Ab Initio Calculations on Large Molecules Using Molecular Fragments. Benzene and Naphthalene Isomer Characterizations and Aromaticity Considerations[1]

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Abstract: An *ab initio* investigation of several benzene and naphthalene isomers and hexatriene has been carried out. It was found that the relative order of total energies for the benzene isomers is benzene > fulvene > 2,3-dimethylenecyclobutene > trimethylenecyclopropane > Dewar benzene. In the naphthalene isomer series, the relative order of total energies was found to be naphthalene > azulene > fulvalene. Examination of the electronic structure of the various isomers permits new insight to be gained into the concept of aromaticity, and also provides a rationalization for some of their chemical behavior in terms of their molecular orbital structure.

Throughout the past century the rationalization of the differences in stability and reactivity of aromatic molecules compared to their open-chain analogs has been recognized as one of considerable importance. Several suggestions as to the most appropriate definition to be used to describe the aromaticity of a given molecule have been proposed[2-6] which use a variety of different criteria for distinguishing the degree of aromaticity that is present. In each of these proposals, a detailed understanding of the electronic and geometric structure of the molecule in question is essential, either explicitly or implicitly, to the development of the proposal.

In the past, many semiempirical techniques have been employed to quantify these notions.[7-9] Despite their several limitations, they have provided considerable insight into the concepts of resonance, delocalization, and aromaticity. However, many of these limitations can be eliminated by the use of *ab initio* quantum mechanical techniques, in which all electrons and nuclei are considered explicitly.

In this study, an *ab initio* technique[10,11] has been applied to several isomers of benzene and naphthalene. 1,3,5-*trans*-Hexatriene, although not an isomer of benzene, has also been included in this study because of its importance to discussions of aromaticity. The *ab initio* method using molecular fragments that is employed in this study is particularly appropriate, for it has been found to be one which allows the determination in a practical manner of the electronic structure of reasonably large molecules of arbitrary geometry. Furthermore, the results are readily interpretable into concepts familiar to chemists. Also, previous studies on benzene itself[11] and other hydrocarbons indicate that the molecular orbital energy level ordering, molecular geometry, Hellman–Feynmann forces and fields at nuclei, and other properties are well predicted.

The isomers chosen for this study do not exhaust all of the possible isomeric forms of benzene and naphthalene. Rather, the particular molecules chosen for inclusion were those in which a structure determination or extensive geometry search had been carried out, either on the parent hydrocarbon or a closely related substituted hydrocarbon. This procedure allows examination of the difference in electronic structure for the molecules as they actually exist, and eliminates perhaps misleading hypothetical structures from consideration.

Theoretical Procedure

The detailed development of the procedure to be used has been given previously[10,11] and will only be summarized briefly here. The basis orbitals that are employed are normalized floating spherical Gaussian orbitals (FSGO), defined by

$$G_i(r) = (2/\pi\rho_i^2)^{3/4} \exp\{-[(\mathbf{r} - \mathbf{R}_i)/\rho_i]^2\} \qquad (1)$$

where ρ_i is the orbital radius and $\mathbf{R}_i$ is the location of the FSGO, relative to some arbitrary origin. When π-type orbitals are used, a linear combination of two FSGO's is employed, *i.e.*

$$G_\pi = (G_\mathrm{u} - G_\mathrm{d})/[2(1 - \Delta_\mathrm{ud})]^{1/2} \qquad (2)$$

where G_u and G_d are FSGO's that are symmetrically placed above and below the plane of atoms, on a line perpendicular to the central atom. The nonlinear parameters for these orbitals are variationally determined by studies on molecular fragments. The parameters for the two molecular fragments of particular interest to these studies, CH_4 and $\cdot CH_3$, are given in Table I. These fragments were found to be particularly suitable for hydrocarbon investigations in a detailed earlier study[11] of various fragment possibilities.

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[1] This work was supported in part by grants from the University of Kansas, the Upjohn Co., Kalamazoo, Mich., and the Deutscher Akademischer Austauschdienst.

[2] (a) See, for example, M. J. S. Dewar and C. DeLlano, *J. Amer. Chem. Soc.*, **91**, 789 (1969), and earlier papers in this series; see also M. J. S. Dewar, "The Molecular Orbital Theory of Organic Chemistry," McGraw-Hill, New York, N. Y., 1969; (b) A. Streitweiser, "Molecular Orbital Theory for Organic Chemists," Wiley, New York, N. Y., 1961.

[3] J. F. Labarre and F. Crasnier, *J. Chim. Phys. Physicochem. Biol.*, **64**, 1664 (1967).

[4] R. W. Hakala, *Int. J. Quantum Chem., Suppl.*, **1**, 187 (1967).

[5] A. Julg and P. Francois, *Theor. Chim. Acta*, **8**, 249 (1967).

[6] D. P. Craig, "Theoretical Organic Chemistry (Kekulé Symposium)," Butterworths, London, 1955, pp 20–34; see also *J. Chem. Soc.*, 3175 (1951).

[7] See, for example, P. B. Empedocles and J. W. Linnett, *Theor. Chim. Acta*, **4**, 377 (1966), and ref 8 and 9; see also ref 2 and 4.

[8] J. D. Roberts, A. Streitweiser, Jr., and C. M. Regan, *J. Amer. Chem. Soc.*, **74**, 4579 (1952).

[9] D. H. Lo and M. A. Whitehead, *Can. J. Chem.*, **46**, 2041 (1968).

[10] R. E. Christoffersen and G. M. Maggiora, *Chem. Phys. Lett.*, **3**, 419 (1969).

[11] R. E. Christoffersen, D. W. Genson, and G. M. Maggiora, *J. Chem. Phys.*, **54**, 239 (1971).

Table I. Molecular Fragment Data[a] (au)[b]

	Orbital radius	Distance from carbon atom
CH_4, tetrahedral,	ρ_{CH} = 1.67251562	1.23379402
R_{CH} = 2.05982176	ρ_C = 0.32784375	0.0
$\cdot CH_3$, planar, sp^2,	ρ_{CH} = 1.51399487	1.13093139
R_{CH} = 1.78562447	ρ_C = 0.32682735	0.0
	ρ_π = 1.80394801	±0.1

[a] See ref 10 and 11 for details of the parameter determination. [b] All distances and energies are reported throughout as unscaled quantities, using Hartree atomic units, unless otherwise stated; see H. Shull and G. G. Hall, *Nature* (*London*), **184**, 1559 (1959).

Using the molecular fragment parameter data of Table I, *ab initio* SCF calculations have been carried out on benzene (I), fulvene (II), 2,3-dimethylenecyclobutene (III), trimethylenecyclopropane (IV), Dewar benzene (V), 1,3,5-*trans*-hexatriene (VI), naphthalene (VII), azulene (VIII), and fulvalene (IX). The geometries that were used are given in Table II, and the coordinate systems are shown in Figure 1.

The molecular orbitals are taken to be a linear combination of fragment FSGO's, *i.e.*

$$\varphi_i = \sum_{A=1}^{P} \sum_{k=1}^{N_A} c_{ki}{}^A G_k{}^A \tag{3}$$

where the $G_k{}^A$'s are the previously determined fragment orbitals, and the $c_{ki}{}^A$'s are the coefficients to be determined by the solution of the SCF equations

$$\mathbf{F}\mathbf{c}_i = \boldsymbol{\Delta}\mathbf{c}_i\boldsymbol{\varepsilon} \tag{4}$$

where **F** is the Fock matrix, $\boldsymbol{\Delta}$ is the overlap matrix over FSGO's, and $\boldsymbol{\varepsilon}$ contains the orbital eigenvalues. For the cases not explicitly given, hydrogen atom positions have been chosen to bisect the corresponding CCC angle. In the case of benzene, the coordinates are those employed by Schulman and Moskowitz.[12] The SCF calculations on benzene were reported earlier,[11] and are summarized here only for completeness. For fulvene, the extensive VESCF studies of bond distances and angles by Brown, Burden, and Williams[13] were employed. For 2,3-dimethylenecyclobutene, the results of extensive geometric variations by Skancke and Skancke[14] were used. For trimethylenecyclopropane and 1,3,5-*trans*-hexatriene, the results of the electron diffraction studies were employed.[15,16] For Dewar benzene, the electron diffraction results of Cardillo and Bauer for the hexamethyl derivative[17] were used. Naphthalene was constructed by fusing two benzene rings, and fulvalene was constructed by fusing two fulvene rings. Azulene coordinates were taken from the crystal structure data of Hanson.[18]

All calculations have been carried out using double-precision arithmetic on a GE-635 computer, and the convergence criterion that was used was

$$|P_{rs}{}^{(i+1)} - P_{rs}{}^{(i)}| < 0.00002 \tag{5}$$

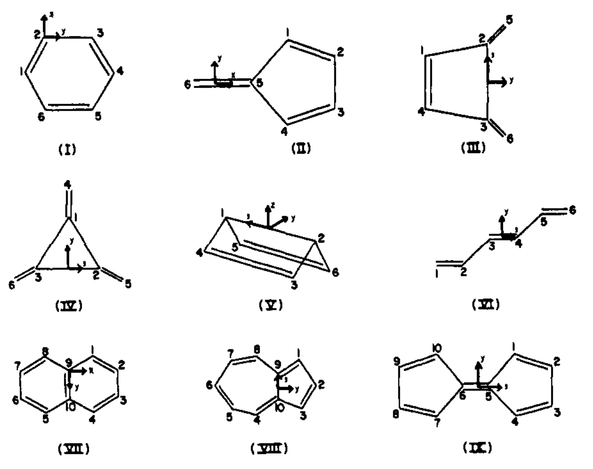

Figure 1. Numbering and coordinate systems. In all cases except Dewar benzene, the positive *z* axis points out of the paper.

This corresponds typically to a root-mean-square error of approximately 10^{-7} or smaller.

All of the benzene (except Dewar benzene) and naphthalene isomers and hexatriene were formed by using the $\cdot CH_3$ fragment parameters for the inner-shell carbon orbital, the π orbital, and the C–C bonding orbitals. The CH bonding orbital was taken from the CH_4 fragment. In each of these cases the position of the off-center FSGO was taken to lie along the internuclear axis, but at the same distance as found in the molecular fragment. Dewar benzene differs from the other isomers in that the bridgehead carbons were treated as sp^3 carbon atoms, *i.e.*, the inner-shell orbitals were taken from the CH_4 fragment, and no π orbitals were used.

Results

Each of the benzene isomers and hexatriene were assembled using the six appropriate $\cdot CH_3$ and CH_4 fragment FSGO's, and the various total energy components resulting from the SCF calculations are given in Table III. Since the scale factors in Table III are all quite similar, it is reasonable to make comparisons directly using the unscaled quantities as listed. Also, since the basis sets used for all of these molecules are identical (except for those of the bridging atoms in Dewar benzene), it is likely that error cancellations will be uniform, and that trends observed by comparisons using the energies and eigenvectors of these calculations would also be observed if more extensive basis sets were employed. Additional evidence supporting the view that the error cancellations are likely to be uniform is found in the per cent of the Hartree–Fock limit that is obtained. For all cases investigated here and previously[10,11] where this limit is known or can be estimated, the SCF calculations resulted in approximately 86% of the Hartree–Fock result, regardless of the particular molecule under consideration.

The molecular orbitals for the benzene isomers and hexatriene are given in Table IV. As noted in the earlier study on hydrocarbons,[11] the ordering of the inner-shell orbitals is not expected to be correct, since the orbitals are nearly degenerate, and a more extensive basis set is needed in order to establish the inner-shell ordering. However, in the outer-shell orbitals of usual interest in chemical reactions, previous studies[11] indi-

(12) J. M. Schulman and J. W. Moskowitz, *J. Chem. Phys.*, **43**, 3287 (1965).

(13) R. D. Brown, F. R. Burden, and G. R. Williams, *Aust. J. Chem.*, **21**, 1939 (1968).

(14) A. Skancke and P. N. Skancke, *Acta Chem. Scand.*, **22**, 12 (1968).

(15) E. A. Dorko, J. L. Hencher, and S. H. Bauer, *Tetrahedron*, **24**, 2425 (1968).

(16) M. Traetteberg, *Acta Chem. Scand.*, **22**, 628 (1968).

(17) M. J. Cardillo and S. H. Bauer, *J. Amer. Chem. Soc.*, **92**, 2399 (1970).

(18) A. W. Hanson, *Acta Crystallogr.*, **19**, 19 (1965).

Table II. Nuclear Geometries

Molecule	Point group	Distance, Å	Angle, deg
Benzene	D_{6h}	$R_{CC} = 1.395$ $R_{CH} = 1.085$	$\angle C_1C_2C_3 = 120.00$
Fulvene	C_{2v}	$R_{C_1-C_5} = 1.460$ $R_{C_1-C_2} = 1.360$ $R_{C_2-C_3} = 1.445$ $R_{C_5-C_6} = 1.360$ $R_{CH} = 1.070$	$\angle C_4C_5C_1 = 103.00$ $\angle C_5C_1C_2 = 110.50$
2,3-Dimethylenecyclobutene	C_{2v}	$R_{C_1-C_2} = 1.468$ $R_{C_1-C_4} = 1.353$ $R_{C_2-C_5} = 1.350$ $R_{C_2-C_3} = 1.456$ $R_{CH} = 1.070$	$\angle C_4C_1C_2 = 92.00$ $\angle C_1C_2C_5 = 137.00$ $\angle C_1C_2C_3 = 88.0$
Trimethylenecyclopropane	D_{3h}	$R_{C=C} = 1.343$ $R_{C-C} = 1.453$ $R_{CH} = 1.108$	$\angle C_2C_5C_3 = 118.00$
Dewar benzene	C_{2v}	$R_{C_3-C_4} = 1.352$ $R_{C_1-C_2} = 1.629$ $R_{C_2-C_3} = 1.523$ $R_{CH} = 1.134$	$\angle C_3C_2C_6 = 124.50$ $\angle C_2C_1H_1 = 115.90$ $\angle C_1C_4H_4 = 120.10$ $\angle H_2C_2C_3 = 110.90$ $\angle C_1C_2C_3 = 84.78$
1,3,5-*trans*-Hexatriene	C_{2h}	$R_{C-C} = 1.458$ $R_{C=C} = 1.337$ $R_{C_3=C_4} = 1.368$ $R_{CH} = 1.104$	$\angle C_1C_2C_3 = 121.7$ $\angle C_2C_3C_4 = 124.4$ $\angle C_2C_1H_2 = 120.5$ $\angle C_4C_3H_4 = 115.0$ $\angle C_1C_2H_3 = 117.0$
Naphthalene	D_{2h}	$R_{CC} = 1.395$ $R_{CH} = 1.085$	$\angle C_1C_2C_3 = 120.0$
Azulene	C_{2v}	$R_{C_9-C_1} = 1.3995$ $R_{C_1-C_2} = 1.3925$ $R_{C_8-C_9} = 1.3910$ $R_{C_7-C_8} = 1.3975$ $R_{C_6-C_7} = 1.3940$ $R_{C_9-C_{10}} = 1.4970$ $R_{CH} = 1.070$	$\angle C_{10}C_9C_1 = 106.315$ $\angle C_{10}C_9C_8 = 127.410$ $\angle C_9C_8C_7 = 128.810$ $\angle C_8C_7C_6 = 129.055$ $\angle C_9C_1C_2 = 108.615$
Fulvalene	D_{2h}	$R_{C_5-C_6} = 1.3600$	[a]

[a] Same ring geometry as fulvene.

Table III. Total Energy Components for Benzene Isomers and Hexatriene

	Energy components[a]						
		Potential					
Molecule	Kinetic	Electron–nuclear	Electron–electron	Nuclear–nuclear	Total energy	$\sum_i^{occ} \epsilon_i(\pi)$	Scale factor[b]
Benzene	182.99669075	−855.31125641	271.12976837	203.83065414	−197.35413742	−0.82536	1.03922869
Fulvene	183.08301544	−850.68164825	269.10876846	201.25369644	−197.23616791	− 0.75075	1.03865227
2,3-Dimethylene-cyclobutene	183.26167107	−843.94989777	265.68368530	197.84906387	−197.15546608	−0.76913	1.03790699
Trimethylene-cyclopropane	183.54508591	−824.18850708	256.02054214	187.60945892	−197.01341438	−0.76124	1.03668942
Dewar benzene	183.38595009	−864.31048584	278.18297195	205.95754433	−196.78401184		1.03652968
Hexatriene	184.52228737	−836.95754242	261.23413467	193.05647087	−198.14464188	−0.74308	1.03691249

[a] All energies and distances are reported throughout as unscaled quantities, using hartree atomic units, unless otherwise stated; see footnote *b*, Table I. [b] See P. O. Löwdin, *J. Mol. Spectrosc.*, **3**, 46 (1959), for the definition of the scale factor.

cate that the ordering of the various symmetries is expected to be correctly given.

The total energy components for the naphthalene isomers, formed from ten $\cdot CH_3$ and CH_4 fragment FSGO's, are summarized in Table V. As in the case of the benzene isomers, the scale factors for the naphthalene isomers are quite similar, so comparisons will be made directly using the unscaled energies given in Table V.

The molecular orbitals and associated symmetries that result from these calculations are given in Table VI. As in the case of the benzene isomers, it is not expected that the molecular orbitals will be well described for the inner-shell electrons. Consequently, most comments will be directed toward the non-inner-shell "valence" orbitals.

Discussion

A. Comparisons with Other Calculations. It is important first to calibrate these results, in order to ascertain the accuracy to be expected. Toward this end, it is instructive to examine where similarities and discrepancies occur between these calculations and more extensive basis set calculations.

In the case of benzene isomers and hexatriene, several comparisons are possible. For benzene itself, it was found in a previous study[11] that the ordering of the molecular orbitals that results using the fragment orbitals described in Table I (a total of 36 FSGO's) is precisely the same for the "valence" orbitals as obtained by using a considerably larger basis set[19] (a total of 222

(19) R. J. Buenker, J. L. Whitten, and J. D. Petke, *J. Chem. Phys.*, **49**, 2261 (1968).

Table IV. Molecular Orbitals for Benzene Isomers and Hexatriene

Benzene		Fulvene		2,3-Dimethylene-cyclobutene		Trimethylene-cyclopropene		Dewar benzene		Hexatriene	
(D_{6h})		(C_{2v})		(C_{2v})		(C_{2v})		(C_{2v})		(C_{2h})	
MO	$-\epsilon$	MO	$-\epsilon$	MO	$-\epsilon$	MO	$-\epsilon$	MO	$-\epsilon$	MO	$-\epsilon$
$1b_{1u}$	9.4535	$1a_1$	9.4265	$1b_2$	9.4419	$1e'$	9.3986	$1b_2$	9.3265	$1b_u$	9.4136
$1e_{2g}$	9.4252	$1b_2$	9.4253	$2b_2$	9.4027	$1e'$	9.3986	$1a_2$	9.3203	$1a_g$	9.4122
$1e_{2g}$	9.4252	$2a_1$	9.4067	$1a_1$	9.3947	$1a_1'$	9.3919	$1a_1$	9.3207	$2b_u$	9.4016
$1e_{1u}$	9.3517	$2b_2$	9.3322	$2a_1$	9.3507	$2e'$	0.3355	$1b_1$	9.2264	$2a_g$	9.3442
$1e_{1u}$	9.3517	$3a_1$	9.3291	$3b_2$	9.3294	$2e'$	9.3355	$2b_2$	9.1974	$3b_u$	9.2833
$1a_{1g}$	9.2684	$4a_1$	9.2419	$3a_1$	9.2431	$2a_1'$	9.2370	$2a_1$	9.0790	$3a_g$	9.2479
$2a_{1g}$	1.0874	$5a_1$	1.0840	$4a_1$	1.1065	$3a_1'$	1.0518	$3a_1$	0.9925	$4a_g$	1.0261
$2e_{1u}$	0.9686	$6a_1$	0.9705	$4b_2$	0.9397	$3e'$	0.9371	$2b_1$	0.8751	$4b_u$	0.9870
$2e_{1u}$	0.9686	$3b_2$	0.8994	$5a_1$	0.9358	$3e'$	0.9371	$3b_2$	0.7437	$5a_g$	0.9130
$2e_{2g}$	0.7605	$7a_1$	0.8042	$6a_1$	0.7469	$4a_1'$	0.8458	$4a_1$	0.6676	$5b_u$	0.7604
$2e_{2g}$	0.7605	$4b_2$	0.6570	$5b_2$	0.7442	$4e'$	0.5947	$2a_2$	0.6389	$6a_g$	0.6732
$3a_{1g}$	0.5848	$8a_1$	0.6371	$6b_2$	0.5788	$4e'$	0.5947	$4b_2$	0.5155	$6b_u$	0.6581
$2b_{1u}$	0.5566	$9a_1$	0.5748	$7a_1$	0.5627	$5a_1'$	0.5277	$5a_1$	0.4962	$7a_g$	0.5252
$1b_{2u}$	0.5031	$5b_2$	0.5034	$8a_1$	0.4993	$5e'$	0.4715	$3b_1$	0.4724	$7b_u$	0.5028
$3e_{1u}$	0.4783	$10a_1$	0.4408	$7b_2$	0.4726	$5e'$	0.4715	$6a_1$	0.3607	$8b_u$	0.4705
$3e_{1u}$	0.4783	$6b_2$	0.4389	$9a_1$	0.4211	$1a_2'$	0.4645	$4b_1$	0.3139	$8a_g$	0.4402
$1a_{2u}$ (π)	0.3915	$11a_1$	0.4030	$1b_1$ (π)	0.3837	$1a_2''$ (π)	0.3587	$5b_2$	0.2530	$9a_g$	0.4051
$3e_{2g}$	0.3900	$1b_1$ (π)	0.3758	$8b_2$	0.3787	$6e'$	0.2734	$3a_2$	0.2047	$9b_u$	0.3993
$3e_{2g}$	0.3900	$7b_2$	0.3652	$10a_1$	0.3424	$6e'$	0.2734	$7a_1$	0.1758	$10a_g$	0.3767
$1e_{1g}$ (π)	0.2169	$2b_1$ (π)	0.2156	$1a_2$ (π)	0.2050	$1e''$ (π)	0.2012	$5b_1$	0.1345	$1a_u$ (π)	0.3320
$1e_{1g}$ (π)	0.2169	$1a_2$ (π)	0.1594	$2b_1$ (π)	0.1803	$1e''$ (π)	0.2012	$8a_1$	0.0546	$1b_g$ (π)	0.2631
										$2a_u$ (π)	0.1480
$1e_{2u}$ (π^*)	-0.2913	$3b_1$ (π^*)	-0.2016	$2a_2$ (π^*)	-0.2654	$2a_2''$ (π^*)	-0.2041	$6b_2$	-0.3790	$2b_g$ (π^*)	-0.2389
$1e_{2u}$ (π^*)	-0.2913	$2a_2$ (π^*)	-0.4293	$3b_1$ (π^*)	-0.3023	$2e''$ (π^*)	-0.4819	$4a_2$	-0.4223	$3a_u$ (π^*)	-0.3782
$1b_{2g}$ (π^*)	-0.5441	$4b_1$ (π^*)	-0.4811	$3a_2$ (π^*)	-0.5572	$2e''$ (π^*)	-0.4819	$7b_2$	-0.7993	$3b_g$ (π^*)	-0.4835
$4e_{2g}$	-0.9999	$8b_2$	-0.9143	$9b_2$	-0.8569	$2a_2'$	-0.7549	$9a_1$	-0.9765	$10b_u$	-0.8496
$4e_{2g}$	-0.9999	$12a_1$	-0.9312	$11a_1$	-0.8765	$7e'$	-0.9752	$6b_1$	-1.0545	$11b_u$	-0.9810
$4e_{2u}$	-1.0406	$9b_2$	-0.9819	$10b_2$	-0.9924	$7e'$	-0.9752	$5a_2$	-1.0758	$11a_g$	-1.0154

Table V. Total Energy Components[a] for Naphthalene Isomers

Energy component	Naphthalene	Azulene	Fulvalene
Kinetic	303.35664749	303.51782608	303.47954559
Electron–nuclear	−1667.78880310	−1653.77546692	−1631.76205444
Electron–electron	574.26500702	567.07115936	556.76239777
Nuclear–nuclear	462.05744553	455.22081757	443.62667084
Total E	−328.10969543	−327.96566010	−327.89342499
$\Sigma_i^{\mathrm{occ}}\epsilon_i(\pi)$	−1.3770	−1.3690	−1.2631
Scale factor	1.04079859	1.04027413	1.04022326

[a] All energies are reported as unscaled quantities.

Gaussians). Furthermore, it was shown that the remaining energetic deficiency of the current description was primarily in the inner-shell-orbital description. It is interesting to note that another investigation,[20] using a larger basis set than the one employed here, did not predict the correct ordering of the valence molecular orbitals, with the ordering of the $1b_{2u}$ and $2b_{1u}$ orbitals switched from that found by Buenker, Whitten, and Petke.[19] Consequently, increasing the size of the basis set does not guarantee more satisfactory results, unless the balance of the basis set can be maintained.

For the case of fulvene, direct comparisons with more extensive calculations are also possible. For a basis set of 174 Gaussians, it was found[21] that all of the filled non-inner-shell molecular orbitals are in exactly the same order as the order given in Table IV. This includes the ordering of most virtual, as well as filled, orbitals. As in the case of benzene, the basis set employed by Praud, *et al.*,[20] does not produce an ordering of molecular orbitals in agreement with Peyerimhoff[21] and the current studies, with the ordering of the $1b_1$ and $11a_1$ orbitals switched. For the case of 2,3-dimethylenecyclobutene, the ordering is the same as that observed by Praud, *et al.*,[20] except for the $6b_2$, 7a pair, which is switched.

It is also possible to make direct comparisons with more extensive basis-set calculations for the naphthalene and azulene molecules.[22] For naphthalene, only one switch in ordering is observed in the filled non-inner-shell orbitals. This occurs in the case of the $9a_g$ and $6b_{1g}$ orbitals, whose energies are very nearly degenerate. In the case of the virtual orbitals, only the ordering of the very high-lying $8b_{3u}$ and $8b_{2u}$ orbitals is interchanged from that of Buenker and Peyerimhoff.[22] Considering the large number of symmetry species that are present (eight irreducible representations), the agreement is remarkably complete. Furthermore, a direct comparison of the molecular orbital coefficients of the π orbitals also shows striking similarities, as indicated in Table VII.

For the case of azulene, the ordering of the molecular orbitals is again found to be identical with that found by Buenker and Peyerimhoff[22] for the chemically inter-

(20) L. Praud, P. Millie, and G. Berthier, *Theor. Chim. Acta*, 11, 169 (1968).

(21) S. D. Peyerimhoff, private communication.

(22) R. J. Buenker and S. D. Peyerimhoff, *Chem. Phys. Lett.*, 3, 37 (1969).

Table VI. Molecular Orbitals for Naphthalene Isomers

Naphthalene (D_{2h}) MO	$-\epsilon$	Azulene (C_{2v}) MO	$-\epsilon$	Fulvalene (D_{2h}) MO	$-\epsilon$
$1b_{2u}$	9.4516	$1a_1$	9.4724	$1b_{1g}$	9.4321
$1b_{1g}$	9.4497	$1b_2$	9.4608	$1b_{2u}$	9.4311
$1a_g$	9.4295	$2a_1$	9.4360	$1b_{3u}$	9.4247
$1b_{3u}$	9.4232	$3a_1$	9.4302	$1a_g$	9.4182
$2b_{2u}$	9.4172	$2b_2$	9.4171	$2b_{3u}$	9.3918
$2b_{1g}$	9.3817	$3b_2$	9.3896	$2a_g$	9.3478
$2a_g$	9.3607	$4a_1$	9.3698	$2b_{1g}$	0.3432
$3b_{2u}$	9.3396	$4b_2$	9.3361	$2b_{2u}$	9.3377
$2b_{3u}$	9.3083	$5a_1$	9.3247	$3b_{3u}$	9.2752
$3a_g$	9.2666	$6a_1$	9.2692	$3a_g$	9.2473
$4a_g$	1.1188	$7a_1$	1.1109	$4a_g$	1.1020
$3b_{3u}$	1.0538	$8a_1$	1.0650	$4b_{3u}$	1.0781
$4b_{2u}$	1.0040	$5b_2$	1.0283	$5a_g$	0.9581
$5a_g$	0.9654	$9a_1$	0.9617	$3b_{2u}$	0.9112
$3b_{1g}$	0.9246	$6b_2$	0.9099	$3b_{1g}$	0.8986
$4b_{3u}$	0.7997	$10a_1$	0.8282	$5b_{3u}$	0.8319
$5b_{2u}$	0.7687	$7b_2$	0.7952	$6a_g$	0.7137
$6a_g$	0.7453	$11a_1$	0.6700	$4b_{2u}$	0.6719
$4b_{1g}$	0.6255	$12a_1$	0.6506	$4b_{1g}$	0.6455
$5b_{3u}$	0.5803	$8b_2$	0.6256	$6b_{3u}$	0.6190
$7a_g$	0.5561	$13a_1$	0.5638	$7a_g$	0.6033
$6b_{2u}$	0.5255	$14a_1$	0.5270	$7b_{3u}$	0.5241
$8a_g$	0.5009	$9b_2$	0.5121	$5b_{2u}$	0.4486
$5b_{1g}$	0.4725	$10b_2$	0.4684	$5b_{1g}$	0.4400
$6b_{3u}$	0.4686	$15a_1$	0.4497	$8a_g$	0.4301
$7b_{2u}$	0.4522	$11b_2$	0.4249	$6b_{2u}$	0.4190
$1b_{1u}(\pi)$	0.4261	$16a_1$	0.4238	$9a_g$	0.4081
$7b_{3u}$	0.4234	$1b_1\ (\pi)$	0.4192	$8b_{3u}$	0.4062
$9a_g$	0.3781	$12b_2$	0.4084	$1b_{1u}\ (\pi)$	0.4026
$6b_{1g}$	0.3755	$17a_1$	0.3653	$6b_{1g}$	0.3574
$1b_{2g}(\pi)$	0.3304	$2b_1\ (\pi)$	0.3410	$1b_{2g}\ (\pi)$	0.3461
$1b_{3g}\ (\pi)$	0.2658	$1a_2\ (\pi)$	0.2982	$2b_{1u}\ (\pi)$	0.1862
$2b_{1u}\ (\pi)$	0.2002	$3b_1\ (\pi)$	0.1808	$1b_{3g}\ (\pi)$	0.1672
$1a_u\ (\pi)$	0.1545	$2a_2\ (\pi)$	0.2198	$1a_u\ (\pi)$	0.1610
$2b_{2g}\ (\pi^*)$	−0.2253	$4b_1\ (\pi^*)$	−0.1822	$2b_{2g}\ (\pi^*)$	−0.1528
$2b_{3g}\ (\pi^*)$	−0.2845	$3a_2\ (\pi^*)$	−0.2137	$3b_{1u}\ (\pi^*)$	−0.3429
$3b_{1u}(\pi^*)$	−0.3502	$5b_1\ (\pi^*)$	−0.4216	$2b_{3g}\ (\pi^*)$	−0.4198
$2a_u\ (\pi^*)$	−0.4475	$6b_1\ (\pi^*)$	−0.4974	$2a_u\ (\pi^*)$	−0.4294
$3b_{3g}\ (\pi^*)$	−0.6310	$4a_2\ (\pi^*)$	−0.5368	$3b_{2g}\ (\pi^*)$	−0.5521
$8b_{3u}$	−0.7721	$18a_1$	−0.8153	$7b_{2u}$	−0.7633
$8b_{2u}$	−0.9363	$13b_2$	−0.8507	$9b_{3u}$	−0.8689

Table VII. π-Orbital Comparisons for Naphthalene

MO	MO coefficients		Atoms[a]
	This work	Ref 22	
$1b_{1u}\ (\pi)$	0.31643	0.31307	9 + 10
	0.21762	0.21139	1 + 4 + 5 + 8
	0.17914	0.17409	2 + 3 + 6 + 7
$1b_{2g}\ (\pi)$	0.21681	0.22442	1 + 4 − 5 − 8
	0.33256	0.32958	2 + 3 − 6 − 7
$1b_{3g}\ (\pi)$	0.27544	0.27703	9 − 10
	0.33897	0.34500	1 − 4 − 5 + 8
	0.15612	0.17837	2 − 3 − 6 + 7
$2b_{1u}\ (\pi)$	0.38484	0.43450	9 + 10
	0.00477	−0.01850	1 + 4 + 5 + 8
	−0.35042	−0.35344	2 + 3 + 6 + 7
$1a_u\ (\pi)$	0.39231	0.40142	1 − 4 + 5 − 8
	0.25709	0.27262	2 − 3 + 6 − 7
$2b_{2g}\ (\pi^*)$	−0.49289	−0.49692	1 + 4 − 5 − 8
	0.31478	0.33223	2 + 3 − 6 − 7
$2b_{3g}\ (\pi^*)$	0.53529	0.57492	9 − 10
	0.00619	0.00268	1 − 4 − 5 + 8
	−0.51041	−0.47500	2 − 3 − 6 + 7
$3b_{1u}\ (\pi^*)$	−0.47722	−0.43572	9 + 10
	0.53877	0.51696	1 + 4 + 5 + 8
	−0.23517	−0.24960	2 + 3 + 6 + 7
$2a_u\ (\pi^*)$	0.39578	0.38763	1 − 4 + 5 − 8
	−0.61809	−0.57368	2 − 3 + 6 − 7
$3b_{3g}\ (\pi^*)$	−0.84964	−0.67857	9 − 10
	0.53395	0.45016	1 − 4 − 5 + 8
	−0.41380	−0.38068	2 − 3 − 6 + 7

[a] Refers to the atom on which the π orbital is located (see Figure 1).

Table VIII. Relative Stability of Benzene and Naphthalene Isomers and Hexatriene

Molecule	Energy difference, kcal/mol	Molecule	Energy difference, kcal/mol
Benzene		Naphthalene	
Fulvene	74		
2,3-Dimethylene-cyclobutene	125	Azulene	90
Trimethylene-cyclopropane	213	Fulvalene	135
Dewar benzene	357		
Hexatriene	−496		

esting valence orbitals, with the exception of the near-degenerate $11b_2$ and $16a_1$ orbitals and the highest virtual orbitals ($18a_1$ and $13b_2$). Detailed comparison of the magnitudes of the individual coefficients also indicates essentially complete agreement, with the largest error being 0.11 in the $4a_2$ orbital, the highest virtual orbital.

Consequently, it is clear that, for the molecules where direct comparisons with more extensive calculations are possible, the electronic structure as predicted by the current procedure is essentially identical, even to the point of detailed comparisons of molecular orbital coefficients. Therefore, comparisons of electronic structure differences in hydrocarbons to be made below are expected to yield reliable and useful measures of the differences in the actual electronic structure of the various molecules. The only exceptions to be expected are for nearly degenerate or very high-lying orbitals, and they will be noted accordingly.

B. Relative Stabilities. Of considerable interest is the relative stability of the various isomers of benzene and naphthalene. The appropriate energy differences for these isomers are presented in Table VIII. It should be pointed out that the absolute magnitude of these energy differences is expected to be exaggerated, for several reasons. First, a similar magnification of energy differences was observed in studies of various hydrocarbon rotomers.[11] Also, the correlation error for decreasing size ring systems will be likely to increase, further exaggerating the effect. Nevertheless, several interesting observations can be made concerning the relative stabilities.

First, it is obvious that hexatriene itself (which is neither isoelectronic nor isonuclear to benzene) is not a useful reference molecule, if total energies are used for the comparisons. Correction for the extra hydrogen atoms does not alter this observation. However, the individual molecular orbital structure is more promising in this regard, as will be discussed later.

Although the magnitude of these energy differences may be reduced by more extensive basis-set calculations, it appears unlikely that the relative ordering of the various isomers will be altered. For comparison purposes, it might be noted that more extensive SCF calculations[21] indicate that benzene is more stable than fulvene by 40.2 kcal/mol, and that naphthalene is more stable than azulene by 50.3 kcal/mol.[22] These very extensive calculations also overestimate the stability difference,[23] emphasizing the difficulty of predicting absolute differences in energies without using configuration interaction techniques.

It should be noted also that the results of semiempirical calculations using both the MINDO technique and a π procedure[24] are not in agreement with the results of the current studies. In particular, the MINDO procedure predicts a relative ordering benzene, fulvene, 2,3-dimethylenecyclobutene, Dewar benzene, trimethylenecyclopropane, while the π procedure predicts a relative ordering benzene, fulvene, trimethylenecyclopropane, 2,3-dimethylenecyclobutene. Since the current calculations (where comparisons are possible) have been found to give electronic structure predictions in essentially complete agreement with the most accurate theoretical calculations available, it is believed that the relative order of stabilities given by the current studies is that expected to be verified experimentally. Consequently, the σ electrons in these systems appear to play a very important role, both with respect to the overall stability and the stability of the π orbitals, and should be explicitly considered if comparisons are to be made.[25]

The ionization potentials, as estimated *via* Koopmans' theorem,[26] are summarized in Table IX. Consistent with earlier observations,[11] the values are found to be too low when compared with more extensive calculations.[19–22] However, the trends appear to be correctly indicated, as for other properties.

Table IX. Ionization Potentials of Benzene and Naphthalene Isomers and Hexatriene

Molecule	IP, eV Calcd	IP, eV Exptl
Benzene	5.90	9.241[a]
Fulvene	4.34	
2,3-Dimethylenecyclobutene	4.91	
Trimethylenecyclopropane	5.48	
Dewar benzene	1.49	
Hexatriene	4.03	
Naphthalene	4.20	8.12[b]
Azulene	3.53	7.41[c]
Fulvalene	4.38	

[a] A. J. C. Nicholson, *J. Chem. Phys.*, **43**, 1171 (1965). [b] K. Watanabe, T. Nakayama, and J. Mottle, *J. Quant. Spectrosc., Radiat. Transfer*, **2**, 369 (1962). [c] T. Kitagawa, H. Inokuchi, and K. Kodera, *J. Mol. Spectrosc.*, **21**, 267 (1966).

It might be noted that the observation of Buenker and Peyerimhoff[22] concerning comparison of inner-shell orbital energies to extract differences in valence–charge distribution is not borne out in these studies. The inner-shell orbitals resulting from the current studies are not localized, so the identification of a given orbital with a particular nucleus (or a set of symmetry-related nuclei) is not possible without performing a separate localization procedure.[27]

C. Molecular Orbital Structure and Chemical Characteristics. Several comments regarding the nature and ordering of the various molecular orbitals are also appropriate. From Tables IV and VI, the first observation of interest is the considerable interspersing of σ and π orbitals. Only hexatriene has all of the π orbitals grouped together as the uppermost filled orbitals. The importance of this is emphasized by the fact that the interspersing is not uniform in the various isomers, *e.g.*, three σ orbitals appear between the $1b_{1u}$ (π) and the $1b_{2g}$ (π) orbitals in naphthalene, and only one σ orbital appears between the same symmetry orbitals in fulvalene.

In the case of Dewar benzene, the lack of planarity destroys any identifiable π orbitals, and the electronic structure is considerably different from that of the other isomers. For example, the b_1 and a_2 orbitals, which appear as π orbitals in the other isomers of C_{2v} symmetry, appear interspersed within the entire set of orbitals, and are not all grouped near the top of the filled orbitals. Indeed, $1a_2$ and $1b_1$ appear as *inner-shell* orbitals.

In the $C_{10}H_8$ isomer series, both naphthalene and fulvalene have D_{2h} symmetry and show several striking similarities in their electronic structure, as seen by examination of Table VI. For example, the number and kind of molecular orbitals that are filled are quite similar, differing only in the number of b_{2u} and b_{3u} orbitals. Furthermore, the highest occupied orbital is $1a_u$ in both cases, and the ionization potentials (Table IX) are quite similar. In addition, the detailed orbital shapes, including FSGO molecular orbital coefficients, are quite similar, as indicated in Figure 2. As seen in the figure, carbons 5 and 6 in fulvalene play a role entirely analogous to that of carbons 9 and 10 in naphthalene, while carbons 2, 3, 8, and 9 in fulvalene correspond to carbons 2, 3, 6, and 7 in naphthalene, and carbons 1, 4, 7, and 10 in fulvalene correspond to carbons 1, 4, 5, and 8 in naphthalene. Similar observations also apply to the shapes of the other filled π molecular orbitals of the same symmetry in naphthalene and fulvalene.

As far as the chemical reactivity of a molecule is determined by the nature of the highest occupied and lowest unoccupied molecular orbitals,[28] naphthalene and fulvalene should possess similar reaction characteristics. Azulene, on the other hand, does not contain a node at carbons 9 and 10 in its highest occupied molecular orbital (as is present at carbons 9 and 10 in naphthalene and carbons 5 and 6 in fulvalene), even though a total of two nodes is still present. Apparently the position of the orbital nodes remains relatively stationary (relative to the $\pm x$ coordinates), and is relatively insensitive to changes in the atomic geometry. Consequently, the susceptibility to electrophilic attack at carbons 9 and 10 in azulene is expected to be greater than at carbons 9 and 10 in naphthalene and carbons 5 and 6 in fulvalene.

The other molecular orbital coefficients in Figure 2 also reveal interesting points concerning the chemistry of these species. In naphthalene, the magnitude of the highest occupied molecular orbital coefficients (a measure of the electron density at various atoms in this molecular orbital) is seen to mimic the chemical reactivity of naphthalene,[29] where electrophilic attack would

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(23) E. Perrottet, W. Taub, and E. Briner, *Helv. Chim. Acta*, **23**, 1260 (1940).

(24) N. C. Baird and M. J. S. Dewar, *J. Amer. Chem. Soc.*, **91**, 352 (1969).

(25) This observation has also been made for other hydrocarbons; see, for example, R. J. Buenker and S. D. Peyerimhoff, *J. Chem. Phys.*, **48**, 354 (1968).

(26) T. A. Koopmans, *Physica*, **1**, 104 (1933).

(27) See, for example, S. F. Boys, *Rev. Mod. Phys.*, **32**, 296 (1960); C. Edmiston and K. Ruedenberg, *ibid.*, **34**, 457 (1963); V. Magnasto and A. Perico, *J. Chem. Phys.*, **47**, 971 (1967).

(28) For many examples of this notion, see R. Hoffmann and R. B. Woodward, *Science*, **167**, 825 (1970), and earlier papers.

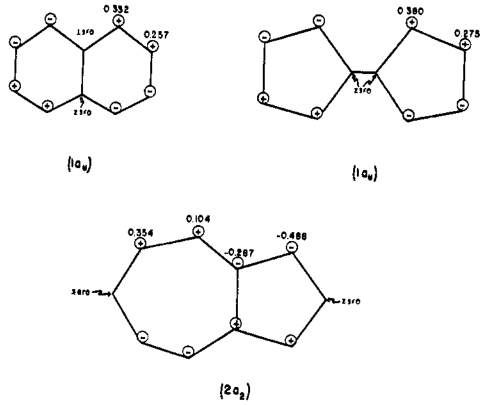

Figure 2. Comparisons of the highest occupied orbitals in the naphthalene isomer series. The magnitude of the coefficient of the FSGO on the respective atoms is also given.

be expected to be most favorable at carbons 1, 4, 5, and 8, and nucleophilic attack would be favored at atoms 9 and 10. Similarly, fulvalene would be expected to be susceptible to electrophilic attack at atoms 1, 4, 7, and 10, and most susceptible to nucleophilic attack at atoms 5 and 6. Azulene, on the other hand, does not have reaction characteristics that can be rationalized by examination of only the highest occupied molecular orbital coefficients, and a larger set of molecular orbitals must be considered. Further investigations are currently in progress to clarify this possibility.

Although it is likely that the ordering of the various molecular orbitals is correctly revealed by these calculations, there are several places at which accidental degeneracies approximately occur, in which the ordering may be altered by more extensive basis set calculations. In addition to those already noted in direct comparisons, one should include the $9a_g$,$9b_u$ pair in hexatriene and the $5b_{2u}$,$5b_{1g}$ pair, the $9a_g$,$8b_{3u}$,$1b_{1u}$ (π) triad, and the $1b_{3g}$ (π),$1a_u$ (π) pair in fulvalene. The ordering of the latter pair is of particular interest, since these orbitals represent the highest occupied orbitals. However, the overall reactivity at various carbon positions in fulvalene is not expected to be affected greatly by the ordering of the $1b_{3g}$ (π),$1a_u$ (π) pair, since both orbitals have nodes at the same atoms (5 and 6 in fulvalene and 9 and 10 in naphthalene) and coefficients whose magnitudes are approximately the same in both molecular orbitals at the various atoms.[30]

D. Aromaticity Considerations. The determination of the electronic structure of the various benzene and naphthalene isomers also can be profitably examined with respect to the concept of aromaticity. This notion, useful in rationalizing the differences in stability of various ring compounds from their open-chain analogs,[31] is connected closely with the presence of delocalized π orbitals in the ring compounds, which impart added stability ("aromaticity") that would not be present if these orbitals were localized. Consequently, some of the currently used procedures[2] for quantification of this notion are based upon a comparison of a molecule of interest with a corresponding hypothetical molecule having all "localized" π orbitals. However, it seems that, if properties that are intrinsically *real* chemical characteristics of molecules are to be compared, it is highly desirable to avoid comparisons based upon *unreal* reference molecules.

It appears from the data presented here that the notion of aromaticity can be rationalized without the introduction of hypothetical reference molecules. Instead, the electronic structure as given by the wave functions for the actual molecules can be used to make the desired comparisons. In particular, the occupied π orbitals resulting from these calculations exhibit characteristics that provide an acceptable framework for both qualitative and quantitative discussions of aromaticity. It must be emphasized at the outset, however, that the relative energies of the π orbitals are strongly dependent upon the particular σ environment that is present. Consequently, explicit consideration of the σ electrons must be included in order to obtain reliable π-orbital determinations. It should also be noted that, since aromaticity is a concept that is concerned only with π orbitals, the aromaticities of a set of molecules need not necessarily parallel the ordering of overall stability of the molecules.

Considering hexatriene and the benzene isomers, we note first that the filled π orbitals in hexatriene all lie above the filled σ orbitals and have not been stabilized by the particular σ-electron and nuclear environment to any extent more than expected from particle-in-a-box considerations.[32] However, in fulvene, the lowest π orbital has been sufficiently stabilized by this particular environment to exchange its position relative to the highest σ orbital ($7b_2$). In 2,3-dimethylenecyclobutene, trimethylenecyclopropane, and benzene itself, the π orbitals are further stabilized, with a pair of σ orbitals separating the lowest π orbital from the other filled π orbitals. Consequently, a qualitative understanding of the aromaticity of these molecules can be obtained from simple examination of the relative ordering of molecular orbitals.

More quantitatively, the amount of lowering of a given π orbital can be estimated by its orbital energy. Since all filled π orbitals contribute to the aromaticity of a given molecule, the sum of the filled π-orbital energies can be used to provide a simple measure of the extent of energy lowering. In Table III, these quantities are given for hexatriene and the benzene isomers. As expected, they parallel the qualitative observations made above, with benzene and hexatriene exhibiting the aromaticity extremes, and the other isomers falling between these two molecules. In addition, the quantitative measure shows that the three-, four-, and five-membered rings all exhibit aromaticities (*i.e.*, $\Sigma_i^{\mathrm{occ}}\epsilon_i(\pi)$) closer to hexatriene than to benzene, in agreement with their chemical behavior.[13,15,33,34] Thus, the overall description that emerges is that the three-, four-, and five-membered ring isomers are primarily *nonaromatic*, with only benzene having considerable aromatic character.

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[29] J. D. Roberts and M. C. Caserio, "Basic Principles of Organic Chemistry," W. A. Benjamin, New York, N. Y., 1965, p 812.

[30] For example, the π FSGO on carbon 4 in fulvalene has a coefficient of ±0.384 in the $1b_{3g}$ (π) orbital, and a coefficient of -0.380 in the $1a_u$ (π) orbital.

[31] See, for example, M. J. S. Dewar, *Tetrahedron Suppl.*, No. **8**, 75 (1966).

[32] R. L. Flurry, Jr., "Molecular Orbital Theories of Bonding in Organic Molecules," Marcel Dekker, New York, N. Y., 1968, Chapter 2.

[33] P. A. Straub, D. Meuche, and E. Heilbronner, *Helv. Chim. Acta*, **49**, 517 (1966).

[34] M. L. Heffernan and A. J. Jones, *Chem. Commun.*, 120 (1966).

Dewar benzene cannot be included in the comparisons, since there are no identifiable π orbitals.

The quantitative description also results in fulvene taking on an interesting role. In particular, its aromatic character is less than that of the three- and four-membered isomers, even though its total stability is greater than that of the other isomers. Consequently, the chemical characteristics of the π electrons in fulvene should exhibit more similarities to those of hexatriene than the other isomers.

A perhaps more convenient quantitative measure of aromaticity can be obtained if the open-chain analog is used as a reference molecule. In this case, one can define the aromaticity (A) of a given molecule (M) as

$$A = \left[\frac{E_\pi(\mathrm{M}) - E_\pi(\mathrm{ref})}{E_\pi(\mathrm{ref})}\right]100 \qquad (6)$$

where $E_\pi(\mathrm{M})$ and $E_\pi(\mathrm{ref})$ are the sum of the occupied π-orbital energies for the molecule in question and the open-chain reference molecule, respectively. Using this measure of aromaticity, the benzene isomer aromaticities are summarized in Table X. Also given for comparison are delocalization energies, computed using Hückel theory.[8]

Table X. Aromaticities of Benzene Isomers

Molecule	Aromaticity (A)[a]	Delocalization[b] Energy[c]
Benzene	11.073	36
Fulvene	1.032	26
2,3-Dimethylenecyclobutene	3.506	22
Trimethylenecyclopropane	2.444	23
Hexatriene	0.000	

[a] Calculated using eq 6. [b] Calculated using β = 18 kcal/mol. [c] See ref 8.

It might also be noted in passing that the terms "aromatic" and "nonaromatic" are not readily separable using this definition, except at the extremes. This is believed to be highly desirable, for it does not require an absolute decision that a particular molecule must be *either* aromatic *or* nonaromatic, but allows for an appropriate gradation of aromaticity that is more characteristic of the real molecules.[35]

The naphthalene isomers provide similar examples of the above notion of aromaticity, as revealed by examination of Tables V and VI. Qualitatively, three σ orbitals separate the lowest π orbital from the others in naphthalene, while in azulene two σ orbitals are present between the π orbitals and only one σ orbital is present in fulvalene between the π orbitals. As noted earlier, the $9a_g$, $8b_{3u}$, and $1b_{1u}$ (π) orbitals have very nearly degenerate energies, and more extensive basis set calculations may lower the relative energy of the $1b_{1u}$ (π) orbital so that its aromaticity is qualitatively more like benzene. However, the quantitative sums over orbital energies in Table V indicate the clear aromaticity decrease from naphthalene to fulvalene. Consequently, even though the orbital structure of fulvalene is quite similar to that of naphthalene, the particular environment in fulvalene does not produce a stabilization of the π orbitals as in the case of naphthalene and the resulting π electrons are expected to be considerably more reactive than those in naphthalene,[36,37] although in reactions similar to those found for naphthalene.

Further investigation of the similarities and differences of these isomers is underway, and various molecular properties (*e.g.*, dipole moments), molecular orbital contours, and a complete population analysis will be reported later.

Conclusions

The studies on the benzene and naphthalene isomers and hexatriene using the molecular-fragment approach allow several conclusions of both theoretical and chemical interest.

(1) The method provides a reliable and computationally convenient means of electronic structure determination of large molecules.

(2) Examination of the filled π orbitals of the benzene and naphthalene isomers provides both a qualitative and quantitative rationalization of aromaticity. However, both σ and π orbitals must be considered explicitly to maintain the usefulness of the concept.

(3) The relative stability of benzene isomers is found to be benzene > fulvene > 2,3-dimethylenecyclobutene > trimethylenecyclopropane > Dewar benzene. Only benzene has been found to have considerable aromaticity.

(4) The relative stability of naphthalene isomers is found to be naphthalene > azulene > fulvalene. The molecular orbital structure of fulvalene is found to closely resemble that of naphthalene, but the molecule is considerably less aromatic.

Acknowledgments. The author wishes to express his gratitude to the University of Kansas for partial support of the computer time required for this work, and to the personnel of the Institute für Physikalische Chemie in Mainz for their gracious hospitality. Also, many constructive discussions with Dr. S. D. Peyerimhoff and help with several computations by Mr. Donald W. Genson are gratefully acknowledged.

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(35) For a definition of antiaromaticity similar in spirit to the proposed definition, see R. Breslow, *Chem. Brit.*, **4**, 100 (1968), and references contained therein.

(36) A. J. Silvestri, L. Goodman, and J. A. Dixon, *J. Chem. Phys.*, **36**, 148 (1962).

(37) W. von E. Doering, *Theor. Org. Chem., Pap. Kekule Symp., 1958*, 35 (1959).