lation as per eq 7, one obtains a back estimate, $\hat{\mathbf{N}}_p$, of the pure component spectrum, $\mathbf{N}_p$. Systematic differences between $\hat{\mathbf{N}}_p$ and $\mathbf{N}_p$ are indicative of matrix effects and other violations of condition b above, while random differences between the two matrices are indicative of the accuracy of the concentration estimate. Using rank annihilation and nonbilinear second-order data, it is then possible to quantitate for an analyte of interest even in the presence of unknown spectral interferents.

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DEWAR-PI Study of Electrophilic Substitution in Selected Polycyclic Fluoranthene Hydrocarbons

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Abstract: DEWAR-PI molecular orbital calculations are reported for 14 nonalternant polycyclic aromatic hydrocarbon derivatives of fluoranthene and for the Wheland intermediates (arenium ions) to study electrophilic substitution at all the methine groups in them. Calculations were also carried out for related alternant aromatic hydrocarbons. The species studied were indeno[1,2,3-*hi*]chrysene (**1**), benz[*def*]indeno[1,2,3-*hi*]chrysene (**2**), fluoreno[3,2,1,9-*defg*]chrysene (**3**), benz[*a*]aceanthrylene (**4**), benz[*e*]acephenanthrylene (**5**), indeno[1,2,3-*cd*]pyrene (**6**), fluoreno[9,1,2,3-*cdef*]chrysene (**7**), benz[*def*]indeno[1,2,3-*qr*]chrysene (**8**), dibenz[*a,e*]aceanthrylene (**9**), dibenz[*a,j*]aceanthrylene (**10**), dibenz[*e,k*]acephenanthrylene (**11**), dibenz[*a,l*]aceanthrylene (**12**), and benzo[*k*]fluoranthene (**13**), benzo[*j*]fluoranthene (**14**), fluoranthene (**15**), phenanthrene (**16**), pyrene (**17**), chrysene (**18**), benzo[*def*]chrysene (**19**), benz[*a*]anthracene (**20**), anthracene (**21**), and naphthalene (**22**).

Interest in higher polyaromatic hydrocarbon derivatives of fluoranthene stems from their widespread prevalence as environmental pollutants. Some of these hydrocarbons can be mutagenic and/or carcinogenic, stimulating cancer research as well as synthetic work. Surprisingly little is known about the chemistry of these polycyclic fluoranthenes or their patterns of electrophilic substitution. Because they are nonalternant hydrocarbons, simple theoretical arguments describing substitution do not exist.

The majority of aromatic electrophilic substitutions occur by the *arenium ion mechanism* as depicted in Scheme I. The electrophile attacks in the first step, generating a positively charged intermediate (the so-called arenium ion or Wheland intermediate), and the leaving group departs in the second step. For the hydrocarbons studied, the leaving group is always hydrogen, and the results discussed in this paper are valid only for electrophiles that follow this type of mechanism.

The rate-determining step is almost always the formation of the Wheland intermediate (WI). Species of this kind are well-known, e.g., the species formed by protonation of aromatic hydrocarbons by strong acids. It can be shown by PMO theory[1] that the activation energy (E_a) for substitution at a given site in an even alternant hydrocarbon (AH) is proportional to the heat of reaction (ΔH_{Rx}) for the formation of the corresponding WI:

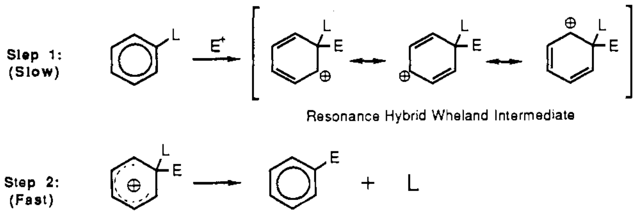
$$E_a = A\Delta H_{Rx} \tag{1}$$

where A is a constant. Thus the difference (ΔE_{XY}) in activation energies for substitution at different positions (X and Y) is proportional to the difference in energies of their respective WIs (E_X and E_Y):

$$\Delta E_{XY} = E_a(X) - E_a(Y) = B(E_X - E_Y) \tag{2}$$

where B is another constant. Thus the quantities of ΔE_{XY} should serve as a measure of the relative reactivities of various positions to electrophilic substitution. In order to predict the favored point of attack in a given aromatic compound, the energies of the WIs have to be evaluated for all possible positions, 14 in the case of indeno[1,2,3-*hi*]chrysene (**1**).

Scheme I



Calculations of this kind for the compounds of interest here by even the simplest ab initio procedures would require an unreasonable amount of computer time. Indeed, the use of even all-valence-electron semiempirical methods would be very expensive. These difficulties can be avoided by using a π-SCF treatment[2] that was developed here some years ago, based on the Pople[3] method together with the Pariser–Parr[4] procedure for allowing for electron correlation. This Pariser–Parr–Pople (PPP) approach, as it is commonly termed, was originally developed for studies of light absorption. Our group was able to show that it could be parametrized to reproduce ground-state properties of conjugated molecules very effectively,[2,5] heats of formation of conjugated and aromatic hydrocarbons being reproduced to within the limits of error of the best thermochemical measurements.

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Table I. Calculated DEWAR-PI Wheland Intermediate Relative Energies δE for Electrophilic Substitution at Various Positions

	rel[b] energies for each molecule, kcal/mol						
positn[a]	**1**	**2**	**3**	**4**	**5**	**6**	**7**
1	11.3	1.1	13.4	11.4	3.8	10.0	7.8
2	11.0	25.3	10.3	17.6	10.6	5.2	23.4
3	15.3	0	18.3	12.7	5.8	0.0	16.5
4	6.8	3.9	6.4	16.3	6.3	21.3	20.8
5	0	18.5	4.7	18.7	6.6	0	17.6
6	11.9	12.5	13.3	22.9	7.0	4.6	19.9
7	5.0	11.3	6.1	12.0	6.2	9.8	12.9
8	11.0	15.9	12.1	0	0	7.6	0
9	7.9	11.8	7.6	12.7	5.2	10.6	12.8
10	7.5	6.4	1.3	23.4	14.3	6.5	29.2
11	6.3	13.1	23.8	19.9	8.4	13.8	16.9
12	8.3	5.4	0	15.9	11.1	1.4	23.8
13	5.7	12.6	1.8				18.8
14	4.5	8.0	17.4				12.5

[a] The position numbers correspond to the numbering system given in the formulas. [b] Energies are relative to the WI with the lowest energy in the *same* molecule.

Table II. Calculated DEWAR-PI Wheland Intermediate Relative Energies (δE) for Electrophilic Substitution at Various Positions

	rel[b] energies for each molecule, kcal/mol						
positn[a]	**8**	**9**	**10**	**11**	**12**	**13**	**14**
1	18.3	10.4	14.2	12.2	20.6	10.1	13.6
2	13.6	19.3	21.5	17.3	19.5	22.5	21.8
3	0	16.2	16.1	13.0	21.9	5.1	9.3
4	13.0	13.5	20.0	15.7	17.4	5.7	6.1
5	29.5	9.6	0	15.4	14.4	22.8	21.7
6	17.0	15.5	8.9	16.4	14.0	10.3	10.0
7	24.3	10.4	17.4	15.0	0	0	8.1
8	18.8	14.9	14.3	6.5	10.4	8.5	13.0
9	17.2	10.1	12.5	0	20.8	14.0	12.5
10	16.7	15.5	9.1	11.5	15.8	13.9	7.5
11	18.3	23.0	13.7	20.2	15.7	8.6	0
12	15.4	17.3	8.0	17.4	12.8	0.3	12.3
13	24.1	21.7	13.5	13.6	16.8		
14	9.1	0	9.3	4.6	11.8		

[a] The position numbers correspond to the numbering system given in the formulas. [b] Energies are relative to the WI with the lowest energy in the *same* molecule.

Table III. Calculated DEWAR-PI Wheland Intermediate Relative Energies (δE) for Electrophilic Substitution at Various Positions

	rel[b] energies for each molecule, kcal/mol						
positn[a]	**15**	**16**	**17**	**18**	**19**	**20**	**21**
1	3.2	0.6	0.1	5.1	7.0	19.0	10.1
2	3.9	7.2	20.5	12.7	30.2	16.4	18.4
3	3.9	4.0	0	9.5	8.3	20.4	18.4
4	3.2	4.1	8.8	8.6	17.2	14.4	10.1
5	5.3	3.9	8.8	9.3	16.7	11.7	0.0
6	13.0	3.9	0.1	0	0	11.7	10.1
7	0	7.0	20.5	5.1	12.1	0	18.4
8	0.5	0.5	0	12.6	28.2	10.0	18.4
9	13.0	0.1	8.8	9.5	16.5	18.1	10.1
10	5.3	0	8.8	8.5	22.6	16.6	0
11				9.3	23.4	11.3	
12				0.0	11.6	2.8	

[a] The position numbers correspond to the numbering system given in the formulas. [b] Energies are relative to the WI with the lowest energy in the *same* molecule.

While it has been overshadowed by the all-valence-electron semiempirical procedures (MINDO/3,[6] MNDO,[7] and AM1[8]) we subsequently developed, no other quantum chemical treatment has rivaled the accuracy it achieves in its admittedly limited range of applicability. It has also proved effective in studies of substitution in a wide range of aromatic AHs and heteroaromatic systems derived from them. However, it has not yet been applied systematically to nonalternant species.

This treatment has recently been updated in the form of a version for the IBM PC computer (and compatibles) and christened DEWAR–PI. The program is especially well suited for this study since it includes an option for calculating the energies of WIs. We have now applied it to a number of nonalternant hydrocarbons for which studies of substitution have been reported or are in progress.[9]

Procedure

Starting geometries were obtained from MM2 calculations,[10] using a modified version of the MODEL[11] program. This provides a fast and efficient method for creating input data files for DEWAR-PI. Removal of the hydrogens was necessary, since DEWAR-PI accepts the carbon skeleton only. Carbon–carbon bond lengths were optimized by the program. All molecules were assumed to be planar.

The calculations were carried out with the recently updated DEWAR-PI program mentioned above which is now available from QCPE.[12] The program approximates the WIs by removing individual atoms from the carbon skeleton, one at a time for each substitution site. The number of C–H bonds is reduced by one. Tests[13] have shown it to account well for the rates and orientation of substitution in aromatic hydrocarbons.

Results and Discussion

Calculations were carried out for 15 nonalternant aromatic hydrocarbons; viz. indeno[1,2,3-*hi*]chrysene (**1**), benz[*def*]indeno[1,2,3-*hi*]chrysene (**2**), fluoreno[3,2,1,9-*defg*]chrysene (**3**), benz[*a*]aceanthrylene (**4**), benz[*e*]acephenanthrylene (**5**), indeno[1,2,3-*cd*]pyrene (**6**), fluoreno[9,1,2,3-*cdef*]chrysene (**7**), benz[*def*]indeno[1,2,3-*qr*]chrysene (**8**), dibenz[*a,e*]aceanthrylene (**9**), dibenz[*a,j*]aceanthrylene (**10**), dibenz[*e,k*]acephenanthrylene (**11**), dibenz[*a,l*]aceanthrylene (**12**), benzo[*k*]fluoranthene (**13**), benzo[*j*]fluoranthene (**14**), and fluoranthene (**15**). Calculations were also carried out for a number of aromatic AHs related to **1**–**15**, i.e., phenanthrene (**16**), pyrene (**17**), chrysene (**18**), benzo[*def*]chrysene (**19**), benz[*a*]anthracene (**20**), anthracene (**21**), and naphthalene (**22**). The numbering of each hydrocarbon is indicated in the corresponding formula.

Tables I–III list the WI relative energies calculated for substitution at all the methine groups in hydrocarbons **1**–**21**. The energies (δE) reported are relative to the WI with the lowest energy in the *same* molecule; thus, a zero entry indicates the preferred site of substitution for a given molecule. The position numbers listed in the tables correspond to the numbering systems given in the formulas. Apart from uncertainty concerning the accuracy of DEWAR-PI in this connection, discrepancies may well arise due to solvation, the calculations referring to isolated molecules while the experimental studies were carried out in solution. All sites within 5 kcal/mol of the site with the lowest total energy were considered possible candidates for electrophilic substitution. The results for each molecule will be discussed separately.

Indeno[1,2,3-*hi*]chrysene (1). Bromination of **1** with bromine in methylene chloride at room temperature gave the 5-bromo derivative,[14] in perfect agreement with DEWAR-PI (Table I).

The AH derived from **1** by dephenylenation is chrysene (**18**), which undergoes chlorination,[15] bromination,[16] or nitration[17]

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(6) Bingham, R. C.; Dewar, M. J. S.; Lo, D. H. *J. Am. Chem. Soc.* **1975**, *97*, 1285, 1294, 1302, 1307.

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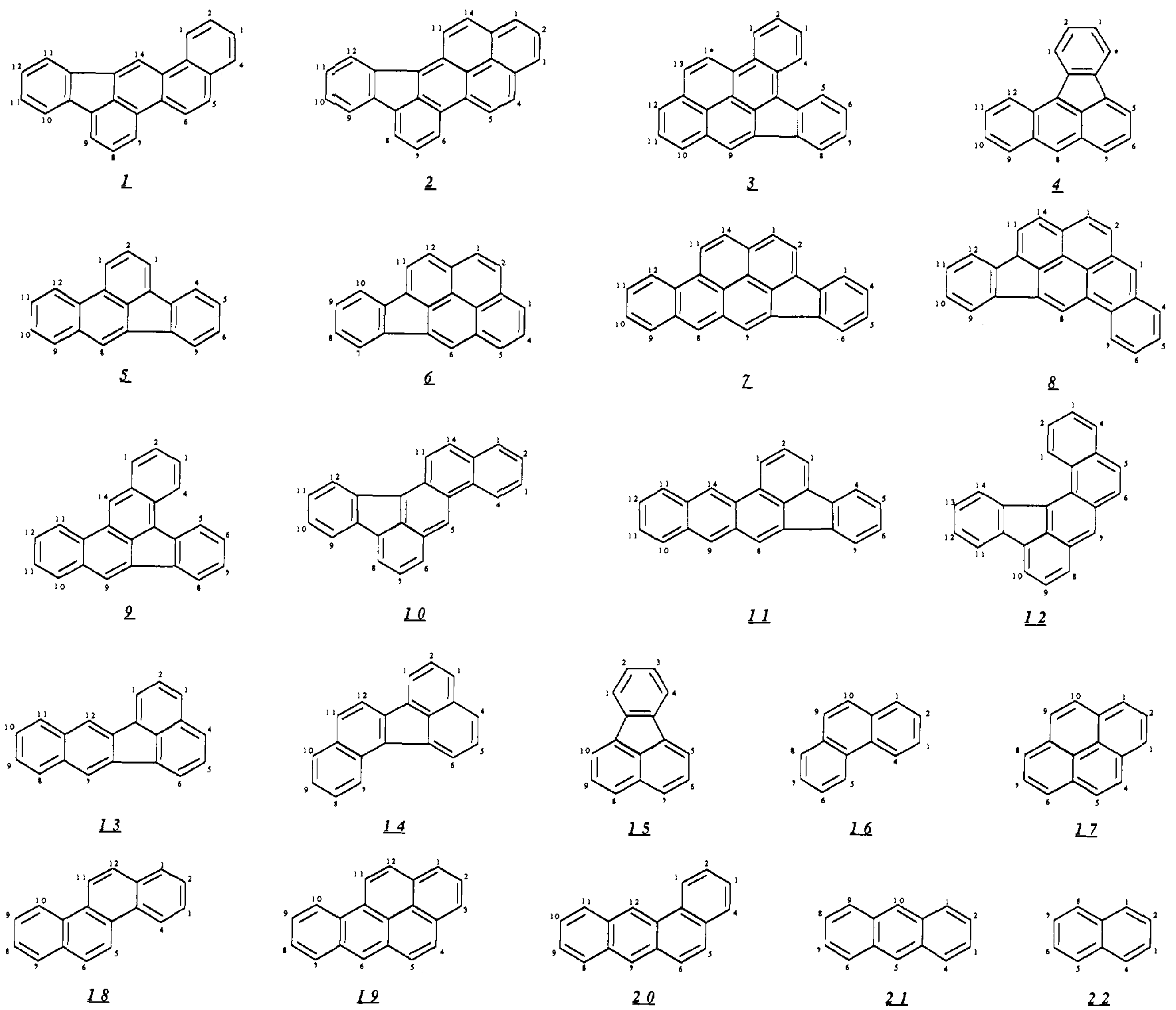
Chart I



preferentially in the 6- and 12-positions, as predicted by DEWAR-PI (Table III). These sites are equivalent and analogous to substitution at the 5-position in **1**.

Benz[*def*]indeno[1,2,3-*hi*]chrysene (2). No experimental data are available for electrophilic substitution in **2**. While DEWAR-PI predicts (Table I) this to be easiest at the 3-position, the value of δE at position 1 is only 1.2 kcal/mol, and the next most reactive position (4) being slightly larger (4.0 kcal/mol). These results illustrate the value of DEWAR-PI in connections such as this in that the 14 sites in **2** are reduced by our calculation to two probables and one marginally possible. It is much easier to confirm a prediction of this kind by experiment than to determine the structure of a completely unknown substitution product.

The related AH, benzo[*def*]chrysene (**19**), chlorinates[18] and nitrates[19] in the 6-position, as predicted by DEWAR-PI (Table III). This position is not open for substitution in **2**. The next most reactive positions in **19**, according to DEWAR-PI, are 1 and 3, with 1 slightly the more reactive. These correspond, respectively, to positions 3 and 1 in **2**. Conversion of **19** to **2** is thus predicted to have no qualitative effect.

Fluoreno[3,2,1,9-*defg*]chrysene (3). No study of electrophilic substitution in **3** has yet been reported. The predictions by DEWAR-PI (Table I) are somewhat uncertain, four possible sites being within the arbitrary 5 kcal/mol limit. The 12-position is the favorite, but the 10- and 13-sites are less than 2.0 kcal/mol higher in energy. Position 5 is next with δE = 4.7 kcal/mol.

The AH related to **3** is again **19**, the most reactive position in which 6 is again blocked. As in **2**, the most reactive (12) and next most reactive (10) sites in **3** correspond, respectively, to the second (1) and third (3) most reactive sites in **19**. Position 13 in **3** corresponds to the fourth most reactive position (12) in **19**. The value of δE is, however, much less for position 13 in **3** (1.8 kcal/mol) than for position 12 in **19** (11.6 kcal/mol).

Benz[*a*]aceanthrylene (4). Bromination[14] of **4** gives the 8-bromo derivative, exclusively. This is exactly as DEWAR-PI predicts (Table I). The second most favored site is the 1-position, for which δE = 11.4 kcal/mol.

The related AH [anthracene (**21**)] undergoes substitution (chlorination,[20] bromination,[20] nitration[21]) exclusively in the 5- and 10-positions to form mono- or disubstituted products. The 5 (10)-position in **21** is predicted by DEWAR-PI (Table III) to be by far the most reactive and is analogous to position 8 in **4**.

Benz[*e*]acephenanthrylene (5). Experimental evidence indicates that bromination of **5** yields primarily the 1-bromo derivative, as discussed previously by Harvey et al.[14] DEWAR-PI predicts (Table I) position 8 to have the lowest energy WI, less than that of position 1 by 3.8 kcal/mol. These are the only sites within the arbitrary 5 kcal/mol limit.

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(18) Windhaus, A.; Raichle, K. *Justus Liebigs Ann. Chem.* **1939**, *537*, 157.

(19) Cook, J. W.; Hewett, C. L. *J. Chem. Soc.* **1933**, 403.

(20) Meyer, K. H.; Zahn, K. *Justus Liebigs Ann. Chem.* **1913**, *396*, 166.

(21) Meisenheimer, J. *Ber. Dtsch. Chem. Ges.* **1900**, *33*, 3547.

The AH related to **5** is phenanthrene (**16**), substitution[22] in which is correctly predicted by DEWAR-PI (Table III) to take place most easily in the 9-position, however all but two sites (2 and 7) were within the 5 kcal/mol limit. The 9-position corresponds to position 8 in **5**, which DEWAR-PI predicts to be the most reactive.

The heats of formation calculated by AM1[8] for the WIs formed from **5** by addition of Br^+ to C_1 and C_8 were degenerate, with energies of 283.19 kcal/mol. The small error in the DEWAR-PI results for **5** could be attributed to a failure to deal explicitly with σ bonds.

Indeno[1,2,3-*cd*]pyrene (6). Harvey and co-workers[14] found that both bromination and Friedel–Crafts acylation of **6** yield 12-substituted products. DEWAR-PI predicts (Table I) the 12-position to be 1.4 kcal/mol higher in energy than the preferred sites, 3 and 5. For reasons indicated above, this is certainly within the limits of error of the DEWAR-PI predictions.

The AH related to **6** is pyrene (**17**). DEWAR-PI correctly predicts (Table III) substitution[23] in **17** at the 1-position, analogous to positions 3, 5, and 12 in **6**.

It has also been reported that nitration of **6** yields an 8- or 9-nitro derivative,[24] contrary to the results predicted by DEWAR-PI. The DEWAR-PI relative energies for these sites are 7.6 and 10.6 kcal/mol, respectively. Given that Harvey and co-workers[14] express serious misgivings concerning the validity of these experimental results, and the large discrepancy in the DEWAR-PI results, further experimental studies would be of interest.

Fluoreno[9,1,2,3-*cdef*]chrysene (7) and Benz[*def*]indeno[1,2,3-*qr*]chrysene (8). No experimental data are available for electrophilic substitution in **7** or **8**, both of which, like **2** and **3**, can be derived by phenylenation of benzo[*def*]chrysene (**19**). Both **7** and **8** differ, however, from **2** and **3** in that the position equivalent to 6 in **19** is free. Since this is predicted by DEWAR-PI to be by far the most reactive in **19** (Table III), it is not surprising that the same is true for the corresponding positions in **7** and **8**, i.e., 8 in **7** and 3 in **8** (Tables I and II). The values of δE for the next most reactive positions, 1 in **7** and 14 in **8**, are very large (7.8 and 9.1 kcal/mol, respectively). There seems little doubt that electrophilic substitution in **7** and **8** will prove to take place as predicted.

Dibenz[*a*,*e*]aceanthrylene (9), Dibenz[*a*,*j*]aceanthrylene (10), Dibenz[*e*,*k*]acephenanthrylene (11), and Dibenz[*a*,*l*]aceanthrylene (12). These hydrocarbons can all be derived from the same AH [benz[*a*]anthracene (**20**)] by introduction of a phenylene substituent in different positions. Again, no experimental data for electrophilic substitution are available for any of them. The calculated results are given in Table II.

DEWAR-PI correctly predicts (Table III) substitution[25] to occur far more readily in **20** at positions 7 and 12 than at any other, with 7 the most reactive. The position predicted to be the most reactive in **11** (9), or **12** (7) corresponds in each case to position 7 in **20**. In **9** and **10**, where this position is blocked, the most reactive positions (14 and 5) correspond to the second most reactive position (12) in **20**. In **11**, where both relevant positions are free, the second most reactive (14) site corresponds to the second most reactive position in **20**.

Benzo[*k*]fluoranthene (13) and Benzo[*j*]fluoranthene (14). **13** and **14** are analogous structural isomers derived from two molecules of naphthalene (**22**) by double union. No experimental data are available for electrophilic substitution in them. The DEWAR-PI results (Table II) indicate that substitution in **13** should be easiest at positions 7 and 12, these being almost equal in reactivity and well ahead of positions 3 and 4, which tie for third and fourth place. In **14**, position 11 is predicted to be by far the most reactive. Each of these sites is analogous to the α position (1) in **22**, predicted by DEWAR-PI to be 7.4 kcal/mol more stable than the β position (2), and the experimentally[26] preferred site of attack. A PMO analysis of these results is given in the next section.

Table IV. Calculated DEWAR-PI Total Energies (E_{tot}), Relative Reactivities ($\Delta\Delta H_{Rx}$), and Heats of Formation (ΔH_f)

molecule	WI,[a] E_{tot}, eV	E_{tot}, eV	$\Delta\Delta H_{Rx}$,[b] kcal/mol	ΔH_f, kcal/mol DEWAR-PI	ΔH_f, kcal/mol expt[c]
1	−183.138	−205.841	−36.7	83.9	
2	−197.882	−220.195	−45.7	94.7	
3	−197.832	−220.203	−44.4	94.5	
4	−149.705	−171.965	−46.9	77.3	
5	−149.456	−172.287	−33.8	69.9	
6	−164.116	−186.707	−39.3	79.2	
7	−198.111	−220.173	−51.5	95.1	
8	−198.111	−220.165	−51.7	95.3	
9	−183.263	−205.451	−48.6	92.9	
10	−183.259	−205.658	−43.7	88.1	
11	−183.264	−205.628	−44.5	88.8	
12	−183.342	−205.596	−47.1	89.5	
13	−149.550	−172.026	−42.0	75.9	
14	−149.527	−172.104	−39.6	74.1	
15	−115.639	−138.636	−29.9	58.2	69.1
16	−100.984	−124.192	−25.1	49.5	49.6
17	−115.913	−138.599	−37.1	59	53.9
18	−134.896	−157.744	−33.4	63.5	64.5
19	−149.937	−172.071	−49.9	74.9	
20	−135.051	−157.554	−41.3	67.9	70
21	−101.307	−123.849	−40.4	57.4	55.2
22	−67.189	−90.550	−21.6	37.5	35.9
benzene	−32.863	−57.158	0.0	19.8	19.8

[a] Wheland intermediate predicted by DEWAR-PI to have the lowest energy. [b] Relative reactivities are relative to benzene. [c] All heats of formation are given by: Pedley, J. B.; Naylor, R. D.; Kirby, S. P. *Thermochemical Data of Organic Compounds*, 2nd ed.; Chapman and Hall: London, 1986.

Fluoranthene (15). DEWAR-PI correctly predicts (Table III) **15** to undergo substitution[27] preferentially in positions 7 and 8. These sites are also equivalent to the most reactive α position in naphthalene (**22**) from which **15** is derived by phenylenation.

The total energies for the DEWAR-PI WI with the lowest energy and the parent hydrocarbon are given in columns 1 and 2 of Table IV for each hydrocarbon. Since the DEWAR-PI WI total energy does not include contributions from the methylene group or the attacking electrophile, the true ΔH_{Rx} (see eq 1) cannot be accurately determined. For a given electrophile, these energy contributions will be approximately constant for most hydrocarbons. Thus the relative reactivity, $\Delta\Delta H_{Rx}$, provides a reasonable estimate of the rates of reaction in different hydrocarbons:

$$\Delta\Delta H_{Rx} = \Delta H_{Rx}(\text{hydrocarbon}) - \Delta H_{Rx}(\text{benzene}) \qquad (3)$$

where ΔH_{Rx} is the DEWAR-PI WI total energy minus the total energy of the parent molecule. Column 3 lists the relative reactivity of each hydrocarbon relative to benzene.

The DEWAR-PI calculated heat of formation for each hydrocarbon is also given in Table IV, along with available experimental heats of formation. The calculated values, with one exception, agree well with the experimental data. The error in the exception (**15**) is due to neglect of ring strain.[5b]

Each of the compounds **1–12** and **15** can be regarded as a 1,2-phenylene derivative of an alternant hydrocarbon. Thus, **1** is derived in this way from chrysene (**18**). As the previous discussion shows, the position (X) in each of these compounds that DEWAR-PI predicts to be the most reactive corresponds in almost all cases to the most reactive position in the associated AH.

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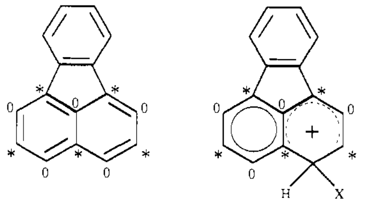


(a) (b)

Figure 1.

Furthermore, the exceptions refer to cases where the value of δE in the AH corresponding to position X was very small. Conversion of an AH to a nonalternant hydrocarbon by phenylenation thus seems to have little effect on the relative reactivities of the various positions in the related AH. An explanation in terms of PMO theory is given in the next section.

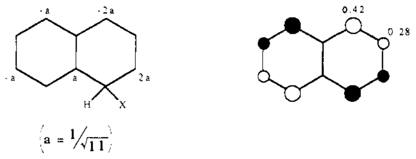
PMO Treatment

PMO theory[1] in its proper form[28] has been shown to account in a very satisfactory way for the rates and orientation of aromatic substitution reactions in alternant hydrocarbons[30] (AH) and isoconjugate heteroaromatic species.[31] As the following discussion shows, it can also account in a simple manner for substitution in the 15 nonalternant compounds (**1**–**15**) considered here.

Compounds **1**–**12** and **15** are derived from even alternant hydrocarbons (AH) by introduction of a 1,2-phenylene substituent, attached to positions of like parity (both starred or both unstarred) in the A*H*; see e.g., Figure 1a. Each is therefore derived by union of an AH (R) with benzene to form a nonalternant hydrocarbon (RBz). According to PMO theory,[1] the energy of union of any two even AHs through a single position in each has a constant value, which is included in the bond energy of the linking CC bond, a "polyene" single bond. It is easy to show that the same is true for each of the bonds linking benzene to R in **1**–**12**. In the PMO sense, the stabilization energies of union are zero, the π energies of R and RBz being the same.

The relative rates of electrophilic substitution at various positions in a group of aromatic compounds run parallel to the differences in π energy between them and the corresponding WIs.[1] The effect of the phenylene substituent in RBz will therefore depend on the π energy of union of benzene with the WI (R_k^+) for substitution at the corresponding position (k) in R.

Since the product of union is nonalternant, the usual first-order PMO treatment[1] is inapplicable. The interaction between R_k^+ and benzene has to be found by using second-order perturbation theory. However, it can be shown that the sum of the terms corresponding to interactions between bonding MOs of each component and antibonding ones of the other has the same value as it has for union of two even AHs. It is therefore included in the bond energies of the linking C–C bonds. The only relevant terms are thus ones corresponding to interactions between the empty nonbonding MO (NBMO) of R_k^+ and the filled bonding MOs of benzene, which are proportional to the squares of the corresponding NBMO coefficients in the WI.



(a) (b)

Figure 2.

As noted above, the atoms (r and s) in R involved in union with benzene are of like parity. In a corresponding WI, they are therefore either both starred or both unstarred. If they are unstarred, the interactions with the benzene vanish. If they are starred, the interactions lead to stabilization. The former condition holds for positions of like parity to the point of attack.

Since the effect of a 1,2-phenylene substituent on electrophilic substitution should be comparable with that of phenyl, and since the latter is small, the phenylene groups in **1**–**12** are unlikely to have any large effect on the orientation of substitution. An effect would be expected only if two of the most reactive positions in R have comparable reactivities and if substitution is assisted by phenylene only in the less reactive. As we have already seen, the positions in **1**–**12** and **15**, which DEWAR-PI predicts to be the most reactive, do indeed correspond to the most reactive positions in the related even AHs. It is also easily seen that the phenylene group is attached in each case to positions that are starred in the corresponding WI; see e.g., Figure 1b.

The situation in **13** and **14** is different, these compounds being derived by union of two molecules of naphthalene. Since the α positions in naphthalene are the most reactive, substitution should take place most easily at positions 3, 4, 7, and 12 in **13** and positions 3, 4, and 11 in **14**. The main contribution to the second-order perturbation in each case should moreover correspond to an interaction between the NBMO of the WI and the HOMO of the naphthalene moiety that is acting as a substituent. The relevant HOMO and NBMO coefficients are shown in Figure 2. The reactivity should run parallel to the absolute magnitude of the sum of the products of coefficients at each point of union.[1] These are shown under the formulas in Figure 2. It will be seen that the points of preferred attack in **13** and **14** are the ones with the largest sums.

This approach should prove useful in predicting the orientation of substitution in other analogous nonalternant hydrocarbons, i.e., ones that can be formed by union of two AHs. The orientation of substitution in even AHs can be predicted semiquantitatively by a "pencil and paper" PMO calculation.[1] The results reported here suggest that the present extension to nonalternant hydrocarbons that can be derived by union of pairs of AHs should also prove effective.

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[28] The term "PMO theory", which was introduced many years ago[29] to describe the general theory of organic chemistry of ref 1, is often misapplied to a treatment of reactions, notably cycloadditions, in which transition states are regarded as perturbed forms of the reactants, their energies being estimated by using second order perturbation theory.

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