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AN IMPROVED CORRELATION BETWEEN POLAROGRAPHIC REDUCTION POTENTIAL AND HUCKEL LUMO ENERGY. APPLICATION TO NON-BENZENOID HYDROCARBONS

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Abstract -- It is shown that the reduction potentials of a wide variety of hydrocarbons, including benzenoid and non-benzenoid polycyclic alternant and non-alternant hydrocarbons, annulenes, cyclophanes, and polyenes (but not Huckel 4n compounds) can be predicted quite well using a modified HMO method in which Coulomb integrals are adjusted iteratively to self-consistency with charge densities, and exchange integrals are adjusted to consistency with pi-bond orders. The median difference between calculated and experimental half-wave potentials is only 39 mV. The correlation (eq 4) involves a simple linear relationship capable of correlating reduction potentials over a range of over 2.5 V, or almost 60 kcal/mole in energy terms.

Many investigations into the cathodic behavior of polycyclic aromatic hydrocarbons (PAH's) have been reported in the literature.[1] One of the earliest and most significant discoveries in this area was the discovery[2] of the rather good correlation between polarographic reduction potential[3] and the energy of the lowest unoccupied molecular orbital (LUMO) of the hydrocarbon as computed by Huckel molecular orbital (HMO) theory. A number of significant points emerged from these studies. First, the correlation is remarkably independent of the nature of the solvent in which the polarographic measurements are made.[2,5] Thus, while the correlation line in 2-methoxyethanol is described by eq 1,[2] where $E_{1/2}$ is the polarographic half-wave potential (in volts) relative to the

$$E_{1/2} = (2.414 \pm 0.092)\mathbf{m} - (0.435 \pm 0.065) \qquad (1)$$

mercury pool and $\mathbf{m}$ (a negative number) is the energy (in units of β) of the LUMO, the line in dimethylformamide (DMF) is very similar (eq 2).[6] The slope

$$E_{1/2} = (2.407 \pm 0.182)\mathbf{m} - (0.396 \pm 0.093) \qquad (2)$$

in 96% dioxane[5] is close to both of these values (eq 3). The intercept is different, but this is simply due to use of a different reference electrode; we shall however return to this point in the Discussion, since it represents a potential stumbling block to interpretation of data measured under different

$$E_{1/2} = (2.368 \pm 0.099)\mathbf{m} - (0.924 \pm 0.109) \qquad (3)$$

conditions. We wish to address in this paper problems surrounding the second major finding by previous investigators in this area. The correlation between $E_{1/2}$ amd $\mathbf{m}$ is relatively good for polycyclic benzenoid hydrocarbons (although, as we shall see, it can be made better); however, the lines represented by eqs 1-3 fail badly when applied to non-alternant hydrocarbons or linear polyenes.[2] For example, eq 2 predicts reduction potentials for azulene, acepleiadiene (1), and 1,4-diphenylbutadiene which are in error by amounts up to and exceeding 0.3 V (vide infra). It has been suggested[2,5] that one might compensate for this deficiency by developing a different correlation line for each class of compounds. In our opinion, however, this represents an inadequate solution, and it suffers from the additional disadvantage that most such lines will not be very precise anyway, having been produced in general from a small number of data points.

This situation is particularly unfortunate, when one considers the fact that correlations such as those represented by eq 1-3 are of relatively little importance if one cannot use them to estimate the reduction potentials of unknown substances. The latter capability is of considerable current interest in a variety of contexts: a) questions related to the physical chemical properties of non-benzenoid hydrocarbons,[7] b) mechanisms of organic reactions such as aromatic $S_{RN}1$ processes[8], and c) the design of organic conductors and other species involving electron-transfer between two components, inasmuch as the formation of charge-transfer complexes, cation or anion radicals, and conducting complexes all depend upon a knowledge of the relative redox potentials of the various components of the system.[9] Our interest in this problem was aroused in the course of recent studies on the electrochemical reduction of non-benzenoid aromatic hydrocarbons.[10] As an adjunct to our other work, we wished to develop a method of estimating the reduction potentials of non-alternant hydrocarbons which would retain the advantages of Huckel molecular orbital theory (simplicity, speed of computation, even for large molecules, and widespread use) while, ideally, being applicable to other unsaturated hydrocarbons as well. This suggested use of a modified HMO method, rather than other theoretical methods such as graph theory[11] or SCF-MO theory[12] which have been used to correlate structure and electrochemical reactivity. It is known that one of the principal reasons why first-order HMO theory handles non-alternant compounds badly is the unequal charge distribution in such substances. Simple Huckel theory assumes identical Coulomb integrals at all carbon atoms, which is manifestly incorrect for non-alternants. Consequently, a number of properties of significance are not computed properly for such substances. Streitwieser has, however, shown[2,13,14] that the properties of charged species can be correlated by a modified HMO method (" ω- technique") in which Coulomb integrals at each carbon are adjusted iteratively to self-consistency with computed charges. We decided to explore the extent to which use of Streitwieser's ω-technique (which can be implemented easily as a subroutine to a standard HMO program) would improve the computed reduction potentials of non-alternant hydrocarbons. At the same time, we felt that it might be possible to further improve the reduction potential-LUMO energy correlation for both alternants and non-alternants, and even for benzenoid compounds, by a second modification to the standard HMO calculation (which assumes all carbon-carbon exchange integrals to be identical) in which carbon-carbon exchange integrals are adjusted iteratively to consistency with computed *pi*-bond orders by assuming empirical bond order-bond length and bond length-exchange integral relationships[15] This procedure has been shown to fit the experimental bond lengths of PAH's quite well,[15a] and a computational procedure including both of these modifications has been shown to afford reliable results when applied to large organic polyanions.[16] We have found that electron-densities calculated by this method agree quite well with those computed for a number of neutral non-alternants by Pariser-Pople-Parr MO theory.[17]

The first question to be addressed was the source of the electrochemical data to be used in developing the correlation. There are a large number of polarographic investigations on polycyclic benzenoid hydrocarbons in the literature, but they have employed a variety of solvents, supporting electrolytes, reference electrodes, and polarographic techniques. We desired data on a large set of hydrocarbons, measured by a single investigator under identical experimental conditions. We therefore chose the data of Bergman,[18] who examined 67 benzenoid and 11 nonbenzenoid hydrocarbons (all of the latter were substituted fluoranthenes) in 2-methoxyethanol/0.1 M tetrabutylammonium iodide by two-electrode polarography, with potentials measured *vs* the mercury pool anode. Bergman's solvent, technique, and reference electrode are rarely used by modern investigators, but this data set represents the largest number of hydrocarbons ever studied in a single investigation of this type and therefore appeared ideal for our purposes. We elected to determine the best correlation line using these data, and then to develop a separate procedure (*vide infra*) for correcting the derived line to conditions generally used by modern experimenters.

The least-squares line representing the correlation between polarographic half-wave potential and LUMO energy computed by the procedure described above was computed using all of the benzenoid hydrocarbons in Bergman's data set, with one exception. We noted that the reduction potential of zethrene (2) measured by Bergman deviated by 4.35 standard deviations from the line composed of all benzenoid hydrocarbons. Like others,[19] we regarded the datum for zethrene as suspect, and excluded it from the correlation line, which was therefore constructed from data for a total of 66 hydrocarbons. With this exception, all of the benzenoid compounds in the Bergman data set were used, even though it appears that certain of his values are less reliable than others (some reduction potentials are reported to fewer significant figures than others) because of the limited solubility of some of the substances.[18] The correlation line is given by eq 4, whose correlation coefficent is 0.980, which we regard as rather high, considering the wide range

$$E_{1/2} = (2.635_4 \pm 0.067)m - (0.129_4 \pm 0.032) \qquad (4)$$

of structures and reduction potentials included in the substances studied by Bergman.[20] The best previous HMO correlation between reduction potentials and LUMO energies is that of Streitwieser (eq 2).[6] It may be seen by inspection of the error limits on the respective slopes and intercepts that eq 4 correlates the reduction potentials of benzenoid hydrocarbons better than does eq 2. One might object that this is true not because construction of eq 4 involved correction of exchange integrals to match computed *pi*-bond orders, but simply because about twice as many points are represented in Bergman's data set as contained in the data set used to construct eq 2.[2,6] We separated these two effects in two ways. First, we computed the least-squares line through the same set of 66 PAH's, but using the Huckel LUMO's. This line is given as eq 5. While this line represents a better correlation between $E_{1/2}$ and LUMO energy than eq 2 (note the narrower error limits on slope and intercept), presumably because it is based on a larger data set, it is not as good as eq 4, which

$$E_{1/2} = (2.543_3 \pm 0.089)m - (0.348_4 \pm 0.036) \qquad (5)$$

incorporates the modified HMO LUMO's: the correlation coefficient for eq 5 is lower (0.963), and (equivalently) the error limits on slope and intercept are larger. This shows that the $E_{1/2}$-LUMO correlation is indeed improved by correcting exchange integrals to match bond orders. Next,we confirmed this point by computing the least-square line through the same data points as were used to construct eq 2, but using the LUMO's computed by the modified HMO method. The resulting line (eq 6), while not as good as eq 4, is much better

$$E_{1/2} = (2.564 \pm 0.074)m - (0.193 \pm 0.038) \qquad (6)$$

than eq 2: the correlation coefficient (0.989) is better, and the error limits are smaller. Eq 4 in fact represents the best method yet reported for predicting the reduction potentials of aromatic hydrocarbons. For example, Dewar described a method for computing the electronic affinities of PAH's, and found a linear correlation between his computed electron affinities and Bergman's polarographic data.[12] This correlation was claimed to be superior to previous correlations such as those in eqs 1-3 on the basis of two criteria: (a) the high correlation coefficient of the line (0.967) and (b) the fact that the standard deviation of the slope of the line is smaller than that of a correlation line constructed similarly to our eq 5, but using a slightly different subset of Bergman's data. The correlation coefficient of our line is even higher (0.980) than that of Dewar's. Furthermore, the second of Dewar's criteria is in fact inappropriate as a measure of the accuracy of the method for predicting reduction potentials; the proper criterion to use is the standard deviation of the half-wave potentials computed using the least-squares line from the corresponding experimental values. This statistical measure of accuracy is 69 mV for our method, 90.5 mV for the Huckel line, and 94 mV for the procedure advocated by Dewar. The substantial superiority of the correlation expressed as eq 4 is therefore clear.

The potentials reported by Bergman were measured in 2-methoxyethanol relative to the mercury pool electrode (which serves as both anode and reference electrode). These conditions are rarely used in modern polarographic practice, which favors a separate reference electrode (most often the saturated calomel electrode, or SCE) and an aprotic solvent such as dimethylformamide or acetonitrile. It is necessary therefore to correct eq 4 appropriately to correct for these differences. This was done in the following way. Streitwieser has tabulated the reduction potentials of a number of hydrocarbons in 75% dioxane relative to SCE.[2] Bergman's data were measured in 2-methoxyethanol relative to mercury pool.[18] There are a number of overlaps. From the somewhat limited data (16 compounds), we noted that reduction potentials measured against SCE in aqueous dioxane average 0.472 ± .040 V more negative than those measured against the mercury pool in 2-methoxyethanol. We were able to find nine hydrocarbons in the literature whose reduction potentials have been measured against SCE in either DMF or acetonitrile; on average, the reduction potential in the aprotic solvent is 0.083 ± 0.063 V negative of that in aqueous dioxane vs the same reference.[1c] Combining these two correction factors, we conclude that potentials measured under modern conditions (aprotic solvent, SCE) are 0.555 V negative of those measured under Bergman's conditions, and that there is a probable cumulative uncertainty of ca 0.075 V involved in the extrapolation. As was indicated in the Introduction, reduction potentials cannot be predicted for nonalternants, nonbenzenoid alternants, or polyenes using eq 2 and LUMO energies computed by the standard Huckel method. Thus, the Huckel LUMO energy of azulene is 0.400,[2] leading to a predicted $E_{1/2}$ from eq 2 of -1.359 V vs mercury pool, while the experimental value is -1.075,[27] an error of .284 V. Likewise, the reduction potentials of a number of 1,n-diphenylpolyenes are also not correlated at all well by eq 2, a fact which led Streitwieser to suggest that a different correlation line should be required for each class of compound.[2]

It should be recalled that only benzenoid species were used in the correlation represented by eq 4, in contrast to eq 2, which incorporates both benzenoid and non-benzenoid substances.[6] Our procedure was chosen because we felt that it would be more challenging to attempt to correlate the reduction potentials of non-alternant and alternant non-benzenoid hydrocarbons using a correlation line which was developed using only benzenoid substances. Our hope was that we could derive a single correlation line which could predict the reduction potentials of a wide range of hydrocarbon structures within 75 mV, i.e., the uncertainty in the extrapolation to modern polarographic conditions, under which most of the relevant data have been measured. The degree to which we were able to achieve this goal may be assessed by examination of the data in Table 1, which includes all of the polarographic data which we have been able to locate in the literature for planar (or nearly so) nonbenzenoid hydrocarbons, as well as benzene itself and a few of its derivatives whose reduction potentials were not available at the time of Bergman's work. For each hydrocarbon, the table contains its experimental reduction potential, corrected to Bergman's experimental conditions as described above, together with reduction potentials computed by equations 2 and 4, using Huckel LUMO energies with eq 2 and LUMO energies computed by the modified HMO method[22] with eq 4. The data in the table show clearly that the modified HMO method represents a substantial improvement over procedures based upon simple Huckel theory. In fact, although it is more successful with alternant compounds than non-alternants, equation 4 predicts the reduction potentials of these 65 hydrocarbons with a median deviation of 39 mV, less than the probable error in the experimental values, and about a factor of three better than when eq 2 is used with LUMO's computed by simple HMO theory. Furthermore, while calculated reduction potentials using simple Huckel theory differ from the experimental values by more than 200 mV in 14 instances, this is true for only 3 compounds when the modified HMO theory is used. We regard the method therefore as successful: reduction potentials encompassing a range of over 2.5 V, or almost 60 kcal/mole, are well correlated by the single linear relationship expressed as eq 4, and the correlation is successful in treating a wide variety of structural types, even though it was derived using only benzenoid hydrocarbons.

The Coulomb integral correction, not that of the exchange integrals, proved, as expected, to be critical in treating the reduction potentials of non-alternant substances. Streitwieser,[6] Hoijtink,[5,13] and Anderson[21] found previously that changing the exchange integrals in the Huckel calculation for such substances to match experimental bond lengths does not lead to better fit to the correlation line, and in fact often produces a worse fit.[23] On the other hand, the improved fit for alternants such as 4n + 2 annulenes and polyenes presumably derives from the improved method of treating exchange integrals in this modified HMO method.

As an example of the results obtained, one can compare the reduction potentials of pyracylene (**3a**) and its four homologues **3b-6** as computed by both Huckel MO theory and the modified HMO method. Huckel theory fails completely at

Table 1. LUMO Energies and Reduction Potentials

(Experimental and Calculated) of Nonbenzenoid Hydrocarbons

Compound	$-E_{1/2}$ Exptl^a	Ref	Huckel ■	 $-E_{1/2}$ Calcd^b	 Dev^d	Modified HMO ■	 $-E_{1/2}$ Calcd^c	 Dev^d
Non-Alternants								
Azulene	1.075	21	.400	1.359	.284	.370	1.104	.029
1,2-Benzazulene	1.018	25	.388	1.330	.312	.399	1.181	.163
5,6-Benzazulene	1.108	25	.317	1.159	.051	.339	1.023	.085
6,6-Diphenylfulvene	0.745	26	.139	0.731	.014	.226	0.725	.020
Azupyrene (**9**)	0.814	21	.362	1.267	.453	.227	0.728	.086
as-Azupyrene (**10**)	0.910	21	.307	1.135	.225	.332	1.004	.094
Aceheptylene (**11**)	0.725	21	.329	1.188	.463	.321	0.975	.250
6,6'-Biazulenyl	0.635	27	.162	0.786	.151	.159	0.548	.087
5,5'-Biazulenyl	0.945	27	.379	1.308	.363	.356	1.067	.122
Dibenzopentalene	0.745	28	.116	0.675	.070	.238	0.757	.012
Acenaphthylene	1.178	29	.285	1.082	.096	.380	1.131	.047
Acepleiadiene	1.163	6	.445	1.467	.304	.426	1.252	.089
Cyclobutadieno-pleiadiene	1.389	30	.328	1.185	.204	.484	1.405	.016
Pleiadiene	1.295	31	.457	1.496	.201	.583	1.666	.371
Tetrabenz[a,d,g,i]-pyracylene (**6**)	0.340	18	.000	0.396	.056	.084	0.351	.011
1,2-Diphenyl-pyracylene (**3b**)	0.500	17	.000	0.396	.104	.148	0.519	.019
Pyracyclene (**3a**)	0.584	17	.000	0.396	.188	.178	0.599	.015
Tribenz[a,d,g]-pyracylene (**5**)	0.600	18	.229	0.947	.347	.253	0.796	.196
Dibenz[a,g]-pyracylene (**4**)	0.900	18	.186	0.844	.056	.281	0.870	.030
1-Phenyl-4-fluoren-eylidenebutadiene	0.988	29	.249	0.995	.007	.357	1.070	.082
1-Phenyl-6-fluoren-ylidenehexatriene	0.878	29	.202	0.882	.004	.317	0.965	.087
1-Phenyl-8-fluoren-ylideneoctatetraene	0.818	29	.170	0.805	.013	.290	0.894	.076
1-Phenyl-12-fluoren-ylidenedodecahexaene	0.778	29	.130	0.709	.069	.255	0.801	.023
1,4-Bis(fluorenyl-idene)-butadiene	0.668	29	.127	0.702	.034	.238	0.757	.089
1,6-Bis(fluorenyl-idene)-hexatriene	0.698	29	.105	0.649	.049	.224	0.720	.022
Fluoranthene^e	1.345	18	.371	1.289	.056	.444	1.300	.045
Benz[a]fluoranthene	0.975	18	.252	1.003	.028	.320	0.973	.002
Dibenz[a,f]-fluoranthene	0.650	18	.160	0.781	.131	.211	0.685	.035
Benz[b]fluoranthene	1.375	18	.345	1.226	.149	.405	1.197	.178
Benz[j]fluoranthene	1.165	18	.312	1.147	.018	.381	1.133	.032
Benz[k]fluoranthene	1.390	18	.401	1.361	.029	.474	1.379	.011
Naphtho[2,3-j]-fluoranthene	1.055	18	.267	1.039	.016	.335	1.012	.043
Naphtho[2,3-k]-fluoranthene	1.375	18	.397	1.352	.023	.474	1.379	.004
Alternants								
Biphenylene	1.793	6	.445	1.467	.326	.586	1.674	.119
2,3-Benzobiphenylene	1.733	6	.502	1.604	.129	.612	1.745	.009
Benzene; [6]Annulene	2.86	32	1.000	2.803	.057	1.034	2.854	.006
[14]Annulenes:								
12	1.315	10c	.445	1.467	.152	.454	1.326	.011
13	1.315	10b	.445	1.467	.152	.454	1.326	.011
14	1.180	10c	.325	1.178	.002	.395	1.170	.010
15	1.160	10c	.325	1.178	.018	.395	1.170	.010
16	0.750	10c	.226	0.940	.190	.244	0.772	.022
17	1.320	10c	.357	1.255	.065	.453	1.323	.003
18	1.030	10c	.285	1.082	.052	.307	0.938	.092
1,3-Butadiene	2.158	29	.618	1.884	.274	.845	2.356	.198
Phenylbutadiene	1.698	29	.474	1.537	.161	.634	1.800	.102
1,4-Diphenyl-butadiene	1.528	29	.386	1.325	.203	.523	1.508	.020
1,6-Diphenyl-hexatriene	1.288	29	.311	1.145	.143	.457	1.334	.046
1,8-Diphenyl-octatetraene	1.148	29	.260	1.022	.126	.408	1.205	.057

1,10-Diphenyldecapentaene	1.068	29	.223	0.933	.135	.371	1.107	.039
1,12-Diphenyldodecahexaene	0.978	29	.196	0.868	.110	.343	1.033	.055
1,3,5-Triphenylbenzene	2.025	33	.662	1.989	.036	.715	2.014	.011
1,3-Diphenylbenzene	2.115	33	.662	1.989	.126	.713	2.008	.107
1,2-Bis(phenalen-1-ylidene)ethane (19)	0.565	34	.138	0.728	.163	.199	0.654	.089
20	1.705	31	.445	1.467	.238	.558	1.600	.105
21	1.135	35	.254	1.007	.128	.388	1.152	.017
22	1.287	35	.323	1.173	.114	.436	1.278	.009
23	1.031	35	.210	0.901	.130	.357	1.070	.039
24	1.087	35	.281	1.072	.015	.401	1.186	.099
25	0.955	35	.183	0.836	.119	.337	1.018	.063
26	1.127	35	.361	1.265	.138	.465	1.355	.228
27	1.141	35	.274	1.056	.085	.394	1.168	.027
28	1.171	35	.288	1.089	.082	.400	1.184	.013
29	1.186	35	.288	1.089	.097	.406	1.199	.013
30	1.457	35	.365	1.275	.182	.480	1.394	.063
31	1.131	35	.254	1.007	.124	.385	1.144	.013

[a] Literature values, as corrected to the solvent and reference electrode used in ref.18. [b] Calculated using Huckel LUMO energies and eq 2. [c] Calculated using HMO LUMO energies (ref 22) and eq 4. [d] Difference between calculated and experimental half-wave potentials. [e] This and the next seven compounds are compounds LXII - LXIX in ref.18. [f] This and the next four entries are compounds 4-8 in ref 10c.

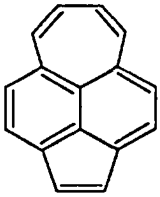
predicting the experimental reduction potentials of these compounds and in fact predicts the same value for three of them; the modified HMO method not only removes this degeneracy, it predicts precisely the order of ease of reduction observed for the five substances.

There are on the other hand some conspicuous failures of the correlation procedure (Table 2). These include primarily Huckel 4n systems, such as cyclobutadiene, but also pentalene. In all cases these substances turn out to be much harder to reduce than expected on the basis of standard or modified Huckel theory. These failures presumably arise from the fact that in general Huckel theory does not handle such compounds at all well; for example, pentalene is predicted to have a very sizeable resonance energy of 2.46 β by Huckel theory, while in fact it appears to be an extremely unstable substance, and in fact has never been isolated except as its tri-t-butyl derivative.[24] On the other hand, benzannelated derivatives of 4n annulenes [e.g., biphenylene, 2,3-benzobiphenylene, benzo- and naphtho-annelated large annulenes uch as **21**, **23**, and **27**, and dibenzopentalene (**8**)] are treated adequately (see Table 1).

Table 2. Unsaturated Substances Whose Reduction Potentials Are Not Predicted Properly by HMO Methods [a]

			Huckel			Modified HMO		
Compound	$E_{1/2}$, Exptl	Ref	■	$E_{1/2}$, Calcd	Dev	■	$E_{1/2}$, Calcd	Dev
Cyclobutadiene	1.6	36	.000	0.396	1.2	.266	0.833	.8
[12]Annulene: **32**	0.935	37	.000	0.396	.539	.271	0.847	.088
[16]Annulene: **33**	0.675	38	.000	0.396	.379	.086	0.359	.326
Pentalene	0.85[b]	39	.000	0.396	.45	-.157[c]	-0.281	1.13

[a] See footnotes a - d of Table 1. [b] Estimated: see ref.36. [c] LUMO is computed to be a bonding orbital.



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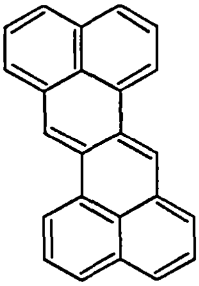

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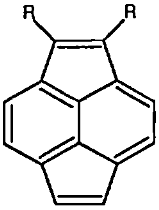

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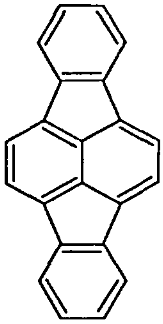

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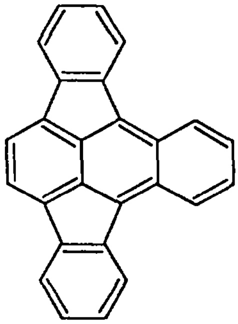

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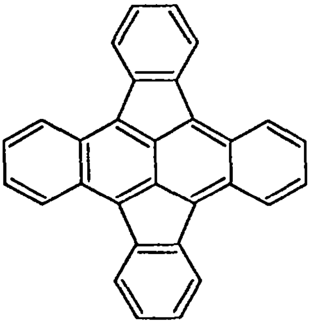

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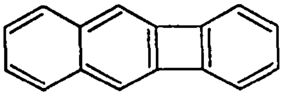

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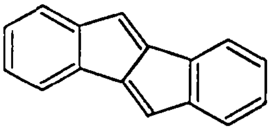

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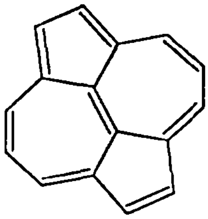

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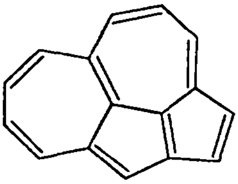

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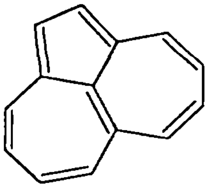

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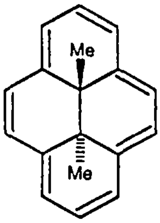

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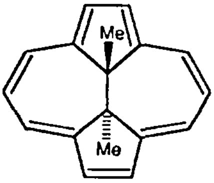

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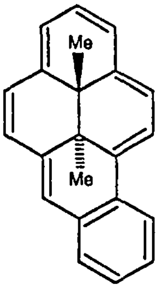

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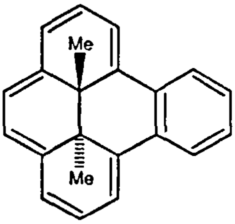

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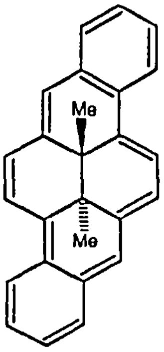

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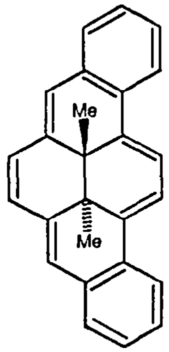

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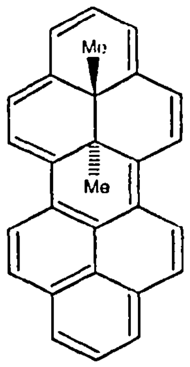

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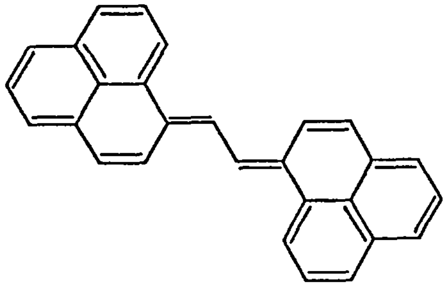

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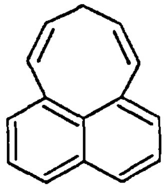

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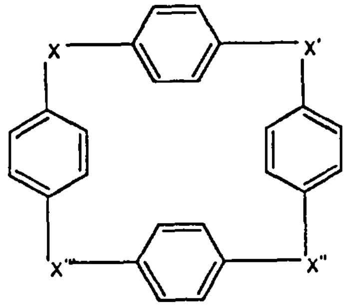
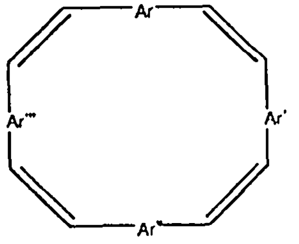
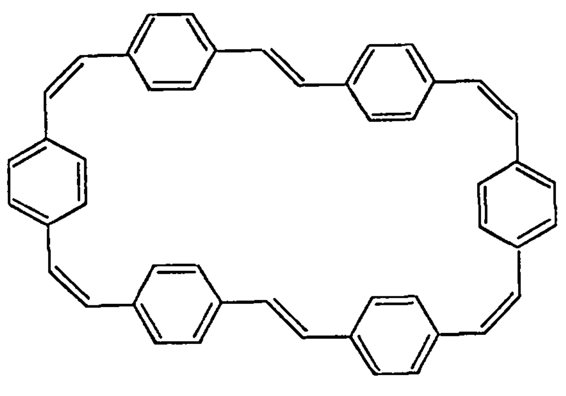


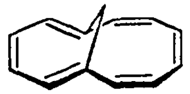
21, X = X' = X'' = X''' = -CH=CH-
22, X = X' = X'' = -CH=CH-; X''' = -CH=CHCH=CH-
23, X = X' = -CH=CH-; X'' = X''' = -CH=CHCH=CH-
24, X = -CH=CH-; X' = X'' = X''' = -CH=CHCH=CH-
25, X = X' = X'' = X''' = -CH=CHCH=CH-



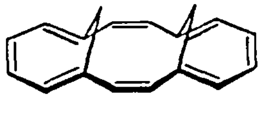
26, Ar = Ar' = Ar'' = p-C_6H_4 ; Ar''' = 2,6 - naphthalenediyl
27, Ar = Ar'' = p-C_6H_4 ; Ar' = Ar''' = 2,6 - naphthalenediyl
28, Ar = Ar' = Ar'' = Ar''' = 2,6 - naphthalenediyl
29, Ar = Ar'' = p-C_6H_4 ; Ar' = Ar''' = p, p'-biphenylyl
30, Ar = Ar'' = p-C_6H_4 ; Ar' = Ar''' = m - C_6H_4



31



32



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Notes and References

(1) For reviews see (a) Peover, M.E. in Bard, A.J., Ed. "Electroanalytical Chemistry", vol. 1; Dekker: New York, 1966; p.1; (b) Fry, A. "Synthetic Organic Electrochemistry"; Harper and Row: New York, 1972; Chap.7; (c) M.M.Baizer and H.Lund, Eds., "Organic Electrochemistry",2nd ed., Dekker: New York, 1983.

(2) The literature on such correlations has been summarized: Streitwieser, A. "Molecular Orbital Theory";Wiley: New York, 1961; Chapter 7.

(3) Most such investigations have been carried out using traditional DC polarography. It should be noted that, for reversible systems (the first electron transfer to aromatic hydrocarbons is reversible in aprotic media), polarographic half-wave potentials are 28 mV positive of linear-sweep voltammetric peak potentials[4] and that the latter must be corrected accordingly to be consistent with polarographic data.

(4) R.S.Nicholson, R.S.and I.Shain, Anal. Chem., **36**, 722 (1964).

(5) G.J.Hoijtink, Rec.trav.chim., **74**, 1525 (1955).

(6) Streitwieser,Jr., A.;Schwager,I J. Phys. Chem. **66**, 2316 (1962).

(7) (a) L.A.Paquette, G.D.Ewing, S.Traynor, and J.M.Gardlik, J.Amer.Chem.Soc., **99**, 6115 (1977); (b) R.H.Mitchell, T.Fyles, and L.M.Ralph, Can.J.Chem., **55**, 1480 (1977); (c) B.C.Berris, G.H. Hovakeemian, Y.-H. Lai, H.Mestdagh, and K.P.C.Vollhardt, J.Amer.Chem.Soc., **107**, 5670 (1985).

t (8) J.M.Saveant, Acc.Chem.Res., **13**, 323 (1980).

(9) (a) R.Gompper and R.Guggenberger, Tetrahedron, **42**, 849 (1986); (b) D.O.Cowan, C.LeVanda, J.Park, and F.Kaufman, Acc.Chem.Res., **6**, 1 (1973); c) see ref. 34.

(10) (a) Fry, A.J., in Fry, A.J. and Britton, W.E., Eds. "Topics in Organic Electrochemistry"; Plenum Press: New York, in press; (b) Fry,A.J.;Powers,T.A.;Mullen,K.;Irmen,W. Tetrahedron Lett., **26**, 4879 (1985); (c) A.J.Fry, J.Simon, M.Tashiro, T.Yamato, R.H.Mitchell, T.W.Dingle, R.V.Williams, R.Mahedevan, Acta Chem.Scand., **37B**, 445 (1983).

(11) A.S.Shawali, W.C.Herndon, and C.Parkanyi, Electrochim.Acta, **27**, 817 (1982).

(12) M.J.S.Dewar, J.A.Hashmall, and N.Trinajstic, J.Amer.Chem.Soc., **92**, 5555 (1970).

(13) A. Streitwieser, Jr., J.Amer.Chem.Soc., **82**, 4123 (1960).

(14) A. Streitwieser, Jr.and P.M.Nair, Tetrahedron, **5**, 149 (1959).

(15) (a)G.V.Boyd, N.Singer, Tetrahedron, **22**, 3383 (1966); (b). J. Koutecky, Electrochim.Acta, **13**, 1079 (1958).

(16) (a) A.Minsky, A.Y.Meyer, R.Poupko, and M.Rabinovitz, J. Amer. Chem. Soc. **105**, 2164 (1983); (b) A.Minsky, A.Y.Meyer, K.Hafner, and M.Rabinowitz, J. Amer. Chem. Soc., **105**, 3975 (1983).

(17) B.M.Trost, G.M.Bright, C.Frihart, and D.Britelli, J. Amer. Chem. Soc., **93**, 737 (1971).

(18) I. Bergman, Trans. Faraday Soc., **50**, 829 (1954).

(19) Streitwieser[6] and Hoijtink[5] also excluded zethrene from their correlation lines.

(20) Eq 4 is cast in a form appropriate for computing half-wave potentials under Bergman's conditions. To compute the half-wave potential of an unknown substance in a dipolar aprotic solvent relative to SCE, change the last term of eq 4 to -0.684.

(21) (a) A.G. Anderson,Jr. and G.M.Masada, J. Org. Chem., **39**, 572 (1974); (b) Anderson and Masada[21a] mistakenly used HOMO, not LUMO, energies in their analysis, but the compounds examined by them would not have fit the Huckel correlation line any better had LUMO energies been used.

(22) The computer program (OMEGAMO) used in this work was Quantum Chemistry Program Exchange (QCPE) # 110. Our revised version of QCPE 110, which uses the treatment of Boyd and Snyder for the bond order-bond length-exchange integral relationship (equations 17 and 18 of ref 15a) and uses an improved matrix diagonalization method, is being filed with QCPE. Serena Software, 489 Serena Lane, Bloomington, IN 47401, distributes a modified Huckel program for the IBM PC which corrects exchange integrals to match bond orders, but does not adjust Coulomb integrals. This program should handle alternant non-benzenoid hydrocarbons about as well as QCPE 110 does, but very likely will not handle non-alternants as well. It could be easily modified to do so, however.

(23) Hoijtink[5] concluded that the poor fit of azulene to the Huckel line is associated with ring strain in azulene, but the fact that we can fit azulene to the benzenoid line using the modified HMO technique demonstrates that strain is not a factor in this case at least.

(24) K.Hafner and H.U.Suss, Angew.Chem.Int.Ed.Engl., **12**, 575 (1973).

(25) E.Heilbronner, in D.Ginsburg, Ed., "Non-Benzenoid Aromatic Compounds", Interscience: New York, 1959, p.251.

(26) Ref. 1b, p. 79.

(27) F.Gerson, J.Lopez, and A.Metzger, Helv.Chim.Acta, 63, 2135 (1980).

(28) I.Willner, J.Y.Becker, and M.Rabinovitz, J.Amer.Chem.Soc., 101, 395 (1979).

(29) Ref. 2, p.178.

(30) R.L.Blankespoor, J.Org.Chem., 50, 3010 (1985).

(31) S.F.Nelsen and J.P.Gillespie, J.Amer.Chem.Soc., 95, 1874 (1973).

(32) J.Mortensen and J.Heinze, Angew.Chem.Int.Ed.Engl., 23, 84 (1984).

(33) D.F.Shriver, D.E.Smith, and P.Smith, J.Amer.Chem.Soc., 86, 5153 (1964).

(34) K.Nakasuji, K.Yoshida, and I.Murata, J.Amer.Chem.Soc., 104, 1432 (1982).

(35) (a) K.Ankner, B.Lamm, B.Thulin, and O.Wennerstrom, .J.Chem.Soc.Perkin II, 1301 (1980); (b) U.Norinder, D.Tanner, B.Thulin, and O.Wennerstrom, Acta Chem.Scand., 35B, 403 (1981); (c) B.Thulin, J.Chem.Soc.Perkin I, 664 (1981); (d) I.Raston and O.Wennerstrom, Acta Chem.Scand., 36B, 655 (1982).

(36) R.Breslow, R.W.Johnson, and A.Krebs, Tetrahedron Lett., 3443 (1975).

(37) J.F.M.Oth, K.Mullen, H.Konigshofen, J.Wassen, and E.Vogel, Helv.Chim.Acta, 57, 2387 (1974).

(38) D.Tanner, O.Wennerstrom, and E.Vogel, Tetrahedron Lett., 1221 (1982).

(39) R.W.Johnson, J.Amer.Chem.Soc., 99, 1461 (1977).