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STABLE π-ELECTRON SYSTEMS AND NEW AROMATIC STRUCTURES

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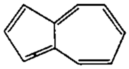
Abstract—Aromatic character, as expressed in the reactions of azulene and its derivatives, is correlated with the development, in the appropriate transition state, of a stable π-electron system (sextet) in the five- or the seven-membered ring.

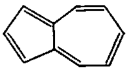
The recognition that considerable stability is associated with the ions and radical derived from perinaphthene leads to the formulation of several new types of hydrocarbons which may be expected to show aromatic character. A brief theoretical consideration of these hydrocarbons is given.

The synthesis of carbocyclic and heterocyclic derivatives of one of these hydrocarbons, *cyclo*-penta[*a*]perinaphthene, is outlined, and a detailed account of their properties is given.

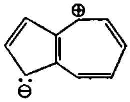
ASIDE from the benzenoid hydrocarbons, azulene and its derivatives constitute the only recognised class of condensed and fully conjugated cyclic hydrocarbons that show pronounced aromatic character. Although azulene is capable of representation as a hybrid of two equivalent, neutral and covalent forms, (Ia) and (Ib), aromatic character in this hydrocarbon has been correlated with effective contribution of dipolar structures, such as (Ic), to the description of the molecule in its reacting form[1] and in the ground state.[2] The implied polarisation of the molecule is considered to be the condition set by two opposing tendencies. The whole assemblage of π-electrons tends to partition itself into two stable π-electron systems (sextets) such that the five-membered ring should assume the form of the *cyclo*pentadienide anion (II), and the seven-membered ring that of the *cyclo*heptatrienylium cation (III). This is opposed by electrostatic forces that work towards the mutual annihilation of charges of opposite sign developed in the polarisation. The observed dipole moment[3] of azulene serves as the best evidence that the molecule is polarised in the ground state, but the low value of the moment ($\mu = 1{\cdot}0$ Debye) emphasises that dipolar forms, e.g. (Ic), contribute to a small extent only. The behaviour of azulene in reactions considered expressive of aromatic character indicates that it is during reaction that importance



I (a)



I (b)



I (c)

II

III

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[1] A. G. Anderson, Jr., J. A. Nelson and J. T. Tazuma, *J. Amer. Chem. Soc.* **75**, 4980 (1953).
[2] W. H. Stafford and D. H. Reid, *Chem. & Ind.* 277 (1954).
[3] G. W. Wheland and D. E. Mann, *J. Chem. Phys.* **17**, 264 (1949).

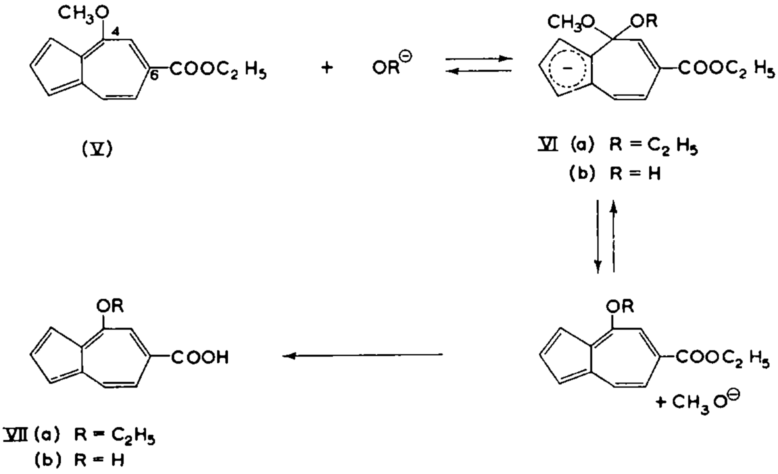
must be attached to the stability of π-electron sextets associated with the five- and seven-membered rings. In general, if attack at a site in one ring is accompanied by the development of a π-electron sextet in the other, the transition-state energy will be favourably low and reaction will be facilitated.

In substitution by an electrophilic reagent $R^{\oplus}$, a process known[1] to occur at (C_1), the transition state may be represented by the Wheland type of structure (IV) in which a sextet of π-electrons becomes associated with the now positively charged seven-membered ring.

(IV)

The characteristically high basicity of azulene is due to the stability of this type of transition state, here the azulenium ion[4] itself (IV, R = H), which results from an electrophilic attack in which the acid transfers a proton to (C_1) of the hydrocarbon base.

It has also been shown that nucleophilic replacement of substituents in the seven-membered ring of azulene may proceed under mild conditions. The ester obtained,[5] *inter alia*, by the action of ethyl diazoacetate on 4-methoxyindane, and considered on spectroscopic grounds to be 4-methoxyazulene-6-carboxylic acid ethyl ester (V), suffers ready replacement of the methoxy group when solvolysed by boiling ethanolic or aqueous potassium hydroxide to give, respectively, 4-ethoxy- and 4-hydroxy-azulene-6-carboxylic acid (VIIa and VIIb). These observations are rationalised by the following reaction scheme:



Nucleophilic attack at the effective site, (C_4), leading to the transition intermediate (VIa, R = C_2H_5; VIb, R = H), is rendered facile through delocalisation of the introduced negative charge by (*i*) the ester group attached to (C_6) and (*ii*) the formation of a π-electron sextet in the five-membered ring.

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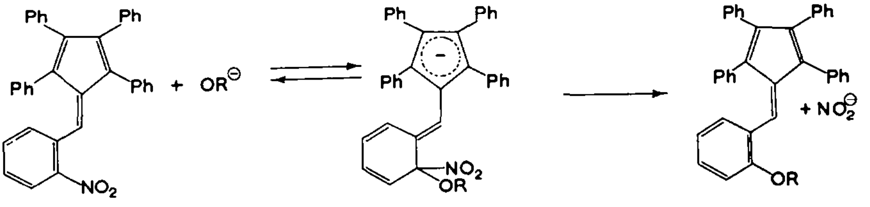
[4] E. Heilbronner and M. Simonetta, *Helv. Chim. Acta* 35, 1049 (1952).
[5] D. H. Reid, W. H. Stafford and J. P. Ward, *J. Chem. Soc.* 1100 (1958).

The view that the development of a π-electron sextet in the five-membered ring plays an important part in creating readily an electron-deficient centre at the point of attack (C_4) receives independent support from the observation that 1-*o*-nitrobenzylidene-2:3:4:5-tetraphenyl*cyclo*pentadiene (VIII) is converted to 1-*o*-alkoxybenzylidene-2:3:4:5-tetraphenyl*cyclo*pentadiene (IX, $R = CH_3$ or C_2H_5) by the action of a boiling solution of potassium alkoxide in the appropriate alcohol. The following representation is in accord with these observations:



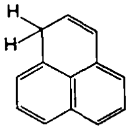
(VIII)

(IX, R=CH₃ or C₂H₅)

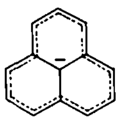
The common feature of the reactions considered is the assistance given to the nucleophilic substitution process by the formation of a π-electron sextet in the five-membered ring; this stabilises the negative charge introduced by the attacking reagent.

Aromatic character is therefore associated with stable π-electron systems that either exist already in the ground state, as in the benzenoid hydrocarbons, or are capable of development during reaction, as in the azulenes. In the aromatic hydrocarbons hitherto studied a single π-electron system, the π-electron sextet, has served in the interpretation of the chemistry of these compounds.

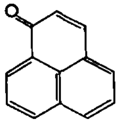
The possibility that other stable mobile-electron systems may be capable of existence has led us to prepare and study new classes of aromatic hydrocarbons in which positively and negatively charged structures other than simple five-, six- and seven-membered rings would serve as frameworks for the delocalisation of stable π-electron systems. In particular, it appeared that the perinaphthene nucleus might serve satisfactorily in both capacities, as judged from a study of the properties of compounds containing this nucleus. An important feature of the chemistry of such compounds is the tendency for the three six-membered rings to function as a structural unit in which a stable system of (fourteen, thirteen or twelve) π-electrons is developed during reaction. Perinaphthene (X) is acidic,[6] and when treated with strong bases, e.g. $CH_3O^{\ominus}$ and $C_6H_5^{\ominus}$, forms the red perinaphthenide anion (XI) in which fourteen π-electrons are delocalised over the tricyclic framework of thirteen carbon nuclei.



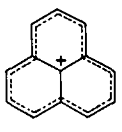
(X)



(XI)



(XII)



(XIII)

The modified carbonyl properties of perinaphthenone (XII) suggest that the perinaphthene nucleus may also give rise to a stable cation when associated with the

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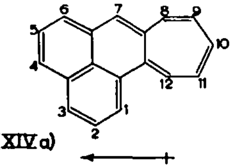
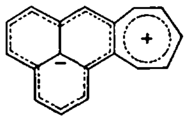
[6] V. Boekelheide and C. E. Larrabee, *J. Amer. Chem. Soc.* 72, 1245 (1950).

appropriate number of π-electrons. Perinaphthenone is unusually highly basic,[7] dissolving reversibly in concentrated hydrochloric acid, and the CO stretching frequency in the infra-red spectrum[8] is abnormally low (1637 cm^{-1}). These properties, reflecting an unusually high polarisation of the carbonyl group, imply that considerable stability must be attributed to the perinaphthenylium cation (XIII) in which twelve π-electrons are delocalised over the perinaphthene nucleus. The preparation in this laboratory of several compounds believed to contain the cation (XIII)[9] will be described below. As a result of the recognition of these stable structures (XI) and (XIII), several new types of potentially aromatic hydrocarbons may be arrived at theoretically, and these are as follows.



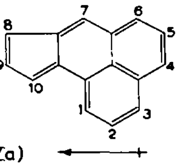
(XIVa)

Direction of π-electron migration



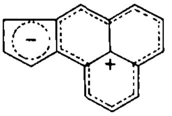
(XIV b)

(*i*) cyclo*Hepta*[a]*perinaphthene*. Fusion of the perinaphthene nucleus to a seven-membered ring gives the skeleton of *cyclo*hepta[*a*]perinaphthene (XIVa). In the completely polarised form of the hydrocarbon fourteen π-electrons are delocalised over the perinaphthene nucleus and a sextet of π-electrons is associated with the seven-membered ring. This limiting structure (XIVb) reflects the sense of the expected polarisation. It may be predicted that electrophilic attack will occur readily at one or more of the chemically recognisable positions (C_1, C_3, C_4, C_6 and C_7) on the periphery of the perinaphthene nucleus, and that the expected high basicity will be associated with the same position(s).



(XVa)

Direction of π-electron migration



(XV b)

(*ii*) cyclo*Penta*[a]*perinaphthene*. The hydrocarbon (XVa) results from fusion of a five-membered ring to the perinaphthene nucleus. In the completely polarised structure (XVb) a sextet of π-electrons is associated with the five-membered ring, which takes the form of the *cyclo*pentadienide anion (II), while the perinaphthene skeleton, embracing twelve π-electrons, assumes the form of the perinaphthenylium cation (XIII). Electrophilic attack is expected to take place at (C_{10}) or (C_8) or both, the positions at which proton uptake in acid media should occur most readily. The synthesis and study of several hydrocarbon and heterocyclic derivatives of *cyclo*-penta[*a*]perinaphthene is described below.

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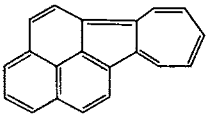
[7] E. Bamberger and M. Philip, *Liebigs Ann.* **240**, 178 (1887); J. W. Cook and C. L. Hewett, *J. Chem. Soc.* 365 (1934).

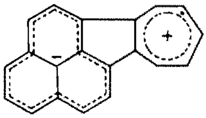
[8] N. H. Cromwell and G. V. Hudson, *J. Amer. Chem. Soc.* **75**, 872 (1953).

[9] D. H. Reid, *Angew. Chem.* 761 (1955); I. M. Aitken and D. H. Reid, *J. Chem. Soc.* 3487 (1956).

Owing to the re-entrant form of the periphery of the perinaphthene skeleton, a further two types of dipolar aromatic hydrocarbons are possible. These are *cyclo*hepta[*cd*]perinaphthene (XVIa) and *cyclo*penta[*cd*]perinaphthene (XVIIa), resulting from a new mode of union of the seven- and the five-membered rings, respectively, with the perinaphthene nucleus.

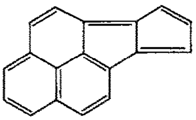


(XVI a)

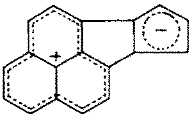


(XVI b)

(*iii*) cyclo*Hepta*[cd]*perinaphthene*. A new structural feature is the formal independence of the π-electron systems in the completely polarised form (XVIb). In this respect *cyclo*hepta[*cd*]perinaphthene differs from the dipolar hydrocarbons previously considered, viz., azulene (I), *cyclo*hepta[*a*]perinaphthene (XIV) and *cyclo*penta[*a*]perinaphthene (XV), in the the completely polarised forms of which a pair of π-electrons is common to both stable π-electrons systems. As in the case of *cyclo*hepta[*a*]perinaphthene, anionic reactivity, including basicity, is expected to be shown by the perinaphthene moiety.



(XVII a)



(XVII b)

(*iv*) cyclo*Penta*[cd]*perinaphthene*. *cyclo*Penta[*cd*]perinaphthene (XVIIa and completely polarised form XVIIb) may be similarly derived by union of a five-membered ring at adjacent positions, with the perinaphthene nucleus at a pair of peri-carbon atoms. Since a five-membered ring shows ionic stability only when associated with a sextet of π-electrons, anionic character and basicity will be shown by the five-membered ring in (XVIIa).

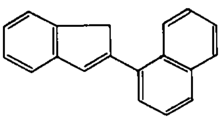
EXPERIMENTAL RESULTS

Indeno[2,1-a]*perinaphthene*[9] (XX)

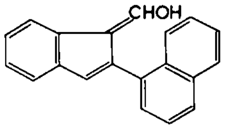
Two positions (C_8 and C_{10}) in the five-membered ring of *cyclo*penta[*a*]perinaphthene (XV) are expected to show nucleophilic reactivity, but they are not equivalent. Indeno[2,1-*a*]perinaphthene (XX), a ring homologue of (XV), possesses one chemically recognisable position in the five-membered ring, and a study of this hydrocarbon was undertaken first.

Synthesis. The reaction of indan-2-one and 1-naphthylmagnesium bromide followed by dehydration of the crude product gave 1-2′-indenylnaphthalene (XVIII), m.p. 90–91°. Condensation of this hydrocarbon with ethyl formate in the presence of potassium methoxide afforded the unstable hydroxymethylene derivative (XIX), which, when treated with 93% sulphuric acid, underwent peri-cyclisation to give indeno[2,1-*a*]perinaphthene (XX) as reddish-brown leaflets, m.p. 210–211°. A second, purple-black, hydrocarbon, m.p. 294–297°, was formed concomitantly in smaller amount. It has been shown to contain two nuclei of indeno[2,1-*a*]perinaphthene and probably possesses structure (XXI).

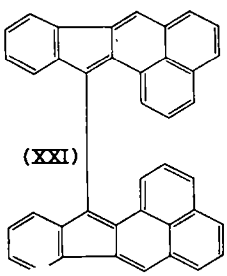
Basicity. The most characteristic property of indeno[2,1-*a*]perinaphthene is its high basicity. The hydrocarbon dissolves reversibly in strong acids, e.g., in 72% perchloric acid and 65% sulphuric acid, to form a green cation. A measure of the basicity was obtained by the procedure of Plattner *et al.*,[10] by which the hydrocarbon was partitioned between *cyclo*hexane and sulphuric acids of different strengths. A linear relation was found to exist between $\log_{10} K'$ (where K' is the apparent partition coefficient) and the Hammett acidity function H_0, and the slope of the straight line was found to approximate closely to two.[11] The H_0 value found (—4·80) for which K' is unity corresponds to an acid concentration of 64% w/w sulphuric acid; this value places indeno[2,1-*a*]perinaphthene alongside the azulenes in order of basicity.[12] In the light of the reasoning outlined above the conjugate acid is considered to possess structure (XXII), resulting from accession of a proton to (C_{12}). Addition of a proton at this position is accompanied by formation, in the perinaphthene nucleus, of the π-electron system present in the perinaphthenylium cation (XIII).



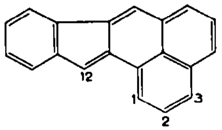
(XVIII)



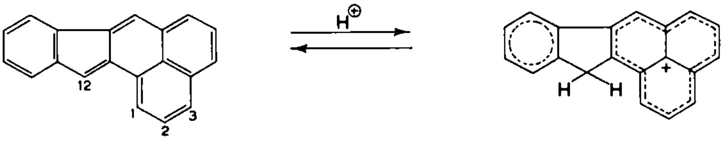
(XIX)



(XXI)



(XX)



(XX) (XXII)

Electrophilic substitution. Substitution occurs readily under mild conditions. The position involved has not yet been determined experimentally, but is held to be the 12-position.

A violet mononitroindeno[2,1-*a*]perinaphthene (XXIIIa), m.p. 186–190° (dec.), is formed at room temperature when (XX) in pyridine–ethanol solution is treated with tetranitromethane. The abnormally low value (1506 cm^{-1}) of the nitro group antisymmetrical N—O stretching frequency* in the infra-red spectrum is consistent with the view that the nitro group occupies the 12-position, structure (XXIIIb) contributing appreciably to the resonance hybrid.

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* An average value given for this vibration is 1518 cm^{-1} (see Randle and Whiffen[13]).

[10] P. A. Plattner, E. Heilbronner and S. Weber, *Helv. Chim. Acta* **32**, 574 (1949).

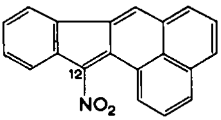
[11] V. Gold and F. L. Tye, *J. Chem. Soc.* 2181 (1952).

[12] D. H. Reid, W. H. Stafford and J. P. Ward, *J. Chem. Soc.* 1193 (1955).

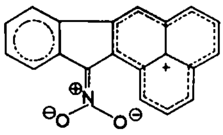
[13] R. R. Randle and D. H. Whiffen, *J. Chem. Soc.* 4153 (1952).

Acylation may be effected by reactive acid halides without the aid of catalysts normally required in reactions of the Friedel–Crafts type. By using acetyl bromide as the reagent a monoacetylindeno[2,1-*a*]perinaphthene was formed.

The course of halogenation is less well defined. Passage of bromine vapour in a stream of nitrogen into a solution of (XX) in carbon tetrachloride at room tempera-

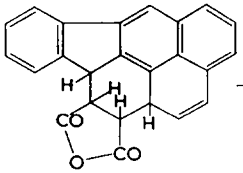


(XXIII a)

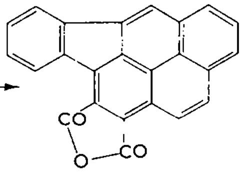


(XXIII b)

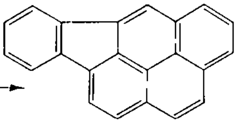
ture gave a mixture of monobromoindeno[2,1-*a*]perinaphthenes, one of which, however, constituted upwards of 95 per cent of the product. It has been established that the predominating isomer is either 1-bromoindeno[2,1-*a*]perinaphthene or 12-bromoindeno[2,1-*a*]perinaphthene, since bromine was lost and the anhydride (XXV) was formed in a Diels–Alder reaction (see next section) with maleic anhydride in nitrobenzene. On theoretical grounds the latter alternative structure is preferred.



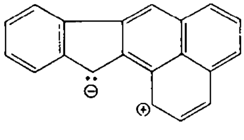
XXIV



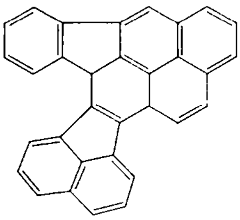
XXV



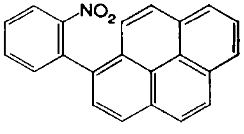
XXVI



XXIX



XXVIII



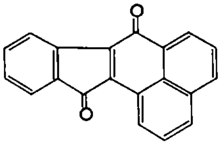
XXVII

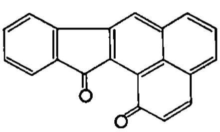
Diene reactivity. Indeno[2,1-*a*]perinaphthene functions readily as the diene in Diels–Alder reactions. Addition has been shown to involve the 1- and the 12-positions. Thus, with maleic anhydride in boiling xylene–acetic acid, it gives a colourless adduct (XXIV). This adduct was dehydrogenated by boiling nitrobenzene, and the resulting fully aromatic anhydride (XXV) was decarboxylated to the yellow hydrocarbon indeno[1,2,3-*cd*]pyrene (XXVI), m.p. 161·5–163°, whose structure was established with the aid of an independent synthesis. A crossed Ullmann reaction between 1-iodopyrene and *o*-bromonitrobenzene gave 1-*o*-nitrophenylpyrene (XXVII), which, by successive reduction to the corresponding amine, diazotisation and treatment with copper bronze, was converted into the same hydrocarbon (XXVI). The synthesis of indeno[1,2,3-*cd*]pyrene from 1-(1-hydroxymethylene-2-indenyl)naphthalene (XIX) and from 1-*o*-nitrophenylpyrene (XXVII) served to establish the constitution of both (XX) and (XXVI).

Other dienophiles that form adducts with (XX) include 1:4-benzoquinone, 1:4-naphthaquinone and 7-bromoacenaphthylene. The reaction of the last-mentioned compound with indeno[2,1-*a*]perinaphthene in nitrobenzene to form (XXVIII) represents the first recorded instance in which 7-bromoacenaphthylene has served as a dienophile.

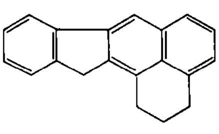
The very ready reactions of indeno[2,1-*a*]perinaphthene with dienophiles reflects the ease with which a pair of π-electrons may be localised at (C_1) and (C_{12}). It is suggested that, in accord with Robinson's views[14] on the mechanism of the Diels–Alder reaction, structure (XXIX) contributes significantly to the electronic description of the transition state.

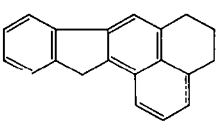
Oxidation. With chromic anhydride in acetic acid as the oxidising agent, quinone formation takes place. The resulting orange-red quinone, m.p. 290–292°, which gives a violet-blue vat with alkaline dithionite, possesses structure (XXX) or (XXXI). The infra-red spectrum is consistent with either structure. Two prominent bands occur in the CO region. One of these, occurring at 1704 cm^{-1}, is close to that of fluorenone[15] (1715 cm^{-1}). The other band appears at 1639 cm^{-1}, thus falling in the region in which perinaphthenones absorb characteristically.*


(XXX)


(XXXI)

Reduction. Chemical reduction of indeno[2,1-*a*]perinaphthene by zinc in acetic acid yielded a homogeneous dihydroindeno[2,1-*a*]perinaphthene, m.p. 169·5–171·5°. Further reduction by catalytic hydrogenation (platinic oxide in acetic acid) afforded a colourless tetrahydroindeno[2,1-*a*]perinaphthene which must possess structure (XXXII) or (XXXIII), since its ultra-violet spectrum resembles closely the ultra-violet spectra of 1:2- and 2:3-benzofluorene. If the possibility is precluded that the dihydroindeno[2,1-*a*]perinaphthene underwent rearrangement under the conditions of the catalytic reduction, it follows that in the course of chemical reduction indeno[2,1-*a*]perinaphthene adds on one hydrogen atom at (C_{12}) and a second at one of the positions (C_1), (C_3), (C_4) and (C_6). Four structures are therefore possible for the dihydroindeno[2,1-*a*]perinaphthene.


(XXXII)


(XXXIII)

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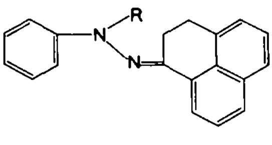
* See ν_{CO} for (XII),[8] (XLII) or (XLIII) and (XLVI).

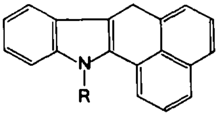
[14] B. J. F. Hudson and R. Robinson, *J. Chem. Soc.* 715 (1941).

[15] E. D. Bergmann, G. Berthier, D. Ginsburg, Y. Hirschberg, D. Lavie, S. Pinchas, B. Pullman and Pullman, *Bull. Soc. Chim. Fr.* **18**, 661 (1951).

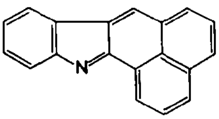
The dihydroindeno[2,1-*a*]perinaphthene undergoes with striking readiness two aromatisation reactions, which reflect the aromatic character of indeno[2,1-*a*]perinaphthene. When a solution of the dihydro derivative in benzene containing pyridine is treated at room temperature with osmium tetroxide, indeno[2,1-*a*]perinaphthene is obtained in fair yield. The parent hydrocarbon is also re-formed when a solution of the dihydroindeno[2,1-*a*]perinaphthene in acetic acid is allowed to stand at room temperature in the presence of 20% palladised charcoal. In boiling solution dehydrogenation is completed in a few minutes.



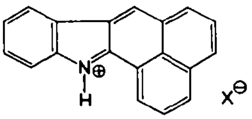
(XXXIV)



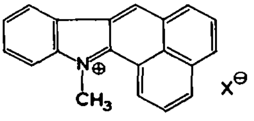
(XXXV)



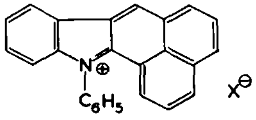
(XXXVI)



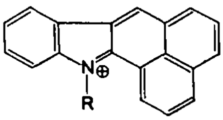
(XXXVII)



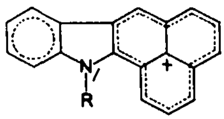
(XXXVIII)



(XXXIX)



(XL a)



(XL b)

Heterocyclic derivatives. The phenylhydrazone (XXXIV, R = H) of perinaphthan-1-one, on being boiled for a short time in acetic acid, is converted into the indole (XXXV, R = H) in low yield. Conversion of (XXXV, R = H) to the fully aromatic base, indolo[2,3,-*a*]perinaphthene (XXXVI), could not be effected by standard dehydrogenation procedures. However, an almost quantitative yield of the hydriodide (XXXVII, X = I) of indolo[2,3-*a*]perinaphthene was obtained by the action of iodine on a boiling solution of (XXXV, R = H) in methanol or acetone. The base (XXXVI) itself is unstable and its orange-red solutions in organic solvents yield an intractable residue on evaporation of the solvent. This accounts for the previously encountered failure to prepare (XXXVI).

Other derivatives, e.g. the picrate (XXXVII, X = picrate) and the perchlorate (XXXVII, X = ClO_4), have been prepared by the action of the corresponding acids on a solution of the hydriodide in methanol. These salts decompose at somewhat elevated temperature without showing definite melting points, and dissolve only in polar solvents, preferably methanol, to give crimson solutions.

In a similar series of reactions the N-methylphenylhydrazone (XXXIV, R = CH_3) was converted into the indole (XXXV, R = CH_3) and thence into the methiodide (XXXVIII, X = I) and the methoperchlorate (XXXVIII, X = ClO_4) of indolo[2,3-*a*]perinaphthene. A superior method for the preparation of (XXXVII, X = ClO_4) and (XXXVIII, X = ClO_4) consists in boiling a solution of the indole (XXXV, R = H or CH_3) in acetic acid containing an excess of 72% $HClO_4$, when the salt is formed directly. The dehydrogenation of these indoles proceeds in the absence of oxygen and requires the presence of a strong acid.

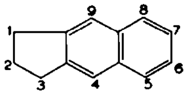
The preparation of the perchlorate (XXXVII, X = ClO_4), the methoperchlorate (XXXVIII, X = ClO_4), and the N-phenylperchlorate (XXXIX) of indolo[2,3-*a*]perinaphthene may be telescoped into a one-step reaction by boiling a solution of perinaphthan-1-one in acetic acid containing phenylhydrazine or the appropriately substituted phenylhydrazine and an excess of 72% perchloric acid.

Undoubtedly the indolo[2,3-*a*]perinaphthenylium structure (XLb, R = H, CH_3 or C_6H_5) makes significant contribution to the resonance hybrid of the cation (XLa, R = H, CH_3 or C_6H_5).

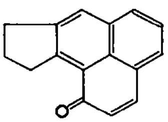
cyclo*Penta*[a]*perinaphthene* (XV)

Preliminary studies on *cyclo*penta[*a*]perinaphthene have been confined to attempts to synthesise compounds containing the carbon skeleton of the hydrocarbon.

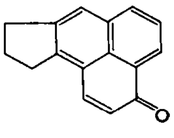
In one approach acetylation of 2:3-*cyclo*pentenonaphthalene (XLI)[16] with acetyl chloride and aluminium chloride in 1:2-dichloroethane gave a mixture in which the



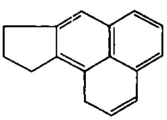
(XLI)



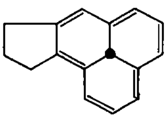
(XLII)



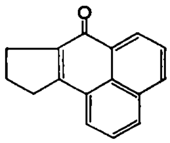
(XLIII)



(XLIV)



(XLV)



(XLVI)

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[16] F. J. McQuillin and R. Robinson, *J. Chem. Soc.* 586 (1941).

presence of two monoacetyl-2:3-*cyclo*pentenonaphthalenes was detected. The predominating isomer was condensed with ethyl formate in the presence of potassium methoxide, and the resulting hydroxymethylene derivative, on cyclisation with 87% sulphuric acid, formed a yellow ketone, m.p. 81–82°. This was reversibly soluble in concentrated hydrochloric acid and showed infra-red carbonyl absorption at 1637 cm^{-1}. The cyclisation product is therefore 8:9-*cyclo*pentenoperinaphthenone (XLII) or 4:5-*cyclo*pentenoperinaphthenone (XLIII), and the monoacetyl-2:3-*cyclo*pentenonaphthalene is, correspondingly, the 4- or the 5-isomer. The isomer isolated in low yield (about 7 per cent) from the acetylation of (XLI) is 6-acetyl-2:3-*cyclo*pentenonaphthalene.

Elimination of oxygen from the *cyclo*pentenoperinaphthenone (XLII) or (XLIII) by the use of lithium aluminium hydride[17,6] afforded in high yield a *cyclo*pentenoperinaphthene, to which structure (XLIV) is arbitrarily assigned. Attempts to dehydrogenate this hydrocarbon to *cyclo*penta[*a*]perinaphthene, catalytically, under a variety of conditions, or, chemically, by heating with sulphur, gave no useful product. When bromination with N-bromosuccinimide was carried out as the initial step in an attempted bromination–dehydrobromination procedure, formation of the transient *cyclo*pentenoperinaphthyl radical (XLV) ensued. This radical subsequently formed a high-melting solid, probably a di*cyclo*pentenoperopyrene (cf. the formation of peropyrene from perinaphthyl).

A second possible route to (XV) that is being currently investigated is based on the observation that 2:3-*cyclo*pentenoperinaphthenone (XLVI), m.p. 147–148° (infra-red CO absorption at 1634 cm^{-1}), is formed in substantial yield when naphthalene is treated with *cyclo*pentene-2-carboxylic acid chloride in the presence of an excess (3 moles) of aluminium chloride.

Perinaphthyl radicals[18]

Synthesis of perinaphthyl. A consideration of the symmetry of the carbon sleketon in perinaphthene (X) has led to the suggestion[6,19,20] that perinaphthyl (XLVII) may be a stable long-lived radical. Four oxygenated derivatives of perinaphthyl have already been reported. One of these, 1-hydroxy-3-phenylperinaphthyl,[20] was isolated as a red solid possessing a definite melting point. The remaining three, 1-methoxyperinaphthyl, 1-acetoxyperinaphthyl and 1-benzoyloxyperinaphthyl, were observed[19] as their blue solutions. Several attempts[6,20] to prepare the parent radical (XLVII) were unsuccessful.

We have observed the formation of this entity in five distinct reactions:

(*i*) In the best method for the preparation of perinaphthyl, the perinaphthenide anion (XI), prepared from perinaphthene and potassium methoxide in a 2% ethanolic ether solution, was shaken at room temperature in the presence of oxygen. Perinaphthyl arose in the process by a spontaneous one-electron transfer from the anion (XI) to molecular oxygen, which was thereby converted to the peroxide anion.

(*ii*) A second method, of theoretical significance, started with the diol (XLVIII), which was obtained as the bimolecular reduction product from perinaphthan-1-one and amalgamated aluminium in ethanol–benzene. The addition of a catalytic

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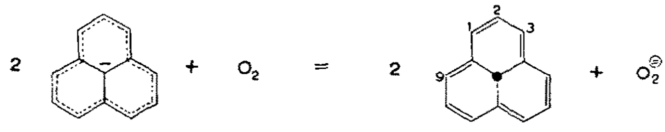
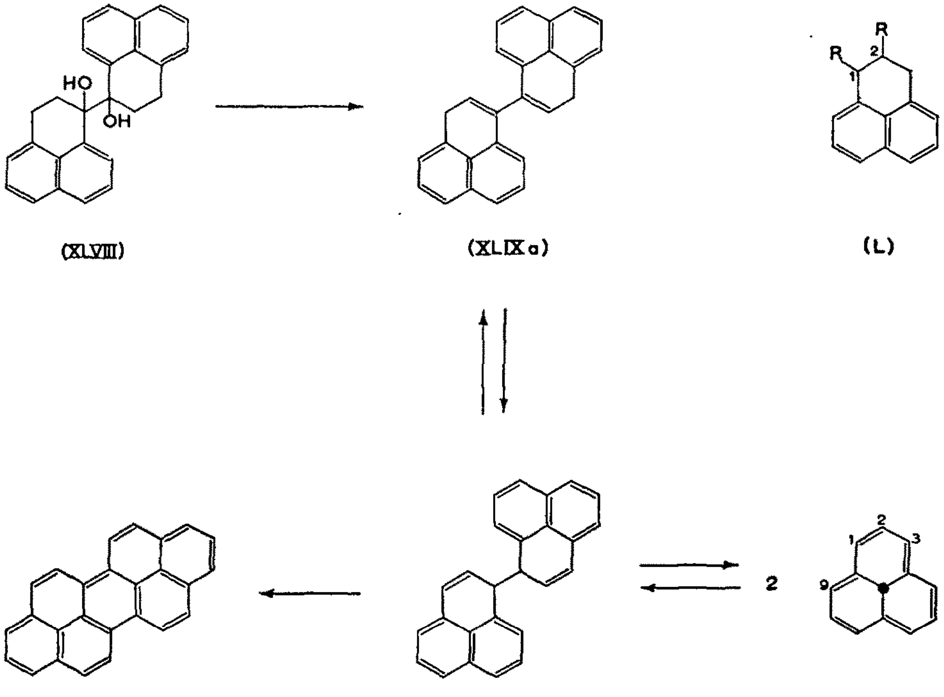
[17] F. A. Hochstein, *J. Amer. Chem. Soc.* **71**, 305 (1949).
[18] D. H. Reid, *Chem. & Ind.* 1504 (1956).
[19] E. Clar, *Aromatische Kohlenwasserstoffe* (2nd Ed.) p. 431. Springer Verlag, Berlin (1952).
[20] V. Boekelheide and M. Goldman, *J. Amer. Chem. Soc.* **76**, 604 (1954).
[21] C. F. Koelsch and J. A. Anthes, *J. Org. Chem.* **6**, 558 (1941).



(XI) (XLVII)

amount of concentrated hydrochloric acid to a solution of the diol (XLVIII) in propionic acid at room temperature resulted in immediate formation of the blue perinaphthyl (XLVII).

Under the prevailing conditions acid-acatalysed prototropy involving the intermediately formed dehydration product (XLIXa) gives rise to isomer (XLIXb), the



(XLVIII) (XLIXa) (L)

(LI) (XLIX b) (XLVII)

dimeric form of perinaphthyl. Subsequent spontaneous fission of the C–C bond joining the perinaphthene moieties in (XLIXb) affords the radical (XLVII).

(*iii*) Treatment of 1:2-dibromoperinaphthane (L, R = Br) with organic bases resulted in the loss of hydrogen bromide and bromine and formation of (XLVII) (see Boekelheide and Larrabee[6]).

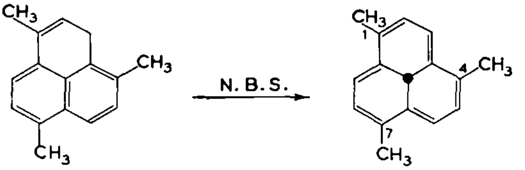
(*iv*) Perinaphthyl also results when perinaphthene is treated with N-bromosuccinimide (see Boekelheide and Larrabee[6]). This procedure assumed importance in the preparation of the substituted perinaphthyls (XLV) and (LIII).

(*v*) Finally, perinaphthyl was formed along with the normal product *cis*-1:2-dihydroxyperinaphthane (L, R = OH), m.p. 142–144°, when perinaphthene was allowed to react with osmium tetroxide and pyridine in benzene solution.

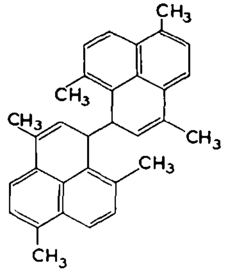
Properties of perinaphthyl. Perinaphthyl is green in the solid state, but has not in this form been isolated pure. It fails to react with nitric oxide. With oxygen it readily affords a green peroxide, $C_{26}H_{18}O_2$, which possesses no definite melting-point and breaks down on being heated *in vacuo* into a mixture of peropyrene (LI) and perinaphthenone (XII). The structure of this somewhat unstable compound is uncertain.

From a consideration of the first two methods of preparation of (XLVII) it follows that an equilibrium between perinaphthyl and its dimeric form is theoretically possible. It has been found, however, that the dimeric form disproportionates into peropyrene (LI) and a hitherto unidentified hydroaromatic product. This irreversible process takes place slowly at room temperature, but it is completed in seconds when the solvent is (benzene or acetic acid) at its boiling point. The thermal instability of the dimeric form of perinaphthyl thus accounts for the earlier failures to prepare this radical.

1:4-7-*Trimethylperinaphthyl* (LIII). The formation of a molecule of peropyrene in the disproportionation process involves the eventual linking of two perinaphthyl radicals, each through a pair of peri-positions (C_1 and C_9). A derivative, 1:4:7-trimethylperinaphthyl (LIII), was therefore synthesised in which one position of each of the three pairs of peri-positions is substituted by a methyl group. Aromatisation of the dimeric form (LIV) is thus impossible. In agreement with expectation the violet-blue radical (LIII) was found to be stable in the absence of oxygen at 240°. It is noteworthy that 1:4:7-trimethylperinaphthyl could not be prepared by the action of oxygen on a solution of (LII) in ethanolic ether containing potassium methoxide. The presence of the three methyl substituents in (LII) suppresses the ionisation of the hydrocarbon to a degree at which, under the reaction conditions, the equilibrium concentration of the corresponding anion is inadequately low.



LII LIII

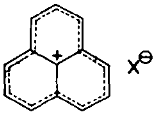


LIV

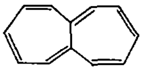
The perinaphthenylium cation (XIII). The possibility of completing the sequence:

perinaphthene → perinaphthenide → perinaphthyl → perinaphthenylium

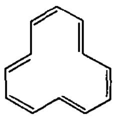
has been realised in the successful conversion of perinaphthyl to perinaphthenylium salts. The halogens chlorine, bromine and iodine all react with the radical to form products whose stabilities follow the order iodide > bromide > chloride. The iodide ($C_{13}H_9I$) is indefinitely stable when stored under nitrogen. The bromide is much less stable and slowly evolves hydrogen bromide, passing over to peropyrene (LI) and a bromine-containing contaminant. The chloride has not been isolated as a solid. Studies in this series have been confined mainly to the iodide. This compound, as isolated by the action of iodine on an ethereal solution of perinaphthyl, is a violet-black solid possessing no definite melting point but decomposing to an orange-yellow solid on being heated. It is insoluble in most organic solvents; it dissolves to a small extent only in nitromethane (green solution), but very readily in pyridine and related bases to form greenish-blue solutions. These solutions contain the perinaphthyl radical, which may be recovered by addition of water and then extraction with ether. In boiling pyridine the iodide is rapidly transformed into peropyrene (LI).



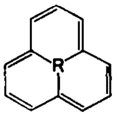
(LV)



(LVI)



(LVII)



(LVIII)

The properties of the iodide (LV, X = I) are consistent with the view that in the solid state the bond between iodine and the organic moiety is largely ionic in character, but that the molecule breaks down homolytically in pyridine to form the radical (XLVII). It is significant that pyridine forms a molecular complex with the iodine molecule,[22] a process that would assist the homolytic cleavage. A marked increase in the stability of the coloured entity is observed when the iodide is added to nitromethane containing a Lewis acid, e.g. aluminium chloride or stannic chloride. The resulting deep-green solutions are stable at the boiling point.

Conversion of the perinaphthyl radical to the perinaphthenylium cation has also been achieved by using as electron acceptor a metallic ion possessing a ready tendency to assume the metallic state. Thus perinaphthyl and anhydrous silver perchlorate react in ether solution to form perinaphthenylium perchlorate (LV, X = ClO_4) and metallic silver. This salt is readily soluble in nitromethane to give yellowish-green solutions, from which it is precipitated as a black solid on the addition of ether. It shows no definite melting point, but it decomposes slowly on being heated and readily undergoes hydrolysis.

The perinaphthenylium cation (XIII) and heptalene (LVI) are isoelectronic with the unknown polyolefin *cyclo*duodecahexaene (LVII), which, however, cannot be planer owing to "H-inside" steric compression. In order to examine further the stability of such peripheral conjugated systems of π-electrons attempts are being made to replace the formally positively charged central carbon atom of (XIII) by tervalent elements, in particular boron. In the resultant neutral molecule (LVIII, R = B) the central hetero-atom serves to hold the peripheral structure in a planar configuration free of "angle" strain.

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[22] L. F. Audrieth and E. J. Birr, *J. Amer. Chem. Soc.* 55, 668 (1933).