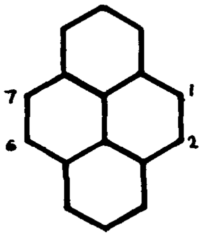
Tetrahedron Letters No. 14, pp. 901-904, 1963. Pergamon Press Ltd.
Printed in Great Britain.

L.C.A.O. - M.O. CALCULATIONS ON PYRENE BENZOLOGUES

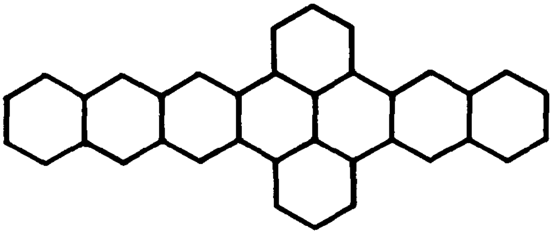
T. H. Goodwin and D. A. Morton-Blake
Chemistry Department, The University, Glasgow, W.2.

(Received 13 March 1963)

AT the suggestion of Dr. E. Clar, we have carried out some calculations on a number of benzologues of pyrene (I)



I



II

in which benzenoid rings are annelated linearly in the 1:2 and 6:7 positions. These have all been found by Clar and his co-workers[1] to have ultra-violet absorption spectrum bands, the positions of which are remarkably independent of the number of rings on the shorter side. If these molecules were thought of as dibenzoacenes this result would not be anticipated, as the absorption spectra would be expected to exhibit a resemblance to those of the corresponding parent acenes and to show marked and progressive displacement towards longer wave-lengths with increasing length of the acene chains. Moreover, the

---

[1] E. Clar, J.-F. Guye-Vuillème, A. McCallum, and I. A. Macpherson (private communication).

positions of the absorption bands of the pyrene benzologues are very different from those of acenes having the same number of collinear rings, thus showing that the former are not just simple derivatives of the latter.

For convenience we shall adopt the following system to describe the pyrene benzologues: if the molecule can be regarded as pyrene with n annelated benzene rings on one side and m on the other (m not greater than n) we shall denote it as nPm. Naphtho-[2'.3':1.2]anthraceno-[2".3":6.7]pyrene (II) will therefore be written 3P2.

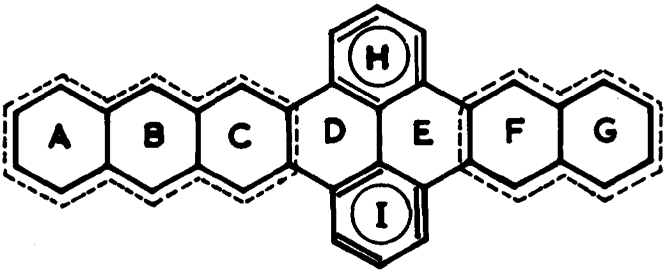
Calculations by the simplest Hückel method, *i.e.* with all overlap integrals neglected and all interaction integrals between orbitals on neighbouring atoms assumed equal to β_0, show moderate consistency in the energies of the highest occupied molecular orbitals, and hence in the transition energies of Clar's p-bands (highest occupied level to lowest unoccupied). If, however, we recognise a fundamental asymmetry[2] in the fully-aromatic benzenoid rings by allotting β-values in accordance with tendency towards the development of single-bond and double-bond character, then much more consistent results obtain.

The molecule 3P2, for example, was supposed to have an electronic structure indicated diagrammatically at (III). The bonds shown as single in rings D, E, H, I are, rather arbitrarily, assigned the value $0.8\beta_0$, those shown as double $1.1\beta_0$ (for pure single and double bonds the assignments would be $0\beta_0$ and $1.20\beta_0$ respectively)

---

[2] E. Clar, *Tetrahedron*, **5**, 98 (1959); **18**, 1471 (1962) etc.

while those forming part of a delocalised acene system[3] and enclosed by broken lines are taken to have values β_o. The "double" bonds in rings H and I have been assumed to



III

have such positions as to provide an induced aromatic sextet[2] in ring D, thus leaving ring E formally empty in accordance with Clar's picture of these molecules.

The π-bond energies $(E - \alpha)$ of the highest occupied molecular orbitals calculated for the pyrene series 3Pm, 2Pm are given in the table together with the measured wavelengths of the p-bands. The consistency of the calculated energies in column 3 is seen to parallel that of the observed wavelengths in column 4. This appears to give strong support to Clar's picture of the aromatic hydrocarbons and, in particular to his conclusion regarding the asymmetry of the benzene ring.

---

[3] E. Clar, Aromatische Kohlenwasserstoffe, p. 79, Springer-Verlag (1952).

MOLECULE	$\alpha - E$(units of β_o) Simplest Hückel	$\alpha - E$(units of β_o) Improved Hückel	Longest p-wavelength measured (Å)
3P3	0.3391	0.3629	4420
3P2	0.3549	0.3656	4390
3P1	0.3570	0.3658	4390
3P0	0.3587	0.3663	4420
2P2	0.4762	0.5117	3420
2P1	0.5009	0.5147	3410
2P0	0.5053	0.5168	3450

The method is being extended to other aromatic hydrocarbon systems.

One of us (D. A. M.-B.) thanks the D.S.I.R. for a maintenance grant.