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## Localized Molecular Orbitals for Polyatomic Molecules. 6. Condensed Aromatic Ring Systems

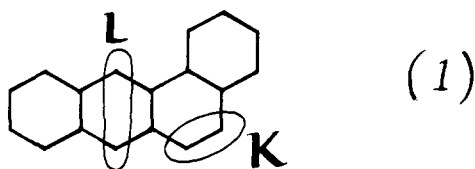
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**Abstract:** Wave functions have been calculated in the approximation of partial retention of diatomic differential overlap (PRDDO) for the molecules naphthalene, anthracene, tetracene, pentacene, phenanthrene, triphenylene, chrysene, benzanthracene, pyrene, 1,2-benzopyrene, and 3,4-benzopyrene. The wave functions are examined in terms of both the canonical molecular orbitals and the localized molecular orbitals obtained using the Boys criterion. Dipole moments for these molecules are presented, along with energy differences for the various isomers. Ionization potentials for the  $\pi$  orbitals are compared with experiment and with those obtained from the simulated ab initio molecular orbital (SAMO) method. The reactivity index most useful for predicting the site of electrophilic attack is the population in the highest occupied molecular orbital. Bond overlap populations are presented and are found to correlate well with the experimental data. Localized molecular orbitals (LMOs) have been obtained for all electrons and for  $\pi$  electrons only. The complete LMOs correspond to Kekulé-type structures with alternating single bonds and pairs of  $\tau$  bonds. Secondary maxima on the LMO hypersurface, found for certain molecules, are related to the Fries rule. A detailed analysis of these LMOs is presented and correlations between bond order and delocalization index are found. The  $\pi$  LMOs are in general two-center bonds that occur between centers which have  $\tau$  bonds in the complete localizations. However, no multiple maxima are observed and the  $\pi$  LMOs tend to be significantly more delocalized than their  $\tau$ -bond counterparts. Three-center  $\pi$  LMOs are found if there are symmetry-related maxima for the complete LMOs.

The approximate molecular orbital method PRDDO<sup>1</sup> (partial retention of diatomic differential overlap) is applied here to several polycyclic aromatic ring systems: benzene, naphthalene, anthracene, tetracene, pentacene, phenanthrene, triphenylene, chrysene, benzanthracene, pyrene, 1,2-benzopyrene, and 3,4-benzopyrene.

One area of biochemical interest is the possible relationship between charge density and carcinogenicity in some of these compounds. Pullman's calculations<sup>2,3</sup> by the Hückel method correlate carcinogenic activity with high  $\pi$ -electron density in the K region, while region L is deactivating, as shown in an example



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and outlined in historical perspective by Herndon.<sup>4</sup> Recent theoretical studies of aromatic hydrocarbons include the use of graph theory<sup>4,5</sup> and of the SAMO (simulated ab initio molecular orbital) method,<sup>6-8</sup> which has given the best previously available wave functions for these molecules. The SAMO studies<sup>6,7</sup> have correlated a high  $\pi$ -bond order in the K region with carcinogenicity but have also indicated that other factors are involved in carcinogenicity. On the experimental side, the recently available photoelectron spectra<sup>9</sup> are particularly relevant to our study.

In this study of 12 aromatic molecules, eigenvalues obtained by the PRDDO method are compared with the photoelectron spectra and with the results of the SAMO method. Also, reactivity predictions<sup>10</sup> are discussed in terms of simple indexes such as group charges, bond overlap populations, HOMO (highest occupied molecular orbital) populations, and total  $\pi$ -orbital populations. In order to analyze the wave functions in simple chemical terms, we have obtained localized molecular orbitals (LMOs)<sup>11</sup> from the Boys criterion<sup>12</sup> using the Edmiston-Ruedenberg procedure<sup>13</sup> for all of the occupied orbitals, and also for the subset of occupied orbitals containing

**Table I.** Comparison of Calculated Properties for Naphthalene

symmetry	Ionization Potentials, eV <sup>a</sup>				
	PRDDO (E) <sup>b</sup>	PRDDO (I) <sup>c</sup>	ab initio	SAMO	expt <sup>d</sup>
a <sub>u</sub>	8.14	7.73	9.30	7.72	8.15
b <sub>1u</sub>	9.01	9.12	10.20	9.62	8.88
b <sub>3g</sub>	10.86	10.94	11.85	11.33	10.08
b <sub>2g</sub>	12.46	12.46	13.51	12.89	10.85
σ	13.36	13.52	14.21	13.76	11.0
b <sub>1u</sub>	15.13	15.26	15.67	14.17 <sup>f</sup>	

atom	Charges <sup>e</sup>			
	charge (E)	charge (I)	group charge (E)	group charge (I)
1	-0.14	-0.13	0.00	0.01
2	-0.15	-0.15	-0.01	-0.01
9	0.03	0.02	0.03	0.02

bond	Bond Properties			
	bond overlap (E)	bond overlap (I)	degree of bonding (E)	degree of bonding (I)
1-2	1.116	1.085	1.63	1.57
1-9	0.967	0.992	1.24	1.28
2-3	0.961	0.988	1.27	1.32
9-10	1.044	1.028	1.35	1.29

<sup>a</sup> Obtained from Koopmans' theorem. <sup>b</sup> E = experimental. <sup>c</sup> I = idealized. <sup>d</sup> Reference 9. <sup>e</sup> Atomic charges in e. Group charges are calculated by adding the charge on a bonded hydrogen to the carbon charge. <sup>f</sup> The SAMO calculation places the b<sub>1u</sub> orbital as the eighth highest occupied orbital while PRDDO and the ab initio calculation place it sixth.

only  $\pi$  electrons. The localizations involving only  $\pi$  electrons are compared to the results obtained by Ruedenberg and co-workers<sup>14</sup> who employed the Edmiston-Ruedenberg energy criterion with modified Hückel wave functions. Finally, we use LMOs and overlap populations to predict bond distortions in going from our idealized geometries to real geometries, and to predict regions of local aromaticity.

**Canonical Molecular Orbitals.** The wave functions were generated from the PRDDO program package<sup>1</sup> using a minimum basis set of Slater orbitals including all electrons. Standard Slater exponents for carbon (1s = 5.70, 2s = 2p = 1.625) were employed while the 1s exponent on hydrogen was set at 1.20. Geometries for all molecules were based on the geometry of benzene; we assumed C-C bond distances of 1.397 Å, C-H bond distances of 1.07 Å, and bond angles of 120°. However, for naphthalene, calculations were performed using both this idealized and the experimental geometry<sup>15</sup> in order to examine the approximations introduced through the use of idealized geometries (Table I). In Table II we report the energy analysis, dipole moments, and computing times for these molecules, and in Table III we present important energy differences. The molecular ionization potentials are given in Table IV, where they are compared with the SAMO results.<sup>6,7</sup> In Table V we report the  $\pi$ -ionization potentials and the onset of the ionization potentials for  $\sigma$  bonds as determined by PRDDO and compare them with the experimental results as determined by photoelectron spectroscopy.

For naphthalene the experimental geometry is 6 kcal/mol more stable than the idealized geometry. The charges for the two geometries are very similar (Table I). The calculated ionization potential for the experimental geometry is in extremely good agreement with experiment. However, the calculated value is too low for the idealized geometry. Comparison of the  $\pi$ -ionization potential obtained with the SAMO method<sup>6,7</sup> and the ab initio results of Buenker and Peyerimhoff<sup>16</sup> is given in Table I. The ionization potential calculated with the

SAMO method<sup>6,7</sup> for the idealized geometry is in good agreement with the PRDDO value. However, since at present the SAMO method<sup>6,7</sup> has been employed only for molecular geometries based on certain pattern molecules, it cannot be used on the experimental geometry. The ionization potential calculated by Buenker and Peyerimhoff<sup>16</sup> for the experimental geometry is too large by more than 1 eV. Agreement between experiment and PRDDO for the second  $\pi$  ionization potential is also good, but the remaining  $\pi$  and the first  $\sigma$  ionization potentials are calculated as larger than experimental values. More severe electronic changes due to ionization occur for the more deeply embedded orbitals so that Koopmans' theorem<sup>17</sup> is no longer appropriate. Alternatively, the basis sets may be inadequate for these embedded orbitals. The ionization potentials for the two geometries do become more similar as the magnitude increases. The SAMO values are always worse than the PRDDO values and even give the wrong ordering for the final  $\pi$  orbital when compared to both the ab initio and PRDDO results. This result is in contrast to a recent statement<sup>8</sup> which claimed that SAMO eigenvalues are better than PRDDO eigenvalues.

The bond orders for the two PRDDO geometries correlate well. As expected, smaller differences are found for the idealized system because the calculation employing the real geometry properly accentuates the differences in the bond orders. Nevertheless, the results for naphthalene suggest that the bond orders from idealized geometries of condensed aromatic ring systems can be used to predict the direction in which changes in bond lengths should occur in going to the optimum geometry. The 1-2 bond (and symmetry-related bonds) is the shortest bond as determined by experiment (1.361 Å) and has the highest bond overlap population (1.085). Similarly we predict, in agreement with experiment, that the 1-9 and 2-3 bonds should be longer because they have the smallest bond overlaps (0.992 and 0.988, respectively), while the 9-10 bond should be of intermediate length. Comparison of the degree of bonding<sup>18</sup> over orthogonal atomic orbitals shows that these results are quite similar for the two geometries. A strong 1-2 bond is indicated from the value of 1.57 found for idealized geometry. This bond has substantially more double bond character than that found for a double bond in benzene for which the value is 1.44. However, the values for the degree of bonding for the idealized geometry do not show the 9-10 bond as the next shortest bond as suggested by the experimental geometry. In agreement with the experimental geometry, the degree of bonding does predict the 9-10 bond to have less double bond character than the 1-2 bond and than a C-C bond in benzene. Thus, both overlap populations and degrees of bonding based on ideal geometries give qualitatively correct predictions of changes in bond lengths toward the optimum geometry.

The dipole moments (Table II), as expected for these extended  $\pi$  systems, are small, ranging from 0.11 to 0.16 D. In order to calibrate these results we note that for azulene our calculated dipole moment is 1.73 D while the experimental result is 1.00.<sup>19</sup> Minimum basis set dipole moments are usually too large by a factor of 2. We therefore estimate that the dipole moments for phenanthrene, benzanthracene, 1,2-benzopyrene, and 3,4-benzopyrene are between 0.05 and 0.10 D. Such a small dipole moment is difficult to determine experimentally and, in fact, the dipole moment of phenanthrene<sup>20</sup> is reported to be zero. Our estimated values would lie within the normal experimental errors of  $\pm 0.1$  D.

Important energy differences are reported in Table III. Naphthalene is 58 kcal/mol more stable than azulene at the PRDDO level which is in good agreement with the difference of 50 kcal/mol as determined by Buenker and Peyerimhoff.<sup>16</sup> Both results are quite far from the experimental value of 30 kcal/mol.<sup>21</sup> Such a large error might be expected for this comparison because the ring sizes are quite different. For the

**Table II.** Energetics and Dipole Moments

molecule	Energies					
	energy <sup>a</sup>	nuclear repulsion	kinetic energy	nuclear attraction	electron repulsion energy	computing time, <sup>b</sup> s
benzene	-230.351	203.556	229.016	-940.709	277.786	11
naphthalene	-382.793	461.131	380.688	-1809.000	548.387	39
phenanthrene	-535.246	785.135	532.409	-2810.294	957.504	94
anthracene	-535.233	773.995	532.415	-2788.068	946.425	93
triphenylene	-687.698	1175.569	684.142	-3944.324	1396.913	198
chrysene	-687.696	1154.412	684.137	-3902.113	1375.867	192
benzanthracene	-687.690	1144.805	684.126	-3883.105	1366.384	192
naphthacene	-687.668	1127.285	684.145	-3847.966	1348.867	182
pentacene	-840.104	1512.385	835.869	-4971.434	1783.076	352
pyrene	-610.925	977.412	606.679	-3370.060	1174.043	133
1,2-benzopyrene	-763.380	1391.127	759.414	-4550.657	1636.734	254
3,4-benzopyrene	-763.371	1372.334	759.420	-4513.169	1618.042	244

Dipole Moments <sup>c</sup>	
molecule	$\mu$
phenanthrene	0.11
benzanthracene	0.16
1,2-benzopyrene	0.14
3,4-benzopyrene	0.14

<sup>a</sup> Energies in atomic units. Virial ratio is 1.005 for all molecules. <sup>b</sup> Computing times (IBM 360/91) for convergence criterion of  $10^{-4}$  for the root mean square change of density matrix elements. <sup>c</sup> Dipole moments in debye.

**Table III.** Energy Differences (kcal/mol)

	no. of carbons	$\Delta E(\text{calcd})^a$	$\Delta E(\text{exptl})^{a,b}$
naphthalene	10	0	0
azulene	10	58	30
phenanthrene	14	0	0
anthracene	14	8	7
triphenylene	18	0	0
chrysene	18	1	0.7
benzanthracene	18	5	6.2
naphthacene	18	18	4.6
1,2-benzopyrene	20	0	0
3,4-benzopyrene	20	5	

<sup>a</sup> Energy above the most stable molecule with the same number of carbons. <sup>b</sup> Reference 22.

cases we have examined where the ring sizes are constant, but are fused in different geometries, much better agreement with experiment is found. As shown in Table III, we are within 1 kcal/mol of the experimental differences<sup>22</sup> for all cases except naphthacene, which the experiments find more stable than predicted by theory. Dewar<sup>22</sup> has argued that the combustion experiments are likely to be in error for this molecule and that the experimental heat of atomization is, consequently, too large. For the two isomers of benzopyrene, we find that the 1,2 isomer is 5 kcal/mol more stable than the 3,4 isomer. The SAMO method<sup>6,7</sup> gives a large error for the energy difference between phenanthrene and anthracene. Whereas we find a difference of 8 kcal/mol as compared to the experimental value of 7 kcal/mol, SAMO gives 18 kcal/mol while a version of SAMO corrected for steric effects yields a difference of 62 kcal/mol.

Before discussing the eigenvalue spectrum in detail and comparing it with the photoelectron spectra, we compare the ionization potentials determined by the PRDDO method with the experimental results<sup>9</sup> and with the SAMO results<sup>6,7</sup> as shown in Table IV. For all cases except naphthalene and benzene, the ionization potentials determined by the SAMO method are smaller than the PRDDO values and thus show a

**Table IV.** Ionization Potentials<sup>a</sup>

molecule	PRDDO	SAMO <sup>b</sup>	expt <sup>c</sup>
benzene	9.26	9.8	9.24
naphthalene	7.73	7.7	8.15
phenanthrene	7.65	7.4	7.86
anthracene	6.69	6.3	7.47
triphenylene	7.92		7.89
chrysene	7.24		7.60
benzanthracene	6.88	6.4	7.47
naphthacene	6.01		7.04
pentacene	5.58		6.74
pyrene	6.80	6.5	7.41
1,2-benzopyrene	7.05		7.43
3,4-benzopyrene	6.42	5.9	7.12

<sup>a</sup> Ionization potentials in eV calculated by Koopmans' theorem. <sup>b</sup> Reference 6. <sup>c</sup> Reference 9.

larger error when compared with experiment. The SAMO method gives too large an ionization potential for benzene while the PRDDO and SAMO values are the same for naphthalene as discussed previously. In general, the PRDDO ionization potentials are too low with respect to experiment; the exceptions are benzene and triphenylene, for which the values are slightly greater (0.02–0.03 eV) than experiment. Reasonable agreement with experiment is found for most of the ionization potentials, and qualitative trends in isomeric molecules are well reproduced by PRDDO. The largest differences between PRDDO and experiment occur for the linear arrays of fused rings, anthracene, naphthacene, and pentacene; the deviation from experiment increases with increasing molecular size. For the isomeric benzopyrenes, the error is greater for the 3,4 isomer than for the 1,2 isomer. The less stable isomer has the lower ionization potential.

In Table V we report our calculated eigenvalue spectrum and compare it with the experimental photoelectron  $\pi$  eigenvalue spectrum.<sup>9</sup> We also report the onset of ionization of electrons from the  $\sigma$  orbitals. The agreement for the first few  $\pi$  ionization potentials is usually quite good. However, the first ionization potential is usually too low and all other ionization

Table V. Orbital Energies<sup>a</sup>

molecule	PRDDO			exptl <sup>c</sup>	
	symmetry	orbital <sup>b</sup>	energy	symmetry	energy
benzene ( <i>D</i> <sub>6h</sub> ) <sup>d</sup>	e <sub>1g</sub>	21	9.26	e <sub>1g</sub>	9.3
	σ <sup>e</sup>	19	13.51	σ	11.4
	a <sub>2u</sub>	17	13.92	a <sub>2u</sub>	12.1
naphthalene ( <i>D</i> <sub>2h</sub> ) <sup>g</sup>	a <sub>u</sub>	34	7.73	a <sub>u</sub>	8.15
	b <sub>1u</sub>	33	9.12	b <sub>1u</sub>	8.88
	b <sub>3g</sub>	32	10.94	b <sub>3g</sub>	10.08
	b <sub>2g</sub>	31	12.46	b <sub>2g</sub>	10.85
	σ	30	13.52	σ	11.0
	b <sub>1u</sub>	27	15.26		
anthracene ( <i>D</i> <sub>2h</sub> ) <sup>g</sup>	b <sub>3g</sub>	47	6.69 (6.34) <sup>f</sup>	b <sub>3g</sub>	7.47
	b <sub>2g</sub>	46	8.98 (9.45)	b <sub>2g</sub>	8.57
	a <sub>u</sub>	45	9.58 (9.86)	a <sub>u</sub>	9.23
	b <sub>1u</sub>	44	11.46 (11.83-b <sub>3g</sub> )	b <sub>3g</sub>	10.26
	b <sub>3g</sub>	43	11.51 (12.14-b <sub>1u</sub> )	b <sub>1u</sub>	10.40
	σ	42	13.41 (13.66)	σ	10.8
	b <sub>2g</sub>	40	13.99 (13.90)		
	b <sub>1u</sub>	36	15.70 (14.27)		
phenanthrene ( <i>C</i> <sub>2v</sub> ) <sup>g</sup>	b <sub>2</sub>	47	7.65 (7.43)	b <sub>2</sub>	7.86
	a <sub>2</sub>	46	8.22 (8.29)	a <sub>2</sub>	8.15
	a <sub>2</sub>	45	9.96 (10.57)	a <sub>2</sub>	9.28
	b <sub>2</sub>	44	10.88 (11.37)	b <sub>2</sub>	9.89
	b <sub>2</sub>	43	12.00 (12.42)	b <sub>2</sub>	10.59
	σ	42	13.31 (13.32)	σ	10.60
	a <sub>2</sub>	40	13.90 (13.83)		
	b <sub>2</sub>	36	15.78 (14.29)		
triphenylene ( <i>D</i> <sub>3h</sub> )	e''	60	7.92	e''	7.89
	a <sub>1''</sub>	58	8.84	a <sub>1''</sub>	8.66
	e''	57	10.74	e''	9.68
	a <sub>2''</sub>	55	11.10	a <sub>2''</sub>	10.06
	σ	54	13.25	σ	10.7
	e''	52	14.04		
	a <sub>2''</sub>	45	16.19		
chrysene ( <i>C</i> <sub>2h</sub> )	a <sub>u</sub>	60	7.24	a <sub>u</sub>	7.60
	a <sub>u</sub>	59	8.22	a <sub>u</sub>	8.10
	b <sub>g</sub>	58	8.87	b <sub>g</sub>	8.68
	b <sub>g</sub>	57	10.34	b <sub>g</sub>	9.46
	a <sub>u</sub>	56	10.78	a <sub>u</sub>	9.76
	b <sub>g</sub>	55	12.14	b <sub>g</sub>	10.52
	a <sub>u</sub>	54	12.82	σ	10.6
	σ	53	13.17		
	b <sub>g</sub>	49	14.75		
	a <sub>u</sub>	44	16.08		
benzanthracene ( <i>C</i> <sub>s</sub> )	a''	60	6.88	a''	7.47
	a''	59	8.05	a''	8.05
	a''	58	9.28	a''	8.86
	a''	57	10.12	a''	9.39
	a''	56	11.02	a''	9.95
	a''	55	11.84	a''	10.41
	a''	54	13.03	σ	10.7
	σ	53	13.33		
	a''	49	14.78		
	a''	44	16.00		
naphthacene ( <i>D</i> <sub>2h</sub> ) <sup>g</sup>	a <sub>u</sub>	60	6.01	a <sub>u</sub>	7.04
	b <sub>3g</sub>	59	8.54	b <sub>1u</sub>	8.44
	b <sub>1u</sub>	58	8.90	b <sub>3g</sub>	8.63
	a <sub>u</sub>	57	10.53	a <sub>u</sub>	9.60
	b <sub>2g</sub>	56	10.80	b <sub>2g</sub>	9.75
	b <sub>3g</sub>	55	11.81	b <sub>3g</sub>	10.26
	b <sub>1u</sub>	54	13.03	σ	10.7
	σ	53	13.33		
	b <sub>2g</sub>	48	14.78		
b <sub>1u</sub>	45	15.92			
pentacene ( <i>D</i> <sub>2h</sub> ) <sup>g</sup>	b <sub>3g</sub>	73	5.58	b <sub>3g</sub>	6.74
	a <sub>u</sub>	72	7.75	a <sub>u</sub>	8.03
	b <sub>2g</sub>	71	8.87	b <sub>2g</sub>	8.40
	b <sub>3g</sub>	70	9.66	b <sub>3g</sub>	9.09
	b <sub>1u</sub>	69	10.37	b <sub>1u</sub>	9.49
	a <sub>u</sub>	68	11.07	a <sub>u</sub>	9.88
	b <sub>3g</sub>	67	11.97	b <sub>3g</sub>	10.33
	b <sub>2g</sub>	66	12.30	σ	10.5
	σ	65	13.31		

Table V (continued)

molecule	PRDDO			exptl <sup>c</sup>	
	symmetry	bital <sup>b</sup>	energy	symmetry	energy
pyrene	b <sub>1u</sub>	62	13.99		
	b <sub>2g</sub>	58	15.24		
	b <sub>1u</sub>	54	16.05		
	b <sub>2g</sub>	53	6.80	b <sub>2g</sub>	7.41
	b <sub>3g</sub>	52	8.57	b <sub>3g</sub>	8.26
	b <sub>1u</sub>	51	9.74	b <sub>1u</sub>	9.00
	a <sub>u</sub>	50	10.50	a <sub>u</sub>	9.29
	b <sub>1u</sub>	49	11.24	b <sub>1u</sub>	9.96
	b <sub>2g</sub>	48	13.25	σ	10.59
	σ	47	13.39		
	b <sub>3g</sub>	45	14.12		
	b <sub>1u</sub>	39	16.32		
	1,2-benzopyrene (C <sub>2v</sub> ) <sup>g</sup>	b <sub>2</sub>	66	7.05	b <sub>2</sub>
a <sub>2</sub>		65	8.05	a <sub>2</sub>	8.04
a <sub>2</sub>		64	9.28	a <sub>2</sub>	8.76
b <sub>2</sub>		63	9.52	b <sub>2</sub>	8.91
a <sub>2</sub>		62	11.07	a <sub>2</sub>	9.76
b <sub>2</sub>		61	11.16	b <sub>2</sub>	9.85
b <sub>2</sub>		60	12.22	b <sub>2</sub>	10.51
σ		59	13.17	σ	
a <sub>2</sub>		56	14.23		
b <sub>2</sub>		54	14.58		
b <sub>2</sub>		47	16.49		
3,4-benzopyrene (C <sub>s</sub> )	a''	66	6.42	a''	7.12
	a''	65	8.30	a''	8.00
	a''	64	9.33	a''	8.73
	a''	63	10.34	a''	8.92
	a''	62	10.50	a''	9.49
	a''	61	11.21	a''	9.95
	a''	60	12.98	σ	10.4
	σ	59	13.25		
	a''	58	13.39		
	a''	53	14.94		
	a''	48	16.41		

<sup>a</sup> All energies in eV. <sup>b</sup> Index of occupied molecular orbital with lowest energy orbital at 1. <sup>c</sup> Reference 9. <sup>d</sup> Molecular symmetry designation. <sup>e</sup> Onset of  $\sigma$  bonding. <sup>f</sup> SAMO results from ref 7. <sup>g</sup> In determining the symmetry species for  $D_{2h}$  and  $C_{2v}$  point groups we have used a different convention to define the  $x$  and  $y$  axes compared with the conventions used in ref 7 and 9. We have changed the symmetry designations of ref 7 and 9 to correspond to our convention.

potentials are too high. Koopmans' theorem may be inappropriate for these more deeply imbedded orbitals, or the wave functions may have inadequate basis sets. In general, the  $\sigma$  ionization potentials are 2.5 eV too large. The order for  $\pi$  and  $\sigma$  ionization potentials given by the PRDDO method is generally in agreement with experiment. As shown in Table V, PRDDO predicts that the b<sub>3g</sub> orbital (43) is lower than the b<sub>1u</sub> orbital (44) in anthracene and in naphthalene the b<sub>1u</sub> orbital (58) is lower than the b<sub>3g</sub> orbital (59); the experimental order is reversed. However, these ionization potentials are rather close. Actually, our PRDDO values may be more nearly correct because the photoelectron assignments are based on semiempirical calculations. Another slight difference is found for chrysene, benzantracene, naphthalene, pentacene, pyrene, and 3,4-benzopyrene: one extra  $\pi$  state before the  $\sigma$  onset is found in PRDDO as compared to the photoelectron results. These results suggest that PRDDO is providing a reasonably accurate description of the electrons in these molecules. In particular, the  $\sigma$  and  $\pi$  systems are well treated. On the other hand, semiempirical methods such as extended Hückel theory and MINDO/2 do not treat the  $\sigma$ - $\pi$  problem properly; for example, they predict that the third highest molecular orbital is usually a  $\sigma$ -type orbital in striking disagreement with experiment.

We compare the eigenvalues for phenanthrene and anthracene obtained by SAMO with the PRDDO eigenvalues in Table V. The PRDDO eigenvalues are in general much better than the SAMO results.<sup>7</sup> The SAMO results tend to

compress the  $\pi$  orbitals; for example, in anthracene the lowest lying b<sub>1u</sub> orbital is too close to the adjacent b<sub>2g</sub> orbital. Moreover, there are no interleaving orbitals between them. However, SAMO does give the same ordering of the b<sub>2g</sub> and b<sub>1u</sub> orbitals as given by the experiments.<sup>9</sup> For phenanthrene the lowest lying b<sub>2</sub> orbital is again too close to the adjacent  $\pi$  orbital. Here, only one  $\sigma$  orbital is interleaved as compared with the three found with PRDDO. As these comparisons show, PRDDO does provide a better spectrum of  $\pi$  eigenvalues than does SAMO for these systems.

Some general conclusions can be made regarding the charge distributions for the polycyclic aromatics. Carbon atoms without an attached hydrogen are more positive than those with an attached hydrogen as seen from an examination of inner shell (1s) eigenvalues for carbon atoms and atomic and group charges. Carbon atoms without an attached hydrogen have inner shell eigenvalues that are lower by 0.02 au than those of carbon atoms with attached hydrogens; this splitting is always found. A decrease in the inner shell eigenvalue implies an increase in the positive charge at the nucleus because the 1s electrons are more tightly bound. We do not report inner shell eigenvalues because, except for the above comment, the differences are too small to be chemically meaningful within the accuracy of the calculation. We report group charges in Table VI rather than atomic charges because the Mulliken population analysis tends to make the C-H bonds too polar. The group charge is calculated by adding the Mulliken charges on the carbon atom and hydrogen atom in a given C-H group.

Table VI. Group Charges

molecule	atom <sup>a</sup>	group charge <sup>b</sup>	molecule	atom <sup>a</sup>	group charge <sup>b</sup>
benzene	1	0.00	naphthacene	1	0.00
naphthalene	1	0.01		2	-0.03
	2	-0.01		5	0.01
	9	0.02		13	0.01
phenanthrene	1	0.00		15	0.02
	2	-0.02	pentacene	1	0.00
	3	-0.02		2	-0.03
	4	0.01		5	0.00
	9	-0.01		6	0.00
	11	0.02		15	0.01
	12	0.03		17	0.01
anthracene	1	0.00	pyrene	1	-0.02
	5	0.01		3	-0.01
	7	-0.02		4	-0.03
	11	0.02		11	0.02
triphenylene	1	0.00		15	0.04
	2	-0.03	1,2-benzopyrene	1	-0.02
	13	0.02		3	-0.02
chrysene	1	-0.01		4	-0.04
	2	-0.03		5	0.00
	3	-0.02		6	0.02
	4	0.01		11	0.00
	5	0.00		12	-0.03
	6	-0.02		15	0.02
	13	0.02		16	0.03
	14	0.02		19	0.04
	15	0.03	3,4-benzopyrene	1	-0.02
benzanthracene	1	0.02		2	-0.01
	2	0.02		3	0.02
	3	-0.03		4	0.02
	4	-0.01		5	0.00
	5	-0.02		6	-0.02
	6	-0.02		7	-0.02
	7	0.00		8	-0.01
	8	0.00		9	-0.03
	9	-0.03		10	-0.01
	10	-0.03		11	-0.01
	11	0.00		12	-0.03
	12	0.02		13	-0.03
	13	0.02		14	-0.01
	14	0.02		15	0.02
	15	0.01		16	0.02
	16	0.03		17	0.03
	17	0.02		18	0.01
	18	0.02		19	0.04
				20	0.04

<sup>a</sup> Symmetry unique atom. See Figure 1 for numbering scheme. <sup>b</sup> Charge in e.

Such an approach works well in the boron hydrides and carboranes<sup>10,23,24</sup> where good correlations between 1s eigenvalues and group charges have been found. The group charges are more positive than the respective carbon atomic charges which are in the range -0.11 to -0.15 e. Carbons without attached hydrogens are slightly positive (0.00-0.03 e) while the carbons with hydrogens have slightly negative group charges (0.01 to -0.04 e). Thus the group charges show, as did the 1s eigenvalues, that carbons without hydrogen tend to be more positive than those with hydrogen.

In the carboranes and boron hydrides<sup>10,23,24</sup> sites of electrophilic and nucleophilic attack are well predicted by the static charge distribution as calculated from the 1s eigenvalues and group charges; the positive centers are susceptible to nucleophilic attack, and negative centers are susceptible to electrophilic attack. Criteria of a difference in 1s eigenvalue of 0.02 au (0.54 eV) and a difference of 0.03 e in charge were used in order to differentiate between sites. For predicting sites of electrophilic attack in the benzenoid aromatic systems the differences in charges or inner shell eigenvalues are not large enough for these criteria to be applied. However, an exami-

nation of the charges should show qualitatively whether electrophilic attack is occurring in the most negative regions. De la Mare and Ridd<sup>25</sup> have tabulated the sites of nitration for the various benzenoid hydrocarbons with respect to the reactivity of benzene. For naphthalene the charges are the opposite of the site of attack; C1 is more positive than C2, but electrophilic attack occurs preferentially at C1 an order of magnitude faster. Examination of phenanthrene shows that the dominant site of electrophilic attack C9 is of intermediate negativity while the second site of electrophilic attack is even more positive. For pyrene and 3,4-benzopyrene the dominant sites of electrophilic attack are the most positive of the available sites. In triphenylene, where the two unique sites have the same reactivity, we find a difference of 0.03 e between them. These examples show that reactivity predictions based on charges cannot be used to predict the site of electrophilic attack in these aromatic molecules at this level of calculation.

In order to ascertain whether other possible theoretical indexes of reactivity are useful, we have examined the population distribution of the HOMO. Simple predictions suggest that the carbon with the largest population in the HOMO is the

most susceptible to electrophilic attack. We have reported the populations  $>0.15 e$  in Table VII along with the experimental results given by De la Mare and Ridd.<sup>25</sup> As can be seen from the comparison with experiment, the largest population always correlates with the site for electrophilic attack. In general, the order for electrophilic attack is given reasonably well. However, it is unlikely that the HOMO population can be used to distinguish between sites that differ in population by a few hundredths of an electron. An example is triphenylene, where the sites 1 and 2 have approximately the same experimental reactivity but we predict 2 to be slightly more susceptible. We point out that in the case of the boron hydrides, the eigenvalues of the HOMO are too close to the other eigenvalues, and such predictions based on the population of the HOMO are not useful. For very large aromatics, where the splitting between orbitals may become quite small, these reactivity predictions may fail.

In Table VIII we present bond overlap populations, degrees of bonding, and the experimental bond distances as determined by x-ray diffraction.<sup>26</sup> The interrelating concepts of degrees of bonding, valencies and local anisotropies have been discussed by Armstrong et al.<sup>18</sup> We report neither valencies nor local anisotropies; the valencies are all greater than 3.99 and the magnitude of the local anisotropy is less than 0.01. However, the degrees of bonding are of significant interest as they correlate very well with bond overlap population but show a wider range of values and are thus more useful in making qualitative chemical interpretations. Benzene is the model aromatic compound; the C-C bonds in this molecule have a degree of bonding of 1.44 and a bond overlap population of 1.034 for an experimental bond distance of 1.397 Å. We expect that bonds with bond orders greater than 1.44 would be shorter than 1.40 Å (the bond length employed in these calculations) and should show greater double bond character, while bonds with bond orders less than 1.44 should be longer than 1.40 Å and more like single C-C bonds.

Naphthalene has been previously discussed, and we note that the shortest bond (1-2) has a degree of bonding of 1.57 and a bond length of 1.371 Å. For anthracene the 1-2 bond is the shortest (1.375 Å) and has the largest degree of bonding (1.61) while the two longest bonds (1-11 and 11-12) have the lowest degree of bonding (1.24). For phenanthrene, the longest bond (12-13) with a bond distance of 1.465 Å has the lowest bond order (1.16) while the shortest bond (9-10 at 1.350 Å) has the highest bond order (1.67). In general, where the experimental results are good, the experimental bond lengths correlate well with the degrees of bonding obtained from the idealized structures. Differences occur only for the two structures which are apparently very poorly determined experimentally—benzanthracene and 3,4-benzopyrene. No experimental data are given for 1,2-benzopyrene. The experimental benzanthracene structure has serious deficiencies, and we point out that there are likely to be major errors in the determination of the 1-13, 5-14, 8-18, and 9-10 bonds which are too short while the 4-14, 7-15, 11-17, 3-4, and 17-18 bonds are too long. In 3,4-benzopyrene the 5-18 bond is too short while the 6-7 and 6-18 bonds are too long.

General trends for regions with significant double-bond character have been found for many of these molecules. The bond orders for molecules with bonds like the 9-10 bond in phenanthrene show high bond orders (greater than 1.60), being 1.67 in phenanthrene, 1.63 for the 6-5 and 11-12 bonds in chrysene, and 1.70 for the 5-6 bond in benzanthracene and for the 6-7 bond in 3,4-benzopyrene. We also note that, as found by experiment, the bonds like the 1-2 bonds in all molecules (except the three based on pyrene) also show strong double-bond character. This result is observed from naphthalene through pentacene. Unless there is a 9-10 phenanthrene-like region, these outer bonds tend to have the highest bond orders

Table VII. HOMO Populations and Electrophilic Reactivities

molecule	atom	HOMO population ( $\geq 0.15$ ) <sup>a</sup>	nitration order <sup>b</sup>
benzene	1	0.67 (2)	
naphthalene	1	0.35	1
	2	0.15	2
phenanthrene	9	0.34	9
	1	0.20	1
	3	0.20	3
anthracene	9	0.36	
	1	0.19	
triphenylene	13	0.25 <sup>c</sup>	
	2	0.23	1 <sup>d</sup>
	1	0.19	2 <sup>d</sup>
chrysene	6	0.28	6
	15	0.17 <sup>c</sup>	
	2	0.16	
benzanthracene	7	0.35	7
	12	0.30	
	8	0.20	
	6	0.18	
	11	0.18	
	5	0.16	
naphthacene	9	0.28	
pentacene	6	0.26	
	7	0.20	
	1	0.20	
pyrene	3	0.25	3
	1	0.18	
1,2-benzopyrene	3	0.34	
	1	0.21	
3,4-benzopyrene	5	0.34	5
	10	0.21	
	8	0.18	
	1	0.16	
	6	0.16	
	7	0.16	

<sup>a</sup> Atomic population in the highest occupied molecular orbital in e if  $\geq 0.15 e$ . <sup>b</sup> Reference 25. <sup>c</sup> No hydrogen atoms are connected to this carbon. <sup>d</sup> Comparable reactivity.

in the molecules.

**Localized Molecular Orbitals (LMOs).** The Edmiston-Ruedenberg (ER) localization<sup>13</sup> maximizes the intraorbital self-repulsion energy, while the Boys procedure<sup>11,12</sup> maximizes the sum of squares of distances of the orbital centroids from an arbitrary origin. The ER procedure can yield  $\sigma$ - $\pi$  separations, but the Boys procedure prejudices against them, as shown in the bonds to carbon in 1,2-C<sub>2</sub>B<sub>4</sub>H<sub>6</sub>.<sup>11</sup> However, the Boys method does yield  $\sigma$ - $\pi$  separation in the tropylium ion (C<sub>7</sub>H<sub>7</sub><sup>+</sup>).<sup>27</sup> In carbon systems containing  $\pi$  electrons, Ruedenberg and co-workers<sup>14</sup> used the ER procedure on Hückel-Wheland wave functions, Switkes and Newton<sup>28a</sup> studied LMOs in benzene using the ER procedure on an ab initio wave function, Kleier et al.<sup>27</sup> used the Boys procedure on monocyclic aromatics C<sub>n</sub>H<sub>n</sub> for 4  $\leq n \leq 10$  for which they compared complete and  $\pi$ -only localizations, and von Nissen<sup>28b</sup> used the Boys method on ab initio wave functions for substituted benzenes.

For benzene, localizations of all occupied orbitals yielded<sup>27</sup> Kekulé structures having alternating  $\sigma$  bonds (13% delocalized,<sup>11</sup> sp<sup>1.9</sup> hybrids, bent 2.6°) and pairs of strongly bent  $\tau$  bonds (19% delocalized, sp<sup>3.9</sup> hybrids, bent 53.4°: the angle between the hybrid orbital and the vector joining the nuclei). Populations of these  $\tau$  bonds are 0.93 e on each bonded C, 0.05 e on each adjacent C, and 0.03 e on the far C. The second derivative test (-3.54) indicates<sup>11</sup> a well-determined bonding pattern. By contrast, owing to the molecular symmetry the localizations of only  $\pi$  orbitals are completely indeterminate,<sup>27</sup>

Table VIII. Properties of Carbon Bonds

molecule	bond	bond overlap	degree of bonding	bond distance <sup>a</sup>	molecule	bond	bond overlap	degree of bonding	bond distance <sup>a</sup>
benzene	1-2	1.034	1.44	1.397	naphthalene	1-2	1.104	1.63	1.381
naphthalene	1-2	1.085	1.57	1.371		1-16	0.958	1.22	1.420
	1-9	0.992	1.28	1.422		2-3	0.958	1.26	1.459
	2-3	0.988	1.32	1.412		12-13	1.012	1.32	1.404
	9-10	1.028	1.29	1.420		12-16	1.056	1.42	1.390
anthracene	1-2	1.099	1.61	1.375		13-14	0.986	1.21	1.460
	1-11	0.968	1.24	1.444	pentacene	15-16	0.988	1.21	1.420
	2-3	0.967	1.28	1.418		1-2	1.107	1.63	1.36
	10-11	1.038	1.38	1.405		1-15	0.954	1.21	1.43
	11-12	1.001	1.24	1.433		2-3	0.953	1.25	1.44
phenanthrene	1-2	1.069	1.52	1.386		13-18	1.030	1.36	1.40
	1-11	1.010	1.32	1.423		14-15	1.064	1.44	1.38
	2-3	1.006	1.36	1.394		14-18	1.000	1.30	1.41
	3-4	1.067	1.52	1.401		15-16	0.981	1.20	1.45
	4-12	1.021	1.33	1.409		17-18	0.977	1.19	1.46
	9-10	1.117	1.67	1.350	pyrene	1-2	1.122	1.68	1.367
	10-11	0.950	1.20	1.453		1-11	0.943	1.19	1.438
	11-12	1.043	1.32	1.420		9-10	1.039	1.45	1.395
	12-13	0.953	1.16	1.465		10-11	1.034	1.37	1.406
triphenylene	1-2	1.058	1.49	1.384		11-15	1.022	1.28	1.425
	1-13	1.031	1.35	1.404		15-16	1.000	1.24	1.430
	2-3	1.016	1.39	1.392	1,2-benzopyrene <sup>b</sup>	1-2	1.120	1.68	
	13-14	1.052	1.34	1.411		1-15	0.944	1.19	
	13-18	0.927	1.13	1.469		7-14	1.032	1.36	
chrysene	1-2	1.073	1.54	1.363		7-16	0.923	1.12	
	1-14	1.002	1.30	1.428		8-9	1.027	1.42	
	2-3	0.999	1.35	1.394		8-16	1.054	1.41	
	3-4	1.072	1.53	1.381		9-10	1.048	1.47	
	4-13	1.012	1.31	1.401		10-15	1.025	1.35	
	11-12	1.105	1.63	1.369		12-13	1.017	1.39	
	11-15	0.975	1.24	1.428		13-14	1.055	1.49	
	12-14	0.964	1.22	1.421		15-19	1.030	1.29	
	13-14	1.038	1.31	1.409		16-19	1.028	1.29	
	13-16	0.968	1.19	1.468		19-20	0.983	1.21	
	15-16	1.068	1.38	1.401	3,4-benzopyrene	1-2	1.108	1.64	1.35
benzanthracene	1-2	1.060	1.50	1.40		1-15	0.958	1.22	1.47
	1-13	1.028	1.35	1.32		2-17	0.970	1.23	1.42
	2-3	1.012	1.38	1.43		3-4	1.026	1.29	1.43
	3-4	1.062	1.51	1.45		3-11	1.003	1.29	1.42
	4-14	1.017	1.33	1.48		3-17	0.985	1.22	1.42
	5-6	1.126	1.70	1.34		4-5	0.994	1.28	1.42
	5-14	0.936	1.18	1.37		4-14	0.988	1.27	1.39
	6-15	0.934	1.18	1.44		5-18	1.076	1.47	1.33
	7-15	1.058	1.42	1.50		6-7	1.129	1.70	1.40
	7-18	1.020	1.34	1.42		6-18	0.928	1.17	1.51
	8-9	1.091	1.59	1.26		7-16	0.927	1.17	1.39
	8-18	0.976	1.25	1.36		8-9	1.025	1.41	1.42
	9-10	0.976	1.30	1.35		8-16	1.046	1.40	1.44
	10-11	1.091	1.59	1.38		9-10	1.051	1.48	1.41
	11-17	0.977	1.25	1.55		10-15	1.018	1.34	1.41
	12-17	1.019	1.33	1.39		11-12	1.078	1.55	1.38
	12-16	1.069	1.44	1.30		12-13	0.989	1.33	1.41
	13-14	1.045	1.33	1.43		13-14	1.081	1.56	1.46
	13-16	0.937	1.14	1.60		15-19	1.026	1.29	1.42
	15-16	1.001	1.25	1.49		16-19	1.016	1.27	1.43
	17-18	1.011	1.26	1.53		17-20	1.053	1.34	1.40
						18-20	0.986	1.21	1.44
						19-20	1.002	1.24	1.43

<sup>a</sup> Reference 26. <sup>b</sup> The crystal structure has not yet been determined.

yielding an infinite number of localized structures between the Kekulé (2a) and three-center (2b) structures. In (2b) each three-center bond has approximate populations of  $e/2$ ,  $e$ , and  $e/2$ .

We show our results for LMOs in Figure 1 (all electrons included) and Figure 2 ( $\pi$  electrons only). Sums of squares<sup>11</sup> are given in Table IX, and population analyses of  $\tau$  bonds (all electrons) are listed in Table X, and of  $\pi$  LMOs are given in Table XI.

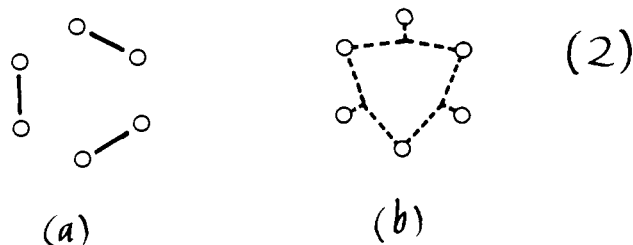




Table IX. Boys Localization Results. The Sum of Squares (SOS)

molecule	primary SOS (full) <sup>a</sup>	$\nu_{\max}^b$	secondary SOS (full) <sup>c</sup>	$\nu_{\max}$	SOS ( $\pi$ ) <sup>d</sup>	$\nu_{\max}$
benzene	183.4	-3.5			9.5	0.0
naphthalene	561.4	-2.2			52.2	-7.6
phenanthrene	1361.9	-2.1	1358.9	-1.3 <sup>e</sup>	156.0	-5.4
anthracene	1537.9	-1.7			180.6	-0.5
triphenylene	2161.7	-1.9	2159.9	-1.5	258.6	-3.3
chrysene	2163.3	-2.1	2159.6	-1.1	260.1	-6.7
benzanthracene	2339.6	-2.0	2337.5	-1.4	284.9	-3.7
naphthacene	2514.9	-1.9			309.1	-2.0
pentacene	4746.7	-3.2			625.0	-1.2
pyrene	1339.5	-1.6			144.3	-1.2
1,2-benzopyrene	2319.3	-1.8	2317.8	-1.5	274.4	-2.4
3,4-benzopyrene	2633.5	-1.8	2632.0	-1.2	321.8	-3.3

<sup>a</sup> Primary SOS corresponds to the value of the dominant structure. See Figure 1. Full implies localization of all electrons. The sum of squared (SOS) distances was computed relative to the following midpoints as origins: benzene (center of molecule), naphthalene (9-10), phenanthrene (11-12), anthracene (11-12), triphenylene (13-14), chrysene (15-16), benzanthracene (15-16), naphthacene (13-14), pentacene (19-20), pyrene (15-16), 1,2-benzopyrene (19-20), 3,4-benzopyrene (19-20). <sup>b</sup>  $\nu_{\max}$  is the highest eigenvalue found in the second derivative test. <sup>c</sup> Secondary SOS corresponds to the value of the secondary structures (see Figure 3). <sup>d</sup> SOS found by localizing only the  $\pi$  orbitals. <sup>e</sup> This value is for structure 3a for phenanthrene. A third structure (3b) has an even lower SOS of 1356.0 with a corresponding  $\nu_{\max}$  of -1.0.

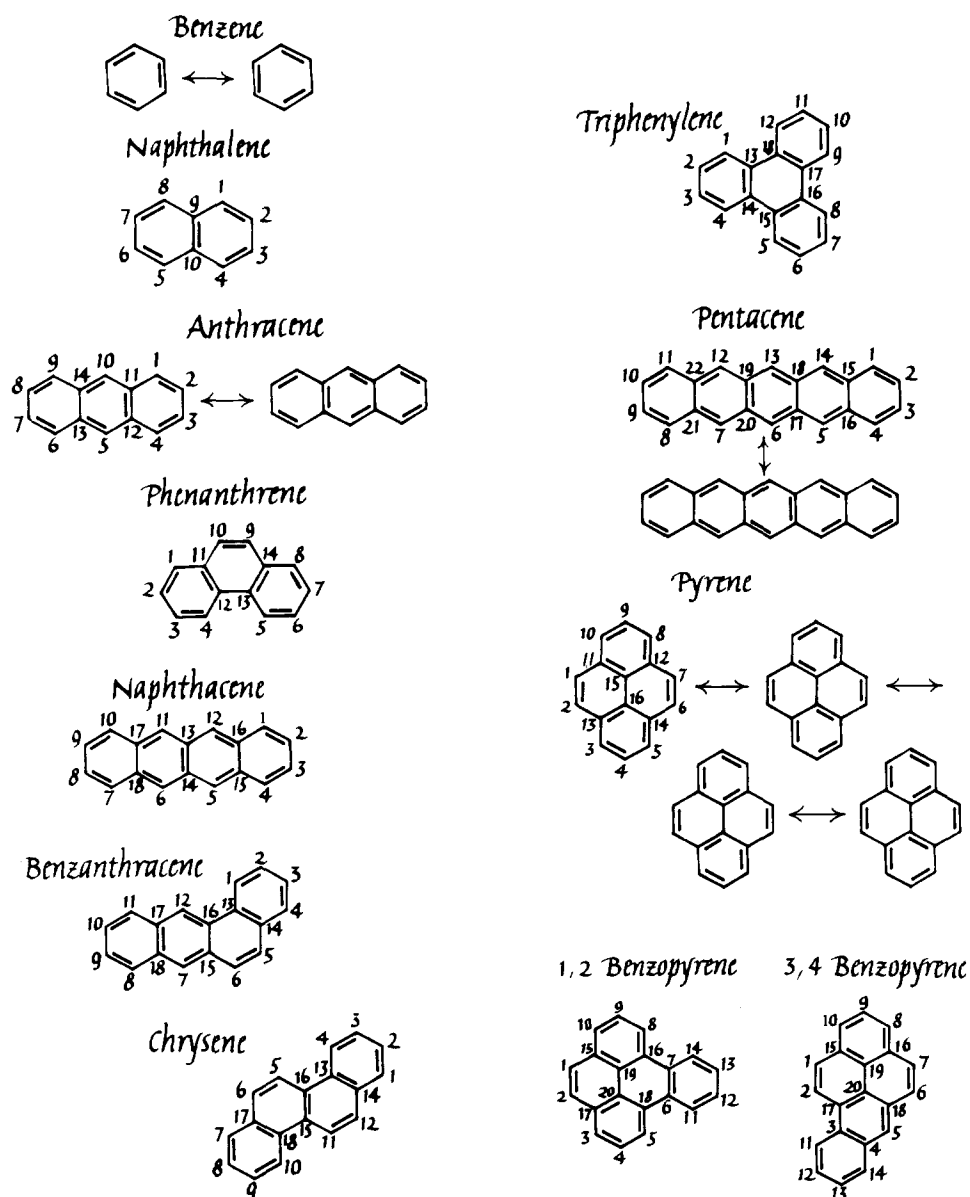
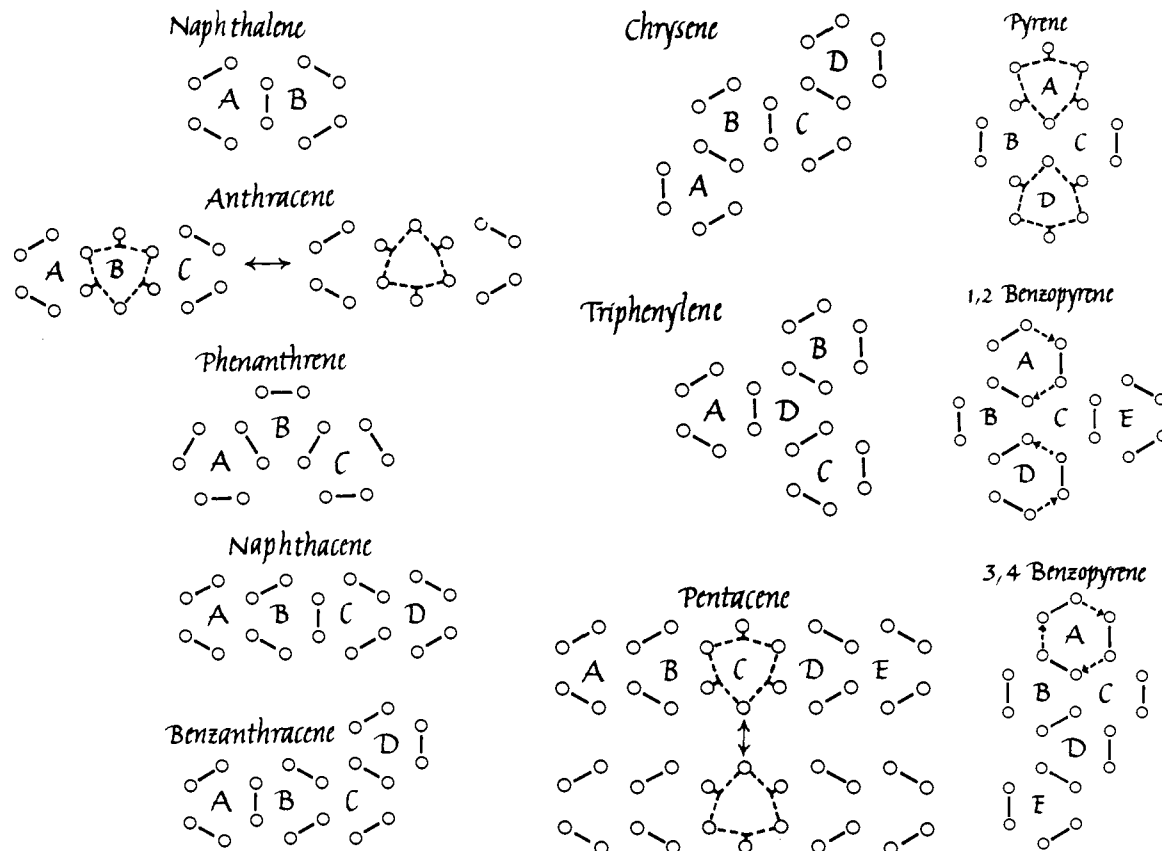
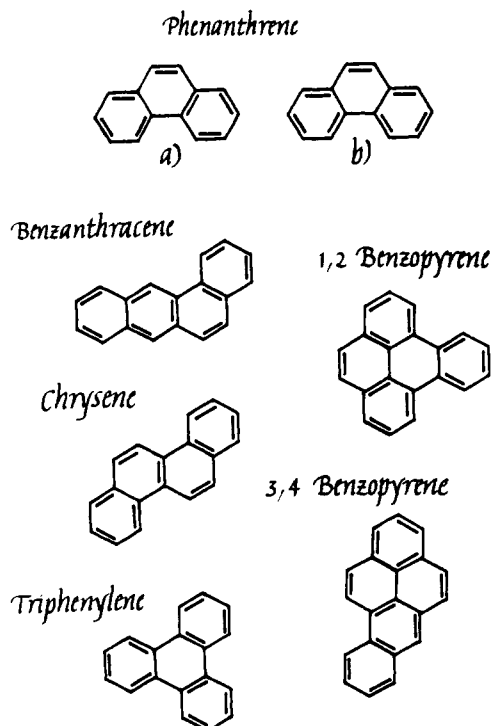


Figure 1. Primary LMOs for localization of all electrons. These are drawn as Kekulé structures. However, the double bonds are not  $\sigma$ - $\pi$  bonds but are equivalent pairs of bent  $\tau$  bonds. The numbering schemes for the paper are also given in this figure.



**Figure 2.** LMOs for  $\pi$ -only localizations. Circles correspond to carbon atoms. Solid lines correspond to two-center  $\pi$  LMOs. The symbol  $\text{---}\text{---}\text{---}$  corresponds to a three-center  $\pi$  LMO with approximately one-half of the density on the central carbon (solid line) and approximately one-quarter of the density on each adjacent carbon (dashed lines). The symbol  $\rightarrow$  in the benzopyrenes shows the direction of significant delocalization of the two-center  $\pi$  LMOs.



**Figure 3.** Secondary LMOs for localization of all electrons. See caption for Figure 1.

For the  $\pi$  localizations, we find (as did England et al.<sup>14</sup>) only one set of LMOs if symmetry equivalence is ignored. Five or more localizations were always carried out from randomized

LMOs in order to search for other maxima. Except for the indeterminant LMOs for benzene for which  $\gamma_{\text{max}}$  (the highest eigenvalue, limited second derivative test LSDT<sup>11</sup>) is zero, all  $\gamma_{\text{max}}$  are negative (Table IX), indicating a local maximum on the LMO hypersurface. These  $\pi$  LMOs are highly delocalized single  $\pi$  bonds between two adjacent centers (cf. diagram 2a). However, for anthracene and pentacene there are two sets of symmetry-related  $\pi$  LMOs which have three-center bonds (cf. diagram 2b), and in pyrene the  $\pi$  LMOs yield a single structure containing three-center bonds. This structure for pyrene is the average of the four sets of two-center bonds found for the full localization (all electrons included). Indeed, all full localizations of these molecules yielded only sets of two-center bonds. For example, in anthracene and pentacene there are two Kekulé structures for the unique center ring in the full localization.

These full localizations often show a complex behavior on the LMO hypersurface, unlike that observed<sup>24</sup> for  $\text{B}_{10}\text{H}_{10}^{2-}$ , where noninterconvertible multiple maxima had the same sum of squares (SOS). Here, the SOSs are significantly different for the different multiple maxima, and those secondary structures (Figure 3) observed for phenanthrene, triphenylene, chrysene, benzanthracene, and the two isomers of benzopyrene are essentially different sets of Kekulé structures. The relationship between the dominant structures (Figure 1), which have the largest SOS, and the secondary structures (Figure 3), which have smaller SOSs (Table IX), is a reorientation of the  $\tau$  bonds within one ring. For example, in phenanthrene rotation of the bonds in one ring lowers the SOS by 3 units for this structure which has a lower number of benzenoid rings than that of Figure 1. An added rotation of bonds in the other outer ring lowers the SOS another 3 units in this molecule.

There is some correlation of the maximum SOS with the

Table X. LMO Populations for Bonds from Primary Full Localizations

molecule	$\tau$ bond <sup>a</sup>	% deloc <sup>b</sup>	populations <sup>c</sup>
naphthalene	7-8	16.6	7 (0.96); 8 (0.95); 6,9 (0.03); 5,10 (0.02)
	9-10	21.0	9,10 (0.91); 1,4,5,8 (0.03); 2,3,7,6 (0.02)
anthracene	1-2	15.8	2 (0.98); 1 (0.95); 3, (0.03); 4,11 (0.02); 12 (0.01)
	6-7	15.7	7 (0.97); 6 (0.95); 8,13 (0.03); 9 (0.02); 14 (0.01)
	10-11	21.3	11 (0.92); 10 (0.91); 14,12 (0.04); 5 (0.03); 13 (0.02)
phenanthrene	13-14	22.6	13,14 (0.90); 5,10 (0.05); 6,7,8,9,11,12 (0.02)
	5-6	17.7	6 (0.96); 5 (0.93); 7,13 (0.04); 8,14 (0.02)
	7-8	17.7	7 (0.95); 8 (0.93); 6,14 (0.04); 5,13 (0.02)
	9-10	14.5	9,10 (0.97); 11,14 (0.02); 12,13 (0.01)
naphthacene	11-12	21.0	11 (0.92); 12 (0.91); 1,4 (0.03); 2,3,10 (0.02); 9,13,14 (0.01)
	7-8	15.0	8 (0.98); 7 (0.95); 5,16,18 (0.02); 17 (0.01)
	11-17	20.2	17 (0.93); 11 (0.92); 13,12,17 (0.03); 14 (0.02)
benzanthracene	13-14	23.0	13,14 (0.89); 9,10,11,12 (0.04); 15,16,17,18 (0.01)
	1-2	18.1	2 (0.96); 1 (0.92); 13 (0.05); 3 (0.04); 1,14 (0.02)
chrysene	3-4	18.0	3 (0.95); 4 (0.93); 2,14 (0.04); 1,13 (0.02)
	5-6	14.0	5 (0.98); 6 (0.97); 15 (0.01)
	7-15	19.9	7,15 (0.93); 16 (0.04); 12,18 (0.03); 17 (0.02); 5 (0.01)
	8-9	16.2	9 (0.97); 8 (0.94); 10,18 (0.03); 11 (0.02); 17 (0.01)
	10-11	16.2	10 (0.97); 11 (0.94); 9,17 (0.03); 8 (0.02); 18 (0.01)
	12-16	19.6	12,16 (0.93); 15,17 (0.04); 7 (0.03); 18 (0.02)
	13-14	21.0	13 (0.93); 14 (0.91); 1,4 (0.03); 2,3 (0.02); 6 (0.01)
	17-18	22.6	18 (0.91); 17 (0.90); 7,8,9,10,11,12 (0.02); 15,16 (0.01)
	5-6	15.3	6 (0.97); 5 (0.96); 16 (0.03); 17 (0.02); 15,18 (0.01)
	7-8	17.4	7 (0.96); 8 (0.94); 9,17 (0.04); 10,18 (0.02)
triphenylene	9-10	17.3	9 (0.96); 10 (0.93); 18 (0.04); 8 (0.03); 7,17 (0.02)
	15-16	19.9	15,16 (0.93); 5,11,13,18 (0.02); 6,12,14, 17 (0.01)
	17-18	21.2	17 (0.92); 18 (0.91); 7,10 (0.03); 5,6,8,9,15 (0.02); 16 (0.01)
pentacene	1-2	18.3	2 (0.95); 1 (0.92); 13 (0.05); 3 (0.04); 4,14 (0.02)
	13-14	20.5	13,14 (0.92); 1,4 (0.03); 2,3 (0.02)
	10-11	15.3	10 (0.98); 11 (0.95); 8,9,22 (0.02); 21 (0.01)
pyrene	12-22	19.9	22 (0.94); 12 (0.92); 7,21 (0.03); 19,20 (0.02); 11 (0.01)
	13-19	21.8	13,19 (0.91); 6,18,20 (0.04); 7,17 (0.02); 12 (0.01)
	17-18	23.3	17 (0.89); 18 (0.88); 6,13 (0.04); 7,12 (0.03); 5,14,19,20 (0.01)
	1-2	14.2	1,2 (0.97); 11,13 (0.02); 15,16 (0.01)
	3-4	19.3	4 (0.95); 3 (0.90); 5 (0.07); 13 (0.04); 14,16 (0.02)
1,2-benzopyrene	5-14	21.0	14 (0.92); 5 (0.91); 16 (0.06); 3,4 (0.03); 13 (0.02); 6,7 (0.01)
	6-7	14.2	6,7 (0.97); 12,14,15,16 (0.01)
	11-15	22.5	11 (0.93); 15 (0.88); 10 (0.05); 8,12 (0.03); 9,16 (0.02); 1,2 (0.01)
	1-2	14.4	1,2 (0.97); 15,17 (0.02); 19,20 (0.01)
	7-6	20.7	6,7 (0.92); 11,14 (0.03); 12,13 (0.02)
	8-16	20.0	8,16 (0.93); 20 (0.05); 9,10 (0.03); 15 (0.02)
	9-10	18.8	9 (0.95); 10 (0.92); 8 (0.06); 16 (0.04); 16,19 (0.02)
	11-12	18.4	12 (0.95); 11 (0.92); 6 (0.05); 13 (0.04); 7,14 (0.02)
	15-19	21.9	15 (0.94); 19 (0.88); 10 (0.04); 8,16 (0.03); 20,9 (0.02); 1,2 (0.01)
	3,4-benzopyrene	1-2	15.0
3-4		21.6	4 (0.92); 3 (0.89); 5,14 (0.03); 11,12,13,17 (0.02); 18,20 (0.01)
5-18		18.6	18 (0.94); 5 (0.93); 20 (0.03); 3,4,17 (0.02)
6-7		14.0	7 (0.98); 6 (0.97); 16,18 (0.01)
8-16		20.2	16 (0.93); 8 (0.92); 19 (0.05); 10,9 (0.03); 15 (0.02); 6,7 (0.01)
9-10		18.6	9 (0.96); 10 (0.91); 8 (0.06); 16 (0.04); 16,19 (0.02)
11-12		17.0	12 (0.96); 11 (0.94); 3 (0.04); 13 (0.03); 4,14 (0.02)
13-14		17.0	13 (0.97); 14 (0.93); 4,12 (0.03); 3,11 (0.02)
15-19		22.0	15 (0.93); 19 (0.88); 10 (0.04); 8 (0.03); 1,9,20 (0.02); 2,17 (0.01)
17-20		22.0	17 (0.93); 20 (0.91); 5 (0.03); 1,3,18,19 (0.02); 2,5,15 (0.01)

<sup>a</sup> Unique  $\tau$  bonds. <sup>b</sup> % delocalization index. <sup>c</sup> Populations (>0.01 e) in the untruncated LMO in units of e.

Fries rule:<sup>29</sup> the Kekulé structure which has the largest number of benzenoid rings is the most stable. However, the second rotation in phenanthrene is not different according to the Fries rule, but it does remove density from the outer regions (and lowers the SOS). In triphenylene and chrysene the secondary structures are less stable by Fries rule. In benzanthracene two LMO structures are found, but both structures have the same number of benzenoid rings. (Even so, ring B of benzanthracene is not like ring C of phenanthrene.) In 3,4-benzopyrene the rotation of bonds occurs in the ring which had two equivalent structures in pyrene, and the secondary structure follows the Fries rule. In 1,2-benzopyrene there are two different structures even though the number of benzenoid rings is constant.

Here, the primary structure is like that of pyrene; by contrast, in the secondary structure one ring has no double bonds.

The equivalence between the  $\pi$  LMO structures and the complete LMO structures with the largest SOS is remarkable. In all cases except where three-center  $\pi$  bonds are found, the  $\pi$  LMOs are the same as the complete LMOs for the dominant structure. The major difference between the complete LMOs and the  $\pi$  LMOs is that the  $\pi$  LMOs tend to be significantly more delocalized. In most cases,  $\tau$  bonds are found where the largest overlap populations occur and where the shortest bonds are found experimentally, for example, the 9-10 bond in phenanthrene. We note that bonds like the 1,2 bonds in naphthalene and anthracene which we call "wing bonds" are

Table XI. LMO Populations for  $\pi$  Bonds from  $\pi$ -Only Localizations

molecule	bond <sup>a</sup>	% deloc <sup>b</sup>	population <sup>c</sup>
naphthalene	7-8	20.6	8 (0.88); 7 (0.87); 6,9 (0.08); 5 (0.05); 10 (0.04)
	9-10	26.8	9,10 (0.78); 1,4,5,8 (0.07); 2,3,7,6 (0.04)
anthracene	10-11-14	21.0	10 (0.99); 11,14 (0.40); 5 (0.17); 11,14 (0.01)
	12-5-11	22.0	12 (0.94); 11 (0.42); 5 (0.40); 4,13 (0.06); 1 (0.04); 3 (0.03); 2 (0.02)
	6-7	19.0	7 (0.90); 6 (0.87); 13 (0.08); 8 (0.05); 9,14 (0.04)
phenanthrene	8-9	19.0	8 (0.92); 9 (0.87); 14 (0.08); 6 (0.06); 7 (0.05); 13 (0.02)
	7-8 <sup>d</sup>	22.2	8 (0.86); 7 (0.85); 6 (0.10); 14 (0.09); 5,13 (0.05)
	9-10	17.4	9,10 (0.91); 11,14 (0.06); 12,13 (0.02)
naphthacene	11-12	26.0	11,12 (0.80); 14 (0.08); 3,13,10 (0.05); 2 (0.04); 9 (0.03); 14 (0.02)
	7-8	18.8	8 (0.90); 7 (0.89); 6 (0.06); 18 (0.05); 5 (0.04); 17 (0.02); 11 (0.01)
	6-18	25.8	18 (0.82); 6 (0.81); 17 (0.09); 13 (0.08); 12 (0.07); 8 (0.03); 5,7,14 (0.02)
benzanthracene	13-14	28.4	13,14 (0.74); 9,10,11,12 (0.09); 15,16,17,18 (0.02)
	1-2	22.8	1 (0.87); 2 (0.83); 13 (0.11); 3 (0.09); 4,14 (0.05)
	3-4	22.8	3,4 (0.85); 2,14 (0.10); 1,13 (0.05)
chrysene	5-6	16.6	5 (0.93); 6 (0.92); 14 (0.05); 15 (0.04); 13 (0.02); 16 (0.01)
	7-15	25.3	15 (0.84); 7 (0.82); 16 (0.10); 18 (0.08); 12 (0.06); 17 (0.05); 6 (0.03); 13 (0.01); 5 (0.02)
	8-9	19.9	8 (0.89); 9 (0.87); 10 (0.08); 18 (0.07); 11 (0.04); 17 (0.03)
	10-11	19.9	11 (0.90); 10 (0.87); 17 (0.08); 9 (0.07); 8 (0.04); 18 (0.03)
	12-16	24.9	12,16 (0.83); 17 (0.09); 15 (0.08); 7 (0.07); 18 (0.04); 13 (0.02); 6,14 (0.01)
	13-14	26.0	13,14 (0.80); 4 (0.09); 1 (0.08); 2,3 (0.05); 5,16 (0.04); 6 (0.03); 15 (0.01)
	17-18	27.0	18 (0.78); 17 (0.76); 7 (0.11); 12 (0.09); 11,8 (0.06); 9,10,15,16 (0.03)
	5-6	18.7	5 (0.91); 6 (0.89); 16 (0.07); 17 (0.06); 15,18 (0.03)
	7-8	21.7	7 (0.87); 8 (0.85); 9,17 (0.09); 10 (0.05); 18 (0.04)
	9-10	21.7	10 (0.88); 9 (0.85); 8,18 (0.09); 7 (0.05); 17 (0.04)
triphenylene	15-16	24.5	15,16 (0.82); 5,11,13,18 (0.05); 6,12 (0.04); 14,17 (0.03)
	17-18	26.2	18 (0.80); 17 (0.79); 7 (0.08); 10 (0.07); 6,15 (0.06); 8,9 (0.04); 5,16 (0.03)
	1-2	23.0	1 (0.86); 2 (0.83); 3,13 (0.10); 4,14 (0.05)
pentacene	13-14	26.0	13,14 (0.81); 1,4 (0.08); 2,3 (0.05); 15,18 (0.03); 16,17 (0.02)
	6-20-17	22.0	6 (0.98); 17 (0.39); 20 (0.37); 13 (0.21)
	19-13-20	23.0	19 (0.93); 20 (0.42); 13 (0.37); 12 (0.12); 7,17 (0.05); 22 (0.02); 21 (0.01)
	7-21	25.0	7 (0.87); 21 (0.78); 20 (0.10); 12 (0.08); 22 (0.06); 19 (0.03); 8,9,11 (0.02)
	8-9	18.4	8,9 (0.90); 10,21 (0.06); 11 (0.04); 12 (0.02); 7 (0.01)
pyrene	10-11	18.6	11 (0.91); 10 (0.89); 9 (0.06); 22 (0.05); 8 (0.04); 12 (0.01)
	12-22	25.0	22 (0.87); 12 (0.77); 21 (0.12); 7,20 (0.05); 10,11 (0.03); 8 (0.02); 13 (0.01)
	9-10-8	16.9	9 (0.98); 10 (0.52); 8 (0.41); 15 (0.07)
	11-10-15	23.9	11 (0.95); 15 (0.47); 10 (0.34); 8 (0.11); 1 (0.05); 2,16 (0.03); 13 (0.01)
	1-2	17.9	1,2 (0.91); 11,13 (0.04); 15,16 (0.03)
1,2-benzopyrene	1-2	17.4	1,2 (0.91); 15,17 (0.05); 19,20 (0.02)
	6-7	25.8	6,7 (0.82); 11,14 (0.08); 12,13 (0.05); 16,18 (0.03); 19,20 (0.01)
	8-16	27.0	16 (0.92); 8 (0.69); 19 (0.17); 10 (0.08); 9 (0.04); 7,15 (0.03); 6 (0.01)
	9-10	28.0	9 (0.91); 10 (0.74); 8 (0.21); 19 (0.06); 15 (0.05); 16 (0.02)
	11-12	23.0	11 (0.86); 12 (0.82); 6 (0.11); 13 (0.10); 7,14 (0.05)
3,4-benzopyrene	15-19	26.5	15 (0.84); 19 (0.72); 10 (0.14); 8 (0.08); 1,20 (0.05); 16 (0.04); 2,9 (0.03); 17 (0.02)
	1-2	18.6	2 (0.92); 1 (0.88); 17 (0.07); 15 (0.05); 19,20 (0.03)
	3-4	26.7	4 (0.81); 3 (0.75); 5 (0.10); 14 (0.08); 11,17 (0.06); 12,13 (0.04); 20 (0.03); 18 (0.02)
	5-18	23.5	18 (0.88); 5 (0.81); 20 (0.09); 4 (0.06); 3,17 (0.04); 6 (0.03); 7 (0.02)
	6-7	16.7	7 (0.93); 6 (0.92); 16,18 (0.04); 5,19 (0.02); 8,20 (0.01)
	8-16	27.2	16 (0.92); 8 (0.67); 19 (0.18); 10 (0.09); 7 (0.04); 9,15 (0.03); 6 (0.02)
	9-10	28.0	9 (0.92); 10 (0.73); 8 (0.21); 17,19 (0.05); 16 (0.01)
	11-12	21.0	11 (0.90); 12 (0.84); 3 (0.10); 13 (0.07); 14 (0.05); 4 (0.03)
	13-14	21.0	13,14 (0.87); 12 (0.09); 4 (0.07); 3,11 (0.04)
15-19	28.3	15 (0.86); 19 (0.68); 10 (0.15); 8 (0.08); 1 (0.06); 20 (0.05); 2,16 (0.03); 9,17 (0.02)	
17-20	26.1	17 (0.81); 20 (0.80); 3 (0.07); 5,19 (0.06); 2,18 (0.05); 1 (0.04); 4 (0.03); 15 (0.02)	

<sup>a</sup> Unique  $\pi$  bond. <sup>b</sup> % delocalization index. <sup>c</sup> Populations (>0.01 e) in the untruncated LMO in units of e. <sup>d</sup> The 5-6 bond is equivalent to the 7-8 bond.

always found to have  $\tau$  bonds (or  $\pi$  LMOs) in agreement with overlap populations. Thus the LMOs provide a mathematically rigorous yet pictorial means of examining the wave function and the bonding in these molecules.

Our  $\pi$  LMOs differ from those obtained by England et al.<sup>14</sup> only in naphthacene, 3,4-benzopyrene, and pyrene. In the first two molecules, our orbitals are more localized. Our LMOs for rings A and D of pyrene (Figure 2) are rotated by 60° from their results. Hence, our structure has higher symmetry, and the centroids are better separated. We do not know whether this difference is due to the better quality of our wave function or to our use of the Boys criterion for localization.

**Details of Bonding from Full Localizations.** In naphthalene,

the unique central  $\tau$  bonds (9-10) have density on all centers, and are more delocalized than the wing  $\tau$  bonds (7-8). These wing bonds have a delocalized electron density of more than 0.01 e only on atoms of the ring containing these wing bonds. A general trend is an increase in localization with increasing distance from the molecular center. Also, carbon 7 has larger density from the wing bonds than does carbon 8.

In anthracene the  $\tau$  bonds of the central ring are more delocalized than are the wing bonds. The  $\tau$  bonds 11-12 are delocalized in two rings, while the  $\tau$  bonds 5-13 have delocalized density in only one ring somewhat like wing  $\tau$  bonds. The 8-9 and 1-2  $\tau$  bonds are essentially equivalent even though the LMO structure appears not to have full molecular symmetry.

(Actually, the sum of all LMO densities when delocalized parts are included must exhibit full molecular symmetry.) These results, and the two equivalent LMO structures for the central ring noted above, suggest that this central ring is significantly benzenoid.

In phenanthrene the 9–10  $\tau$  bonds are highly localized (cf. the overlap population). Again, central  $\tau$  bonds between two rings delocalize over both rings, while wing bonds delocalize over one ring.

Naphthacene has bonding which is similar to that in naphthalene, although its unique central  $\tau$  bonds are more delocalized than in naphthalene. Here, the decrease in delocalization with increasing distance from the molecular center and the correlation of increased localization with increased overlap population and shorter interatomic distance are especially clear.

In triphenylene, the wing  $\tau$  bonds are especially delocalized, while the central  $\tau$  bonds delocalize only into the outer ring. Thus, these outer rings are highly benzenoid.

In chrysene, the 5–6  $\tau$  bonds, like the 9–10  $\tau$  bonds in phenanthrene, are the most localized, while the 15–16 central bonds are most delocalized.

Benanthracene shows, in the 5–6  $\tau$  bonds, especially highly localized bonds, more like a double bond than an aromatic bond. The 11–10 and 8–9 wing  $\tau$  bonds are more delocalized than the 1–2 and 3–4 wing  $\tau$  bonds, a result which might be predicted from the greater delocalization of wing  $\tau$  bonds in phenanthrene than in anthracene. The central  $\tau$  bonds 13–14 and 17–18 are quite delocalized, and so are the 12–16 and 7–15  $\tau$  bonds of the dominant structure of benanthracene.

Pentacene follows these trends: the central 19–20  $\tau$  bonds are highly delocalized while the 13–18 and 6–17  $\tau$  bonds are next most delocalized. These three sets of bonds are involved in the symmetry equivalent maxima. The outer wing  $\tau$  bonds are the most delocalized.

In pyrene, which we relate below to the peri-condensed molecules, the 1–2 and 6–7  $\tau$  bonds (like the 9–10  $\tau$  bonds of phenanthrene) are highly localized. As expected, the 11–15 central  $\tau$  bonds are the most highly delocalized, while the 5–14  $\tau$  bonds to a highly branched carbon are also quite delocalized. The 3–4 wing bonds are more delocalized than we expected and may indicate benzenoid character for rings A and D.

In 1,2-benzopyrene the bonding is similar to that in pyrene except that rings A and D have specific localization schemes and the 7–6  $\tau$  bonds are more delocalized due to the addition of the new ring. The 11–12 and 13–14 wing bonds are more delocalized than we expected, and taken together with the occurrence of multiple maxima, these results suggest that ring E is significantly benzenoid.

In 3,4-benzopyrene, also similar in bonding to pyrene, the asymmetric location of the new ring makes the 6–7  $\tau$  bonds more highly localized than the 1–2  $\tau$  bonds. Thus this molecule has some benanthracene-like character. In addition, the ring containing the 6–7  $\tau$  bonds has little benzenoid character. The other  $\tau$  bonds are similar to those discussed above.

We close by relating the three-center  $\pi$  orbitals to the complete localizations. These three-center orbitals are found in the  $\pi$  LMOs of anthracene, pentacene, and pyrene, while very asymmetric three-center bonds occur in the benzopyrenes. In anthracene there are different three-center bonds. The unique 11–10–14 bond is symmetric with 0.99 e on 10 and only 0.40 e on 11 and 14. Significant density, 0.17 e, is found on 5 which is not adjacent to any of the centers involved in the three-center bond. The two equivalent three-center bonds, which delocalize into two rings, do not have symmetric bonding from the center carbon to the other two carbons. The three-center bonds in pentacene are essentially the same as those in anthracene except that a higher density of 0.21 e is found on the nonadjacent carbon of the unique bond. In pyrene there

are two equivalent rings with three-center bonds, so we restrict our discussion to one ring. The unique three-center bond is more highly localized than are its counterparts in anthracene and pentacene: only 0.07 e is on the nonadjacent center. The other two three-center orbitals, which have populations of 0.34 and 0.47 e on the outer carbons of this orbital, are quite asymmetric. Significant density, 0.11 e, is also observed on the nonadjacent carbon in the ring. The bonding in the benzopyrenes reflects the pyrene backbone. Thus, the 9–10 and 8–16 bonds in 1,2-benzopyrene are quite delocalized with 0.21 and 0.17 e on adjacent carbons, respectively. In 3,4-benzopyrene the 9–10, 8–16, and 15–19 bonds show some partial three-center character similar to that found in the 1,2 isomer.

## Conclusions

The general behavior of the LMOs and features of the CMOs allow us to relate these electronic characteristics to certain molecular properties. Most of these characteristics show that molecules that exhibit carcinogenic behavior have highly localized double-bond regions typical of the 9–10 bond in phenanthrene. The carcinogenic behavior which is observed for benanthracene and 3,4-benzopyrene can be correlated with the large double-bond character in the K region. The delocalization index is only 14% for these bonds, the lowest value found for the molecules that were studied here. This delocalization index would most likely be even smaller if the experimental bond distances were used. Thus, our calculations demonstrate the high degree of electron localizability in this region.

The concept of local aromaticity has always intrigued organic chemists. As suggested in ref 27 the "second derivative test" for the  $\pi$ -only localizations may give some information about aromaticity in ring systems of the sort studied here. Specifically, it was suggested that a small magnitude for the highest eigenvalue of the second derivative matrix may be associated with aromaticity. Thus, the highest eigenvalue for the  $\pi$ -only localization of benzene was zero corresponding to a completely indeterminate localization and suggesting significant aromaticity for the prototype aromatic system.

As judged by the symmetry related LMO structures (Figures 1 and 3) for linear acenes possessing an odd number of rings, we would expect that the central ring in these molecules would possess considerable aromatic character. This is confirmed by the  $\nu_{\max}$  values for the  $\pi$ -only localizations given in Table IX for benzene, anthracene and pentacene. An examination of the eigenvectors corresponding to these eigenvalues shows that the least determined  $\pi$ -LMOs are indeed in the central ring of these odd linear acenes. Furthermore, we observe that as we proceed from benzene and anthracene to pentacene the localizations become more determinate ( $\nu_{\max} = 0.0, -0.5, \text{ and } -1.2$ , respectively) indicating some loss in aromaticity as we proceed to larger odd acenes. This result is in keeping with Clar's concept<sup>30</sup> of the aromatic sextet for this type of molecule.

Interestingly, according to Clar<sup>30</sup> phenanthrene should possess two sextets rather than the one possessed by anthracene. Although  $\nu_{\max}$  for the  $\pi$ -only localization on phenanthrene is more negative than that for anthracene, the value for phenanthrene is very nearly doubly degenerate, the corresponding eigenvectors indicating near indeterminacy in the localizations for rings A and C, the same rings Clar claims for the aromatic sextets! In triphenylene aromatic sextets should reside in rings A, B, and C. Once again the second derivative test is consistent with this conclusion. The eigenvalue with the smallest magnitude is nearly triply degenerate and well separated from the remaining eigenvalues. The corresponding eigenvectors speak of indeterminacy among the LMOs in rings A, B, and C.

The multiple localized structures in the full localizations for

pyrene suggest significant aromatic character for rings A and D. This is consistent with two sextets residing in these rings as suggested by Clar<sup>30</sup> and once again the second derivative test suggests indeterminacy for LMOs in these rings. The magnitude of the highest eigenvalue  $\nu_{\max}$  (Table IX) is very low and furthermore the eigenvalue is very nearly doubly degenerate, the eigenvectors suggesting an indeterminacy for the LMOs in rings A and D.

As additional rings are fused to pyrene forming the benzopyrenes benzenoid character is partially lost in rings A and D. This is particularly true for ring D in 3,4-benzopyrene. Here the two  $\nu$  values of smallest magnitude ( $-3.3$  and  $-7.9$ ) for the  $\pi$ -only localization are clearly nondegenerate and significantly more negative than those in pyrene. The eigenvector corresponding to the highest eigenvalue gives the LMOs in ring A as least determinate, while the second eigenvector gives those in rings D and E. The aromatic sextet theory predicts that one sextet should reside in ring A and another in rings D and E completely consistent with the second derivative results. The situation for 1,2-benzopyrene suggests that rings A, D, and E have some aromatic character since the  $\nu_{\max}$  value is nearly triply degenerate (highest eigenvalues are  $-2.40$ ,  $-2.73$ , and  $-2.92$ ) and the corresponding eigenvectors show that the LMOs in rings A, D, and E are least determinate. Once again these are precisely the rings predicted by Clar to contain aromatic sextets.

Chrysene and benzantracene are very interesting cases. In both cases two aromatic sextets are predicted. For benzantracene one should reside in ring D with another shared between rings A and B. The second derivative test gives two relatively large  $\nu$  values, one corresponding to LMOs in ring D and the other to the LMOs in ring B. For chrysene two aromatic sextets should be present, one shared between rings A and B and the other between rings C and D. The second derivative test gives a nearly doubly degenerate  $\nu_{\max}$  value suggesting that the LMOs in rings A and D are least well determined.

From the discussion above it is clear that there is a connection between the near indeterminacy of LMOs in  $\pi$ -only localizations and the concepts of local aromaticity and the aromatic sextet. Thus, molecular orbital localizations and the corresponding second derivative tests seem to provide a new and objective way of judging local aromaticity in condensed aromatic systems.

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