(27) R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **11**, 781 (1969).
(28) N. T. Anh, "Les règles de Woodward-Hoffmann", Ediscience, Paris, 1970, p 156.
(29) W. A. Goddard III, *J. Am. Chem. Soc.*, **94**, 793 (1972).
(30) F. D. Mango and J. H. Schachtschneider, *J. Am. Chem. Soc.*, **89**, 2484 (1967).
(31) I. Tvaroška, V. Klimo, and L. Valko, *Tetrahedron*, **30**, 3275 (1974).

Simulated ab Initio Molecular Orbital Technique. II. Benzenoid Aromatic Hydrocarbons[1a]

James E. Eilers,*[1b] Brian O'Leary, Arno Liberles, and Donald R. Whitman

Contribution from the Chemistry Department, State University of New York, College at Brockport, Brockport, New York 14420, the Department of Theoretical Chemistry, The University of Oxford, England, and the Chemistry Department, Case Western Reserve University, Cleveland, Ohio 44106. *Received July 15, 1974*

Abstract: The successful application of the simulated ab initio molecular orbital (SAMO) technique to benzenoid ring systems is reported. Wave functions for benzene, naphthalene, anthracene, and phenanthrene were obtained through the transfer of Fock matrix elements from ab initio calculations on two "pattern molecules", *s-cis-* and *s-trans*-butadiene. The "pattern molecules" were calculated at geometries chosen to coincide with the benzenoid structure. The SAMO results for benzene are compared to a completely analogous ab initio calculation and the SAMO results for both benzene and naphthalene are compared to published ab initio results using other basis sets; the agreement is satisfactory and demonstrates that SAMO calculations can correctly predict features for the large molecules that are not present in the "pattern molecules". In all cases, the SAMO calculations were performed on computers of moderate size and used substantially less time and storage than is required for traditional ab initio methods.

Although ab initio calculations on a few large molecules of chemical interest are now beginning to appear in the literature, the prediction that such calculations would soon be routine[21] has yet to be realized. Such calculations are still terribly expensive and very demanding of computer resources; even for molecules of modest size, it is difficult to justify the cost of ab initio calculations if results of similar accuracy can be obtained much less expensively or with less elaborate computing facilities. The recently reported simulated ab initio molecular orbital (SAMO) technique[2] shows promise of providing just such an inexpensive means of calculating wave functions for large molecules using computers of modest size. The early results[2,3] indicate a rather successful mimicry of ab initio calculations using identical basis sets and geometries.

Earlier papers[2,3] reported the successful application of the SAMO techniques to saturated hydrocarbon chains and polymers. We demonstrate here the applicability of the SAMO approach to conjugated ring systems by reporting the results of SAMO calculations on benzene, naphthalene, anthracene, and phenanthrene. These systems provide a valuable test of the SAMO technique because: (1) they involve conjugated unsaturated systems; (2) rings are being simulated from "pattern molecules" which, in this case, are small open-chain molecules; (3) the geometry of these "pattern molecules" is chosen to mirror structural aspects of the molecule of interest; (4) we are able to simulate ab initio calculations on a whole range of large molecules by taking a limited number of these "pattern molecules"; and (5) we expect to be able to predict features in the large molecules that are not present in the "pattern molecules".

We would emphasize that our sole aim is to mimic ab initio results; hence our method, since it makes no direct appeal to the variational theorem, can only be judged by direct comparison with ab initio results or with experiment. Further, since the method avoids the calculation and storage of all two-electron integrals, it represents a considerable saving in both computer time and storage.

Method

The SAMO method arises from the observation by Eilers and Whitman[2] that matrix elements over the converged Hartree–Fock operator in an LCAO-SCF-MO treatment are closely similar for analogous pairs of basis functions in a range of similar molecules. Thus the converged Fock matrix elements from small "pattern molecules" provide an excellent estimate of the converged Fock matrix elements in large molecules; and hence they provide a direct noniterative means of calculating the molecular orbitals for large molecules. This transferability is neither readily seen nor easily exploited unless calculations are carried out in a basis of hybridized atomic orbitals. The reason for this is that hybrids point along bonds and are therefore defined by the internal reference framework of the molecule, while nonhybridized s and p functions are defined by reference to an often arbitrary external coordinate system.

Certain features of the SAMO methods circumvent many of the difficulties encountered by earlier workers on Fock matrix transference.[22,23] Since in SAMO both off-diagonal and diagonal elements are obtained by transference, there is no need to use the Wolfsburg–Helmholtz approximation[24] which is known to be unsatisfactory for kinetic energy. The use of hybrid orbitals with internally defined orientations permits a more precise identification of basis orbital types and environments while completely avoiding any need to explicitly consider rotational invariance. Moreover, the present availability and use of more and somewhat larger "pattern molecules" allows one to make more environmental distinctions and to demand greater similarity of "pattern" and "target molecules".

The SAMO Procedure. The SAMO method for closed-shell molecules generates the molecular orbitals and orbital energies by a single solution of the eigenvalue problem

$$\mathbf{FC} = \mathbf{SC}\lambda$$

where **S** is the matrix of overlap integrals (all of which are

Table I. Eigenvalue Spectrum and Total Energy (hartrees) for Benzene

MO	Ab initio	SAMO	Ref 7[a]	Ref 8[b]	Ref 9[c]	Ref 25[e]
$1a_{1g}$	−11.4028	−11.3993	−11.30	−11.354	−10.78	−11.2050
$1e_{1u}$	−11.6027	−11.3992	−11.30	−11.354	−10.77	−11.2048
$1e_{2g}$	−11.4020	−11.3988	−11.29	−11.353	−10.77	−11.2042
$1b_{1u}$	−11.4016	−11.3984	−11.29	−11.352	−10.77	−11.2039
$2a_{2g}$	−1.2069	−1.2003	−1.168	−1.173	−0.9895	−1.1024
$2e_{1u}$	−1.0650	−1.0628	−1.037	−1.043	−0.8909	−0.9672
$2e_{2g}$	−0.8605	−0.8653	−0.846	−0.848	−0.7139	−0.7773
$3a_{1g}$	−0.7380	−0.7197	−0.738	−0.741	−0.5709	−0.6699
$1b_{1u}$	−0.6664	−0.6693	−0.654	−0.674	−0.5625	−0.5624
$2b_{2u}$	−0.6602	−0.6616	−0.662	−0.660	−0.4482	−0.6040
$3e_{1u}$	−0.6223	−0.6205	−0.622	−0.626	−0.4792	−0.5428
$1a_{2u}(\pi)$	−0.5573	−0.5019[d]	−0.535	−0.538	−0.4519	−0.4676
$3e_{2g}$	−0.5258	−0.5269	−0.524	−0.526	−0.3742	−0.4428
$1e_{1g}(\pi)$	−0.3966	−0.3640	−0.373	−0.379	−0.2877	−0.2937
$1e_{2u}(\pi^*)$	+0.1130	+0.0696	+0.127	+0.139	+0.1923	+0.2478
$1b_{2g}(\pi^*)$	+0.3475	+0.1468	+0.372	+0.372	+0.4101	+0.4803
Total energy	−229.7039	−229.5297	−230.463	−230.3745	−220.068	−230.2131

[a] A very good set of contracted Gaussians [3221] from 162 primitives, ref 7. [b] A very good set of Gaussians from 180 primitives grouped to 42 before SCF, ref 8. [c] A minimal set 60 uncontracted Gaussians, ref 9. [d] Note incorrect ordering. [e] A minimal Slater set optimized in the molecule, ref 25.

evaluated exactly, λ is the diagonal matrix of eigenvalues or orbital energies, **C** is the matrix whose columns are the eigenvectors (LCAO expansion coefficients), and **F** is the matrix over the Hartree-Fock operator. The SAMO method obtains the elements of **F** by transferring values, truncated to four decimal figures, from ab initio calculations on similar small molecules known as "pattern molecules". In those cases where interactions between distant orbitals are unavailable from the "pattern molecules", the Fock elements are usually small and can consequently be set to zero when constructing the Fock matrix for the large molecule.

The total energy is given by

$$E_T = \sum_{\text{occ}} (\epsilon_i^{(0)} + \lambda_i) + V_{NN}$$

where the $\epsilon_i^{(0)}$ are the expectation values of the one-electron operator, the λ_i are the eigenvalues of the Hartree-Fock operator, V_{NN} is the nuclear repulsion energy, and the summation is over the occupied orbitals.

Since the above energy is calculated only once from estimated Fock matrix elements, the variational theorem is not operable, and the usual criterion of lowest energy cannot be used to choose between two SAMO calculations on the same molecule. However, when comparing a SAMO calculation with the ab initio calculation that it attempts to mimic, the total energy is a useful measure of the similarity in the two calculations. The energy also can be used for virial theorem tests and can help detect errors in applying the SAMO procedure. Our experience with saturated systems[2,23] has been that the energy from a carefully done SAMO calculation will differ from the ab initio energy obtained with the same basis set by about ±0.05 au or 1.1%. Thus comparing the energy from a SAMO calculation with that from an ab initio calculation using a different basis set serves little purpose other than to emphasize the differences (or similarities) of the basis sets.

The final basis for both the SAMO and "pattern molecule" calculations consisted of three sp^2 hybrid orbitals, one 1s orbital and one p_π orbital for each trigonal carbon and one 1s orbital for each hydrogen. The hybrid orbitals which were obtained as linear combinations of optimized atomic orbitals were in turn expressed as fixed linear combinations (contractions) of a 5s 3p set of primitive Gaussian functions. The optimized exponents and contraction coefficients were obtained from Whitman and Hornback.[5] A detailed discussion of the basis set is given in paper I[2] of this series.

Notation. Recognizing that the Fock matrix element F_{ij} is given by

$$F_{ij} = \langle \chi_i | F | \chi_j \rangle$$

where F is the Fock operator, and χ_i and χ_j are basis orbitals, we make the following definition.

A 1,1-interaction refers to any Fock element where χ_i and χ_j are located within the same -CH- group. Similarly, a 1,2-interaction refers to any Fock element where χ_i and χ_j are located on neighboring -CH- groups. Continuing in this manner, a 1,*n*-interaction refers to any Fock element where χ_i and χ_j are located on different -CH- groups of a chain, such that the two groups are separated by $(n - 2)$ intervening -CH- groups. In general the above notation will refer to the shortest bonding pathway.

Benzene

As the "pattern molecule" for benzene we chose a distorted *s-cis*-butadiene. Here the bond angles are taken to be 120° and all bond lengths are set equal to those found in benzene[6] (2.6408 au for the carbon-carbon distance and 2.0605 au for the carbon-hydrogen distance). Since the environment of the internal groups is clearly more benzene like, all Fock elements of the 1,1 and 1,2 type were chosen from the internal rather than the terminal positions in the "pattern molecule". It was only necessary to involve terminal groups for the 1,3 and 1,4 interactions.

The results of this calculation together with ab initio results using a wide range of basis sets are presented in Table I. The total energy and eigenvalue spectrum are in fairly good agreement with our ab initio calculation using the same basis set and geometry. However, the agreement is not as good as that found for saturated systems.[2] A noteworthy feature of the SAMO result is that the π orbitals are more compressed than those of any of the full ab initio calculations. This effect is most noticeable in the low-lying virtual orbitals and also causes a shift in the $a_{2u}(\pi)$ and $3e_{2g}(\sigma)$ ordering.

Table II compares eigenfunction coefficients obtained by the SAMO technique with those from our ab initio calculation. Only representative MO's are included: the lowest valence orbital, the highest occupied orbital, the "out of prop-

Table II. Ab initio and SAMO Eigenfunction Coefficients for Benzene

Basis orbital type	Ab initio	SAMO	Basis orbital type	Ab initio	SAMO
	$2a_{2g}$			$2b_{1u}$	
C_s	0.0345	0.0341	C_s	0.0100	0.0076
C_H	0.0965	0.1030	C_H	0.2730	0,2761
C_C	0.1721	0.1717	C_C	0.0502	0.0646
H	0.0471	0,0463	H	0.1998	0.1966
	$1e_{1g}(\pi)$			$1a_{2u}(\pi)$	
$C_p(1)$	0.5214	0.5216	C_p	0.3078	0.3078
$C_p(2)$	0.2698	0.2608			
$C_p(3)$	0.2516	0.2608			

Table III. Extrapolated Values of Long-Range π-π Interactions

Interaction	r, au	$(T + V_{ne})$	V_{ee}	Fock element, hartrees
Calcd				
1,1	0			−0.2691
1,2	2.6408			−0.2407
1,3	4.5740	−0.5708	+0.5018	−0.0690
cis-1,4	5.2817	−0.2476	+0.2529	+0.0053
trans-1,4	6.8970	−0.0289	+0.0444	+0.0155
Exptl				
1,5 (AB')	7.9225	−0.0089	+0.0171	+0.0082
1,5 (BB)	9.1480	−0.0019	+0.0049	+0.0030
1,6	9.5215	−0.0012	+0.0033	+0.0021
1,6 3rd ring	10.5633	−0.0003	+0.0012	+0.0008
1,6 3rd ring	11.5110	−0.0001	+0.0004	+0.0003
1,7	12.1017	−0.0000	+0.0002	+0.0002
1,8	13.3600	−0.0000	+0.0001	+0.0001

er order" a_{2u} orbital, and the $2b_{1a}$. Only the absolute value of the coefficients for the unique orbital types are explicitly listed in the table; the sign and values for the other orbitals are apparent from symmetry. As in paper I[2] the symbols C_s and C_p indicate unhybridized s or p orbitals on carbon while C_{3H} and C_{3C} refer to sp^2 hybrids directed toward a hydrogen and carbon, respectively, and H indicates a hydrogen orbital. The correspondence is quite good but somewhat less so than with the unsaturated systems. The ionization potential from SAMO is found by Koopmans' theorem to be 9.8 eV in better agreement with the experimental value of 9.24 eV[10,11] than the ab initio result.

Although neglect of terms arising from 1,4 interactions has been shown to have little effect on straight chain calculations,[2] some of these interactions are as large as 0.1 au in benzene, and we find that their neglect leads to a total energy that is 5 hartrees below the ab initio result. This demonstrates that the usual criterion of lowest total energy cannot be used as a guide to the accuracy of SAMO results; this is not surprising since the method makes no direct appeal to the variational theorem.

It is worth noting that, assuming the prior availability of the necessary Fock elements, the simulated ab initio calculation takes 234 sec on the UNIVAC 1108 whereas a full ab initio treatment would require a few hours.

Naphthalene

The geometry of naphthalene presents certain difficulties for a SAMO treatment. Bond lengths are unequal and differ slightly from the values in benzene.[6] Furthermore, the carbon atoms are not equivalent; there are three different types present in the molecule. Since it is more practical not to introduce all these factors into a simulated calculation, naphthalene was assumed to consist of two regular hexagons with bond lengths equal to those in benzene. The "pattern molecules" were *s-cis*-butadiene in the geometry mentioned earlier and *s-trans*-butadiene, also in a benzene-like geometry.

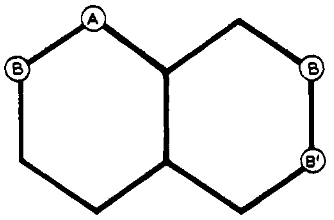

Figure 1. Long-range interactions in naphthalene.

The Fock matrix for naphthalene contains interactions of the 1,5 and 1,6 types. Figure 1 illustrates the two types of 1,5 interactions (AB' and BB) and the 1,6 (heteroannular BB') interaction. The pattern molecules, since they contain only four carbon atoms, obviously afford no values for these long-range Fock elements. However, since these terms might be expected to be small, the Fock matrix for naphthalene was initially completed by setting all such Fock elements equal to zero. This calculation gave a negative energy for the first virtual orbital, a π molecular orbital. This phenomenon might be attributed to the neglect of long-range interactions. Indeed, if these long-range values are positive, symmetry requires that they contribute in an antibonding fashion to this first virtual orbital. Hence, we approximated the 1,5 and 1,6 π-π interactions and recalculated the eigenvalue spectrum.

At first sight, the available Fock elements (Table III) show no obvious trend. The 1,1; 1,2; and 1,3 elements are negative and decrease in magnitude as a function of r, the internuclear distance. However, the 1,4 interactions are positive, and, while the p atomic orbitals are more separated in *s-trans*-butadiene, the value for this interaction is larger than that found in the s-cis conformation. This sign change cannot be a property of radial nodes since our p orbitals contain no such nodes.

The Fock matrix element, F, can be expressed as

$$F = (T + V_{ne}) + V_{ee} \tag{1}$$

When $(T + V_{ne})$ and V_{ee} are considered separately, they are found to decay in a near exponential fashion as a function of r, the distance between the respective carbons. Further, since they are of opposite sign and decay at different rates, their sum might be expected to change its sign. Indeed, the Fock element associated with the 1,4 interaction in *s-cis*-butadiene is near to the crossover point. In view of the above we extrapolated the one- and two-electron components using eq 2, where the constants A_1, A_2, B_1, and B_2 are determined from the values of the 1,4 interactions occurring in *cis*- and *trans*-butadiene. Extrapolated values for use with naphthalene, anthracene, and phenanthrene are presented in Table III.

$$\begin{aligned} (T + V_{ne}) &= A_1 e^{(-B_1 r)} \\ V_{ee} &= A_2 e^{(-B_2 r)} \end{aligned} \tag{2}$$

Although these extrapolated values can only be considered as a first approximation to the correct values for these Fock elements, their sign and order of magnitude are probably correct. No attempt was made to extrapolate the long-range σ-σ interaction, because they presented orientation difficulties and were not involved in this first virtual orbital.

The eigenspectrum resulting from this calculation is presented in Table IV and compared with the ab initio results of Buenker and Peyerimhoff.[12] We should emphasize that

Table IV. Simulated and ab initio Eigenvalue Spectra for Naphthalene

MO symmetry	Ab initio[a]	SAMO	MO symmetry	Ab initio[a]	SAMO
$1a_g$	−11.3926	−11.4008	$6b_{2u}$	−0.6689	−0.6557
$1b_{2u}$	−11.3916	−11.3993	$8a_g$	−0.6616	−0.6479
$2a_g$	−11.3628	−11.3992	$5b_{1g}$	−0.6347	−0.6119[b]
$1b_{3u}$	−11.3628	−11.4005	$6b_{3u}$	−0.6305	−0.6141
$1b_{1g}$	−11.3620	−11.3992	$7b_{2u}$	−0.6094	−0.5854
$2b_{2u}$	−11.3620	−11.3989	$1b_{1u}(\pi)$	−0.5758	−0.5207[b]
$2b_{3u}$	−11.3599	−11.3991	$7b_{3u}$	−0.5673	−0.5598
$3a_g$	−11.3599	−11.3992	$6b_{1g}$	−0.5300	−0.5167
$2b_{1g}$	−11.3599	−11.3986	$9a_g$	−0.5221	−0.5058
$3b_{2u}$	−11.3598	−11.3985	$1b_{2g}(\pi)$	−0.4966	−0.4739
$4a_g$	−1.2133	−1.2315	$1b_{3g}(\pi)$	−0.4355	−0.4163
$3b_{3u}$	−1.1455	−1.1534	$2b_{1u}(\pi)$	−0.3750	−0.3536
$4b_{2u}$	−1.0898	−1.1091	$1a_u(\pi)$	−0.3418	−0.2838
$5a_g$	−1.0466	−1.0703			
$3b_{1g}$	−1.0249	−1.0221	$2b_{2g}(\pi^*)$	+0.0771	+0.0048
$4b_{3u}$	−0.8866	−0.8908	$2b_{3g}(\pi^*)$	+0.1045	+0.0715
$5b_{2u}$	−0.8719	−0.8712	$3b_{1u}(\pi^*)$	+0.1892	+0.1478
$6a_g$	−0.8512	−0.8413	$2a_u(\pi^*)$	+0.2849	+0.1629
$4b_{1g}$	−0.7484	−0.7288	$3b_{3g}(\pi^*)$	+0.4250	+0.2143
$5b_{3u}$	−0.7447	−0.7166	$8b_{2u}$	+0.5290	+0.4351[b]
$7a_g$	−0.7178	−0.7045	$8b_{3u}$	+0.5437	+0.4215
Total energy	−382.7883[a]	−380.8468			

[a] Reference 12. [b] Note incorrect ordering.

considering the limited basis set used in the SAMO scheme, we could not expect results that precisely agree with those of Buenker and Peyerimhoff. Again the π orbitals appear somewhat compressed resulting in $1b_{1u}$ being out of order when compared with the ab initio results. However, the overall comparison between the SAMO and ab initio orbital energies is quite good.

The ionization potential is found by Koopman's theorem to be 7.7 eV, in better agreement with the experimental value of 8.12 eV[11] than the ab initio prediction. The computer time required for the simulated calculation was only 742 sec on the UNIVAC 1108.

Anthracene

A treatment of anthracene presents problems similar to those encountered with naphthalene. A number of different bond lengths and angles are found in the system,[12,14] but the molecule was assumed to be three regular hexagons with benzene-like bond distances. The Fock matrix elements are again obtained from the *s-cis-* and *s-trans*-butadienes.

Here again the first virtual orbital (π symmetry) has a slight negative value. Although inclusion of extrapolated long-range π–π terms from Table III does improve the situation, it does not completely correct it. The results of the calculation which included all long-range π–π elements are presented in Table V. Unfortunately, no ab initio calculations using similar basis sets are available for comparison. Preuss and Janoschek[15] report having made such calculations but do not present results. We suspect, however, that again the π orbitals are somewhat compressed in our simulation. Comparison with Christoffersen's FSGO molecular fragments results[26] would imply that the $1b_{1u}$ orbital (the lowest lying π) should be below the $10b_{2u}$ and $10b_{3u}$.

The chemical behavior of anthracene supports the idea of a low-lying virtual orbital,[16] but a negative virtual orbital is unlikely. The Koopman's ionization potential is 6.3 eV, while the experimental value is 7.38 eV.[17]

The anthracene calculation required only 2462 sec. An ab initio calculation using a comparable basis set on a molecule of this size is beyond the scope of all but the largest computers and even then would require many hours.

Table V. Eigenvalue Spectrum for Anthracene

MO	Energy	MO	Energy
$1b_{2u}$	−11.4009	$7b_{3u}$	−0.7686
$1a_g$	−11.4008	$7b_{2u}$	−0.7264
$1b_{1g}$	−11.4005	$9a_g$	−0.7105
$1b_{3g}$	−11.4005	$6b_{1g}$	−0.6671
$2a_g$	−11.3993	$10a_g$	−0.6652
$2b_{2u}$	−11.3993	$8b_{3u}$	−0.6647
$2b_{3u}$	−11.3992	$8b_{2u}$	−0.6553
$2b_{1g}$	−11.3991	$7b_{1g}$	−0.6212
$3a_g$	−11.3990	$9b_{3u}$	−0.6000
$3b_{2u}$	−11.3989	$9b_{2u}$	−0.5885
$3b_{3u}$	−11.3988	$11a_g$	−0.5755
$4a_g$	−11.3988	$10b_{3u}$	−0.5576
$3b_{1g}$	−11.3985	$10b_{2u}$	−0.5252
$4b_{3u}$	−11.3985	$1b_{1u}(\pi)$	−0.5243
$5a_g$	−1.2447	$1b_{3g}(\pi)$	−0.5107
$4b_{2u}$	−1.1989	$8b_{1g}$	−0.5089
$6a_g$	−1.1291	$12a_g$	−0.5020
$5b_{3u}$	−1.1236	$2b_{1u}(\pi)$	−0.4464
$4b_{1g}$	−1.0740	$1b_{2g}(\pi)$	−0.4347
$5b_{2u}$	−1.0713	$1a_u(\pi)$	−0.3623
$6b_{3u}$	−0.9952	$2b_{3g}(\pi)$	−0.3473
$7a_g$	−0.9160	$2b_{2g}(\pi)$	−0.2329
$5b_{1g}$	−0.8771	$3b_{1u}(\pi^*)$	−0.0399
$6b_{2u}$	−0.8464	$2a_u(\pi^*)$	+0.0959
$8a_g$	−0.8436	$3b_{3g}(\pi^*)$	+0.1097

Total energy = −532.1250

Phenanthrene

The treatment of phenanthrene is similar to that of anthracene in that it was considered to be three fused regular hexagons. Again, the Fock matrix elements were obtained from *s-cis-* and *s-trans*-butadiene.

In benzene, naphthalene, and anthracene the choice of Fock elements has been unambiguous. In phenanthrene,

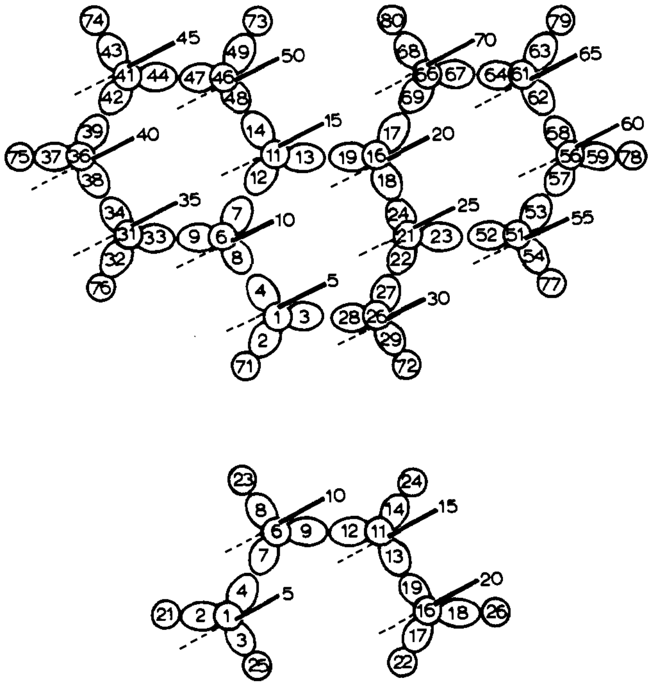

Figure 2. Top: atomic orbitals for phenanthrene. Bottom: atomic orbitals for *s-cis*-butadiene.

however, two of the hydrogens (73 and 80 in Figure 2) are fairly close to one another. This steric effect, while not large enough to distort the molecule from planarity, may have an effect on the Fock elements, particularly those involving orbitals 49, 73, 68, and 80 (see Figure 2, top).

All interfragment interactions (e.g., $F_{73,68}$ or $F_{49,17}$) are readily and unambiguously obtained from *s-cis*-butadiene (see Figure 2, bottom). However, choosing the correct values for the intrafragment interactions of the two hindered C–H groups is less straightforward. In general the Fock elements for 1,1- and 1,2-type interactions have been obtained from the central carbons of the "pattern molecules" because these central carbons are in a more benzene-like environment. Thus, if no steric effect was suspected, intrafragment elements such as $F_{73,73}$ and $F_{49,73}$ would be treated like all other C–H groups in these ring compounds, in that the Fock matrix elements would be obtained from the central positions in *s-cis*-butadiene. Any steric effect present in phenanthrene should also be present in the *s-cis*-butadiene and affect the corresponding $F_{22,22}$ and $F_{17,22}$ butadiene elements (see Figure 2, bottom). One approach would be to use these elements directly. Such a direct approach would introduce other errors since orbitals 17 and 22 are part of a terminal group.

An alternative approach is to apply a steric correction to the values that are obtained from the internal orbitals. For example

$$F_{49,73} = F_{14,24} + (F_{17,22} - F_{18,26}) \tag{3}$$

where $F_{49,73}$ is the Fock element for phenanthrene and the other Fock elements refer to the *s-cis*-butadiene numbering scheme. The rationale for the rather ad hoc introduction of eq 3 is as follows. It is quite possible that intrafragment matrix elements involving orbitals 49 and 73 of phenanthrene will have slightly different values than similar matrix elements involving orbitals 43 and 74, or 37 and 75. It is tempting to attribute such difference to the proximity of orbitals 49 and 73 to orbitals 68 and 80. To see if such an effect in phenanthrene could be expected to be nonnegligible, one need only inspect Fock matrix elements in *s-cis*-butadiene. $F_{17,22}$ and $F_{18,26}$ (Figure 2, bottom) are similar interactions except that 17 and 22 would appear to be subject to the steric effect under discussion while $F_{18,26}$ would not. Thus the difference between $F_{17,22}$ and $F_{18,26}$ is thought to be due to a steric effect (arising from the proximity of orbitals 17 and 22 to orbitals 3 and 25). Since $F_{49,73}$ (phenanthrene) is subject to a similar steric effect, the usual value (chosen from the central groups) is modified by the addition of this steric split. For phenanthrene, the splits were less than 0.002 au.

Table VI. Eigenvalue Spectrum for Phenanthrene

	Energy			Energy	
MO	No steric correction	With steric correction	MO	No steric correction	With steric correction
$1a_1$	−11.4009	−11.4009	$13b_2$	−0.7560	−0.7559
$1b_2$	−11.4008	−11.4008	$14a_1$	−0.7328	−0.7322
$2a_1$	−11.4006	−11.4006	$15a_1$	−0.7116	−0.7112
$2b_2$	−11.4003	−11.4003	$16a_1$	−0.6965	−0.6960
$3a_1$	−11.3993	−11.3993	$14b_2$	−0.6747	−0.6745
$3b_2$	−11.3993	−11.3993	$15b_2$	−0.6430	−0.6425
$4a_1$	−11.3992	−11.3992	$17a_1$	−0.6364	−0.6353
$4b_2$	−11.3991	−11.3991	$18a_1$	−0.6168	−0.6168
$5a_1$	−11.3991	−11.3991	$16b_2$	−0.6114	−0.6102
$5b_2$	−11.3989	−11.3989	$19a_1$	−0.5943	−0.5942
$6a_1$	−11.3989	−11.3989	$17b_2$	−0.5759	−0.5758
$6b_2$	−11.3987	−11.3987	$20a_1$	−0.5470	−0.5460
$7a_1$	−11.3985	−11.3985	$18b_2$	−0.5331	−0.5325
$7b_2$	−11.3985	−11.3985	$1b_1(\pi)$	−0.5253	−0.5253
$8a_1$	−1.2477	−1.2477	$21a_1$	−0.5117	−0.5115
$8b_2$	−1.1928	−1.1927	$1a_2(\pi)$	−0.5081	−0.5081
$9a_1$	−1.1414	−1.1413	$19b_2$	−0.4913	−0.4896
$10a_1$	−1.1138	−1.1138	$2b_1(\pi)$	−0.4564	−0.4564
$9b_2$	−1.0881	−1.0880	$3b_1(\pi)$	−0.4180	−0.4180
$10b_2$	−1.0369	−1.0368	$2a_2(\pi)$	−0.3886	−0.3886
$11a_1$	−1.0230	−1.0229	$3a_2(\pi)$	−0.3045	−0.3045
$12a_1$	−0.8963	−0.8960	$4b_2(\pi)$	−0.2729	−0.2729
$11b_2$	−0.8895	−0.8895	$4a_2(\pi^*)$	+0.0105	+0.0105
$13a_1$	−0.8663	−0.8661	$5b_2(\pi^*)$	+0.0448	+0.0447
$12b_2$	−0.8288	−0.8284	$6b_2(\pi^*)$	+0.1101	+0.1101

Total energy = −532.0262
Total energy (with steric corrections) = −532.0960

We report two calculations on phenanthrene; the first uses no steric correction and the second corrects for the steric effects as illustrated in eq 3. Unlike anthracene, all virtual orbitals are positive in both calculations. The eigenvalue spectra are presented in Table VI. Using the steric correction seems to have little effect on the eigenvalue spectra. We are now in the process of examining the influence of steric effects in other molecules. The π orbital compression is thought to be present in phenanthrene too. Again comparison to FSGO results[26] indicates that the $1b_{1a}(\pi)$ orbital should be lower in energy than the $20a_1$ and $18b_2$ orbitals.

It is worthwhile noting that the SAMO methods predict anthracene to be more stable than phenanthrene by 18 kcal/mol when steric effects are ignored and by 62 kcal/mol when steric effects are taken into account. Experimentally phenanthrene is more stable by 6.9 kcal/mol.[18]

The ionization potential for phenanthrene is found, by both methods, to be 8.4 eV, while the experimental value is 8.03 eV.[19] Thus, both methods correctly predict phenanthrene to have a higher ionization potential than anthracene. The time required for the calculation was 2374 sec.

Population Analysis

A Mulliken population analysis[20] was carried out to determine the simulated method's prediction of electronic distribution within the various molecules. For benzene and naphthalene a check against ab initio results is possible. The numbering system for the molecules is shown in Figure 3.

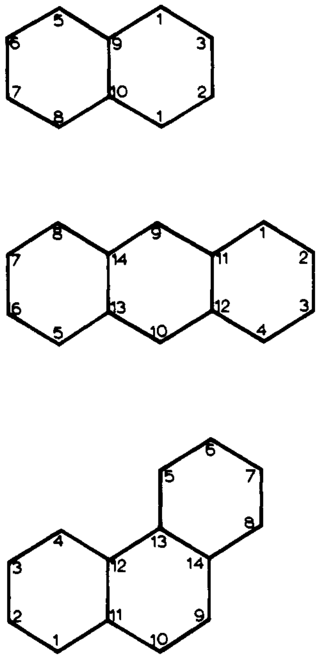

Figure 3. Numbering scheme used for naphthalene, anthracene, and phenanthrene.

Table VII. Orbital Populations in Benzene

Orbital	Ab initio	SAMO
C_s	2.004	2.004
C_{3C}	0.993	0.993
C_{3H}	1.219	1.215
C_p	1.000	1.000
H	0.792	0.795

Table VIII. Atom Populations in Naphthalene

Atom	Population	Atom	Population
C_9, C_{10}	5.851	H_1, H_4, H_5, H_8	0.796
C_1, C_4, C_5, C_8	6.259	H_2, H_3, H_6, H_7	0.794
C_2, C_3, C_6, C_7	6.226		

The agreement for benzene (Table VII) is excellent.

Table VIII represents the total electronic density at the various positions in naphthalene. Our calculation agrees with that of Buenker and Peyerimhoff,[12] and with reactivity measurements, in that we find the fused carbon atoms (C_9 and C_{10}) to be most positive and the α-carbon atoms (C_1, C_4, C_5, and C_8) most negative. When the σ and π components of the atom populations are considered separately, we find this unequal distribution of charge to be almost exclusively in the π system, again in agreement with Buenker and Peyerimhoff.

It should be emphasized that the Fock matrix elements for all the carbon positions were chosen in the same manner from the same "pattern molecules". However, the various carbon positions, because of their differing environments, do experience different combinations of these same interactions. Thus the molecular orbitals resulting from such matrices can reveal details of charge distribution that are quite unlike those found in the "pattern molecules".

The electronic density in anthracene is given in Table IX. The situation here is similar to that found in naphthalene; the fused positions (C_{11}, C_{12}, C_{13}, and C_{14}) are positively charged while the central carbons (C_9 and C_{10}) are most negatively charged. Of the hydrogens, H_9 and H_{10} have the greatest electron density; hence we observe a "piling up" of electrons in the center of the molecule.

Table IX. Atom Populations in Anthracene

Atom	Populations	Atom	Populations
C_1, C_4, C_5, C_8	6.254	H_1, H_4, H_5, H_8	0.798
C_2, C_3, C_6, C_7	6.231	H_2, H_3, H_6, H_7	0.795
C_9, C_{10}	6.335	H_9, H_{10}	0.799
$C_{11}, C_{12}, C_{13}, C_{14}$	5.855		

Table X. Atom Populations in Phenanthrene

	Population	
Atom	No steric correction	Steric correction
C_1, C_8	6.268	6.268
C_2, C_7	6.237	6.236
C_3, C_6	6.236	6.236
C_4, C_5	6.281	6.254
C_9, C_{10}	6.270	6.270
C_{11}, C_{14}	5.862	5.862
C_{12}, C_{13}	5.886	5.886
H_1, H_8	0.797	0.797
H_2, H_7	0.795	0.795
H_3, H_6	0.795	0.795
H_4, H_5	0.778	0.806
H_9, H_{10}	0.796	0.796

Table X shows the atom populations in phenanthrene. Here again, it is the fused positions that are more electron deficient. As expected the primary difference between the sterically corrected and uncorrected values is at positions 4 and 5. The steric correction results in charge moving from carbon 4 to hydrogen 4, making this the most electron-rich hydrogen position.

The results of a Mulliken population analysis are sometimes used to explain chemical behavior. However, the electronic density and bond order at each position are insufficient criteria for explaining such behavior. When determining the site of reaction in a molecule, one must also consider either the transition state for rates or the products for equilibria. Since it rarely suffices to regard only the reactant, we present the electronic density for the various molecules but are reluctant to explain chemical behavior on this basis.

Discussion

The results of this work show that the SAMO technique is applicable to benzenoid-type ring systems as well as to chain hydrocarbons. However, the results appear to be somewhat less accurate. The small changes introduced by using ideal as opposed to real geometries should have little, if any, effect on the electronic structure of these molecules. At this stage in our investigations we cannot say whether or not the SAMO approach would be successful for highly strained rings.

As demonstrated here, the inherent economic advantages of the SAMO system are further enhanced when the application is to highly symmetric "target molecules" or to a series of similar "target molecules", where repeated use can be made of a small number of "pattern molecules". For example, the introduction of ideal hexagonal ring symmetry to this study, while unnecessary to the SAMO approach, had considerable economic advantage by reducing the total number of "pattern molecules" to two. With the ideal geometry, each "pattern molecule" was able to geometrically mimic more than one region of the "target molecule". Clearly less symmetric "target molecules" would require the calculation of additional "pattern molecules" with geometries chosen to exactly mirror the geometries of different regions in the large molecules and therefore be more expensive. For example, experimental naphthalene would need four patterns rather than the two used here and nearly double the cost. However, that would still be much less expensive than the ab initio and those four "pattern molecules" could also be used for anthracene, etc.

In our previous work[2] on straight-chain hydrocarbons, it was necessary to include only three classes of interaction, namely, the 1,1, 1,2, and 1,3 interactions. In the present work, results of comparable accuracy could only be obtained by also including all 1,4 interactions and in some cases longer-range π-π terms.

In all cases, the SAMO results are in fairly good agreement with the available ab initio results. Our eigenvalue spectra for benzene and naphthalene are in good agreement with the ab initio results, except for a general compression of the π orbital eigenvalue spread that has the lowest-lying π orbital out of order with at least one σ orbital. We expect the anthracene and phenanthrene eigenvalue spectra to have similar validity. Comparison to FSGO fragment calculations indicates a problem with the order of the lowest lying π for these molecules also.

Our earlier work[2] had indicated that an accuracy of ±0.005 could be expected for the orbital expansion coefficients. For benzene some coefficients differed by twice this amount from our ab initio ones. For the rest of the calculations, a direct comparison of the SAMO and ab initio eigenvectors is not possible (comparisons of expansion coefficients between calculations using different basis sets are meaningless). An indirect comparison is achieved through a Mulliken population analysis. Consideration of these results serves to show that, for large molecules, the SAMO method is able to predict electron density distributions and allied properties that are not present in their associated "pattern molecules".

Some comment is necessary on the SAMO method's ability to predict energy differences between various isomers or different conformations of a given molecule. Since (1) we are considering small energy differences between large molecules, (2) we cannot be certain that the calculation on each molecular arrangement differs in the same manner from a full Roothaan-Hartree-Fock calculation, and (3) the effect of idealizing the geometry may be different in differing molecular arrangements, we feel that such energy differences must be treated with some degree of skepticism. A clear example of this limitation occurs with anthracene and phenanthrene.

The SAMO results fail to show a sufficient spread in the eigenvalues for the π molecular orbitals. This is clearly seen when the benzene and naphthalene results are compared to the available ab initio results. Recalling that, in both anthracene and phenanthrene, the first virtual orbital is abnormally low lying, we are led to suspect that this compression of π orbitals is a characteristic feature of the SAMO method as applied to the condensed ring systems. We have shown that this can partially be corrected by the inclusion of long-range π-π interactions. However, this π orbital compression may not result solely from omitting certain long-range interactions; rather it may be a consequence of ring closure. Since, in the benzene ring, the 1 and 4 positions are free to "interact" through two bonding pathways (butadiene is restricted to one), we may well be underestimating the size of all 1,4 interactions. This question is currently under investigation. Comparison of ab initio and SAMO calculations using precisely the same basis set and geometries is underway for the cyclohexane conformers.

The result of applying the steric correction is not clear-cut. There is little change in the eigenvalue spectrum, but the electron distribution within the sterically interacting C-H bonds is altered. Subsequent work has demonstrated the correctness and usefulness of this modification to the SAMO technique. We are inclined to think the sterically corrected result is better, even though this leads to a poorer value for the anthracene-phenanthrene energy difference.

The work reported here serves to illustrate the power of the SAMO technique in that it clearly demonstrates the method's remarkable ability to provide a means of calculating the molecular orbitals for a whole range of large molecules from ab initio calculations on one or two small, but suitably chosen "pattern molecules". Indeed, we have recently developed computer programs that, to a large measure, automate the tedious and error-prone tasks of storing, retrieving, and deploying the Fock elements. We are further utilizing the Fock elements from the two butadienes used in this work to perform SAMO calculations on benzonaphthacene, 1,2:5,6-dibenzanthracene, 3,4-benzopyrene, 3,4:9,10-dibenzopyrene, anthanthrene, 1,2-benzanthracene, pyrene, dimethyldibenzopyrene, and dimethylanthanthrene, molecules that are of interest as carcinogens.

Conclusion

The SAMO procedure reproduces ab initio results for benzenoid aromatic hydrocarbons nearly as well as it did in the case of saturated hydrocarbons. Molecules containing any number of fused benzene rings can be calculated from the two butadiene "pattern molecules" with a small expenditure in computing time. Clearly, from a costwise consideration this method has tremendous potential and seems particularly suitable for attacking problems on very large molecules such as carcinogenic aromatic hydrocarbons.

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References and Notes

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(2) J. E. Eilers and D. R. Whitman, *J. Am. Chem. Soc.*, **95**, 2067 (1973).
(3) B. J. Duke and B. O'Leary, *Chem. Phys. Lett.*, **20**, 459 (1973).
(4) E. Clementi and D. R. Davis, *J. Chem. Phys.*, **45**, 2593 (1966).
(5) D. R. Whitman and C. Hornback, *J. Chem. Phys.*, **51**, 398 (1969); C. J. Hornback, Ph.D. Thesis, Case Institute of Technology, 1967.
(6) L. E. Sutton, "Tables of Interatomic Distances and Configurations in Molecules and Ions", The Chemical Society, London, 1958, p M196.
(7) J. M. Schulman and J. W. Moskowitz, *J. Chem. Phys.*, **47**, 3491 (1967).
(8) R. J. Buenker, J. L. Whitten, and J. D. Petke, *J. Chem. Phys.*, **49**, 2261 (1968).
(9) J. M. Schulman and J. W. Moskowitz, *J. Chem. Phys.*, **43**, 3287 (1965).
(10) M. I. Al-Joboury and D. W. Turner, *J. Chem. Cos.*, **4**, 4434 (1961).
(11) K. Watanabe, *J. Chem. Phys.*, **26**, 542 (1957).
(12) R. J. Buenker and S. D. Peyerimhoff, *Chem. Phys. Lett.*, **3**, 37 (1969).
(13) J. M. Robertson, H. M. M. Sherer, G. A. Sim, and D. G. Watson, *Nature (London)*, **182**, 177 (1958).
(14) C. A. Coulson, R. Daudel, and J. M. Robertson, *Proc. R. Soc., Ser. A*, **207**, 306 (1951).
(15) H. Preuss and R. Janoschek, *J. Mol. Struct.*, **3**, 423 (1969).
(16) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists", Wiley, New York, N.Y., 1961, p 218.
(17) A. Terenin and F. Vilessov, *Adv. Photochem.*, **2**, 385 (1964).
(18) A. Magnus, H. Hartmann, and F. Becker, *Z. Phys. Chem.*, **197**, 75 (1951).
(19) M. E. Wacks and V. H. Dibeler, *J. Chem. Phys.*, **31**, 1557 (1959).
(20) R. S. Mulliken, *J. Chem. Phys.*, **23**, 1833 (1955).
(21) E. Clementi, *Proc. Natl. Acad. Sci. U.S.*, **69**, 2942 (1972).
(22) M. D. Newton, F. P. Boer, and W. N. Lipscomb, *J. Am. Chem. Soc.*, **88**, 2353 (1966); D. B. Boyd and W. N. Lipscomb, *J. Chem. Phys.*, **48**, 4955 (1968).
(23) See B. O'Leary, B. J. Duke, and J. E. Eilers, *Adv. Quantum Chem.*, in press, for a general discussion of such methods.
(24) M. Wolfsberg and L. Helmholtz, *J. Chem. Phys.*, **20**, 837 (1952).
(25) R. M. Stevens, E. Switkes, E. A. Laws, and W. N. Lipscomb, *J. Am. Chem. Soc.*, **93**, 2603 (1971).
(26) R. E. Christoffersen, *Int. J. Quantum Chem., Symp.*, 7, 169 (1973).