strain energy of cyclotetradecane is but 1.4 kcal mol^{-1}.

In summary, we have examined cyclotetradecane using an approach that combines intuition about ring-size effects, estimates and measurement of heats of phase changes, and molecular mechanical calculations. Table II summarizes all of the individual results, where all unreferenced quantities are from the current study. We conclude that the strain energy of cyclotetradecane is in line with comparably sized cycloalkanes.

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Supplementary Material Available: The salient MM3 output for the lowest four conformers of cyclotetradecane and both the raw and plotted heat of vaporization and sublimation data (23 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

Dication Formation by Oxidation of Hydrocarbons with SbF_5. Correlation between Ionization Potential, Heat of Formation, and Dication Formation

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The ability of unsaturated hydrocarbons to be oxidized to dications by SbF_5 was examined through AM1, MNDO, and MINDO/3 calculations on 53 compounds whose reactions under these conditions were reported in the literature. A positive correlation existed for first ionization potentials calculated by AM1 for substituted and unsubstituted polycyclic aromatic hydrocarbons, with oxidation to dications occurring when the ionization potential was ≤8.3 eV. The correlation was poor for nonbenzenoid precursors. A much better correlation for all hydrocarbon precursors was with the difference between the heats of formation of the dication and its neutral precursor ($\Delta\Delta H_f$). Both AM1 and MINDO/3 were equally satisfactory in their correlation with $\Delta\Delta H_f$ ceilings of 463 ± 4 kcal/mol (AM1) and 430 ± 4 kcal/mol (MINDO/3) for dication formation.

We are interested in preparing novel hydrocarbon dications from unsaturated precursors by oxidation with SbF_5 in SO_2ClF, particularly those which might possess nonclassical structures like the pyramidal $C_6(CH_3)_6$ dication.[1] Because the synthesis of the unsaturated precursor can involve a major committment of time and effort, it was important to us to be able to easily identify those unsaturated precursors which are most likely to form dications under our conditions. We report here data from AM1, MNDO, and MINDO/3 calculations on 53 compounds whose attempted oxidation by SbF_5 in SO_2ClF was reported in the literature.

There are two types of data from molecular orbital calculations which could be used with experimental data to predict the likelihood of dication formation. Since the formation of dications from unsaturated precursors involves the loss of electrons, the magnitude of the ionization potential(s) might allow precursors to be grouped according to whether they could or could not form dications. Similarly, a comparison of the energy of the dication ($\Delta H_{\text{formn dication}}$) with the energy of the neutral species ($\Delta H_{\text{formn neutral hydrocarbon}}$) or $\Delta\Delta H_f$ might allow a similar grouping of precursors.

Results

Calculation of Ionization Potentials. We chose to calculate first and second ionization potentials using the AM1[2] method because it reliably reproduces higher ionization energies, as does the MNDO[3] method, and because we intended ultimately to examine molecules with moderate to severe steric congestion and the AM1 method is superior to MNDO in dealing with sterically congested molecules.[4] We chose not to use the PM3 method[5] because it has not yet received the verification in the literature to date of AM1. We chose to calculate both first and second ionization potentials for a subset of the precursors to be considered because it was not obvious that the same trends would appear in the formation of cation radicals and in the formation of dications. Because the calculation of the first ionization potential is based on Koopman's theorem, in which all orbitals are unchanged upon going from the molecule to the cation radical, we performed a closed-shell calculation of the second ionization potential using the geometry calculated for the neutral molecule which was assigned a charge of 1 in the calculation. That is, the cation radical was assumed to have the geometry of the neutral molecule for the purpose of calculating its ionization potential, or the energy required to make the dication.

Previous work with a variety of benzenoid aromatic hydrocarbons[6] found that their ability to form dications, as opposed to cation radicals, could be rationalized by a

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Table I. Ionization Potentials of Substituted and Unsubstituted Polycyclic Aromatic Hydrocarbons from AM1 Calculations[a]

unsubstd PAH[b]	first IP	second IP	substd anthracenes[d]	first IP	second IP
benzene	9.7[c]	16.2	9,10-dibromoanthracene[e]	**8.4**	**12.6**
naphthalene	8.7[c]	12.7	9,10-dichloroanthracene	**8.3**	**12.5**
triphenylene	8.7[c]	13.8	9-bromoanthracene[e]	**8.3**	**12.5**
phenanthrene	8.6[c]	13.0	9-chloroanthracene	**8.2**	**12.5**
chrysene	8.4[c]	12.4	[anthracene]	**8.1**	**12.5**
picene	8.4[c]	13.0	9-chloro-10-methylanthracene	**8.1**	**12.3**
benzo[*b*]triphenylene	8.3[c]	12.0	2-methylanthracene	**8.1**	**12.4**
dibenz[*a*,*h*]anthracene	**8.3**[c]	**11.9**	9-phenylanthracene	**8.0**	**12.1**
tetrabenzonaphthalene	**8.2**	**11.8**	9-methylanthracene	**8.0**	**12.3**
coronene	**8.2**	**11.8**	9,10-diphenylanthracene	**8.0**	**11.8**
benz[*a*]anthracene	**8.2**[c]	**11.5**	9,10-dimethylanthracene	**7.9**	**12.2**
pyrene	**8.1**	**12.3**	1,4-dimethoxyanthracene	**7.8**	**11.9**
anthracene	**8.1**[c]	**12.5**			
benzoperylene	**8.0**	**11.8**	substituted naphthalenes[b,f]		
benzopyrene	**7.9**	**11.7**	[naphthalene]	8.7	13.8
perylene	**7.9**	**11.6**	1,2,3,4-tetramethylnaphthalene	8.7	13.8
naphthacene	**7.7**[c]	**11.7**	1,2,3,6,7,8-hexahydropyrene	8.2	12.7
pentacene	**7.5**[c]	**11.1**	1,4,5,6-tetramethylnaphthalene	**8.1**	**12.7**
			octamethylnaphthalene	**8.0**	**12.3**

[a] Precursors which form dications are shown in bold-face type; those in which dication is in equilibrium with cation radical are underlined. [b] Reference 6. [c] First ionization potentials for compounds marked are in agreement with those from: Herndon, W. C.; Connor, D. A.; Lin, P. *Pure Appl. Chem.* **1990**, *62*, 435–444. Dication or cation radical formation reported in ref 6; dication formation from coronene reported in ref 10. [d] Reference 9. [e] These values may be too high due to neglect of the inner electrons (the core approximation). Cf. Similar results for MNDO in: Healy, E.; Dewar, M. J. S. *J. Comput. Chem.* **1983**, *4*, 542–551. [f] Reference 8.

consideration of the energy of the highest occupied π molecular orbital (HOMO) of the neutral precursor calculated by the simple Huckel molecular orbital method.[7] Because of the limitations of the Huckel method, including its inability to handle substituent effects, we recalculated the energy of the HOMO (which is the negative of the ionization potential) using the more sophisticated AM1 method and report those results in terms of ionization potentials (Table I). We extended the series to include substituted naphthalene[6,8] and anthracene precursors[9] to confirm that trends apparent for unsubstituted benzenoid hydrocarbons were found in substituted benzenoid hydrocarbons. Finally, since our interest is in cations generated from nonbenzenoid hydrocarbons, we report calculations on a variety of dications prepared by oxidation with SbF_5 in SO_2ClF from nonbenzenoid precursors (Table II).

It is apparent that for polycyclic aromatic hydrocarbons a consideration of the first ionization potential calculated by the AM1 method gives a fairly close relationship between the ionization potential and the ability to form dications for most precursors with dication formation occurring when the first ionization potential is less than about 8.3 eV. Although Forsyth et al.[6] observed only the cation radical upon oxidation of coronene with SbF_5/SO_2ClF, Krusic et al.[10] very recently reported its oxidation at room temperature to give the triplet. This would be consistent with its calculated first ionization potential. The relationship between dication formation and first ionization potential continues to hold up fairly well for substituted anthracenes and naphthalenes. With the exception of hexahydropyrene and dibrominated anthracenes, compounds with ionization potentials greater than 8.3 eV do not form dications.

There is not a direct relationship between first and second ionization potentials as can be seen from Table I in which the first ionization potentials for each grouping of compounds is listed in decreasing order. Even so, the threshold appears to be approximately 12.7 eV. Since the demarcation for dication formation seemed slightly better for the first ionization potentials, we chose to use them to examine oxidation of nonbenzenoid compounds.

Table II. Ionization Potentials of Nonbenzenoid Hydrocarbons from AM1 Calculations[a]

cyclooctatetraenes[b]	first IP	other hydrocarbons	first IP	
1b	9.0	**6**[c]	**8.2**	
1c	8.9	**7**[c]	**8.2**	
1a	8.7	**8**[c]	**8.2**	
1d	8.7	**9**[d]	**8.3**	
2c	**8.6**			
3	8.5	**10a**[e]	**8.8**	
5	**8.5**	**10b**[e]	**8.7**	
2a	8.5			
4a	**8.5**	**11**[f]	**8.6**	
4b	**8.5**	**12**[g]	**10.1**	**14.0**
2b	8.5			

[a] Precursors which form dications are shown in bold-face type. [b] Reference 11. [c] Reference 13. [d] Reference 14. [e] Reference 15. [f] Reference 17. [g] Reference 18.

The correlation between first ionization potential and dication formation is not demonstrated for the compounds categorized as nonbenzenoid precursors, compounds **1–13** (Table II). These compounds fall into four classes based on their anticipated geometrical reorganization upon ionization and on their mode of ionization. Compounds **1–5**[11] are cyclooctatetraenes and would be expected to move from a tublike geometry to a planar one upon conversion to dications. The cyclooctatetraene cation radical appears to be nonplanar[12] and possibly tub-shaped while the observation of a ring current of large magnitude has been used as strong evidence[11] for planarity in cyclooctatetraene dications. Compounds **6–9**[13,14] contain planar π-systems and might be expected to be similar to the benzenoid

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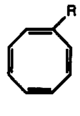
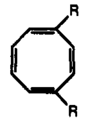
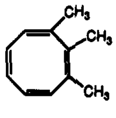


1a, R=H
b, R=Br
c, R=Cl
d, R=CH_3



2a, R=C_6H_5
b, R=OC_2H_5
c, R=CH_3



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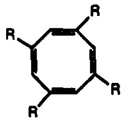
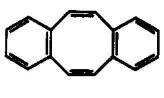


4a, R=C_6H_5
b, R=CH_3



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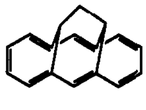

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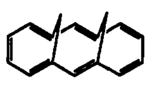

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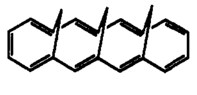

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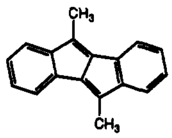

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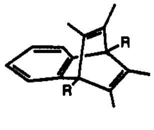
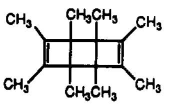


10a, R=H
b, R=CH_3



11

12

precursors in terms of ionization.

Barrelene, the parent of **10a** and **10b** is the three dimensional analogue of cyclooctatetraene, and a 6π-electron Möbius antiaromatic system which could become a Möbius aromatic system upon two-electron oxidation,[15] which would not result in a change in geometry. Alternatively, MINDO/3 calculations on barrelene suggested its rapid rearrangement to a bicyclo[3.3.0]octane dication[16] with a drastic change in geometry, which was verified experimentally.[15] Finally, compounds **11**[17] and **12**[18] differ from the others because they form dications upon oxidation of a σ rather than a π bond.

Compounds **6**–**9** possess ionization potentials of 8.3 eV or less, in agreement with their oxidation to dications. A major discrepancy lies with compounds **1**–**5** and **10**. There is poor internal consistency within the cyclooctatetraene family with ionization potentials of 8.5 eV for both precursors which form dications and for those which do not. In addition, oxidation of **2c** occurs, even though its first ionization potential is greater than 8.3 eV. Compounds **10a** and **10b** are even further from the value determined for the benzenoid series. As might be expected there is little correlation between the ionization potentials for **11** and **12**, which ionize by loss of electrons from a C–H or C–C single bond with the cutoff value of approximately 8.3 eV calculated for compounds which ionize via the π system.

Calculation of $\Delta\Delta H_{\mathrm{formn}}$. An explanation for the inability of calculated ionization potentials to accurately predict the ability of a cyclooctatetraenes and barrelenes to be oxidized by SbF_5 might lie in the extensive geometrical reorganization upon ionization anticipated for these hydrocarbons. Since Koopman's theorum, upon which the ionization potential calculations were based, requires that there be no difference in geometry between neutral precursor and cation radical, ionization potentials calculated for compounds which do undergo geometrical reorganization would be anticipated to be in error. In order to accommodate geometrical changes, we next calculated the difference ($\Delta\Delta H_{\mathrm{formn}}$) between ΔH_f for the dication, with fully optimized geometry, and ΔH_f for the neutral species. We initially chose to examine the results from AM1, MNDO, and MINDO/3 calculations on a subset of benzenoid precursors. Little information[19] exists in the literature concerning the ability of the AM1 method to accurately model the behavior of dications. While MNDO performs better than MINDO/3 for polycyclic structures[3,20] the known tendency[3,21,22] of MNDO to prefer classical structures in contrast to MINDO/3[23,24] might lead to unrealistic relative destabilization of the nonclassical structures we hope ultimately to examine. The subset, Table III, showed a clear correlation between $\Delta\Delta H_f$ and dication formation and effectively no advantage of one method over another. AM1 calculations suggested a $\Delta\Delta H_f$ ceiling of approximately 460 kcal/mol; MNDO suggested 452 kcal/mol and MINDO/3 suggested 425 kcal/mol. Because of our interest in nonclassical dications, we chose to use MINDO/3 to calculate $\Delta\Delta H_f$ for all dications under examination. We also calculated $\Delta\Delta H_f$ for all these dications using AM1 because of its ability to accurately model highly hindered species.[4] Since we anticipate using sterically hindered polyphenyl-substituted hydrocarbons as precursors to our dications of interest, the AM1 method has some obvious strengths for us. The results are grouped according to precursor and are given in Tables IV and V. The correlation is good for both methods with the exception of a few compounds for which there is "poor correlation". Over three fourths of the "poor correlations" are common to both calculational methods. That is, poor correlations are shown for compounds **12**, **2a**–**c**, **10a**, 1,2,3,4-tetramethylcyclooctatetraene, 1,2,3,6,7,8-hexahydropyrene, and chrysene for $\Delta\Delta H_f$ calculated by either AM1 or MINDO/3. It should be noted that almost half of the poor correlations occur within a 3.2 kcal/mol range for AM1 (464.4–461.3 kcal/mol) and within a 6.8 kcal/mol range (433.8–427.1 kcal/mol) for MINDO/3. The difference between experimental and calculated ΔH_f may be considered 4 kcal/mol for both methods[5] because of the inaccuracy of current experimental data, thus giving a ceiling for dication formation of $\Delta\Delta H_f = 463 \pm 4$ kcal/mol (AM1) and 430 ± 4 kcal/mol (MINDO/3). Compounds **12**, **2a**–**b**, **10a**, chrysene, and the hexahydropyrene (AM1) still lie outside these ranges.

The lack of correlation of **12** is not surprising. Strictly speaking, the calculation of $\Delta\Delta H_f$ from neutral precursor alone for this species is incorrect because the dication was formed by oxidation of two C–H bonds[18] rather than a π bond, so the discrepancy is not unexpected. Chrysene shows a poor correlation by both methods while the hexahydropyrene is near the edge of the acceptable range by MINDO/3 and outside the range by AM1. Examination of the geometries calculated for the dications of chrysene and hexahydropyrene shows the planar geometry observed

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Table III. Comparison of Differences in Heats of Formation Calculated by AM1, MNDO, MINDO/3[a]

	AM1			MNDO			MINDO/3		
	$\Delta H_{f\,\mathrm{neutral}}$	$\Delta H_{f\,\mathrm{cation}}$	$\Delta\Delta H_f$	$\Delta H_{f\,\mathrm{neutral}}$	$\Delta H_{f\,\mathrm{cation}}$	$\Delta\Delta H_f$	$\Delta H_{f\,\mathrm{neutral}}$	$\Delta H_{f\,\mathrm{cation}}$	$\Delta\Delta H_f$
	Polycyclic Aromatic Hydrocarbons[b]								
benzene	22.0[c]	586.3	564.3	21.3	577.9	556.6	28.4	551.9	523.5
naphthalene	40.6[c]	534.7	494.1	38.3	524.5	486.2	55.4	520.8	465.4
phenanthrene	57.4[c]	527.0	469.6	55.7	521.9	466.2	82.5	518.0	435.5
benzo[*b*]triphenylene	95.6[c]	540.2	444.6	95.6	531.5	435.9	137.8	548.3	410.5
dibenz[*a*,*h*]anthracene	**94.2**[c]	**528.2**	**434.0**	**91.4**	**516.5**	**425.1**	**137.7**	**534.8**	**397.1**
anthracene	**62.9**[c]	**515.3**	**452.4**	**58.9**	**505.3**	**446.4**	**86.1**	**508.7**	**422.6**
benzopyrene	**87.5**	**514.2**	**426.7**	**81.0**	**501.0**	**420.0**	**127.3**	**520.4**	**393.1**
naphthacene	**87.0**[c]	**511.6**	**424.6**	**80.9**	**500.3**	**419.4**	**119.0**	**521.3**	**402.3**
pentacene	**111.9**[c]	**516.5**	**404.6**	**103.9**	**504.0**	**400.1**	**151.3**	**524.8**	**373.5**
	Substituted Anthracenes and Naphthalenes[d,e]								
9-methylanthracene	**59.1**	**503.7**	**444.7**	**58.8**	**501.3**	**442.5**	**88.3**	**503.6**	**415.3**
9-chloroanthracene	**58.5**	**510.8**	**452.3**	**55.1**	**506.7**	**451.6**	**79.2**	**500.7**	**421.5**
9-bromoanthracene	**71.4**	**526.9**	**455.0**	**65.9**	**516.2**	**450.3**	(no parameters)		
9-phenylanthracene	**92.2**	**525.6**	**433.4**	**88.8**	**521.9**	**433.1**	**79.8**	**535.6**	**455.8**
1,2,3,4-tetramethylnaphthalene	18.4	479.7	461.3	28.6	495.9	467.2	54.7	486.4	431.7
1,4,5,8-tetramethylnaphthalene	**26.3**	**477.5**	**451.2**	**35.2**	**497.3**	**462.1**	**58.8**	**483.0**	**424.2**
octamethylnaphthalene	**5.7**	**440.9**	**435.2**	**26.7**	**479.2**	**452.5**	**66.6**	**473.8**	**407.2**

[a] $\Delta\Delta H_f$ for precursors which form dications are shown in bold-face type; those for precursors in which dications are in equilibrium with cation radicals are underlined. [b] Reference 6. [c] Values are in agreement with those from: Herndon, W. C.; Connor, D. A.; Lin, P. *Pure Appl. Chem.* **1990**, *62*, 435–444. [d] Reference 8. [e] Reference 9.

Table IV. Differences in Heats of Formation Calculated by MINDO/3[a]

	benzenoid precursors				nonbenzenoid precursors		
	$\Delta H_{f\,\mathrm{neutral}}$	$\Delta H_{f\,\mathrm{cation}}$	$\Delta\Delta H_f$		$\Delta H_{f\,\mathrm{neutral}}$	$\Delta H_{f\,\mathrm{cation}}$	$\Delta\Delta H_f$
triphenylene	112.9	541.5	428.6	**1a**	56.9	506.3	449.4
chrysene	111.5	524.2	421.7	**1b**	(no parameters)		
picene	140.0	537.9	397.9	**1c**	48.9	500.3	451.4
tetrabenzonaphthalene	**189.6**	**582.9**	**392.3**	**1d**	53.3	496.1	442.8
coronene	**142.3**	**549.0**	**400.7**	**2a**	137.2	529.6	392.4
benz[*a*]anthracene	**111.6**	**520.8**	**409.2**	**2b**	−58.6	340.5	399.1
pyrene	**97.1**	**513.7**	**416.5**	**2c**	**50.3**	**484.1**	**433.8**
benzoperylene	**138.5**	**535.6**	**397.1**	**3**	55.3	490.0	434.7
perylene	**131.2**	**522.8**	**391.6**	**4a**	**233.1**	**608.3**	**375.2**
9,10-dichloroanthracene	**73.2**	**493.0**	**419.8**	**4b**	**43.9**	**474.4**	**430.5**
9,10-dibromoanthracene	(no parameters)			**5**	**106.0**	**525.5**	**419.5**
9,10-dimethylanthracene	**91.5**	**499.2**	**407.7**	**6**	**142.3**	**549.4**	**407.1**
9,10-diphenylanthracene	**178.0**	**566.9**	**388.9**	**7**	**142.3**	**548.9**	**406.6**
9-chloro-10-methylanthracene	**81.4**	**496.0**	**414.6**	**8**	**141.3**	**548.0**	**406.7**
1,4-dimethoxyanthracene	**−5.2**	**372.0**	**377.2**	**9**	**115.6**	**524.1**	**408.5**
2-methylanthracene	**79.8**	**497.5**	**417.7**	**10a**	**80.9**	**508.8**	**427.9**
1,2,3,6,7,8-hexahydropyrene	35.0	462.1	427.1	**10b**	**111.3**	**527.6**	**416.3**
				11	**89.8**	**468.4**	**378.6**
				12	**37.9**	**492.9**	**455.0**

[a] $\Delta\Delta H_f$ for precursors which form dications are in bold-face type; those for precursors which form dications in equilibrium with cation radicals are underlined.

for the dications of other substituted and unsubstituted polycyclic aromatic compounds, so the discrepancy does not lie with the geometry calculated by either method. Poor correlation is also seen for **2a** and **b**. We had anticipated that the cyclooctatetraene dications would minimize to planar species;[11] however, examination of the ΔH_f calculated for dications with a variety of initial geometries shows that the species with the lowest ΔH_f was not necessarily planar. These results from AM1 calculations are shown in Table VI with the conformation with the lowest ΔH_f for each compound given in terms of dihedral angle along with the ΔH_f for the most planar. For those compounds for which the more planar form has the lowest ΔH_f, the geometry of the compound with the next lowest ΔH_f is reported. The degree of planarity of the ring is apparent from the sum of the dihedral angles of the cyclooctatetraene. Of the five compounds for which a planar or nearly planar (sum ≤11°) geometry resulted from geometry optimization via AM1, for only one compound (**1a**) was the ΔH_f calculated for that geometry lower than that calculated for a less planar geometry. Excluding **1a**, the average dihedral angle summation for the lowest energy conformation is 205.9°. It should be noted that the difference between the ΔH_f's reported in the table is normally fairly small (≤3.0 kcal/mol), suggesting a reasonable conformational flexibility for the dications under the conditions of the calculation.

The poor correlation of the disubstituted cyclooctatetraenes is not, therefore, due to an abnormal geometry, at least in comparison with the results from calculations on other substituted cyclooctatetraenes. No conclusions of a similar sort can be drawn for compound **10a** because there are too few compounds with similar geometry to serve as models.

If compound **12** is removed from consideration because the calculation of $\Delta\Delta H_f$ is inappropriate, AM1, with a ceiling of 463 ± 4 kcal/mol for $\Delta\Delta H_f$ for dication formation, correctly predicts the behavior of 48 of the 53 compounds surveyed, or 92%. MINDO/3, with a ceiling of 430 ± 4 kcal/mol for $\Delta\Delta H_f$ for dication formation, gives accurate prediction for 43 of the 48 compounds examined, or 90%.

Table V. Differences in Heats of Formation Calculated by AM1[a]

	benzenoid percursors				nonbenzenoid precursors		
	$\Delta H_{f\,\mathrm{neutral}}$	$\Delta H_{f\,\mathrm{cation}}$	$\Delta\Delta H_f$		$\Delta H_{f\,\mathrm{neutral}}$	$\Delta H_{f\,\mathrm{cation}}$	$\Delta\Delta H_f$
triphenylene	75.5[b]	541.9	466.4	**1a**	63.5	544.7	481.2
chrysene	76.2[b]	524.5	448.3	**1b**	67.9	555.2	487.3
picene	94.3[b]	530.6	436.3	**1c**	56.0	540.3	484.3
tetrabenzonaphthalene	**125.5**	**557.4**	**431.9**	**1d**	56.3	494.9	472.7
coronene	**96.2**	**536.0**	**439.7**	**2a**	116.5	540.5	424.0
benzanthracene	**78.3[b]**	**522.0**	**443.7**	**2b**	−20.9	408.8	429.7
pyrene	**67.4**	**515.7**	**448.3**	**2c**	**49.3**	**512.6**	**463.3**
benzoperylene	**87.5**	**514.2**	**426.7**	**3**	44.2	507.8	463.6
perylene	**89.2**	**514.4**	**425.1**	**4a**	173.1	**598.4**	**425.3**
				4b	**35.2**	**492.1**	**456.9**
9,10-dichloroanthracene	**54.7**	**507.1**	**452.3**	**5**	**110.5**	**547.7**	**437.2**
9,10-dibromoanthracene	**80.8**	**539.2**	**458.4**	**6**	**142.3**	**537.6**	**395.4**
9,10-dimethylanthracene	**55.3**	**491.8**	**436.5**	**7**	**107.3**	**537.8**	**430.5**
9,10-diphenylanthracene	**121.8**	**540.7**	**418.9**	**8**	**118.0**	**550.2**	**432.2**
9-chloro-10-methylanthracene	**54.9**	**499.5**	**444.5**	**9**	**101.7**	**546.4**	**444.7**
1,4-dimethoxyanthracene	**−11.0**	**409.3**	**420.3**	**10a**	**43.4**	**507.9**	**464.5**
2-methylanthracene	**55.1**	**502.7**	**447.8**	**10b**	**41.8**	**511.7**	**470.0**
2,7-dimethylanthracene	**51.2**	**485.3**	**434.1**	**11**	**85.3**	**513.2**	**427.9**
				12	**−71.8**	**412.5**	**484.3**
1,2,3,6,7,8-hexahydropyrene	10.2	165.8	452.6				

[a] $\Delta\Delta H_f$ for precursors which form dications are in bold-face type; those for precursors which form dications in equilibrium with cation radicals are underlined. [b] Values are in agreement with those from: Herndon, W. C.; Connor, D. A.; Lin, P. *Pure Appl. Chem.* **1990**, *62*, 435–444.

Table VI. ΔH_f of Substituted Cyclooctatetraene Dications as a Function of Geometry

compd	$\Delta H_{f\,\mathrm{dication}}$ from planar starting geom	sum of dihedral angles of ring	$\Delta H_{f\,\mathrm{dication}}$ from MMX-optimized geom	sum of dihedral angles of ring	diff in ΔH_f
1a	544.4	1.95	544.7	118.31	0.3
1b	555.9	0.00	555.2	196.12	0.7
1c	541.6	0.00	540.3	167.11	1.3
1d	529.8	65.35.	529.0	180.74	0.8
2a	540.5	243.08	551.0	302.31	10.5
2b	408.8	234.02	421.9	303.35	13.1
2c	515.3	0.00	512.6	206.17	2.7
3	507.8	209.34	507.9	223.36	0.1
4a	601.4	35.22	598.4	229.48	3.0
4b	494.9	76.67	492.1	182.12	2.8
5	552.4	10.78	547.7	210.55	4.7

Conclusion

This study has shown that ionization potentials calculated by AM1 are reasonable predictors of dication formation by direct oxidation when there is no geometrical rearrangement of the neutral precursor and that the threshhold for oxidation lies below a first ionization potential of approximately 8.3 eV. The correlation is poor for nonbenzenoid compounds undergoing geometrical change upon ionization. Good correlation between $\Delta\Delta H_f$ and dication formation is shown by both benzenoid and nonbenzenoid precursors. AM1 predicts dication formation when $\Delta\Delta H_f \leq 463 \pm 4$ kcal/mol. MINDO/3 predicts dication formation when $\Delta\Delta H_f \leq 430 \pm 4$ kcal/mol.

Because of the difficulty in obtaining reliable thermodynamic data for the highly reactive dications, the good correlation for $\Delta\Delta H_f$ calculated by AM1 is also indirect verification of the reliability of the method applied to dications.

Experimental Section

Methods of Calculation. The MINDO/3,[25] MNDO,[3] and AM1[2] calculations were conducted using the standard methods as implemented in the MOPAC 5.0 semiempirical molecular orbital package[26] running on a Sun SPARCstation 1 computer. The starting geometries were created using the PCMODEL program.[27] The molecular mechanics calculations were performed using the MMX software program on a Macintosh IIci computer with geometry optimization begun after an SCF calculation. Geometries were optimized in internal coordinates and were terminated when Herbert's test was satisfied in the BFGS method. All optimizations were terminated when the change in energy on successive iterations was less than 0.00001 kcal/mol and the change in density matrix elements on two successive iterations was less than 0.001. All calculations were performed with closed-shell structures using the restricted Hartree–Fock (RHF) method with full optimization of all geometrical variables (bond lengths, bond angles, and dihedral angles) without imposition of symmetry restrictions. Since an optimized geometry may turn out to be a local minimum, the optimization was begun from at least two starting geometries in order to verify global minima. For the dications of the cyclooctatraene derivatives, starting geometries were obtained not only from geometries minimized through MMX calculations, which were nonplanar, but also from replacement of hydrogens with the appropriate substituent(s) of a cyclooctatetraene dication which had been "minimized" as a planar structure. In this case, calculation with AM1 or MINDO/3 with incomplete geometry optimization (dihedral angles not optimized) of a cyclooctatetraene dication which had been drawn planar gave a planar cyclooctatetraene dication which could be modified by substitution of the desired substitutents for hydrogens. Recalculation of the newly substituted cyclooctatetraene with full geometry optimization gave the ΔH_f discussed in the body of the paper.

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Registry No. **1a**, 629-20-9; **1a**$^{2+}$, 37306-59-5; **1c**, 29554-49-2; **1c**$^{2+}$, 37306-59-5; **1d**, 2570-12-9; **1d**$^{2+}$, 84550-78-7; **2a**, 121590-73-6;

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[27] The PCMODEL (version 4.0) and MMX (version 87.2) programs were obtained from Serena Software, Box 3076, Bloomington, IN 47402. The MMX program is mainframe software adapted to Macintosh microcomputers by Drs. J. J. Gajewski and K. E. Gilbert from QPCE 395 and 318 programs (Buckert, U.; Allinger, N. L. *Molecular Mechanics*; American Chemical Society: Washington, DC, 1982).

2a^{2+}, 72866-06-9; **2b**, 138878-63-4; **2b**$^{2+}$, 138878-65-6; **2c**, 29554-56-1; **2c**$^{2+}$, 63397-56-8; **3**, 63318-58-1; **3**$^{2+}$, 138878-66-7; **4a**, 35087-43-5; **4a**$^{2+}$, 63832-64-4; **4b**, 29212-88-2; **4b**$^{2+}$, 59227-70-2; **5**, 262-89-5; **5**$^{2+}$, 63397-57-9; **6**, 25835-57-8; **6**$^{2+}$, 109124-31-4; **7**, 14458-51-6; **7**$^{2+}$, 77966-08-6; **8**, 78038-55-8; **8**$^{2+}$, 68630-17-1; **9**, 65549-72-6; **9**$^{2+}$, 65583-97-3; **10a**, 104720-28-7; **10a**$^{2+}$, 112532-59-9; **10b**, 104701-63-5; **10b**$^{2+}$, 112532-58-8; **11**, 1448-74-4; **11**$^{2+}$, 60790-15-0; **12**, 2292-79-7; **12**$^{2+}$, 95531-36-5; SbF_5, 7783-70-2; triphenylene, 217-59-4; triphenylene dication, 138878-64-5; chrysene, 218-01-9; chrysene dication, 115949-55-8; picene, 213-46-7; picene dication, 60670-20-4; tetrabenzonaphthylene, 191-68-4; tetrabenzonaphthylene dication, 60670-18-0; coronene, 191-07-1; coronene dication, 62683-79-8; benz[*a*]anthracene, 56-55-3; benz[*a*]anthracene dication, 60670-19-1; pyrene, 129-00-0; pyrene dication, 60670-21-5; benzoperylene, 191-24-2; benzoperylene dication, 60829-72-3; perylene, 198-55-0; perylene dication, 60670-21-5; 9,10-dichloroanthracene, 605-48-1; 9,10-dichloroanthracene dication, 87517-70-2; 9,10-dimethylanthracene, 781-43-1; 9,10-dimethylanthracene dication, 75309-26-1; 9,10-diphenylanthracene, 1499-10-1; 9,10-diphenylanthracene dication, 70470-09-6; 9-chloro-10-methylanthracene, 19096-07-2; 9-chloro-10-methylanthracene dication, 87517-72-4; 1,4–dimethoxyanthracene, 13076-29-4; 1,4-dimethoxyanthracene dication, 87517-74-6; 2-methylanthracene, 613-12-7; 2-methylanthracene dication, 87517-75-7; 1,2,3,6,7,8-hexahydropyrene, 1732-13-4; 1,2,3,6,7,8-hexahydropyrene dication, 72287-34-4.

Computer-Assisted Mechanistic Evaluation of Organic Reactions. 20. Ene and Retro-Ene Chemistry

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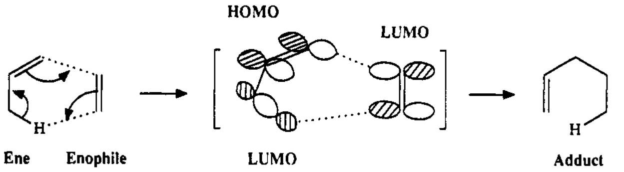
The pericyclic module of the computer program CAMEO has been expanded to encompass ene and retro–ene reactions. The implementation of ene chemistry required substantial modifications to the existing algorithm for the estimation of FMO energies as well as enhancements in the perception phase of the module for the recognition of additional π systems. New equations for computing the FMO energies of 2π and cumulene parent systems have been developed and implemented in the program. Ene reactions have been analyzed by using a frontier molecular orbital approach. Consequently, predictions of regiochemistry in ene additions are based on the relative magnitude of the terminal coefficients of the frontier orbitals and on the topological geometry of the reacting molecules. Analyses of retro-ene fragmentations are made by applying empirical rules derived from literature precedents. Several examples of synthetic sequences that demonstrate the current predictive capabilities of CAMEO are presented.

Introduction

CAMEO is an interactive computer program that predicts the products of organic reactions through the application of mechanistic logic.[1] Given the reactants and conditions, the program typically arrives at its predictions by simulation of reaction mechanisms. Recent extensions to the program include the mechanistic treatment of hydride reductions[2a] and the development of a reaction model that mimics free-radical chain processes.[2b,c] Other types of reactions that are currently handled by CAMEO include base-catalyzed and nucleophilic,[3] acid-catalyzed and electrophilic,[4] thermal pericyclic,[5] oxidative,[6] and heterocycle-forming reactions.[7] The incorporation of ene and retro-ene reactions into the pericyclic module of CAMEO is addressed in this paper.

Scheme I



The philosophy behind CAMEO's approach to reaction prediction is that diverse organic processes can be treated as a sequence of basic mechanistic steps. Thus, reaction analysis is greatly simplified by focusing on a small set of fundamental processes. Competitions between these processes are generally assessed by application of empirically-derived rules or known physical–organic principles. When available, a well-established theory behind a mechanistic process is applied in the analyses of reactions. Thus, the pericyclic module utilizes frontier molecular orbital (FMO) theory[8] in predicting both the feasibility and regiochemistry of thermal cycloadditions. The same approach has been utilized for the evaluation of ene reactions.

The implementation of ene chemistry in CAMEO entailed not only enhancements in the perception of π systems but

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