

529. *Molecular-orbital Calculations for Some Aromatic Hydrocarbons. Part I.*

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Molecular-orbital calculations of π -electron densities, mobile bond orders, free valencies, resonance energies, and spectra are presented for the hydrocarbons *s*-indacene, *as*-indacene, pyracylene, and dibenzopyracylene. The results are used to predict the chemical properties of the molecules. Comparisons are drawn between the electronic structures of these four molecules and other related non-alternant hydrocarbons.

The observed spectrum of dibenzopyracylene agrees surprisingly well with that calculated by the simplest L.C.A.O. approximation.

In two earlier papers (Brown, *Trans. Faraday Soc.*, 1949, **45**, 296; 1950, **46**, 146) the results of molecular-orbital calculations were presented for four simple non-benzenoid hydrocarbons with a view to predict their chemical properties. In the present paper this study is extended to four additional non-benzenoid hydrocarbons. The results are of particular interest because one of the compounds considered has recently been synthesised (Clar, Stubbs, and Tucker, *Nature*, 1950, **166**, 1075) and so offers a further opportunity to test the reliability of the simplest molecular-orbital approximation, in particular when used to predict the chemistry of non-alternant hydrocarbons. So far the only study of the substitution in a non-alternant hydrocarbon is that of azulene (Anderson and Nelson, *J. Amer. Chem. Soc.*, 1950, **72**, 3824), which confirms some of the properties predicted by the M.O. approximation (Brown, *Trans. Faraday Soc.*, 1948, **44**, 984).

Method of Computation.—The usual L.C.A.O. approximation (Coulson and Longuet-Higgins, *Proc. Roy. Soc.*, 1947, *A*, **191**, 39) was employed; some complementary details of the method have been summarised elsewhere (Brown, *Austral. J. Sci. Res.*, 1949, *A*, **2**, 564). The Coulomb integrals of all atoms and the resonance integrals of all bonds were taken to be the same, no attempt being made to correct the former for the variation of the charges, q , from unity, or to correct the resonance integrals for variations in mobile bond order, p . The energy quantities were computed, the overlap integral, S , between adjacent atomic orbitals being assumed to be (i) zero, and (ii) 0.25. The symbolism employed to distinguish these two cases has already been described by the author (*loc. cit.*, 1950). The calculated values of p and q are independent of the value assumed for S (Löwdin, *J. Chem. Physics*, 1950, **18**, 365; Chirgwin and Coulson, *Proc. Roy. Soc.*, 1950, *A*, **201**, 196). For the sake of uniformity the free valency numbers, F , were computed by using $N_{\max.} = 4.680$ (see Brown, *Trans. Faraday Soc.*, 1949, **45**, 296), although theoretically $3 + \sqrt{3}$ is preferable.

The assumptions implied in the correlation of the various theoretically-defined M.O. quantities with chemical properties have been discussed (Brown, *loc. cit.*, 1950). Again, a high value of F has been taken to indicate a high homolytic reactivity although the precise significance of free valency is still *sub judice*.

An interesting case of accidental degeneracy occurs in both pyracylene and dibenzopyracylene. The degeneracy occurs in both molecules in the totally symmetric factor of the secular determinant. Consequently, care must be taken to select orthogonal solutions in calculating q and p . In the author's experience this behaviour is unique in such small molecules,* the only cases previously encountered being degeneracies among energy levels of different symmetry classes, when the solutions are of course necessarily orthogonal.

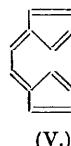
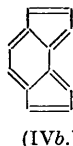
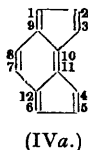
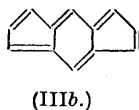
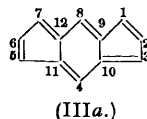
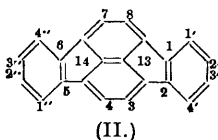
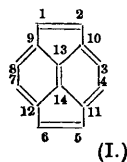
Nomenclature.—The hydrocarbon $C_{14}H_8$ (I) has not hitherto been prepared. Attempts were made to prepare the 1 : 2 : 5 : 6-tetrahydro-derivative by Fleischer and Wolff (*Ber.*, 1920, **53**, 925), who suggested the name pyracene for this reduced derivative. From analogy with acenaphthylene and acenaphthene the name *pyracylene* suggests itself for (I). The compound synthesised by Kloetzel and Chubb (*J. Amer. Chem. Soc.*, 1950, **72**, 150) could then be termed 1 : 2-dihydro-4 : 5-benzopyracylene instead of 1 : 2-dihydrocyclopenta[*cd*]fluoranthene, and the compound (II) could be termed 1 : 2-5 : 6-dibenzopyracylene in preference to bis*peri*phenylene-naphthalene.

Results.—The hydrocarbons studied were *s*-indacene (III), † *as*-indacene (IV), pyracylene (I),

* It is, however, found in the higher polyphenyls and other large molecules.

† That is, the "Ring Index" indacenes, $C_{12}H_8$, and not the compounds $C_{12}H_{10}$ often called indacenes.

and 1:2-5:6-dibenzopyracylene (II). We first consider *s*-indacene. The resonance-energy data (see table) show that *s*-indacene is more stable than its *as*-isomer, a result which can be explained qualitatively in terms of the simplest "resonance" concepts. *s*-Indacene has two equivalent most stable contributing structures, (IIIa) and (IIIb), as does benzene. On the other hand, the two most stable contributing structures, (IVa) and (IVb), for *as*-indacene are



Resonance energies.

Hydrocarbon.	$R(-\beta)$.	$R'(-\gamma)$.	Hydrocarbon.	$R(-\beta)$.	$R'(-\gamma)$.
<i>s</i> -Indacene	4.2314	1.9757	1:2-5:6-Dibenzopyracylene	9.2842	4.5865
<i>as</i> -Indacene	3.8987	1.6912	Difulvyl	3.4680	1.5472
Pyracylene	5.4156	2.5578			

not equivalent. The mobile-order results (see below) indicate a greater contribution from (IVb). It is of interest in view of this to compare the resonance energy of difulvyl (V), which has for convenience been included in the above table. The increase in R' for indacene is -0.14γ , considerably smaller than the increase (-0.29γ) accompanying the analogous structural change from stilbene to phenanthrene.

The π -electron densities, q , the free valencies, F , and mobile orders, p , of *s*-indacene are listed in the following table. The data for q indicate a high electrophilic reactivity at position 2

s-Indacene.

Position.	q .	F .	Bond.	p .	Position.	q .	F .	Bond.	p .
1	0.952	0.480	1:2	0.658	4	0.776	0.490	4:10	0.595
2	1.109	0.363	9:1	0.542	9	1.106	0.075	9:10	0.468

(position 9, of course, does not carry a hydrogen to be substituted), while position 4 should be most susceptible to nucleophilic attack; methyl groups in this position would be expected to be relatively reactive with aldehydes for example. The free valencies point to homolytic attack at position 4 also. Comparison of the charge-density data with the corresponding results for pentalene (Brown, *loc. cit.*, 1949) reveals that the insertion of a benzene ring between the two five-membered rings leaves the relative charge distribution in the latter unaltered. The mobile orders show that the bonds are all relatively inert so that reaction with osmium tetroxide will not occur.

The corresponding results for *as*-indacene are tabulated below. For this molecule we should expect electrophilic substitution to occur at position 2 and nucleophilic reactivity to be greatest at position 7, as judged by the π -electron densities. The free valencies are all unusually

as-Indacene.

Position.	q .	F .	Bond.	p .	Position.	q .	F .	Bond.	p .
1	1.043	0.501	1:2	0.790	7	0.811	0.475	3:10	0.676
2	1.069	0.385	2:3	0.495	9	0.988	0.126	9:10	0.464
3	0.978	0.501	7:8	0.503	10	1.111	0.124	8:9	0.702
								10:11	0.416

high and indicate position 3 as the centre of radical attack. In this case the bond orders show a much greater variation and indicate a high reactivity for the 1:2 bond. The mobile order of

this bond (0.790) is similar to that of the reactive bonds in angular polycyclic hydrocarbons and so *as*-indacene might be expected to react with osmium tetroxide.

Comparison of these results with those for the interesting hydrocarbon fulvalene (Brown, *loc. cit.*, 1949; *Nature*, 1950, **165**, 566) shows that the addition of the ethylene bridge leaves the π -electron densities in the five-membered rings qualitatively unaltered, although there is a considerable rearrangement in the bond orders.

We now consider pyracylene (I), for which the results are given below. They indicate positions 1 and 3 as the sites of electrophilic and nucleophilic substitutions, and greatest homolytic reactivity at position 3. The mobile orders indicate a high reactivity for the 1:2-bond. For comparison, the positions in acenaphthylene corresponding to 1 and 3 in pyracylene have q values of 1.066 and 0.909, respectively, and the order of its 1:2-bond is 0.796 (the data for acenaphthylene given by Sandorfy, *Compt. rend.*, 1948, **227**, 198, would appear to contain a numerical error). This shows that the addition of the ethylene bridge to

Pyracylene.

Position.	q .	F .	Bond.	p .	Position.	q .	F .	Bond.	p .
1	1.042	0.444	1:2	0.830	9	0.996	0.106	9:1	0.406
3	0.917	0.417	3:4	0.610				10:3	0.652
								13:14	0.531
								9:13	0.516

acenaphthylene does not very greatly disturb the electronic structure of the molecule. Pyracylene may alternatively be considered to be derived from fulvalene by addition of two ethylene bridges; comparison with the data for fulvalene (*loc. cit.*) reveals great reorganisation of the π -electrons accompanying this structural change. Pyracylene differs from *as*-indacene by an ethylene bridge, and here again the π -electron densities and mobile orders of corresponding positions show a marked similarity in these two molecules.

1:2-5:6-Dibenzopyracylene.

Position.	q .	F .	Bond.	p .	Position.	q .	F .	Bond.	p .
1'	0.988	0.388	1':2'	0.665	9	1.001	0.122	1:2	0.565
2'	1.003	0.359	2':3'	0.656	14	1.050	0.104	1:9	0.385
3	0.958	0.395	3:4	0.631				9:13	0.520
1	1.026	0.103	1:1'	0.627				8:9	0.654
								13:14	0.536

Finally, we consider dibenzopyracylene. The dibenz-annulation is seen (table) to have the effect of making the π -densities more uniform. We should expect electrophilic attack at positions 2' and nucleophilic substitution at position 3, but the values of q are so similar that the self-atom-polarisabilities may well be more important in determining the course of substitution reactions. The free valencies indicate high homolytic reactivity at position 1'. It will be noticed that the mobile orders are all lower than the benzene value of 0.667, so we should expect dibenzopyracylene to be inert to bond reagents such as osmium tetroxide. These predictions for dibenzopyracylene are of particular interest since the synthesis of this compound has recently been announced, and the ultra-violet absorption spectrum published (Clar, Stubbs, and Tucker, *loc. cit.*). The spectra of the compounds whose chemistry has just been considered are listed below. These results have been derived by the simplest L.C.A.O. treatment, including overlap, but not antisymmetrizing or allowing for configurational interaction. These latter refinements seem to be rather important in the case of small alternant hydrocarbons such as butadiene (Parr and Mulliken, *J. Chem. Physics*, 1950, **18**, 1338), benzene (Parr, Craig, and Ross, *ibid.*, p. 1561), and naphthalene (Jacobs, *Proc. Physical Soc.*, 1949, **62**, 710), and presumably the same applies to larger hydrocarbons, including non-alternants. However, such an elaborate treatment would be extremely tedious for molecules as large as those considered here, and there is some evidence (Pullman, *Compt. rend.*, 1949, **229**, 887) that the present semi-empirical approach is reasonably good for larger hydrocarbons.

There is little point in discussing the first three spectra apart from pointing out that the results for pyracylene will be particularly unreliable since there is an accidental degeneracy for two of the B_{2u} levels (see above). In this case configurational interaction will be of particular importance in determining the position of these levels relative to the others. In the case of dibenzopyracylene, however, the spectrum has already been observed experimentally and the observed band positions have been converted into transition energies for inclusion in the table.

Absorption spectra.

Hydrocarbon.	Transition.*	Transition energy, ev.		Polarization.*
		Calc. †	Found.	
<i>s</i> -Indacene	$A_g - B_{3g}$	1.8	—	forbidden
	$A_g - B_{1u}$	1.8	—	<i>z</i>
	$A_g - B_{2u}$	3.0	—	<i>y</i>
<i>as</i> -Indacene	$A_1 - B_2$	0.2	—	<i>y</i>
	$A_1 - B_2$	2.0	—	<i>y</i>
	$A_1 - A_1$	2.6	—	<i>z</i>
Pyracylene	$A_g - B_{3g}$	1.3	—	forbidden
	$A_g - B_{1u}$	2.7 ‡	—	<i>y</i>
	$A_g - B_{1u}$	2.7	—	<i>z</i>
Dibenzopyracylene	$A_g - B_{3g}$	2.4	2.5	forbidden
	$A_g - B_{1u}$	2.5	3.0	<i>z</i>
	$A_g - B_{2u}$	3.4	4.3	<i>y</i>

* The yz plane has been taken to correspond to the molecular plane. Where there are two symmetry axes in the molecular plane the z axis is taken to be the longer dimension of the molecule.

† The transition energies have been converted into ev. by use of the conversion factor $-\gamma = 3.4$ ev. which was employed by Brown (*loc. cit.*, 1950).

‡ In the approximation employed there is here an accidental degeneracy of two excited B_{2u} levels.

The agreement is quite good, the more so because the first transition has an intensity of the order of magnitude expected for a symmetry-forbidden transition, while the other two have the appearance of permitted transitions. A similar agreement with observation was found in the case of diphenylene (*Trans. Faraday Soc.*, 1950, **46**, 146). Such results suggest that the simple M.O. treatment of spectra may be reasonably satisfactory for larger molecules where it is impracticable to carry through the more complete treatment incorporating configurational interaction.

APPENDIX.

For convenience, the following data are added.

Energies (β) of the occupied molecular orbitals.

<i>s</i> -Indacene.		<i>as</i> -Indacene.		Pyracylene.		Dibenzopyracylene.	
2.4383	1.1386	2.4605	1	2.5616	1	2.6597	1
2	0.6180	1.9377	0.8323	2	1	2.3315	1
1.3028	0.6180	1.1442	0.3046	1.7321	0.4142	1.8549	1
				1		1.7746	0.6180
						1.5208	0.5798
						1.3028	

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