A Prediction of the Reactivity of Some Penta- and Hexa-cyclic Hydrocarbons.

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Dewar's simplified M.O. treatment has been applied to more complex polycyclic hydrocarbons, *viz.*, anthanthrene, the five dibenzophenanthrenes, the five dibenzopyrenes, and zethrene. Results obtained have been correlated with the geometry of the systems. Some recorded experimental results are discussed, including the abnormal acidity of 1 : 2-6 : 7-dibenzopyren-3-ol and the structure of the cation formed by zethrene in acid media.

The simplified molecular-orbital method devised by Dewar (*J. Amer. Chem. Soc.*, 1952, **74**, 3357; *Ann. Reports*, 1951, **48**, 116; "Progress in Organic Chemistry," ed. Cook, Butterworths Scientific Publ., London, 1953, Vol. II, p. 1) for the evaluation of the reactivity of the substituent positions of even alternant hydrocarbons has given results in excellent general agreement with experiment. The present contribution is an extension of the method to some higher ring systems.

3 : 4-8 : 9-Dibenzopyrene (I) is substituted readily in the 5- and the 5 : 10-positions (Ioffe and Efros, *J. Gen. Chem., U.S.S.R.*, 1946, **16**, 111). ΔE_π values * were accordingly determined by Dewar's (*loc. cit.*) procedure; the lowest value was found for the 5-position, in agreement with experiment. Further, the observed value of ΔE_π $(1{\cdot}01\beta)$ is lower than for any other hydrocarbon previously investigated (except pentacene), and the dibenzopyrene (I) should therefore be very reactive. This hydrocarbon is further of interest because of its carcinogenic properties (Kleinenberg, *Arch. Sci. biol., U.R.S.S.*, 1938, **51**, No. 3, 127; 1939, **56**, No. 3, 39; Tretyakova, *Bull. Biol. Med. Exp. U.R.S.S.*, 1941, **11**, 496; *Chem. Abs.*, 1947, **41**, 6621).

Evidence concerning the "reactivity" of 1 : 2-6 : 7-dibenzopyrene (II) is indirect: Clar (*Ber.*, 1943, **76**, 609) showed that the acidity of its 3-hydroxy-derivative is abnormally low for a polycyclic phenol. ΔE_π values of the various positions of (II) were therefore obtained: as can be seen, the 3-position should be most readily substituted. Normally a tendency for substitution at a given position is related to the extent of conjugation between the ring system and a substituent group in that position. It follows that the 3-phenol of (II) ought to have the highest acid strength, comparable with that of α-naphthol. The abnormal acidity must be connected with the sterically hindered nature of this position. The large hydroxyl group will almost certainly be displaced out of the plane of the rings by steric interference with the hydrogen atom in the 4′-position and this (cf. Dewar, *loc. cit.*; Brown, *J.*, 1952, 2231; Guy, *J. Chim. phys.*, 1949, **46**, 469) would lower the conjugative interaction between the *p*-electrons of the hydroxyl-oxygen atom and the π-electron system of the polycyclic hydrocarbon residue. In this manner the low acidity of 3-hydroxy-1 : 2-6 : 7-dibenzopyrene is accounted for, as well as the surprisingly similar absorption spectrum of the phenol and the parent hydrocarbon (Clar, *loc. cit.*). In a like manner, other sterically hindered derivatives of polycyclic hydrocarbons may be predicted to behave abnormally: *e.g.*, the 4-derivatives of phenanthrene and the 1-derivatives of triphenylene should show a low acidity of the hydroxy- and carboxy-derivatives, and a high basic strength for the amines. Steric hindrance can be appreciable in the 1-triphenylene position, as Rapson (*J.*, 1941, 15) showed that 1-methoxytriphenylene resisted demethylation. However, it is possible, in these simpler cases, that conjugation occurs to an appreciable extent, with buckling of the ring system (as in the related cases of "intramolecular overcrowding;" cf. Newman *et al.*, *J. Amer. Chem. Soc.*, 1947, **69**, 978, 3023; 1948, **70**, 1913; 1949, **71**, 3664; 1952, **74**, 3225; Bell and Waring, *J.*, 1949, 2689; Badger, Campbell, Cook, Raphael, and Scott, *J.*, 1950, 2326; Hernik, Herbstein, and Schmidt,

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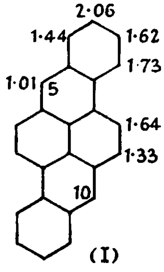
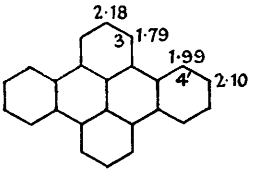
* $\Delta E_\pi = \pi$-electron localisation energy (in terms of β) at the point of attack $= 2\beta(a_1 + a_2) = 2\beta S$, where a_1 and a_2 are the NBMO coefficients of the transition state (as visualised by Wheland, *J. Amer. Chem. Soc.*, 1942, **64**, 900) at the carbon atoms next to the one substituted (cf. Dewar, *locc. cit.*).

Nature, 1951, **168**, 158), in which case the 3-hydroxydibenzopyrene would be abnormal owing to the greater rigidity of the ring system (II).

The data for the isomeric dibenzopyrenes are given in (III—V), and those for the related anthanthrene in (VI). The study of 1 : 12-benzoperylene (VII) appeared relevant on account of the formation of alkyl derivatives of unknown orientation from zinc dust fusion of erythroaphin-*sl* (Brown, Johnson, Quayle, and Todd, *J.*, 1954, 107). Certain pentacyclic hydrocarbons which were not investigated by Dewar, *viz.*, (VIII—XII), are also included. Not only were theoretical data available for only one of these known substances,* but they would prove of value in testing a proposed correlation between predicted reactivity and the geometry of polycyclic hydrocarbons. Such a correlation can now be stated : the reactivity of even complex systems can be predicted qualitatively by reference to simpler component structures.



(I)



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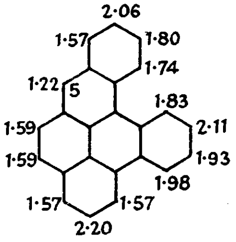
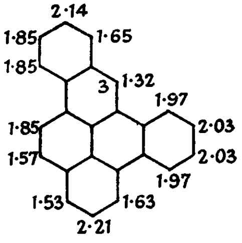


(III)



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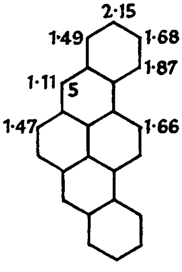

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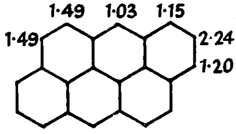

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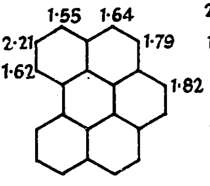
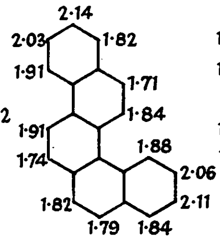


(VII)



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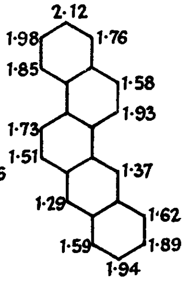

(IX)

Thus, in anthanthrene and each of the dibenzopyrenes the most reactive carbon atom corresponds to the *meso*-position in anthracene. For the derivatives of pyrene, this position corresponds also to one of the four most reactive positions of pyrene itself (in which these are equivalent). In this fashion the susceptibility to substitution of a position may be regarded as an additive property of component structures.

By angular superposition of two naphthalene structures the reactivity of the phenanthrene positions can be gauged : 9- (one α plus one β), 1- and 4- (one α), and 2- and 3- (one β), which is roughly the sequence of ΔE_π values quoted by Dewar (*loc. cit.*).

According to Dewar's ΔE_π values, the most reactive component hydrocarbon of 1 : 2-benzonaphthacene is naphthacene; this has four equivalent very reactive *meso*-positions, which in this benzo-derivative are different. To determine which of these will be the most reactive, the structure is separated into two components, either a naphthalene and a phenanthrene (division at *a* in XIII), or into an anthracene and a naphthalene unit (*b*) : in both cases the 9- and the 10-position are the most reactive. Choice between these two is obtained by consideration of a third component system, benzene and 1 : 2-benzanthracene (*c*). By using the analogy with 1 : 2-benzanthracene it will be concluded that

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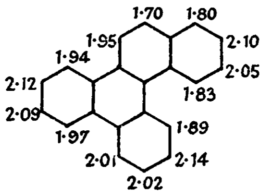
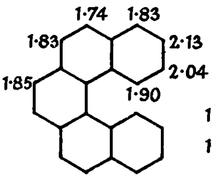
* 1 : 2-3 : 4-Dibenzophenanthrene (X) was examined by Buu-Hoï, Daudel, and Vroelant (*Bull. Soc. chim.*, 1949, 211) by the method of molecular diagrams, and reactivity predicted in the sequence $8 > 5 = 1' = 4' = 1'' = 4'' > 9 > 10 > 6 = 7 = 2' = 3' = 2'' = 3''$, these differing appreciably from our results. This hydrocarbon is of interest on account of its carcinogenic nature (Harris and Bradsher, *Cancer Res.*, 1946, **6**, 671).

ΔE_π values of the positions of 1 : 2-benzonaphthacene should increase in the sequence $10 < 9 < 11 < 12$, etc., as found by Dewar (*loc. cit.*).

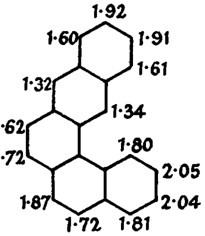
This method of geometrical analysis of investigating " reactivity " has been applied to all the hydrocarbons mentioned in this paper, and those given by Dewar (*loc. cit.*), and only a verv few exceptions were noted.



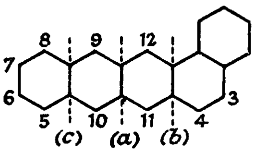
(X)



(XI)



(XII)



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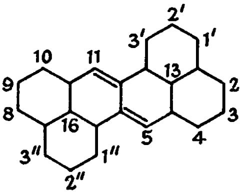
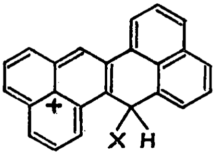
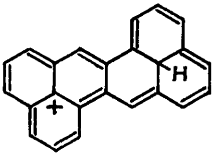


(XIV)



(XIVa)



(XIVb)

Zethrene.—Clar's hydrocarbon zethrene (*op. cit.*) (XIV), being a system where two naphthalene residues are linked by a butadiene bridge in each Kekulé structure, should exhibit high reactivity on account of the apparent bond localisation (cf. Dewar and Longuet-Higgins, *Proc. Roy. Soc.*, 1952, **214**, *A*, 482; Dewar, *loc. cit.*). Analysis of zethrene by Dewar's procedure proved of interest. ΔE_π values for the 3′- (1·02β), 1′- (0·95β), 2- (0·86β), and 4-position (0·88β) were obtained in a normal fashion, the 2′- and the 3-position (2·12β) behaving like isolated β-naphthyl positions, whilst the 5-position, though abnormal in that $C_{(16)}$ becomes inactive with complete isolation of one naphthalene unit, gave $\Delta E_\pi = 0{\cdot}81\beta$, pointing to very high reactivity of the order of the *meso*-position in pentacene ($\Delta E_\pi = 0{\cdot}80\beta$, Dewar, *loc. cit.*). Coulson and Moser (*J.*, 1953, 1341) in a detailed M.O. investigation obtained the same sequence for free valences in the ground state of zethrene, pointing to the same sequence of reactivity in radical reactions. Here too (free valence for the 5-position = 0·210) the reactivity is to be expected to be appreciably higher than for, say, anthracene (free valence for the *meso*-position = 0·202; Burkitt, Coulson, and Longuet-Higgins, *Trans. Faraday Soc.*, 1951, **47**, 553). In an electrophilic substitution of zethrene by means of a reagent X^+, the transition state (XIV*a*) (Wheland, *loc. cit.*; cf. Dewar, *loc. cit.*), involving entry of the group at the 5-position, is resonance-stabilised, the formal charge being able to be written on seven carbon atoms.

In acid solution (XIV*a*; X = H) might be formed in this manner, and this could account for the formation of the " zethrenium " cation under acidic conditions (Clar, *op. cit.*, p. 95). This would require the hydrogen ion to be an electrophilic reagent, a behaviour which is now well established (Ingold, Raisin, and Wilson, *Nature*, 1934, **134**, 734; *J.*, 1936, 915, 1637; Gold and Long, *J. Amer. Chem. Soc.*, 1953, **75**, 4543). The present case differs from the examples of isotopic hydrogen exchange cited in that the transition state is apparently much more stable than usual, and elimination of a proton is not favoured. In Clar's alternate formulation of this cation (XIV*b*) (*op. cit.*), both naphthalene systems become degenerate and the hydrogen becomes attached to the somewhat hindered 13-position. In the absence of published experimental data, structure (XIV*a*) is therefore considered more likely for the " zethrenium " cation.

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