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Localized π-Orbitals, Pauling Bond Orders, and the Origin of Aromatic Stability*

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Energy-localized π-orbitals are obtained for twenty-one cata- and peri-condensed hydrocarbons in the Hückel approximation. Coefficients for the localized orbitals are given. Four different orbital types are found to occur. Rules are given relating the localized orbitals to Pauling bond orders and an interpretation of the theoretical resonance energy is offered.

Energielokalisierte π-Elektronenorbitale für 21 kata- und perikondensierte Kohlenwasserstoffe werden im Rahmen der Hückelschen Näherung angegeben. Es zeigt sich, daß vier verschiedene Arten von ihnen auftreten und daß sich Regeln für ihre Beziehung zu den Paulingschen Bindungsordnungen finden lassen. Die lokalisierte Formulierung erlaubt eine einleuchtende Interpretation der theoretischen Resonanzenergie.

Obtention d'orbitales de Hückel π localisées selon le critère d'énergie pour 21 hydrocarbures cata- et peri-condensés. Donnée des coefficients des orbitales localisées. On trouve quatre types d'orbitales. On donne des règles reliant les orbitales localisées aux indices de liaison de Pauling et une interprétation de l'énergie de résonance théorique est proposée.

Introduction

In this research we discuss the localization of orbitals which describe electrons that are usually considered as delocalized in the molecular orbital theory, namely, π-electrons in conjugated aromatic hydrocarbons. The σ-orbitals are left unchanged. To obtain results for many systems, two simplifications are used: the Hückel-Wheland approximation for the π-orbitals (which includes the effect of neighbour overlap in the definition of the orbitals), and the Mulliken approximation for the electron repulsion integrals needed for localization (which incorporates the effect of the neighbour overlap into the localization) [1]. Inasmuch as both of these approximations have provided useful results in the past, we believe our results are significant.

The first section contains the theory and describes the computational method employed. In the second part all localized orbitals for twenty-one cata- and peri-condensed hydrocarbons are tabulated. These are found to give rise to orbitals resembling one of four prototypes, and each is found to extend over at least three centers. In the last two parts we give rules which relate the Pauling bond orders of each molecule to its localized representation and report a novel interpretation of aromatic stability.

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1. Theory

Canonical MO's

We are presently interested in whether or not it is sensible to undertake a localization of electrons which traditionally have been considered as delocalized in the MO theory. To pursue this we need not employ orbitals from some of the refined MO approximations, but any set of orbitals which represents the essential features of the π-electron problem will suffice. Therefore, the LCAO-MO theory on which the present calculations are based is the π-electron theory with neglect of overlap between non-neigbours. The π-electronic MO's are given by

$$\Phi_i = \sum_{P=1}^{N} C_{Pi}\chi_P, \tag{1}$$

where $\chi_P (P = 1, 2, \dots N)$ is the $2p\pi$ atomic orbital on atom P. Since we consider only hydrocarbons, these AO's are all identical, and since we consider all neighbour atoms equidistant (1.4 Å), the value of a certain integral for a neighbour pair is the same for all neighbour pairs. Thus, the overlap matrix of the AO's is

$$\boldsymbol{S} = \boldsymbol{I} + S\boldsymbol{M} \tag{2}$$

and the matrix of the effective one-electron Hamiltonian with respect to the AO's is

$$\boldsymbol{H} = \alpha\boldsymbol{I} + \beta\boldsymbol{M}. \tag{3}$$

Here, S, α, β are the overlap, coulomb and resonance integral, respectively, whereas $\boldsymbol{I}$ is the unit matrix and the "topological" matrix $\boldsymbol{M}$ is defined by

$$M_{PQ} = \begin{cases} 1, \text{ if } P \text{ and } Q \text{ are neighbours,} \\ 0, \text{ otherwise.} \end{cases} \tag{4}$$

The coefficients C_{Pi} of the i^{th} MO (1) are found to be

$$C_{Pi} = C'_{Pi}/(1 + Sm_i)^{1/2}, \tag{5}$$

where m_i is an eigenvalue and $\{C'_{Pi}\}$ $(P = 1, 2, \dots N)$ the corresponding normalized eigenvector of the matrix $\boldsymbol{M}$. There are N eigenvectors and hence N MO's (1), where N is the number of atoms as apparent from (1). In virtue of Eqs. (2)–(4), the orbital energies for these MO's are

$$\varepsilon_i = \langle \Phi_i | \boldsymbol{H} | \Phi_i \rangle = \alpha + \gamma m_i/(1 + Sm_i), \tag{6}$$

where

$$\gamma = \alpha - \beta S \approx -2 \text{ eV} \tag{7}$$

is the resonance integral. The overlap integral, S, is taken to be equal 0.25.

Furthermore, we are interested only in closed-shell systems [2], so that the occupied MO's of the ground state are those $\{\Phi_i\}$ $(i = 1, 2, \dots N/2)$ which associate to the $N/2$ lowest eigenvalues of $\boldsymbol{M}$.

Localization Criterion

Energy localized molecular orbitals (LMO's) are those which maximize [3, 4]

$$D = \sum_{i=1}^{N/2} [\Phi_i \Phi_i | \Phi_i \Phi_i] \tag{8}$$

against orthogonal transformations among the closed-shell MO's, where

$$[f | g] = \int \mathrm{d}V_1 \mathrm{d}V_2 f(1) g(2)/r_{12} . \tag{9}$$

Two other equivalent definitions are that LMO's are orbitals which minimize

$$C' = \sum_{i=1}^{N/2} \sum_{j}{}' [\Phi_i \Phi_i | \Phi_j \Phi_j] \tag{10}$$

or

$$X' = \sum_{i=1}^{N/2} \sum_{j}{}' [\Phi_i \Phi_j | \Phi_i \Phi_j] \tag{11}$$

against the same transformations [4], where the primed summation indicates that the $j = i$ terms are omitted.

The Edmiston-Ruedenberg algorithm requires knowledge of all two-electron molecular repulsion integrals in some MO basis [4, 5]. Following an earlier suggestion [6], these are presently calculated using the Mulliken approximation [7]. In virtue of (5), the MO basis (1) is particularly convenient, giving

$$[\Phi_i \Phi_j | \Phi_k \Phi_l] = 1/4\, (\sigma_i + \sigma_j)(\sigma_k + \sigma_l) \sum_{P,Q} I_{PQ} C_{Pi} C_{Pj} C_{Qk} C_{Ql} , \tag{12}$$

where

$$\sigma_i = 1 + S m_i \qquad (i = 1, 2 \ldots N/2) \tag{13}$$

are the $N/2$ lowest eigenvalues of $\boldsymbol{S}$, and

$$I_{PQ} = [\chi_P \chi_P | \chi_Q \chi_Q] \tag{14}$$

is an atomic two-center coulomb repulsion integral.

It may be of interest to note that, under the assumption of the Mulliken approximation, molecular coulomb integrals can be written

$$[\Phi_i \Phi_i | \Phi_j \Phi_j] = 1/4 \sum_P \sum_Q q^i(P) q^j(Q) I_{PQ} , \tag{15}$$

where the

$$q^i(P) = 2 C_{Pi} \left[C_{Pi} + S \sum_Q C_{Qi} \right] \tag{16}$$

sum to Mulliken's gross atomic populations [8]. Alternatively, the same integrals can be written

$$[\Phi_i \Phi_i | \Phi_j \Phi_j] = 1/4 \sum_{\substack{\text{neighbour} \\ \text{bonds}}} \sum r^i(PQ) r^j(RS) [\chi_P^2 + \chi_Q^2 | \chi_R^2 + \chi_S^2] , \tag{17}$$

where

$$r^i(PQ) = (T_P^2 C_{Pi}^2 + T_Q^2 C_{Qi}) + 4 S C_{Pi} C_{Qi} \tag{18}$$

sum to the cellular bond populations of Platt, Scherr, and Ruedenberg [9], and

$$T_P=\begin{cases}1, \text{ if } P \text{ is not a joint atom}\\(2/3)^{1/2}, \text{ if } P \text{ is a joint atom.}\end{cases} \tag{19}$$

Because of the assumptions employed in the previous sections, we need formulae only for the two-center overlap and coulomb repulsion integrals. The Hamiltonian (3) does not concern us here since we determine the MO's from Eq. (5). Formulae for the integrals were given earlier by one of us [10], and in keeping with the conclusions from that work the orbital exponents of the $2p\pi$ atomic orbitals are chosen as

$$\zeta(2p\pi)=1.6178932 \text{ a.u.} \tag{20}$$

Choice of Starting Orbitals

It is not unreasonable to expect that the sets of LMO's for the cata- and peri-condensed hydrocarbons considered will in some way be related to classical Kekulé structures [11]. Therefore, we constructed several sets of orbitals in the closed-shell MO space corresponding to appropriate Kekulé structures, and begun localization with each of these sets.

These Kekulé-type MO's were prepared as follows. Let

$$\hat{K}_\nu=\sum_P A_{P\nu}\chi_P \qquad (\nu=1,2,\dots N/2) \tag{21}$$

be a normalized orbital, extending only over two centers of a double bond, so that $A_{P\nu}$ is non-zero for two values of P only, corresponding to two neighbour atoms. Let, further, the $\hat{K}_\nu$ be that set of two-center orbitals corresponding to all double bonds in one Kekulé structure. In general, these orbitals do not lie in the function space spanned by the occupied MO's of Eq. (1) and we, therefore, form the projections $\bar{K}_\nu$ of the $\hat{K}_\nu$ in the space of the occupied MO's

$$\bar{K}_\nu=\sum_{i=1}^{N/2} B_{\nu i}\Phi_i, \tag{22}$$

where

$$B_{\nu i}=\langle\hat{K}_\nu|\Phi_i\rangle=\sigma_i\sum_P C_{Pi}A_{P\nu}\Bigg/\left[\sum_{i=1}^{N/2}\Big(\sigma_i\sum_P C_{Pi}A_{P\nu}\Big)^2\right]^{1/2}. \tag{23}$$

The MO's of Eq. (23) are those within the space of the occupied MO's which are closest to the two-center MO's of Eq. (21). However, they are not orthogonal to one another. Therefore, we finally form a set of mutually orthonormal orbitals $K_\nu(\nu=1,2,\dots,N/2)$ from the $\bar{K}_\nu$ by symmetric orthogonalization [12]. They differ from the $\bar{K}_\nu$ least in the mean squares sense defined by Carlson and Keller [13] and are given by

$$K_\nu=\sum_{\mu=1}^{N/2}(\Delta^{-1/2})_{\mu\nu}\bar{K}_\mu. \tag{24}$$

$\Delta^{-1/2}$ is constructed as

$$(\Delta^{-1/2})_{\mu\nu}=\sum_{\alpha=1}^{N/2}T_{\mu\alpha}T_{\nu\alpha}/(\lambda_\alpha)^{1/2}, \tag{25}$$

where T and λ are obtained from the eigenvalue problem

$$\sum_{\nu=1}^{N/2} \Delta_{\mu\nu} T_{\nu\alpha} = \lambda_\alpha T_{\mu\alpha} \tag{26}$$

for the overlap matrix

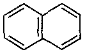
$$\Delta_{\mu\nu} = \langle \bar{K}_\mu | \bar{K}_\nu \rangle = \sum_i B_{\mu i} B_{\nu i} \,. \tag{27}$$

The orbitals defined by Eq. (24) therefore fulfill the following three conditions:

1. They lie in the space of the occupied MO's.
2. They are mutually orthonormal.
3. They are as close as possible to two-center MO's.

We call them "Kekulé-type occupied MO's."

As an example, the two-center orbitals ($\hat{K}_\nu$) and the Kekulé-type occupied MO's (K_ν) corresponding to two resonance hybrids of naphthalene,



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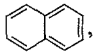


,

are shown in Table 1. These are referred to as I and II, respectively, and the numbering of the atoms is given in Fig. 1. It is interesting that, when neighbour

Table 1. *The orbitals $\hat{K}_\nu$ and K_ν in naphthalene*

AO	Case I, $\hat{K}_\nu$'s					Case II, $\hat{K}_\nu$'s				
	1	2	3	4	5	1	2	3	4	5
1	0.6332	0	0	0	0	0.6332	0	0	0	0
2	0.6332	0	0	0	0	0.6332	0	0	0	0
3	0	0.6332	0	0	0	0	0.6332	0	0	0
4	0	0.6332	0	0	0	0	0.6332	0	0	0
5	0	0	0.6332	0	0	0	0	0.6332	0	0
6	0	0	0.6332	0	0	0	0	0	0.6332	0
7	0	0	0	0.6332	0	0	0	0	0.6332	0
8	0	0	0	0.6332	0	0	0	0	0	0.6332
9	0	0	0	0	0.6332	0	0	0	0	0.6332
10	0	0	0	0	0.6332	0	0	0.6332	0	0

	Case I, K_ν's					Case II, K_ν's				
	1	2	3	4	5	1	2	3	4	5
1	0.5710	−0.1727	0.1630	−0.0473	−0.0012	0.5737	−0.1669	0.0548	0.1383	−0.0748
2	0.5694	0.1736	−0.1431	−0.0349	−0.0589	0.5706	0.1645	−0.0893	−0.1118	0.0799
3	0.1736	0.5694	−0.1431	−0.0589	−0.0349	0.1645	0.5706	−0.1118	−0.0893	0.0799
4	−0.1727	0.5710	0.1630	−0.0012	−0.0473	−0.1669	0.5737	0.1383	0.0548	−0.0748
5	−0.1399	0.1619	0.5185	−0.1399	0.1619	−0.0989	0.1448	0.5249	0.1745	−0.1540
6	0.1619	−0.1399	0.5185	0.1619	−0.1399	0.1448	−0.0989	0.1745	0.5249	−0.1540
7	−0.0473	−0.0012	0.1630	0.5710	−0.1727	−0.1133	0.0658	−0.1871	0.5363	0.2117
8	−0.0349	−0.0589	−0.1431	0.5694	0.1736	−0.0811	0.0812	−0.1608	0.2121	0.5436
9	−0.0589	−0.0349	−0.1431	0.1736	0.5694	0.0812	−0.0811	0.2121	−0.1608	0.5436
10	−0.0012	−0.0473	0.1630	−0.1727	0.5710	0.0658	−0.1133	0.5363	−0.1871	0.2117

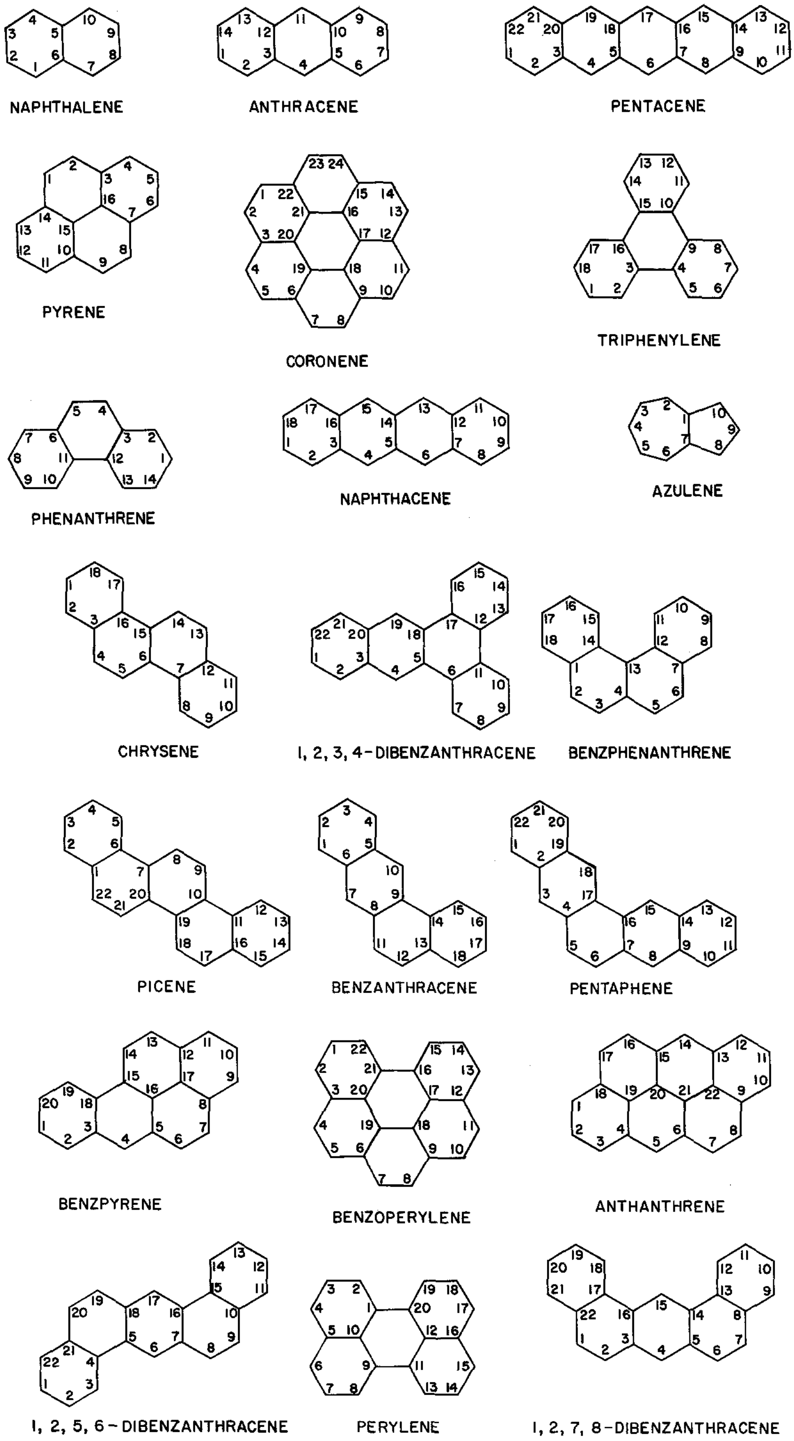


Fig. 1. Numbering of atoms and basis functions

overlap is included, the orthogonal molecular orbitals in the closed-shell Hückel space which differ least from Kekulé orbitals in a mean squares sense extend appreciably over more than two centers. This was found to be true for all molecules considered.

2. Localized π-Orbitals

General Results

The systems studied are given in Fig. 1. The same figure also contains the numbering of the atoms.

As indicated in the previous section, several localization processes were carried out for a given molecule, each one starting from a different set of Kekulé-type occupied MO's. It was initially thought that each of these might iterate to a different set of LMO's and, in that case, each of these sets of LMO's would have corresponded to a different Kekulé structure. However, this did not turn out to be the case. In all molecules considered, the same LMO structure was obtained from the localization process, regardless which set of Kekulé-type occupied MO's was used as starting functions.

In fact, all LMO's in all molecules are basically related to one of four types, called $\pi l2$, $\pi l2'$, $\pi l3$, $\pi l4$ respectively. These are illustrated in Fig. 2. However, in many cases intermediate types (e.g. $\pi l23$) are also found.

Specific Results

The resulting LMO's for the molecules of Fig. 1 are listed in Table 2 by their expansions in terms of atomic π-orbitals. The heading for each LMO indicates the type as defined in Fig. 2. These results are illustrated in Figs. 3, 4, and 5. For

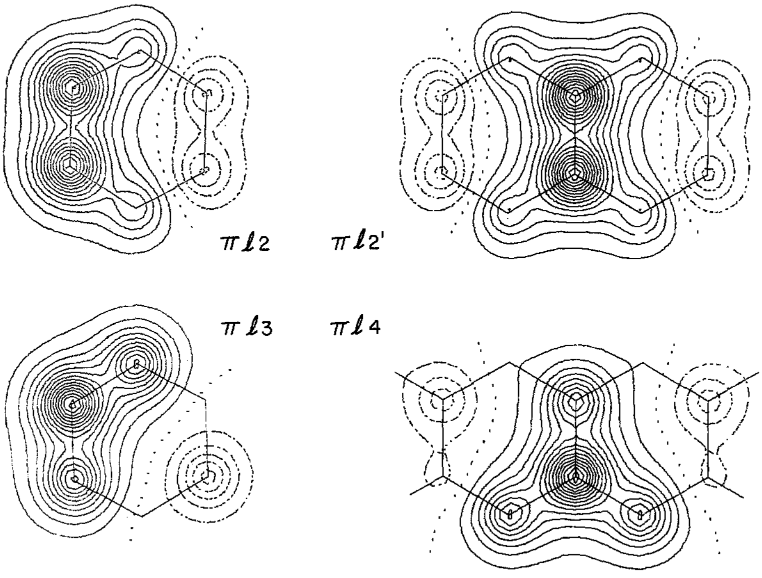


Fig. 2. Prototype localized π-orbitals

Table 2. *Expansions of localized π-orbitals in terms of atomic π-orbitals*

PERYLENE

AO	$\pi\ell 42'$	$\pi\ell 42'$	$\pi\ell 34$	$\pi\ell 34$	$\pi\ell 34$	$\pi\ell 34$	$\pi\ell 2$	$\pi\ell 2$	$\pi\ell 2$	$\pi\ell 2$
1	0.1310	0.0017	-0.5584	0.0266	0.0355	0.1032	0.1477	-0.0062	-0.0185	0.0352
2	-0.1563	0.0208	-0.5430	0.0356	-0.0454	-0.1138	-0.2059	0.0586	0.0235	-0.0570
3	-0.1349	0.0026	-0.1550	-0.0449	-0.0115	-0.0342	-0.5764	-0.0253	0.0067	-0.0150
4	0.1850	-0.0136	0.1813	-0.0046	0.0327	0.0718	-0.5558	-0.0502	-0.0196	0.0421
5	0.5399	-0.0048	0.1221	0.1221	-0.0027	0.0027	-0.1396	0.1396	0.0018	0.0018
6	0.1850	-0.0136	-0.0046	0.1813	-0.0718	-0.0327	0.0502	0.5558	0.0421	-0.0196
7	-0.1349	0.0026	-0.0449	-0.1550	0.0342	0.0115	0.0253	0.5764	-0.0150	0.0067
8	-0.1563	0.0208	0.0356	-0.5430	0.1138	0.0454	-0.0586	0.2059	-0.0570	0.0235
9	0.1310	0.0017	0.0266	-0.5584	-0.1032	-0.0355	0.0062	-0.1477	0.0352	-0.0185
10	0.4971	0.0318	-0.1853	-0.1854	0.0431	-0.0431	0.1469	-0.1469	-0.0235	-0.0235
11	-0.0017	-0.1310	0.0355	-0.1032	-0.5584	-0.0266	-0.0185	-0.0352	0.1477	0.0062
12	-0.0318	-0.4970	0.0431	0.0431	-0.1854	0.1854	-0.0235	0.0235	0.1470	0.1470
13	-0.0208	0.1563	-0.0454	0.1138	-0.5430	-0.0356	0.0235	0.0570	-0.2060	-0.0586
14	-0.0026	0.1349	-0.0115	0.0342	-0.1550	0.0449	0.0067	0.0150	-0.5764	0.0253
15	0.0136	-0.1853	0.0327	-0.0718	0.1813	0.0046	-0.0196	-0.0422	-0.5558	0.0502
16	0.0048	-0.5399	-0.0027	-0.0027	0.1220	-0.1220	0.0018	-0.0018	-0.1396	-0.1396
17	0.0136	-0.1850	-0.0718	0.0327	-0.0046	-0.1813	0.0421	0.0196	0.0502	-0.5558
18	-0.0026	0.1349	0.0342	-0.0115	-0.0449	0.1550	-0.0150	-0.0067	0.0253	-0.5764
19	-0.0208	0.1563	0.1138	-0.0454	0.0356	0.5432	-0.0570	-0.0235	-0.0586	-0.2060
20	-0.0017	-0.1310	-0.1032	0.0355	0.0266	0.5584	0.0352	0.0185	0.0062	0.1477

BENZPYRENE

AO	$\pi\ell 2'4$	$\pi\ell 42'$	$\pi\ell 42'$	$\pi\ell 34$	$\pi\ell 3$	$\pi\ell 34$	$\pi\ell 23$	$\pi\ell 23$	$\pi\ell 23$	$\pi\ell 23$
1	-0.1652	0.0595	-0.0287	-0.0163	0.0185	-0.0516	0.5471	0.2106	0.0257	-0.0133
2	0.1146	-0.0039	0.0146	-0.0126	0.0017	-0.0334	0.5884	-0.1535	-0.0233	-0.0238
3	0.4625	-0.1384	0.0419	0.0433	-0.0329	0.2238	0.2077	-0.1596	-0.0297	0.0529
4	0.0986	-0.1228	-0.0130	0.0610	-0.0235	0.5895	-0.0317	-0.0090	0.0543	0.1115
5	-0.1469	0.2033	-0.0322	-0.0866	0.0437	0.5060	-0.0508	0.0674	-0.0114	-0.1576
6	-0.0386	0.0227	-0.0137	-0.1227	0.0426	0.0882	0.0001	0.0132	-0.0004	-0.5984
7	0.0686	-0.0744	0.0122	0.1619	-0.0556	-0.1326	0.0257	-0.0388	0.0054	-0.5706
8	0.0253	-0.0285	0.0460	0.5840	-0.0788	-0.0385	-0.0056	-0.0022	-0.0053	-0.0960
9	-0.0443	-0.0326	-0.1999	0.4585	0.3205	0.0876	-0.0232	0.0328	0.0836	0.1204
10	-0.0177	0.0289	-0.0779	0.0605	0.6049	0.0165	0.0082	-0.0033	-0.0141	0.0317
11	0.0493	0.0011	0.2939	-0.2099	0.4812	-0.0743	0.0162	-0.0292	-0.0843	-0.0941
12	0.0186	-0.0723	0.5819	-0.0703	0.0549	-0.0038	-0.3154	0.0127	0.0914	-0.0088
13	-0.0569	-0.1625	0.2049	0.0118	-0.0579	0.0917	-0.0214	0.0371	0.5476	0.0122
14	-0.0130	0.0876	-0.1163	0.0275	-0.0036	-0.0238	0.0229	-0.0265	0.5994	-0.0019
15	0.2080	0.4638	-0.1430	-0.0511	0.0628	-0.1792	0.0083	-0.0533	0.2106	-0.0244
16	-0.0865	0.5723	0.0677	0.0104	-0.0214	0.0967	0.0307	-0.0156	-0.1022	0.0644
17	-0.0232	0.2249	0.4147	0.2793	-0.1739	-0.0085	0.0115	-0.0040	-0.1481	0.1063
18	0.5605	0.0848	-0.0041	-0.0338	0.0196	-0.1005	-0.1113	0.1268	-0.0329	-0.0492
19	0.2122	-0.0488	0.0325	0.0045	-0.0142	0.0039	-0.1825	0.5475	-0.0408	-0.0059
20	-0.1285	-0.0150	-0.0101	0.0189	-0.0072	0.0437	0.1382	0.5838	0.0272	0.0300

CORONENE

AO	$\pi\ell 2'$	$\pi\ell 2'$	$\pi\ell 2'$	$\pi\ell 2'$	$\pi\ell 2'$	$\pi\ell 2'$	$\pi\ell 2$	$\pi\ell 2$	$\pi\ell 2$	$\pi\ell 2$	$\pi\ell 2$	$\pi\ell 2$
1	0.1525	0.0205	-0.0122	-0.0596	0.0279	-0.1641	0.5686	0.0372	-0.0296	-0.0379	0.0114	0.0454
2	-0.1385	-0.0256	0.0520	0.0137	-0.0179	0.1439	0.5797	-0.0276	0.0339	-0.0394	0.0093	0.0300
3	-0.5081	-0.0175	-0.0176	0.1367	-0.0353	0.1360	0.1718	-0.0507	0.0208	0.1712	-0.0208	-0.0507
4	-0.1388	0.0520	-0.0257	0.1447	-0.0178	0.0136	-0.0392	0.0300	-0.0093	0.5794	-0.0339	-0.0276
5	0.1519	-0.0122	0.0206	-0.1636	0.0278	-0.0594	-0.0380	0.0454	-0.0114	0.5689	0.0296	0.0372
6	0.1212	-0.1211	0.0318	-0.5315	0.0127	0.0129	0.0444	-0.1484	0.0182	0.1490	0.0443	0.0182
7	0.0122	-0.1519	0.0205	-0.1643	-0.0596	0.0279	0.0296	-0.5687	0.0372	-0.0453	-0.0381	-0.0114
8	-0.0520	0.1387	-0.0256	0.1441	0.0138	-0.0179	-0.0339	-0.5796	-0.0276	-0.0301	-0.0392	-0.0093
9	0.0175	0.5078	-0.0174	0.1368	0.1368	-0.0351	-0.0208	-0.1715	-0.0507	0.0505	0.1720	0.0208
10	0.0256	0.1380	0.0523	0.0139	0.1441	-0.0178	0.0093	0.0393	0.0300	0.0276	0.5797	0.0340
11	-0.0205	-0.1525	-0.0124	-0.0595	-0.1642	0.0278	0.0114	0.0380	0.0455	-0.0371	0.5685	-0.0296
12	-0.0315	-0.1212	-0.1221	0.0127	-0.5315	0.0128	-0.0182	-0.0444	-0.1484	-0.0183	0.1484	-0.0444
13	-0.0205	-0.0121	-0.1526	0.0278	-0.1640	-0.0596	-0.0372	-0.0296	-0.5686	0.0113	-0.0454	0.0380
14	0.0255	0.0520	0.1385	-0.0178	0.1439	0.0137	0.0276	0.0340	-0.5797	0.0094	-0.0299	0.0393
15	0.0174	-0.0176	0.5081	-0.0351	0.1358	0.1365	0.0507	0.0208	-0.1718	-0.0207	0.0507	-0.1716
16	0.0208	-0.0205	0.5376	0.0448	-0.1401	-0.1393	-0.0172	-0.0256	0.1268	0.0256	-0.0172	0.1271
17	0.0531	0.1686	0.1676	0.0243	-0.5141	0.0242	0.0274	0.0163	0.1382	0.0274	-0.1381	0.0162
18	0.0206	0.5379	-0.0208	-0.1392	-0.1391	0.0447	0.0256	0.1272	0.0173	-0.0171	-0.1266	-0.0256
19	-0.1683	0.1684	-0.0528	-0.5140	0.0243	0.0240	-0.0162	0.1384	-0.0274	-0.1379	-0.0160	-0.0274
20	-0.5376	-0.0206	-0.0205	-0.1395	0.0446	-0.1399	-0.1269	0.0172	-0.0256	-0.1272	0.0257	0.0172
21	-0.1678	-0.0530	0.1683	0.0242	0.0239	-0.5141	-0.1383	-0.0275	0.0162	-0.0163	0.0274	0.1382
22	0.1219	0.0316	-0.1213	0.0128	0.0130	-0.5315	0.1483	0.0182	-0.0443	0.0444	-0.0182	-0.1485
23	0.0123	0.0206	-0.1522	0.0278	-0.0593	-0.1641	-0.0455	-0.0113	0.0381	0.0296	-0.0371	-0.5687
24	-0.0522	-0.0256	0.1386	-0.0178	0.0135	0.1441	-0.0299	-0.0093	0.0392	-0.0340	0.0276	-0.5796

ANTHRACENE

AO	$\pi\ell 34$	$\pi\ell 34$	$\pi\ell 3$	$\pi\ell 23$	$\pi\ell 23$	$\pi\ell 23$	$\pi\ell 23$
1	0.1119	-0.0150	-0.0004	-0.5936	0.0076	-0.0184	0.1211
2	-0.2040	0.0737	-0.0495	-0.5489	0.0284	-0.0083	-0.1840
3	-0.5869	0.0074	0.0101	-0.0927	-0.0243	0.0334	-0.0763
4	-0.3879	-0.3879	0.2572	0.1043	-0.1043	0.0406	0.0406
5	0.0074	-0.5869	0.0101	0.0243	0.0928	-0.0763	0.0333
6	0.0737	-0.2040	-0.0495	-0.0284	0.5489	-0.1840	-0.0083
7	-0.0150	0.1119	-0.0004	-0.0076	0.5936	0.1211	-0.0184
8	-0.0792	0.1356	0.1052	0.0394	0.2086	0.5456	0.0257
9	0.0269	-0.0749	-0.0226	-0.0046	-0.1507	0.5965	0.0096
10	0.1692	-0.3372	-0.3801	-0.0752	-0.1456	0.2073	-0.0643
11	0.0303	0.0304	-0.6171	-0.0236	0.0236	-0.0647	-0.0647
12	-0.3372	0.1692	-0.3800	0.1455	0.0752	-0.0643	0.2074
13	-0.0749	0.0269	-0.0226	0.1507	0.0046	0.0097	0.5965
14	0.1356	-0.0792	0.1051	-0.2085	-0.0394	0.0257	0.5465

Table 2 (continued)

1,2,3,4-DIBENZANTHRACENE

AO	πℓ2'	πℓ2'	πℓ2'	πℓ34	πℓ34	πℓ2	πℓ2	πℓ2	πℓ2	πℓ2	πℓ2
1	-0.1452	0.0094	0.0242	-0.0359	-0.0547	-0.0068	0.0156	-0.0109	-0.0048	0.1670	-0.5706
2	0.1628	0.0178	-0.0030	-0.0448	-0.0028	0.0131	-0.0092	0.0067	0.0151	-0.1722	-0.5711
3	0.5192	-0.0377	-0.0464	0.1654	0.1309	0.0056	-0.0212	0.0134	-0.0030	-0.1296	-0.1603
4	0.1768	-0.0952	-0.0284	0.5559	0.1790	-0.0435	0.0144	-0.0155	-0.0509	0.0027	0.0507
5	-0.1342	0.1020	0.0708	0.5494	-0.1556	-0.0072	0.0242	-0.0143	0.0204	0.0515	0.0325
6	-0.0424	0.5238	0.1015	0.1064	-0.0304	0.1927	-0.0308	0.0442	0.1600	0.0077	-0.0053
7	0.0229	0.1692	0.0128	-0.0617	0.0121	0.5676	-0.0124	0.0161	0.1639	-0.0166	-0.0126
8	0.0111	-0.1682	-0.0527	-0.0083	0.0170	0.5560	0.0239	-0.0320	-0.1934	0.0034	0.0072
9	-0.0236	-0.1586	0.0119	0.0527	-0.0151	0.1749	0.0132	-0.0066	-0.5655	0.0155	0.0099
10	-0.0012	0.1890	0.0540	-0.0176	-0.0178	-0.1725	-0.0326	0.0348	-0.5583	-0.0087	-0.0084
11	0.0422	0.5366	-0.1079	-0.0875	0.0452	-0.1499	-0.0108	-0.0189	-0.1731	-0.0181	-0.0083
12	0.0445	0.1150	-0.5281	-0.0490	0.0888	-0.0184	0.1858	-0.1568	0.0127	0.0092	0.0192
13	-0.0003	-0.0525	-0.1759	0.0165	0.0178	0.0331	0.5646	-0.1672	0.0303	0.0082	0.0086
14	-0.0254	-0.0137	0.1650	0.0172	-0.0544	-0.0068	0.5594	0.1869	-0.0136	-0.0106	-0.0162
15	0.0098	0.0509	0.1621	-0.0160	0.0065	-0.0303	0.1813	0.5623	-0.0220	-0.0069	-0.0033
16	0.0246	-0.0128	-0.1825	-0.0140	0.0637	0.0164	-0.1693	0.5615	0.0123	0.0133	0.0173
17	-0.0406	-0.0989	-0.5326	0.0305	-0.0996	0.0417	-0.1533	0.1800	0.0278	0.0044	-0.0080
18	-0.1398	-0.0730	-0.1086	0.1669	-0.5424	-0.0162	-0.0200	-0.0090	-0.0260	-0.0356	-0.0545
19	0.1620	0.0282	0.0943	-0.1720	-0.5636	-0.0143	0.0483	-0.0398	-0.0129	-0.0479	-0.0012
20	0.5082	0.0481	0.0399	-0.1372	-0.1790	0.0151	0.0024	0.0067	0.0228	0.1695	0.1352
21	0.1528	0.0033	-0.0170	0.0003	0.0413	0.0068	-0.0144	0.0123	0.0091	0.5750	0.1692
22	-0.1490	-0.0250	-0.0102	0.0581	0.0403	-0.0119	0.0051	-0.0071	-0.0164	0.5667	-0.1745

NAPHTHALENE

AO	πℓ2'	πℓ2	πℓ2	πℓ2	πℓ2
1	-0.1602	0.5724	-0.1714	-0.0450	-0.0025
2	0.1491	0.5693	0.1726	-0.0361	0.0579
3	0.1489	0.1724	0.5684	0.0578	-0.0363
4	-0.1604	-0.1715	0.5722	0.0025	-0.0461
5	-0.5182	-0.1359	0.1658	-0.1359	0.1658
6	-0.5182	0.1661	-0.1360	0.1661	-0.1360
7	-0.1600	-0.0460	0.0025	0.5724	-0.1714
8	0.1491	-0.0361	0.0579	0.5682	0.1727
9	0.1490	0.0578	-0.0360	0.1724	0.5684
10	-0.1602	0.0035	-0.0461	-0.1716	0.5722

AZULENE

AO	πℓ3'	πℓ3	πℓ34	πℓ23	πℓ3
1	-0.1265	0.1101	0.3794	-0.2154	-0.3999
2	-0.4826	0.1701	0.1836	-0.1271	-0.0693
3	-0.5903	-0.0448	-0.0752	0.0926	0.1055
4	-0.3210	-0.4202	-0.1868	0.0803	0.0079
5	0.0481	-0.6017	0.0001	-0.0754	-0.0764
6	0.1720	-0.3916	0.3567	-0.0591	0.0533
7	0.0219	-0.0024	0.5725	0.1861	0.1246
8	-0.0582	0.0795	0.1408	0.6473	0.1545
9	0.0273	-0.0394	-0.1957	0.5039	-0.3298
10	0.0839	-0.0679	-0.0862	-0.0019	-0.6733

PENTACENE

AO	πℓ4	πℓ4	πℓ34	πℓ34	πℓ3	πℓ3	πℓ23	πℓ23	πℓ3	πℓ23	πℓ23
1	0.0352	0.0606	-0.0200	0.1033	-0.1220	-0.0177	0.0107	-0.1870	0.0457	-0.5586	0.0061
2	-0.0129	-0.0324	0.0044	-0.0692	0.0675	0.0004	-0.0013	0.1585	-0.0127	-0.5915	0.0022
3	-0.0654	-0.1245	0.0353	-0.2471	0.4691	0.0345	-0.0180	0.1210	-0.1021	-0.1796	-0.0115
4	0.0143	0.0414	-0.0016	0.1186	0.6057	0.0073	-0.0010	-0.0446	0.0065	0.0925	-0.0081
5	0.1407	0.2969	-0.0699	0.1431	0.2692	-0.0846	0.0338	-0.0643	0.3715	0.0636	0.0251
6	0.0306	-0.0306	-0.0196	-0.0196	-0.0511	-0.0512	0.0114	0.0114	0.6206	-0.0261	0.0261
7	-0.2969	-0.1407	0.1431	-0.0698	-0.2846	0.2691	-0.0643	0.0338	0.3715	-0.0261	-0.0636
8	-0.0415	-0.0144	0.1186	-0.0017	0.0072	0.6057	-0.0446	-0.0009	0.0066	0.0081	-0.0925
9	0.1245	0.0654	-0.2471	0.0352	0.0345	0.4691	0.1210	-0.0180	-0.1021	0.0115	0.1796
10	0.0324	0.0129	-0.0692	0.0044	0.0004	0.0675	0.1585	-0.0013	-0.0127	-0.0022	0.5915
11	-0.0606	-0.0352	0.1033	-0.0200	-0.0177	-0.1220	-0.1870	0.0107	0.0457	-0.0061	0.5586
12	-0.0346	-0.0071	0.1175	0.0016	0.0057	-0.0300	-0.5890	-0.0023	-0.0000	0.0055	0.1323
13	0.0655	0.0288	-0.1722	0.0134	0.0072	0.0622	-0.5609	-0.0065	-0.0218	0.0019	-0.1781
14	0.0689	0.0088	-0.5789	-0.0045	-0.0097	0.0655	-0.1045	0.0044	0.0018	-0.0083	-0.0764
15	-0.2717	-0.0916	-0.4790	-0.0390	-0.0227	-0.2398	0.1179	0.0182	0.0733	-0.0064	0.0524
16	-0.5930	-0.0109	-0.0553	0.0162	0.0220	-0.0523	0.0316	-0.0113	-0.0065	0.0156	0.0337
17	-0.3768	0.3768	0.1095	0.1095	0.0678	0.0678	-0.0445	-0.0445	-0.2700	0.0179	-0.0179
18	0.0109	0.5930	0.0162	-0.0553	-0.0523	0.0220	-0.0113	0.0316	-0.0065	-0.0337	-0.0156
19	0.0916	0.2718	-0.0390	-0.4789	-0.2398	-0.0227	0.0182	0.1179	0.0733	-0.0524	0.0054
20	-0.0088	-0.0688	-0.0045	-0.5789	0.0655	-0.0097	0.0044	-0.1045	0.0018	0.0764	0.0083
21	-0.0288	-0.0655	0.0134	-0.1722	0.0622	0.0072	-0.0065	-0.5609	-0.0218	0.1781	-0.0019
22	0.0071	0.0346	0.0016	0.1175	-0.0300	0.0058	-0.0023	-0.5390	-0.0000	-0.1323	-0.0055

PYRENE

AO	πℓ4	πℓ4	πℓ4	πℓ3	πℓ3	πℓ3	πℓ23	πℓ23
1	-0.1274	0.0175	0.1954	0.0612	-0.1089	0.0983	0.5520	0.0066
2	0.0454	0.0082	-0.1150	-0.0192	0.0261	-0.0345	0.6059	0.0004
3	0.3419	-0.0540	-0.1218	-0.0593	0.3744	-0.2071	0.1998	-0.0147
4	-0.0179	-0.0245	0.0263	-0.0014	0.6146	-0.0174	-0.0672	-0.0491
5	-0.1833	0.0604	0.0604	0.0458	0.4054	0.4053	-0.0581	0.0581
6	-0.0179	0.0263	-0.0245	-0.0014	-0.0173	0.6146	0.0491	0.0672
7	0.3418	-0.1218	-0.0540	-0.0592	-0.2071	0.3745	0.0147	-0.1998
8	0.0454	-0.1150	0.0082	-0.0192	-0.0346	0.0261	-0.0004	-0.6059
9	-0.1274	0.1954	0.0175	0.0612	0.0979	-0.1090	-0.0065	-0.5520
10	-0.0422	0.5937	-0.0150	0.0156	0.0147	-0.0049	0.0021	-0.0900
11	-0.0154	0.3797	-0.2137	-0.4058	-0.0709	0.0789	0.0945	0.1078
12	0.0248	-0.0145	-0.0146	-0.6136	-0.0042	-0.0041	-0.0192	0.0192
13	-0.0154	-0.2137	0.3796	-0.4059	0.0789	-0.0709	-0.1078	-0.0945
14	-0.0422	-0.0151	0.5937	0.0155	-0.0049	0.0147	0.0800	-0.0021
15	0.2488	0.3440	0.3441	0.1799	-0.0166	-0.0165	-0.1298	0.1297
16	0.5943	0.0243	0.0243	0.0191	-0.0141	-0.0140	-0.0697	0.0697

Table 2 (continued)

BENZOPERYLENE

AO	π*l*2'	π*l*2'	π*l*2'	π*l*2'	π*l*34	π*l*34	π*l*2	π*l*2	π*l*2	π*l*2	π*l*2
1	-0.0439	0.0234	0.1390	-0.0118	0.0362	0.1600	-0.5727	0.0201	-0.0302	-0.0227	-0.0001
2	0.0063	-0.0346	-0.1933	0.0186	-0.0677	-0.1809	-0.5508	-0.0408	0.0333	-0.0599	-0.0150
3	0.1112	-0.0174	-0.5352	0.0170	-0.0087	-0.1342	-0.1495	-0.0098	0.0400	0.1397	0.0091
4	0.1505	0.0600	-0.1554	0.0140	0.0228	-0.0048	0.0361	0.0136	-0.0382	0.5741	0.0358
5	-0.1355	-0.0132	0.1401	-0.0141	-0.0037	0.0551	0.0333	0.0019	-0.0348	0.5831	-0.0210
6	-0.5154	-0.1369	0.1249	-0.0133	-0.0389	-0.0303	-0.0463	-0.0233	0.1677	0.1621	-0.0506
7	-0.1517	-0.1504	0.0109	0.0516	-0.0299	-0.0354	-0.0308	-0.0341	0.5732	-0.0457	0.0310
8	0.1521	0.1570	-0.0527	-0.0109	0.0358	0.0309	0.0349	0.0316	0.5708	-0.0325	0.0469
9	0.1339	0.5201	0.0127	-0.1227	0.1285	0.0381	0.0225	0.0448	0.1628	0.0494	-0.1579
10	0.0125	0.1401	0.0143	-0.1418	-0.0572	0.0036	-0.0022	-0.0357	-0.0360	0.0212	-0.5812
11	-0.0584	-0.1492	-0.0137	0.1506	0.0060	-0.0223	-0.0131	-0.0344	-0.0365	-0.0351	-0.5762
12	0.0185	-0.1142	-0.0173	0.5300	0.1387	0.0089	0.0101	0.1568	0.0411	-0.0093	-0.1442
13	0.0340	-0.0066	-0.0175	0.1856	0.1779	0.0668	0.0397	0.5549	0.0327	0.0146	0.0583
14	-0.0242	0.0452	0.0119	-0.1425	-0.1676	-0.0371	-0.0204	0.5693	-0.0308	0.0003	0.0240
15	-0.0389	-0.0187	0.0221	-0.1634	-0.5432	-0.1059	-0.0516	0.2059	-0.0254	-0.0180	-0.0622
16	0.0445	-0.0352	-0.0086	0.1463	-0.5510	0.1055	0.0401	-0.1488	0.0346	0.0093	0.0078
17	0.0164	0.1559	0.0385	0.5119	-0.1834	-0.0497	-0.0293	-0.1472	-0.0193	0.0205	0.1320
18	-0.1586	0.5294	0.0320	0.1396	0.0098	-0.0471	-0.0351	-0.0177	-0.1356	-0.0120	0.1304
19	-0.5340	0.1529	-0.1337	-0.0313	0.0456	-0.0087	0.0180	0.0345	-0.1333	-0.1283	0.0123
20	-0.1614	-0.0171	-0.5058	-0.0405	0.0502	0.1905	0.1503	0.0301	-0.0192	-0.1341	-0.0208
21	0.0344	-0.0433	-0.1389	0.0089	-0.1023	0.5547	0.1451	-0.0397	0.0341	-0.0082	-0.0093
22	0.0192	0.0397	0.1670	-0.0235	0.1068	0.5385	-0.2134	0.0530	-0.0259	0.0638	0.0185

BENZPHENANTHRENE

AO	π*l*2'	π*l*2'	π*l*2'	π*l*2	π*l*2	π*l*2	π*l*2	π*l*2	π*l*2
1	-0.5199	0.0182	0.1212	-0.0115	0.1719	0.0184	0.1424	-0.1537	0.0443
2	-0.1450	-0.0518	0.1505	-0.0318	-0.0334	0.0226	0.0068	-0.5784	-0.0309
3	0.1449	0.0087	-0.1480	0.0216	-0.0411	-0.0177	-0.0614	-0.5774	-0.0406
4	0.1229	0.1229	-0.5280	0.0446	0.0446	-0.0265	0.0265	-0.1537	0.1536
5	0.0087	0.1449	-0.1480	-0.0411	0.0216	0.0614	0.0177	0.0406	0.5774
6	-0.0518	-0.1450	0.1506	-0.0334	-0.0318	-0.0068	-0.0226	0.0309	0.5784
7	0.0182	-0.5199	0.1212	0.1719	-0.0115	-0.1424	-0.0184	-0.0443	0.1537
8	0.0185	-0.1652	-0.0003	0.5696	0.0077	-0.1702	0.0016	-0.0209	-0.0545
9	-0.0177	0.1537	-0.0508	0.5655	0.0058	0.1769	0.0126	0.0316	-0.0286
10	-0.0206	0.1536	0.0295	0.1761	-0.0131	0.5657	-0.0092	0.0104	0.0603
11	0.0273	-0.1678	0.0407	-0.1701	-0.0012	0.5685	-0.0112	-0.0324	-0.0049
12	0.0266	-0.5237	-0.1440	-0.1423	0.0244	0.1721	0.0270	0.0121	-0.1279
13	-0.1444	-0.1444	-0.5346	-0.0036	-0.0036	-0.0349	0.0349	0.1388	-0.1388
14	-0.5237	0.0266	-0.1440	0.0244	-0.1423	-0.0270	-0.1721	0.1279	-0.0121
15	-0.1678	0.0273	0.0407	-0.0012	-0.1701	0.0112	-0.5685	0.0049	0.0324
16	0.1536	-0.0206	0.0295	-0.0131	0.1762	0.0092	-0.5657	-0.0603	-0.0104
17	0.1537	-0.0177	-0.0508	0.0058	0.5655	-0.0125	-0.1769	0.0286	-0.0316
18	-0.1652	0.0185	-0.0003	0.0077	0.5696	-0.0016	0.1702	0.0545	0.0209

PENTAPHENE

AO	π*l*2'	π*l*2'	π*l*34	π*l*34	π*l*34	π*l*34	π*l*2	π*l*2	π*l*2	π*l*2	π*l*2
1	-0.1625	-0.0024	-0.0441	0.0144	-0.0068	-0.0029	0.0070	0.1723	0.5712	0.0068	-0.0264
2	-0.5186	0.0238	0.1677	-0.0246	-0.0414	0.1294	0.0053	0.1287	0.1594	0.0109	0.0427
3	-0.1788	0.0236	0.5542	-0.0550	-0.0127	0.1775	-0.0162	-0.1023	-0.0515	-0.0112	0.1185
4	0.1319	-0.0337	0.5427	0.0519	0.0499	-0.1538	-0.0018	-0.1501	-0.0315	-0.0101	-0.1264
5	0.0470	-0.0593	0.1152	0.1300	0.0517	-0.0275	0.0300	-0.0102	0.0049	0.0159	-0.5872
6	-0.0599	0.0472	-0.1301	-0.1165	-0.0272	0.0527	-0.0101	0.0303	0.0162	0.0052	-0.5869
7	-0.0333	0.1305	-0.0511	-0.5443	-0.1511	0.0498	-0.0494	-0.0017	-0.0099	-0.0308	-0.1254
8	0.0239	-0.1824	0.0552	-0.5523	0.1791	-0.0129	-0.0027	-0.0164	-0.0114	-0.0532	0.1169
9	0.0235	-0.5212	0.0241	-0.1644	0.1278	-0.0411	0.1273	0.0052	0.0107	0.1572	0.0423
10	-0.0026	-0.1648	-0.0145	0.0450	-0.0035	-0.0067	0.1730	0.0070	0.0069	0.5702	-0.0267
11	-0.0122	0.1439	-0.0070	0.0354	-0.0535	0.0257	-0.1643	-0.0063	-0.0090	0.5719	-0.0088
12	0.0086	0.1497	0.0178	-0.0591	0.0415	-0.0056	-0.5655	-0.0069	-0.0046	0.1763	0.0342
13	0.0081	-0.1500	-0.0002	0.0009	0.0405	-0.0230	-0.5762	0.0076	0.0088	-0.1680	-0.0074
14	-0.0220	-0.5045	-0.0283	0.1389	-0.1822	0.0336	-0.1722	0.0068	0.0007	-0.1361	-0.0585
15	-0.0424	-0.1582	-0.0287	0.1709	-0.5647	0.1028	0.0473	-0.0169	-0.0245	0.0010	-0.0221
16	0.0402	0.1405	0.0288	-0.1680	-0.5411	-0.1019	0.0365	-0.0045	0.0077	0.0549	0.0812
17	0.1392	0.0398	0.1652	-0.0289	-0.1004	-0.5428	-0.0043	0.0358	0.0541	0.0078	0.0807
18	-0.1618	-0.0428	-0.1725	0.0293	0.1033	-0.5629	-0.0172	0.0479	0.0013	-0.0247	-0.0221
19	-0.5072	-0.0217	-0.1374	0.0281	0.0331	-0.1789	0.0057	-0.1701	-0.1348	0.0006	-0.0581
20	-0.1523	0.0083	-0.0003	-0.0000	-0.0232	0.0414	0.0077	-0.5753	-0.1688	0.0099	-0.0073
21	0.1489	0.0084	0.0582	-0.0176	-0.0054	0.0405	-0.0058	-0.5664	0.1746	-0.0045	0.0339
22	0.1448	-0.0125	-0.0364	0.0073	0.0259	-0.0543	-0.0064	-0.1661	0.5710	-0.0091	-0.0089

TRIPHENYLENE

AO	π*l*2'	π*l*2'	π*l*2'	π*l*2	π*l*2	π*l*2	π*l*2	π*l*2	π*l*2
1	0.1614	-0.0182	-0.0501	-0.0174	-0.0314	-0.1842	0.5612	-0.0097	0.0237
2	-0.1738	-0.0475	0.0079	0.0327	0.0192	0.1682	0.5652	0.0341	-0.0163
3	-0.5278	0.1213	0.1066	0.0178	0.0425	0.1532	0.1816	-0.0141	-0.0282
4	-0.1190	0.5303	0.1057	-0.1782	-0.0273	0.0143	-0.0173	-0.1514	0.0417
5	0.0480	0.1774	0.0077	-0.5636	-0.0163	-0.0345	-0.0332	-0.1697	0.0193
6	0.0176	-0.1598	-0.0495	-0.5628	0.0232	0.0096	0.0173	0.1810	-0.0310
7	-0.0501	-0.1614	0.0182	-0.1842	0.0174	0.0314	0.0237	0.5612	-0.0097
8	0.0079	0.1738	0.0475	0.1682	-0.0327	-0.0192	-0.0163	0.5652	0.0341
9	0.1066	0.5278	-0.1213	0.1532	-0.0178	-0.0425	-0.0281	0.1816	-0.0141
10	0.1057	0.1189	-0.5303	0.0143	0.1782	0.0273	0.0417	-0.0173	-0.1514
11	0.0078	-0.0480	-0.1774	-0.0345	0.5636	0.0163	0.0193	-0.0332	-0.1697
12	-0.0495	-0.0175	0.1598	0.0096	0.5628	-0.0232	-0.0310	0.0173	0.1810
13	0.0182	0.0501	0.1614	0.0314	0.1842	-0.0174	-0.0097	0.0237	0.5612
14	0.0475	-0.0079	-0.1738	-0.0192	-0.1693	0.0327	0.0341	-0.0163	0.5652
15	-0.1213	-0.1065	-0.5278	-0.0425	-0.1532	0.0179	-0.0141	-0.0281	0.1816
16	-0.5303	-0.1057	-0.1190	0.0273	-0.0143	-0.1782	-0.1514	0.0417	-0.0173
17	-0.1774	-0.0079	0.0480	0.0163	0.0345	-0.5636	-0.1697	0.0193	-0.0332
18	0.1598	0.0495	0.0176	-0.0232	-0.0096	-0.5628	0.1810	-0.0310	0.0173

Table 2 (continued)

PICENE

AO	$\pi\ell 2'$	$\pi\ell 2'$	$\pi\ell 2'$	$\pi\ell 2'$	$\pi\ell 2$	$\pi\ell 2$	$\pi\ell 2$	$\pi\ell 2$	$\pi\ell 2$	$\pi\ell 2$	$\pi\ell 2$
1	-0.5220	-0.0178	0.1189	-0.0349	0.1703	0.0094	-0.1424	-0.0054	-0.0143	-0.1511	-0.0182
2	-0.1676	0.0004	-0.0015	-0.0211	0.5683	0.0057	-0.1710	-0.0056	0.0101	0.0555	-0.0232
3	0.1536	0.0107	-0.0486	0.0260	0.5662	-0.0079	0.1758	0.0057	0.0051	0.0269	0.0195
4	0.1553	-0.0051	0.0292	0.0135	0.1788	-0.0037	0.5641	0.0054	-0.0116	-0.0613	0.0276
5	-0.1673	-0.0088	0.0387	-0.0291	-0.1691	0.0082	0.5686	-0.0070	-0.0014	0.0066	-0.0321
6	-0.5236	0.0151	-0.1407	0.0050	-0.1448	-0.0003	0.1755	-0.0046	0.0161	0.1285	-0.0367
7	-0.1393	0.0371	-0.5293	0.1302	-0.0039	-0.0246	-0.0326	0.0199	0.0172	0.1344	0.1624
8	0.0297	-0.0306	-0.1565	0.1512	0.0290	-0.0152	-0.0327	0.0272	-0.0651	0.0156	0.5722
9	0.0306	-0.0297	0.1512	-0.1565	-0.0152	0.0290	0.0272	-0.0327	0.0156	-0.0651	0.5722
10	-0.0371	0.1393	0.1302	-0.5293	-0.0246	-0.0039	0.0199	-0.0325	0.1344	0.0172	0.1623
11	-0.0151	0.5235	0.0050	-0.1407	-0.0003	-0.1448	-0.0045	0.1756	0.1285	0.0161	-0.0367
12	0.0088	0.1673	-0.0291	0.0387	0.0082	-0.1690	-0.0070	0.5686	0.0066	-0.0014	-0.0321
13	0.0051	-0.1553	0.0135	0.0292	-0.0037	0.1788	0.0054	0.5641	-0.0613	-0.0116	0.0276
14	-0.0107	-0.1535	0.0260	-0.0486	-0.0079	0.5662	0.0057	0.1757	0.0269	0.0051	0.0195
15	-0.0004	0.1676	-0.0211	-0.0015	0.0057	0.5683	-0.0056	-0.1710	0.0556	0.0101	-0.0232
16	0.0178	0.5221	-0.0349	0.1189	0.0094	0.1702	-0.0054	-0.1424	-0.1510	-0.0143	-0.0182
17	0.0123	0.1453	0.0355	0.1499	-0.0088	-0.0323	0.0120	-0.0083	-0.5776	-0.0322	0.0657
18	-0.0216	-0.1436	0.0245	-0.1474	-0.0071	-0.0404	0.0015	0.0611	-0.5775	0.0290	-0.0163
19	0.0233	-0.1219	-0.1488	-0.5281	0.0204	0.0433	-0.0193	-0.0250	-0.1562	0.0445	-0.1385
20	0.1218	-0.0033	-0.5281	-0.1488	0.0433	0.0204	-0.0250	-0.0190	0.0445	-0.1562	-0.1385
21	0.1436	0.0216	-0.1475	0.0245	-0.0405	-0.0071	0.0611	0.0015	0.0290	-0.5775	-0.0163
22	-0.1453	-0.0123	0.1499	0.0354	-0.0323	-0.0088	-0.0082	0.0120	-0.0322	-0.5776	0.0657

CHRYSENE

$\pi\ell 2'$	$\pi\ell 2'$	$\pi\ell 2'$	$\pi\ell 2$	$\pi\ell 2$	$\pi\ell 2$	$\pi\ell 2$	$\pi\ell 2$	$\pi\ell 2$
0.1532	0.0244	0.0494	-0.0082	0.1756	0.5663	-0.0137	-0.0279	0.0190
-0.1665	-0.0193	0.0018	-0.0075	-0.1710	0.5689	-0.0011	-0.0545	-0.0233
-0.5213	-0.0339	-0.1206	0.0177	-0.1418	0.1700	0.0219	0.1527	-0.0164
-0.1465	0.0321	-0.1522	0.0283	-0.0073	-0.0336	0.0157	0.5769	0.0674
0.1437	0.0261	0.1502	-0.0313	0.0607	-0.0402	-0.0268	0.5763	-0.0175
0.1240	-0.1414	0.5310	-0.0340	-0.0258	0.0445	0.0030	0.1575	-0.1378
0.0052	-0.5232	0.1425	0.1746	-0.0170	0.0189	0.1438	-0.0394	-0.1287
-0.0269	-0.1669	-0.0390	0.5689	0.0046	-0.0113	0.1694	-0.0308	-0.0058
0.0122	0.1545	-0.0300	0.5646	0.0103	-0.0069	-0.1780	0.0285	0.0608
0.0243	0.1532	0.0494	0.1755	-0.0082	0.0137	-0.5664	0.0180	-0.0279
-0.0193	-0.1665	0.0018	-0.1710	-0.0075	0.0011	-0.5689	-0.0233	-0.0545
-0.0339	-0.5214	-0.1206	-0.1418	0.0177	-0.0219	-0.1700	-0.0164	0.1527
0.0321	-0.1466	-0.1522	-0.0073	0.0283	-0.0157	0.0336	0.0674	0.5769
0.0261	0.1437	0.1502	0.0607	-0.0313	0.0268	0.0401	-0.0175	0.5763
-0.1414	0.1240	0.5310	-0.0258	-0.0340	-0.0030	-0.0445	-0.1378	0.1575
-0.5232	0.0052	0.1425	-0.0170	0.1745	-0.1438	-0.0188	-0.1287	-0.0394
-0.1669	-0.0269	-0.0390	0.0046	0.5688	-0.1694	0.0113	-0.0058	-0.0308
0.1545	0.0122	-0.0300	0.0103	0.5646	0.1779	0.0069	0.0607	0.0295

1,2,5,6-DIBENZANTHRACENE

AO	$\pi\ell 2'4$	$\pi\ell 34$	$\pi\ell 34$	$\pi\ell 2'4$	$\pi\ell 23$	$\pi\ell 23$	$\pi\ell 3$	$\pi\ell 23$	$\pi\ell 23$	$\pi\ell 23$	$\pi\ell 23$
1	0.1775	-0.0383	0.0465	-0.0171	0.5356	0.0082	0.0517	-0.2299	0.0108	-0.0119	-0.0363
2	0.1276	-0.0019	-0.0151	-0.0051	0.1306	-0.0036	0.0113	-0.5862	-0.0023	-0.0116	0.0517
3	-0.2289	0.0379	-0.0363	0.0187	-0.1872	-0.0069	-0.0670	-0.5365	-0.0102	0.0169	-0.0039
4	-0.5664	-0.0240	0.0575	-0.0044	-0.1151	0.0075	0.0225	-0.1225	0.0083	0.0091	-0.1038
5	-0.1799	-0.1811	0.3450	-0.0661	-0.0060	0.0271	0.3900	0.0338	0.0349	-0.0553	-0.1316
6	0.0522	-0.0275	-0.0280	-0.0190	0.0297	-0.0174	0.6148	0.0242	-0.0149	-0.0697	0.0096
7	0.0556	0.3424	-0.1843	0.1255	-0.0133	-0.0289	0.3812	-0.0264	-0.0448	0.1906	0.0788
8	-0.0011	0.0602	-0.0316	0.1265	-0.0097	0.0472	0.0296	-0.0106	0.0245	0.6001	0.0135
9	-0.0236	-0.1259	0.0862	-0.1784	0.0126	-0.0063	-0.1090	0.0176	0.0380	0.5600	-0.0453
10	0.0082	-0.0775	0.0132	-0.5645	0.0081	-0.1101	-0.0030	0.0063	-0.1165	0.1030	0.0005
11	0.0119	0.0008	-0.0221	-0.2307	-0.0032	-0.1894	0.0377	-0.0063	-0.5360	-0.0752	0.0165
12	-0.0091	0.0353	0.0004	0.1260	-0.0054	0.1258	-0.0097	-0.0029	-0.5884	-0.0110	-0.0063
13	-0.0079	-0.0361	0.0311	0.1814	0.0056	0.5321	-0.0313	0.0069	-0.2337	0.0758	-0.0180
14	0.0108	-0.0365	-0.0064	-0.1121	0.0047	0.5904	0.0151	0.0018	0.1417	-0.0142	0.0107
15	0.0015	0.1799	-0.0591	-0.4717	-0.0106	0.2350	0.0280	-0.0088	0.1751	-0.1368	0.0227
16	-0.0283	0.5933	-0.0105	-0.0665	-0.0162	-0.0182	-0.0114	-0.0099	0.0074	-0.0745	-0.0207
17	-0.0279	0.3951	0.3883	0.0802	0.0332	-0.0583	-0.2348	0.0333	-0.0544	0.0166	-0.1073
18	0.0632	-0.0081	0.5890	0.0184	0.0215	0.0128	-0.0085	0.0099	0.0058	0.0380	0.0893
19	0.1485	-0.0600	0.1851	-0.0129	-0.0634	0.0157	0.0217	-0.3789	0.0137	0.0061	0.5600
20	-0.0900	0.0149	-0.1183	-0.0074	-0.0136	-0.0115	0.0047	0.0176	-0.0080	-0.0250	0.6012
21	-0.4721	0.0615	-0.1128	0.0217	0.2282	-0.0132	-0.0720	0.1745	-0.0150	0.0105	0.1823
22	-0.1133	0.0103	0.0069	0.0088	0.5893	0.0022	-0.0197	0.1445	-0.0002	0.0122	-0.0516

PHENANTHRENE

$\pi\ell 2'$	$\pi\ell 2'$	$\pi\ell 2$	$\pi\ell 2$	$\pi\ell 2$	$\pi\ell 2$	$\pi\ell 2$
-0.1549	0.0474	0.5654	0.0302	0.0231	0.1772	-0.0252
0.1689	0.0009	0.5677	-0.0243	-0.0237	-0.1707	-0.0579
0.5228	-0.1149	0.1720	-0.0403	-0.0233	-0.1444	0.1481
0.1407	-0.1444	-0.0291	0.0420	0.0627	-0.0101	0.5808
-0.1443	0.1404	-0.0419	0.0290	-0.0101	0.0626	0.5809
-0.1151	0.5225	0.0404	-0.1724	-0.1446	-0.0239	0.1484
0.0009	0.1685	0.0243	-0.5679	-0.1705	-0.0237	-0.0578
0.0475	-0.1551	-0.0302	-0.5652	0.1775	0.0231	-0.0253
-0.0272	-0.1563	-0.0154	-0.1792	0.5639	0.0256	0.0622
-0.0394	0.1698	0.0335	0.1692	0.5674	-0.0347	-0.0079
0.1355	0.5257	-0.0055	0.1461	0.1760	-0.0296	-0.1275
0.5254	0.1358	-0.1463	0.0055	-0.0297	0.1764	-0.1276
0.1694	-0.0393	-0.1690	-0.0334	-0.0347	0.5676	-0.0079
-0.1565	-0.0273	0.1796	0.0154	0.0256	0.5637	0.0623

Table 2 (continued)

ANTHANTHRENE

AO	$\pi\ell 4$	$\pi\ell 4$	$\pi\ell 4$	$\pi\ell 34$	$\pi\ell 34$	$\pi\ell 34$	$\pi\ell 3$	$\pi\ell 3$	$\pi\ell 3$	$\pi\ell 23$	$\pi\ell 23$
1	0.0859	0.0191	0.0073	0.0240	0.0582	0.0088	0.5975	0.0880	-0.0342	-0.0951	0.0272
2	0.1679	0.0346	-0.0647	-0.0173	0.0445	-0.0199	0.2903	0.5005	0.0633	-0.0553	-0.0156
3	-0.0591	-0.0192	0.0013	-0.0193	-0.0465	-0.0052	-0.1115	0.6029	0.0328	0.0640	-0.0242
4	-0.4007	-0.0433	0.1467	0.0480	-0.0342	0.0343	-0.1874	0.2654	-0.2503	0.0153	0.0563
5	-0.0592	0.0058	0.1087	0.0601	0.0449	0.0244	-0.0163	-0.0176	-0.5999	-0.0069	0.1069
6	0.1434	0.0369	-0.2242	-0.0939	-0.0062	-0.0465	0.0806	-0.0704	-0.4887	-0.0002	-0.1670
7	0.0310	0.0102	-0.0210	-0.1213	0.0013	-0.0417	0.0169	-0.0064	-0.0781	-0.0023	-0.6006
8	-0.0683	-0.0133	0.0834	0.1677	0.0036	0.0568	-0.0450	0.0342	0.1317	-0.0004	-0.5669
9	-0.0181	-0.0361	0.0212	0.5863	-0.0086	0.0766	-0.0096	0.0016	0.0345	0.0064	-0.0923
10	0.0342	0.1906	0.0442	0.4537	0.0875	-0.3205	0.0607	-0.0487	-0.0955	-0.0462	0.1209
11	0.0133	0.0734	-0.0219	0.0547	-0.0081	-0.6067	0.0011	0.0037	-0.0146	0.0048	0.0301
12	-0.0389	-0.2889	-0.0106	-0.2064	-0.0874	-0.4809	-0.0552	0.0397	0.0795	0.0415	-0.0938
13	-0.0144	-0.5888	0.0541	-0.0582	0.0614	-0.0465	0.0121	-0.0140	0.0014	-0.0269	-0.0063
14	0.0312	-0.2637	0.1862	0.0160	0.4896	0.0728	0.0990	-0.0719	-0.1052	-0.1298	0.0127
15	0.0159	0.0793	-0.0529	0.0208	0.5831	0.0028	-0.0350	0.0285	0.0217	0.0959	-0.0026
16	0.0947	0.0547	-0.0201	0.0057	0.1624	-0.0141	-0.1262	0.0888	0.0059	0.5677	0.0021
17	-0.0257	-0.0387	0.0167	-0.0138	-0.1235	-0.0007	0.0712	-0.0458	-0.0086	0.5999	0.0013
18	-0.2584	-0.0469	0.0533	0.0021	-0.0914	0.0163	0.4666	-0.1871	-0.0095	0.1683	-0.0050
19	-0.5847	0.0111	-0.0473	-0.0226	-0.0021	-0.0144	0.0613	-0.0732	0.0743	-0.0659	-0.0419
20	-0.2602	0.1398	-0.4164	-0.0534	0.2387	-0.0619	-0.0345	-0.0029	0.1760	-0.0930	-0.0226
21	0.0592	-0.0382	-0.5873	0.0017	-0.0791	0.0140	-0.0025	0.0180	-0.0730	0.0124	0.0589
22	0.0352	-0.3807	-0.2647	0.2819	-0.1518	0.1686	-0.0332	0.0349	0.0215	0.0657	0.1067

BENZANTHRACENE

$\pi\ell 42'$	$\pi\ell 2'$	$\pi\ell 34$	$\pi\ell 34$	$\pi\ell 2$	$\pi\ell 2$	$\pi\ell 23$	$\pi\ell 23$	$\pi\ell 2$
0.1334	0.0007	0.0027	-0.0310	-0.0103	0.0112	-0.5823	0.1641	-0.0212
-0.1523	0.0258	-0.0630	-0.0523	0.0128	-0.0168	-0.5607	-0.1856	-0.0145
-0.1366	-0.0135	0.0293	0.0467	0.0107	-0.0075	-0.1532	-0.5777	0.0297
0.1781	-0.0155	0.0493	0.0098	-0.0150	0.0155	0.1769	-0.5648	-0.0026
0.5369	0.0418	-0.1416	-0.1172	-0.0106	0.0009	0.1172	-0.1427	-0.0542
0.4832	-0.0547	0.1473	0.2134	-0.0149	0.0235	-0.1828	0.1418	0.0514
0.1361	-0.0436	0.1607	0.5746	0.0236	-0.0183	0.0475	-0.0011	0.1091
-0.1485	0.0899	-0.1932	0.5173	0.0135	-0.0272	0.0395	-0.0975	-0.1432
-0.1208	-0.1018	-0.5587	0.1313	0.0142	0.0137	-0.0447	0.0267	0.0828
0.2101	0.0930	-0.5362	-0.2003	0.0471	-0.0513	-0.0085	0.0603	-0.0334
-0.0495	0.1382	-0.0467	-0.1005	-0.0604	0.0387	-0.0063	-0.0092	-0.5882
0.0680	-0.1393	0.0726	-0.1286	0.0154	0.0237	-0.0186	0.0331	-0.5805
0.0409	-0.5377	0.0850	-0.0470	0.1380	-0.1580	0.0147	-0.0043	-0.1299
-0.0541	-0.5130	-0.1229	0.0468	-0.1995	0.1597	-0.0022	-0.0133	0.1251
0.0164	-0.1557	0.0559	-0.0029	-0.5740	0.1599	0.0156	-0.0127	0.0146
0.0198	0.1696	0.0150	-0.0309	-0.5526	-0.1991	-0.0072	0.0128	-0.0682
-0.0194	0.1500	-0.0481	0.0106	-0.1624	-0.5721	-0.0139	0.0088	0.0168
-0.0094	-0.1928	0.0123	0.0315	0.1768	-0.5567	0.0121	-0.0133	0.0678

1,2,7,8-DIBENZANTHRACENE

AO	$\pi\ell 2'4$	$\pi\ell 2'4$	$\pi\ell 34$	$\pi\ell 34$	$\pi\ell 23$	$\pi\ell 23$	$\pi\ell 3$	$\pi\ell 23$	$\pi\ell 23$	$\pi\ell 23$	$\pi\ell 23$
1	-0.0159	-0.0902	-0.1185	0.0165	-0.0130	-0.0135	0.0028	0.0088	0.0177	-0.6012	0.0052
2	0.0012	0.1484	0.1826	-0.0600	0.0115	-0.0634	0.0239	-0.0085	-0.0789	-0.5608	0.0217
3	0.0271	0.0626	0.5891	-0.0148	0.0162	0.0212	-0.0036	-0.0102	0.0099	-0.0892	-0.0190
4	0.0264	-0.0283	0.3980	0.3851	-0.0337	0.0335	-0.2345	0.0333	0.0334	0.1086	-0.1068
5	-0.0633	-0.0279	-0.0032	0.5893	-0.0216	-0.0159	-0.0143	0.0102	-0.0098	0.0206	0.0890
6	-0.1487	-0.0012	-0.0586	0.1845	0.0635	-0.0114	0.0217	-0.0790	-0.0084	-0.0215	0.5603
7	0.0898	0.0161	0.1130	-0.1184	0.0137	0.0129	0.0069	0.0174	0.0087	-0.0058	0.6014
8	0.4715	-0.0131	0.0619	-0.1135	-0.2283	0.0087	-0.0710	0.1744	0.0110	0.0291	0.1826
9	0.1132	-0.0093	0.1114	0.0064	-0.5893	-0.0032	-0.0199	0.1446	-0.0005	0.0098	-0.0515
10	-0.1774	0.0129	-0.0391	0.0472	-0.5356	-0.0056	0.0510	-0.2296	-0.0086	-0.0225	-0.0366
11	-0.1275	0.0078	-0.3027	-0.0149	-0.1306	0.0048	0.0119	-0.5862	0.0029	-0.0042	0.0516
12	0.2285	-0.0169	0.0390	-0.0373	0.1870	0.0040	-0.0659	-0.5367	0.0085	0.0232	-0.0035
13	0.5665	-0.0035	-0.1239	0.0582	0.1148	-0.0085	0.0197	-0.1224	-0.0085	-0.0085	-0.1037
14	0.1819	0.0572	-0.1842	0.3507	0.0061	-0.0127	0.3813	0.0342	-0.0264	-0.0793	-0.1327
15	-0.0503	0.0531	-0.0345	-0.0221	-0.0291	0.0294	0.6150	0.0239	0.0237	-0.0111	0.0089
16	-0.0560	-0.1801	0.3391	-0.1843	0.0132	-0.0065	0.3932	-0.0267	0.0336	0.1309	0.0790
17	0.0034	-0.5661	0.3566	-0.0255	0.0086	-0.1152	0.0242	-0.0086	-0.1229	0.1039	0.0088
18	0.0165	-0.2283	-0.3359	0.0386	-0.0041	-0.1870	-0.0666	0.0086	-0.5368	0.0039	-0.0231
19	-0.0076	0.1279	-0.0153	-0.0015	-0.0048	0.1309	0.0107	0.0029	-0.5860	-0.0519	0.0041
20	-0.0127	0.1774	0.0458	-0.0389	0.0056	0.5357	0.0518	-0.0086	-0.2295	0.0362	0.0224
21	0.0091	-0.1137	0.0075	0.0102	0.0032	0.5892	-0.0195	-0.0005	0.1447	0.0519	-0.0096
22	0.0129	-0.4723	-0.1111	0.0623	-0.0089	0.2281	-0.0731	0.0111	0.1744	-0.1816	-0.0291

NAPHTHACENE

$\pi\ell 4$	$\pi\ell 34$	$\pi\ell 34$	$\pi\ell 3$	$\pi\ell 3$	$\pi\ell 23$	$\pi\ell 23$	$\pi\ell 23$	$\pi\ell 23$
-0.0688	0.0386	-0.1135	0.1184	0.0383	0.5545	0.0121	0.0201	0.1943
0.0325	-0.0099	0.0703	-0.0537	-0.0031	0.5936	0.0044	-0.0025	-0.1559
0.1437	-0.0728	0.2742	-0.4448	-0.0877	0.1892	-0.0252	-0.0356	-0.1291
-0.0249	-0.0002	-0.0939	-0.6118	-0.0244	-0.0842	-0.0194	-0.0046	0.0389
-0.3320	0.1551	-0.1551	-0.3036	0.3036	-0.0651	0.0650	0.0693	0.0693
-0.0249	0.0940	0.0002	0.0244	0.6118	0.0194	0.0842	0.0389	-0.0046
0.1437	-0.2742	0.0728	0.0877	0.4448	0.0252	-0.1892	-0.1291	-0.0356
0.0325	-0.0703	0.0099	0.0031	0.0537	-0.0044	-0.5936	-0.1559	-0.0025
-0.0688	0.1135	-0.0386	-0.0383	-0.1184	-0.0121	-0.5545	0.1943	0.0201
-0.0295	0.1152	-0.0000	0.0083	-0.0211	0.0099	-0.1280	0.5909	-0.0042
0.0698	-0.1831	0.0291	0.0163	0.0596	0.0038	0.1801	0.5568	-0.0131
0.0533	-0.5832	-0.0062	-0.0165	0.0434	-0.0160	0.0752	0.0992	0.0095
-0.3081	-0.4540	-0.0967	-0.0596	-0.2487	-0.0141	-0.0497	-0.1152	0.0391
-0.5914	-0.0381	0.0381	0.0444	-0.0444	0.0338	-0.0338	-0.0296	-0.0296
-0.3081	0.0967	0.4540	0.2487	0.0596	0.0497	0.0141	0.0391	-0.1152
0.0533	0.0062	0.5832	-0.0434	0.0165	-0.0752	0.0160	0.0095	0.0992
0.0698	-0.0291	0.1832	-0.0596	-0.0163	-0.1801	-0.0038	-0.0131	0.5568
-0.0295	0.0000	-0.1152	0.0210	-0.0083	0.1280	-0.0099	-0.0042	0.5909

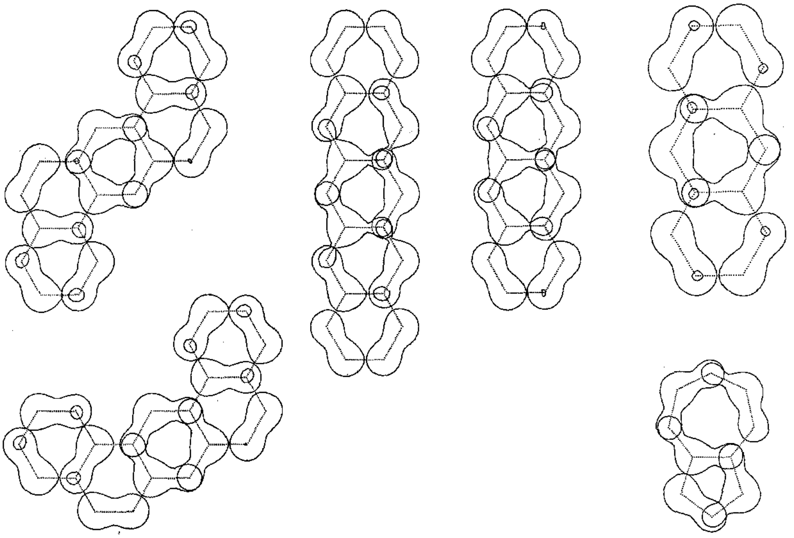


Fig. 4. Non-Kekulé-type localized MO structures

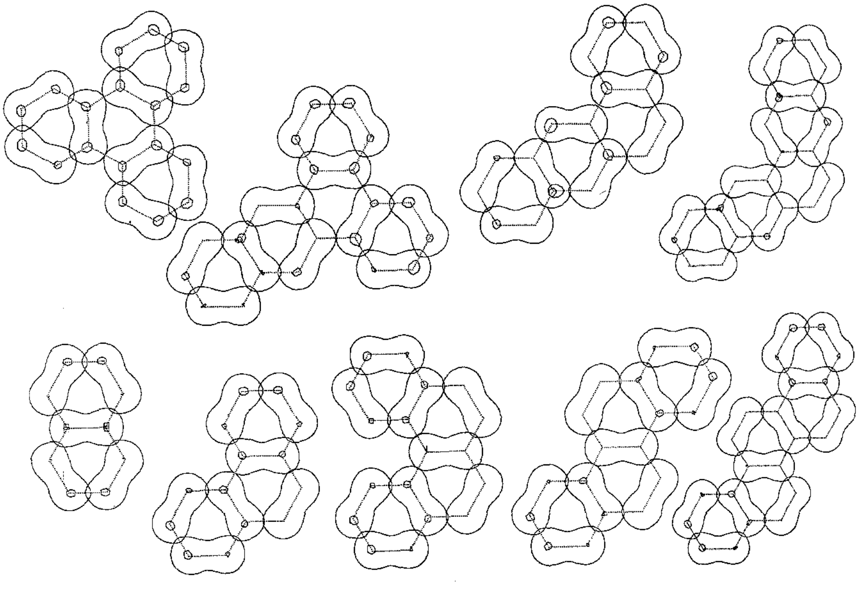


Fig. 3. Kekulé-type localized MO structures

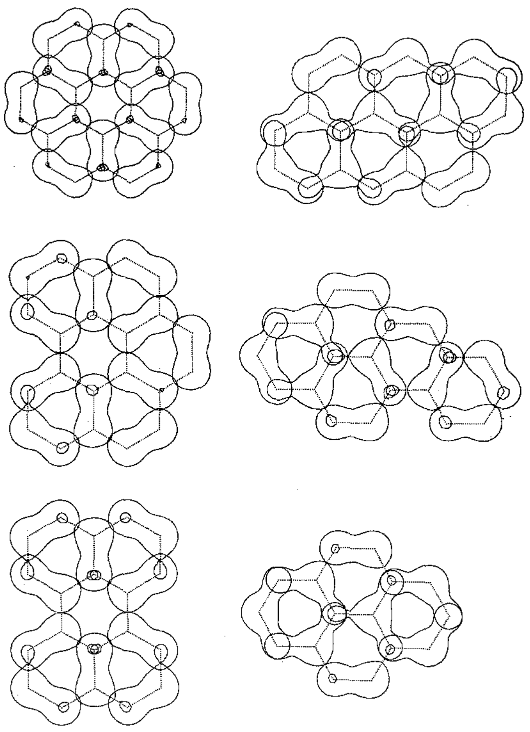


Fig. 5. Kekulé- and non-Kekulé-type localized MO structures in peri-condensed hydrocarbons

each molecule, each LMO is represented by a contour which, in fact, would be the fifth strongest contour in a complete contour diagram such as given in Fig. 2. More complete pictorial representations will be given elsewhere [14].

In symmetric molecules, there is often a symmetry operation under which the LMO's are equivalent, e.g. a σ_v reflection in anthracene, but this is also frequently not the case, e.g. 1,2,3,4-dibenzanthracene. The ways in which the LMO's align around the fused rings may be useful for the discussion of some of the properties of these molecules.

3. Localized Structures and Pauling Bond Orders

Kekulé-Type Localized Structures

A molecule which contains *only* LMO's of types $\pi l2$ and $\pi l2'$ will be said to have a Kekulé-type localized MO structure, since each of the LMO's appears to describe a "double bond". All molecules on Fig. 3 and some on Fig. 5 are of this type.

Relation to Pauling Bond Orders

Is it possible to predict which molecules will have Kekulé-type LMO structures – and, if so, is it furthermore possible to predict the localization of the LMO's? Both questions can indeed be answered with the help of Pauling bond orders [15].

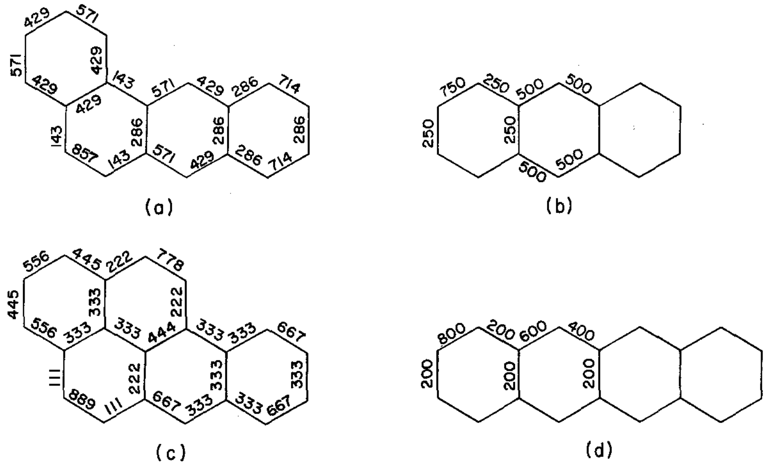
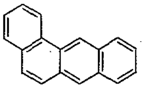


Fig. 6. Pauling bond orders. The numbers given are $100 \cdot P(I, J)$

According to Platt, Ham, and Ruedenberg [9], the latter can be calculated from the canonical MO's of Eq. (1) by

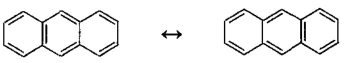
$$P(I, J) = \sum_{i=1}^{N/2} C_{Ii} C_{Ji} \sigma_i / m_i \,. \tag{28}$$

The answer to the second question follows: If a molecule has a Kekulé-type LMO structure, then the LMO's fall on that set of non-neighbouring bonds $B_1, B_2, \ldots B_{N/2}$ for which the sum of the Pauling bond orders, $\sum_i P(B_i)$ is maximal. This set must correspond to *one* of the possible Kekulé structures. E.g., in Fig. 6a the bond orders define the Kekulé-type LMO structure.



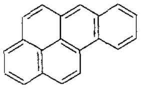
Using this result, the first question can now be answered. A molecule does *not* have a Kekulé-type LMO structure if:

1. Its Pauling bond orders do not uniquely define a specific Kekulé structure in the manner described above. E.g., in Fig. 6b the bond orders define either of two equivalent Kekulé structures



and non-Kekulé-type orbitals are found on the center ring.

2. One, and only one, of the single bond bond orders in a given ring within the structure is larger than that of a nearest neighbour double bond in the same ring. This is exemplified by benzpyrene where, in virtue of Fig. 6c and the predicted Kekulé-type localized structure

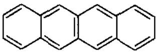


non-Kekulé orbitals occur on the upper left ring.

Table 3. *Localized orbital structures for cata- and peri-condensed hydrocarbons*

Kekulé type Localized structures	Non-Kekulé type Localized structures	
Naphthalene	Azulene	(1,2)
Triphenylene	Anthracene	(1)
Phenanthrene	Naphthacene	(3)
1,2,3,4-dibenzanthracene	Pentacene	(1,3)
Benzphenanthrene	1,2,5,6-dibenzanthracene	(1)
Benzanthracene	1,2,7,8-dibenzanthracene	(1)
Chrysene	Pyrene	(1,2)
Picene	Benzpyrene	(2)
Pentaphene	Anthanthrene	(2)
Perylene		
Benzoperylene		
Coronene		

3. There are double bond bond orders in the structure which are less than or equal to 0.2. An example is provided by Fig. 6d, where the bond orders define the Kekulé structure



and non-Kekulé orbitals obtain on both middle rings.

Each of the molecules presently studied can be analyzed this way and, hence, statements one thru three are *criteria for the occurence of localized Kekulé-type structures using Pauling bond orders.* Table 3 contains a list of Kekulé-type and non-Kekulé-type molecules. The parenthetical numbers accompanying the non-Kekulé-type localized structures refer to the criteria which apply, and two numbers are quoted when either of two criteria are satisfied. However, no cases were found where more than one criterion was *needed* to obtain a single non-Kekulé localized structure.

Localized Orbitals and Cellular Bond Populations

The cellular bond populations of Eq. (18) were also examined to see if they could be used as criteria in a manner similar to the Pauling bond orders. It was found, however, that these populations sometimes did not clearly support any Kekulé-type structure and, furthermore, they were similarly distributed in molecules where the localized orbitals were not.

4. Origin of Aromatic Stability

It is well known that for systems such as the ones discussed here, the sum of the occupied canonical orbital energies satisfies the inequality

$$2\sum_{i=1}^{N/2} \varepsilon_i - N\varepsilon(\text{ethylene}) < 0\,, \tag{29}$$

where the ε_i are defined by Eq. (6) and

$$\varepsilon(\text{ethylene}) = \alpha + 0.80\,\gamma \tag{30}$$

is the π-orbital energy in ethylene. The inequality (29) is considered to have an intrinsic relation to the stability of aromatic systems, and the left-hand-side is called the theoretical resonance energy. *In terms of the canonical* MO's *the reason for* (29) *is by no means obvious, as some of the* ε_i *are more negative than* ε *(ethylene), and others are less negative than* ε *(ethylene).*

Since the trace of the Hamiltonian matrix is invariant against orthogonal transformations, we have

$$\sum_i \varepsilon_i = \sum_i \eta_i \tag{31}$$

if the η_i are the orbital energies of the LMO's, and hence

$$\text{Theoretical Resonance Energy} = \sum_i 2[\eta_i - \varepsilon(\text{ethylene})]\,. \tag{32}$$

Table 4. *Values of orbital energies* ($\gamma \approx -2$ eV)

Ethylene	$\varepsilon = \alpha + 0.80\,\gamma$
$\pi l2$	$\alpha + 0.90\,\gamma < \eta < \alpha + 0.98\,\gamma$
$\pi l3$	$\alpha + 0.92\,\gamma < \eta < \alpha + 1.08\,\gamma$
$\pi l4$	$\alpha + 1.08\,\gamma < \eta < \alpha + 1.12\,\gamma$
$\pi l2'$	$\alpha + 1.08\,\gamma < \eta < \alpha + 1.12\,\gamma$
Canonical MO's	$\alpha + 0.20\,\gamma < \varepsilon < \alpha + 1.60\,\gamma$

Eq. (32) is of interest because of the numerical values given in Table 4 for the orbital energies of the LMO's. From the fact that *each* LMO is lower in energy than ethylene, it is readily seen that the resonance energy *must* be negative. The reason for the low orbital energies of the LMO's can be perceived by comparing the shapes of the localized π orbitals with that of the ethylene π orbital. All of the former have a positive lobe which extends over *at least three* atoms. In contrast, the ethylene orbital is strictly limited to *two* atoms. Thus, the ethylene π orbital is considerably more localized than even the maximally localized orbitals occurring in the aromatic systems. This, then, is the origin of the theoretical resonance energy: *the additional stabilization that is found in aromatic conjugated systems arises from the fact that even the maximally localized* π *orbitals are still more delocalized than the ethylene orbital.* The localized description permits us therefore to be more precise than the canonical description and suggests that resonance stabilization in aromatic molecules be ascribed to a "*local delocalization*" *of each localized orbital.*

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