the latter conditions, the protonation being due to the hydrochloric acid formed from partial hydrolysis of benzyl chloride in the aqueous solvent in which the reaction was carried out. While **3** is soluble in CH_2Cl_2, its monosodium salt, **2**, is not. When **3** is dissolved in a more polar solvent, MeOH, the phenolic OH bond dissociates. Additional structural proof was obtained by the addition of a few drops of HCl to either a solution of **2** or **3** in MeOH. The absorption spectrum of the resulting solution was the same as that of a solution of **3** in CH_2Cl_2. The acidity of the phenolic proton and the solvent dependence of the structure of **3** might interfere with its effectiveness as a singlet oxygen sensitizer, especially in the synthesis of acid-sensitive hydroperoxides.

In order to block the phenolate function, an attempt was made to prepare the 6-*O*- acetyl derivative of **3** by refluxing with acetic anhydride. Surprisingly, this reaction did not yield the expected orange-red 6-*O*-acetyl rose bengal benzyl ester, **4**, but the colorless diacetyl derivative of the lactonic form of rose bengal, **8** (IR band at 1780 cm^{-1}). Its structure was also firmly established by independent synthesis from **1** via the lactonic modification of rose bengal, **7**.[12] Both **7** and **8** are colorless compounds soluble in CH_2Cl_2 with no absorption in the visible region and no absorption for **8** in MeOH. The absorption spectrum of **7** in MeOH, however, is the same as that of **1** indicating complete dissociation with accompanying conversion to the quinoid modification. We suggest that **8** is formed instead of **4** as a consequence of the highly polarized character of the C–O bond in the benzyl ester. After the introduction of the first acetyl function at the 6-O position, the 3-O attacks acetic anhydride aided by an electron push caused by attack of the ester oxygen on the slightly positively polarized C(9). This forces elimination of the benzyl cation.

In a slightly different approach, **1** was converted to its ethyl ester **5**, which has a less polarized C–O bond.[13] Refluxing with acetic anhydride yielded the bright red colored 6-*O*-acetyl rose bengal ethyl ester, **6** (1780 and 1730 cm^{-1} for acetyl and carboxylate esters, respectively).[14] The absorption spectrum of **6** is the same in MeOH and in CH_2Cl_2. The evolution of the spectra of **1**–**6** with structure resembles that observed for the ionization of eosin.[7q] Furthermore, a 6-O monoester of fluorescein described recently had an absorption spectrum similar to **8**, though shifted to shorter wavelengths.[15]

The work presented above shows the elusive structural nature of rose bengal and the dependence of its structure on subtle changes of environment. The close relationship between the dissociation state of the xanthene moiety of rose bengal and the appearance of the absorption spectrum has been clearly established.

Preliminary experiments have shown that **6** is a useful singlet oxygen sensitizer. Our work is continuing with an investigation of the experimentally discernable differences in the photochemistry of the structurally modified rose bengal derivatives.[16]

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work.

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(12) Compound **7** was prepared by dropwise addition of concentrated HCl to an aqueous solution of **1**. Then, **8** was prepared by refluxing **7** with acetic anhydride.

(13) Synthesis of **5** by refluxing a solution of **1** with 5 equiv of ethyl iodide in acetone/water 50% v/v. When a smaller excess of EtI is used a $\nu_{C=O}$ corresponding to a lactone is found in the IR spectrum.

(14) Spectral parameters of **6**: UV–vis λ_{max} (log ϵ) 494 nm (4.03), 395(4.22), λ_{min} (log ϵ) 441 nm (3.87); 80 MHz ^1H NMR ($CDCl_3$, $Me_4Si\delta$, 0.98 (t, CH_3, 3 H, $J = 7.1$ Hz), 2.48 (s, $CH_3C{=}O$, 3 H), 4.01 (q, CH_2, 2 H, $J = 7.1$ Hz), 7.41 (s, 1 H, xanthene H), 7.65 (s, 1 H, xanthene H).

(15) Melhado, L. L.; Peltz, S. W.; Leytus, S. P.; Mangel, W. F. *J. Am. Chem. Soc.* **1982**, *104*, 7299.

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On the Stability of the Polygonal H_n Systems. Simple Models of Aromaticity and Antiaromaticity

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Received June 13, 1983

Aromaticity and antiaromaticity have been the most difficult and the most fascinating subjects in organic chemistry ever since Kekule's intuitive idea in 1865.[1] The Hückel aromaticity rule has played the leading role in the theory of aromaticity[2] providing one a simple method of prediction that in the cyclic conjugate π-electron system such an aromaticity appears if the number of the atoms in the conjugated system is $4n + 2$ whereas antiaromatic unstability dominates if the number is $4n$. The Hückel rule is generally obtained by solving the secular equation consisting of unspecified quantities, α and β, which are called Coulomb and resonance integrals. Although most of aromaticity and antiaromaticity are realized in the π-electron systems, the Hückel secular determinant does not restrict the type of basic atomic orbitals. This suggests that such an effect can be reproduced in the arrangement of hydrogen atoms serving a simple model for energetic analysis of aromaticity or antiaromaticity. Along such a guiding line, we performed an MO theoretical calculation on the system placed as a regular polygons.

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(1) Kekule, A. *Bull. Soc. Chim. Fr.* **1865**, *3*, 98.

(2) (a) Armit, J. W.; Robinson, R. *J. Chem. Soc.* **1925**, 1604. (b) Robinson, R. *Spec. Publ.-Chem. Soc.* **1967**, *No. 21*, p 47.

(3) STO-6G is a code which shows that a Slater-type atomic orbital is simulated by six Gaussian functions (Hehre, W.; Ditchfield, R.; Stewart, R. F.; Pople, J. A. *J. Chem. Phys.* **1970**, *52*, 2769).

(4) (Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 650) In the 6-311G** method the 1s orbital of hydrogen is expressed by three groups of Gaussian functions with different orbital exponents plus p-type functions called polarization functions.

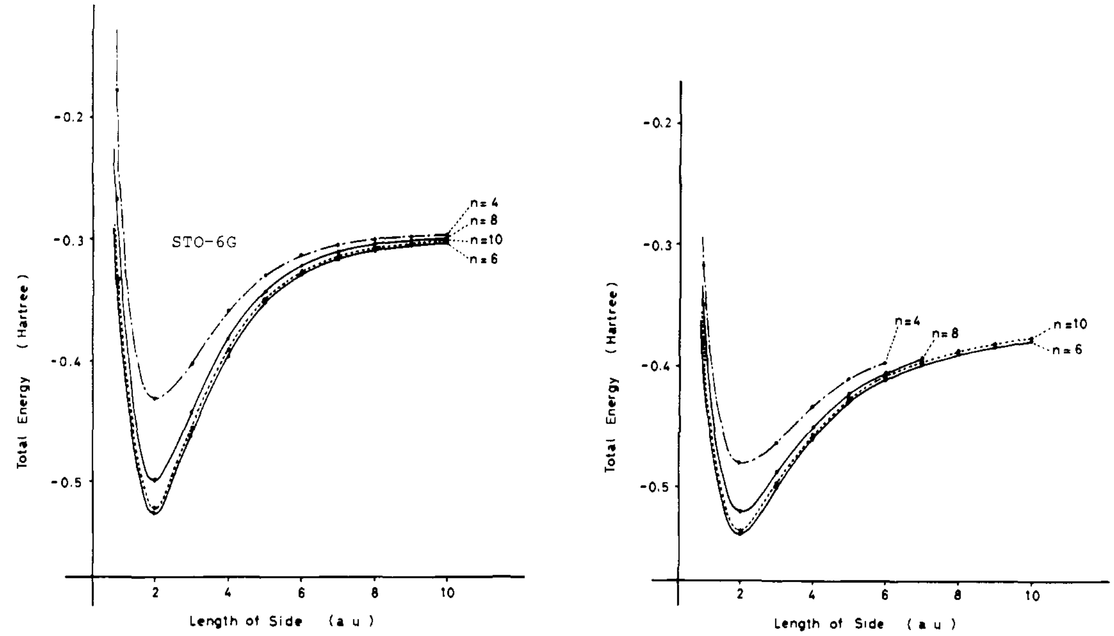

Figure 1. Total energies per atom of polygonal H_n system (n = 4, 6, 8, and 10) by STO-6G and 6-311G** methods.

Table I. The Total and Partitioned Energies of the Optimized *Dnh* Hydrogen Systems (STO-6G)[a]

		H_4	H_6	H_8	H_{10}
R, Å		1.1161	0.9553	0.9997	0.9455
E^V	dia	−2.22461	−2.23344	−2.63824	−2.66671
	nondia other	−0.01929	−0.28319	−0.26854	−0.42369
	peri	−0.24072	−0.66146	−0.53350	−0.72999
	total	−2.48462	−3.17809	−3.44028	−3.82038
E^J	dia	0.64105	0.71223	0.88869	0.93137
	nondia other	−0.01215	0.07802	0.07861	0.13877
	peri	0.06492	0.20162	0.17551	0.24907
	total	0.69382	0.99187	1.14280	1.31920
E^T	dia	0.68284	0.53279	0.58281	0.52984
	nondia other	0.01677	0.05806	0.04236	0.05706
	peri	0.01787	0.05283	0.03642	0.04958
	total	0.71748	0.64367	0.66159	0.63648
E	dia	−0.90072	−0.98843	−1.16674	−1.20550
	nondia other	0.39002	0.58813	0.72405	0.82829
	peri	0.07913	−0.13005	−0.05693	−0.15151
	total	−0.43157	−0.53035	−0.49961	−0.52872

[a] Energies are expressed per atom in terms of Hartree.

Method. As MO methods, we adopted the STO-6G[3] and 6-311G**[4] methods.[5] In order to obtain qualitative energetic pictures inside the system the total energy (E) was expressed as a sum of monocentric (E_A) and bicentric (E_{AB}) terms,[6]

$$E = \sum_{A} E_A + \sum_{A>B} E_{AB} \tag{1}$$

These terms were further partitioned into one-electron potential energies (E_A^V, E_{AB}^V), two-electron potential energies (E_A^J, E_{AB}^J), kinetic energies (E_A^T, E_{AB}^T), and nuclear repulsion energy (E_{AB}^N) as

$$E_A = E_A^V + E_A^J + E_A^T \tag{2}$$

$$E_{AB} = E_{AB}^V + E_{AB}^J + E_{AB}^T + E_{AB}^N \tag{3}$$

Results and Discussion. Figure 1 shows the changes of total energy per atom with respect to the side (R) of the *Dnh* polygonal structures, where the units in energy and length are expressed in terms of atomic unit (au). Both STO-6G and 6-311G** methods give the similar results indicating little influences of split valence and polarization. In all cases, the systems have a minimum energy at R being around 2 au. It is found that when n = 6, the total energy per atom is the lowest, and that when n = 10, the second lowest, reproducing the Hückel rule. Table I shows the partitioned energies (per atom) at the optimized structures by STO-6G within the restriction of keeping the *Dnh* symmetries, where dia and nondia represent the first and second terms in eq 1, respectively. The nondia term is partitioned into pericyclic interactions (peri for instance, when $n = 4$ $(E_{12} + E_{23} + E_{34} + E_{41})/4$) and other bicentric interactions (other). Energy analysis in Table I shows that relatively low energy in the hexagonal or decagonal system is caused mainly by the pericyclic interaction of one-electron potential energy. It is also worth noting that the kinetic energies on atoms decrease at n being 6 and 10 if compared to those at n being 4 and 8. These observations indicate that in the 6- and 10-membered system, the electrons tend to delocalize between atoms in a pericyclic manner lowering the one-electron potential energy between atoms and the kinetic energy on each atom. The latter may correspond to releasing the *kinetic pressure*[7] on the atom by allowing delocalization between atoms. Since there is not an essential difference between s atomic orbitals in polygonal hydrogen systems and p atomic orbitals, which make the cyclic π-electron system, the results obtained here may represent the behavior of π-electrons in aromatic compounds, and it could be analogously said that the aromaticity in π-electron system essentially parallels the lowering of one-electron potential energy between atoms and relaxation of the *kinetic pressure* on atoms.

Registry No. Atomic hydrogen, 12385-13-6.

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(5) We have used GAUSSIAN80 program (QCPE No. 437, Indiana University, IN) to which new subroutines for energy partitioning were added.

(6) The method of energy partitioning has been used in both semiempirical and ab initio methods. E.g.: (a) Gordon, M. S. *J. Am. Chem. Soc.* **1969**, *91*, 3122. (b) Kollmar, H. *Theor. Chim. Acta* **1978**, *50*, 235.

(7) Feinber, M. J.; Ruedenberg, K. *J. Chem. Phys.* **1971**, *54*, 1495 (where the kinetic pressure is correlated with the Heisenberg's uncertainty principle).