## *Non-benzenoid Aromatic Hydrocarbons.*

### By Wilson Baker, M.A., D.Sc.

A Tilden Lecturer is expected to review the progress in some branch of chemical science. In dealing with the present position of our knowledge of the chemistry of the non-benzenoid aromatic hydrocarbons the Lecturer is aware that there are few outstanding recent developments to report. A survey of these compounds at the present time may, however, be of value, as they are of considerable practical and theoretical interest, and this interest is reflected in the number of papers published during the last few years dealing with the chemical and physical aspects of such organic systems. The literature of the non-benzenoid aromatic hydrocarbons contains some material that is of doubtful value, and if part of this account is of a critical character, it is in the hope that thereby a more sound foundation may be laid for future developments.

In discussing the characteristics of benzene in a paper appearing in the *Journal* of the Chemical Society in 1888 (**53**, 888) Sir William Tilden wrote as follows :

" 1. The six atoms of carbon in benzene form a very stable group, which is not easily broken up by heat or by chemical reagents.

" 2. The carbon atoms are all in the same condition, and the hydrogen is distributed equally among them.

" 3. The carbon atoms are not united together by ethylenic bonds.

" 4. There are three, and only three, disubstitution derivatives."

These statements are of equal value to-day as when they were written, though some additions might profitably be made. In the same paper Sir William Tilden, in referring to the Kekulé formula for benzene, pointed out the objection to the use of the same symbol to denote the chemically reactive carbon–carbon bond in ethylene and three of the comparatively inert carbon–carbon bonds in benzene, but he added " Doubtless most chemists have been in the habit of indulging in a mental reservation as to the significance of the double bond in a closed chain. This, however, does not justify the employment of the same symbol to express two different things." This criticism is still effective, and will remain so until a convenient, simple, chemical symbol is adopted to represent the hybrid aromatic bond.

In the absence of this chemical symbol the aromatic formulæ in this lecture will be represented by conventional Kekulé structures, but the mental reservation must be made that these double bonds are not fixed, nor are the compounds tautomeric mixtures of the structures with various arrangements of the valency bonds, but are resonance-hybrid molecules. In these molecules the stability and tendency towards saturation are consequences of this hybrid character, and a molecule may be said to be of aromatic type if it is a cyclic unsaturated compound containing at least two conjugated double bonds in the ring when represented by the conventional symbols, and in which these bonds interact to a greater or lesser extent, thus bringing about a certain stabilisation of the molecule by resonance, which will in consequence be more saturated than if the double bonds were fixed and purely olefinic in character. A benzenoid aromatic compound contains a six-membered ring and the equivalent of three double bonds, as in benzene and pyridine; aromatic compounds not of the benzene type may be described as non-benzenoid.

The degree to which aromatic stability and saturation are developed is represented quantitatively by the resonance energy of the molecule, calculated from the value either of the heat of combustion or of the heat of hydrogenation (Kistiakowsky and co-workers, *J. Amer. Chem. Soc.*, 1935—1939). For benzene this amounts to some 39 kg.-cals. per g.-mol, and for naphthalene to 75 kg.-cals. per g.-mol. With *cyclo*pentadiene (I) and *cyclo*heptatriene (tropilidine) (II) the values calculated from the heats of hydrogenation are only about 3 and 6·7 kg.-cals. per g.-mol. respectively, so these molecules do not appear to possess a greater degree of resonance energy than the corresponding open-chain compounds, which they resemble in their general chemical reactivity. *cyclo*Pentadiene and *cyclo*heptatriene cannot, therefore, be said to be markedly aromatic in type, and a significant degree of aromatic character can only be developed in a molecule if it is more fully conjugated, as in those cases where there are completed cyclic conjugated systems, *e.g.*, benzene.

The present review will deal with the monocyclic *cyclo*butadiene, *cyclo*octatetraene, and the fulvenes; the dicyclic pentalene and azulene systems; and the tricyclic diphenylenes, with an additional note on four-membered rings fused to a benzene nucleus.
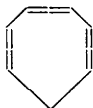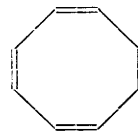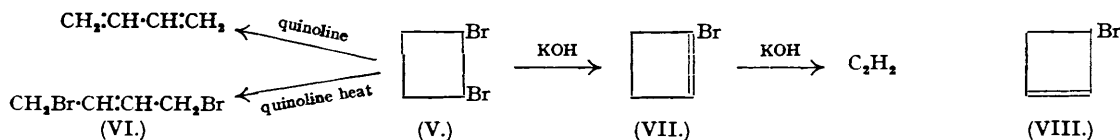


(I.)                    (II.)                    (III.)                    (IV.)

The simplest hydrocarbons which might exhibit aromatic stability and properties are *cyclo*butadiene (III) and *cyclo*octatetraene (IV). It is commonly stated in text books of organic chemistry that *cyclo*butadiene is too

instable to exist, and that *cyclo*octatetraene, although capable of independent existence, is quite unlike benzene and behaves as a typical polyolefin. Statements to the same effect are also to be found in papers of a physico-mathematical nature dealing with the structure of benzene, and unless such statements are well founded any conclusions which may be drawn from them may be invalid. It is, therefore, of some importance to examine closely the evidence upon which these statements are based, and an attempt is made to do this in the following two sections.

*cycloButadiene.*—Chemical literature contains only one reference to the attempted preparation of *cyclo*butadiene. Willstätter and von Schmaedel in 1905 (*Ber.*, **38**, 1992), by the thermal decomposition of *cyclo*butyltrimethylammonium hydroxide, prepared *cyclo*butene, which was then converted into *cyclo*butene dibromide (V). When (V) was distilled, it gave 1 : 4-dibromo-$\Delta^2$-butene (VI), and when boiled with quinoline, gave a trace of butadiene. *cyclo*Butene dibromide, when heated with potassium hydroxide at 100—105°, gave the stable 1-bromo*cyclo*butene (VII), which reacted further with potassium hydroxide at 210° to give a 30% yield of acetylene.

$$CH_2{:}CH{\cdot}CH{:}CH_2 \xleftarrow{\text{quinoline}}$$
$$CH_2Br{\cdot}CH{:}CH{\cdot}CH_2Br \xleftarrow{\text{quinoline heat}}$$
(VI.)

(V.) $\xrightarrow{\text{KOH}}$ (VII.) $\xrightarrow{\text{KOH}}$ C$_2$H$_2$ (VIII.)

These facts suggest that *cyclo*butadiene is not a very stable compound, but do not prove that *cyclo*butadiene is incapable of existence. From a knowledge of the behaviour of *cyclo*propane and *cyclo*butane and derivatives, the ring systems of which are readily broken, the molecule of *cyclo*butadiene would certainly be expected to be somewhat instable, and, owing to increased angular strain, would doubtless be less stable than *cyclo*butene and *cyclo*butane. In passing from *cyclo*butene to *cyclo*butadiene, however, the increased angular strain might be compensated, at least in part, by resonance interaction between the conjugated double bonds. There is thus a possibility that *cyclo*butadiene might be prepared if the final reaction leading to its formation were of a not too vigorous character, and the most promising line of attack would be to prepare 1-bromo-$\Delta^2$-*cyclo*butene (VIII) (probably by the bromination of *cyclo*butene with N-bromosuccinimide; Ziegler, Späth, Schaaf, and Schumann, *Annalen*, 1942, **551**, 80) and to eliminate hydrogen bromide directly or to replace the bromine atom by the dimethylamino-group and proceed by exhaustive methylation. The process of exhaustive methylation has already proved successful in the preparation of the highly strained molecule of *cyclo*propene in 45% yield from *cyclo*propyltrimethylammonium hydroxide at 320—330° (Demjanov and Dojarenko, *Bull. Acad. Sci. Russ.*, 1922, **6**, 297; *Ber.*, 1923, **56**, 2200; Schlatter, *J. Amer. Chem. Soc.*, 1941, **63**, 1733).

A few examples are to be found in the literature of compounds which have been supposed to be derivatives of *cyclo*butadiene or of the *cyclo*butadiene type. Thus Ruhemann and Merriman (J., 1905, **87**, 1383) have described some derivatives of *cyclo*butadiene, but the suggested formulæ are highly speculative and are not supported by adequate chemical evidence. Again, Curtius and Thun (*J. pr. Chem.*, 1891, **44**, 175) suggested that the azine produced from hydrazine hydrate and diacetyl was of the butadiene type, but it was later shown by Zimmermann and Lochte (*J. Amer. Chem. Soc.*, 1936, **58**, 948) to be a polyazine of moderately high molecular weight.

*cycloOctatetraene.*—The preparation and properties of the hydrocarbon believed to be *cyclo*octatetraene were described by Willstätter in two papers in 1911 and 1913 (Willstätter and Waser, *Ber.*, 1911, **44**, 3423; Willstätter and Heidelberger, *Ber.*, 1913, **46**, 517). The starting material was the pomegranate alkaloid ψ-pelletierine, which contains the *cyclo*octane nucleus bridged by an NMe group. The steps of the preparation are shown in the following scheme :
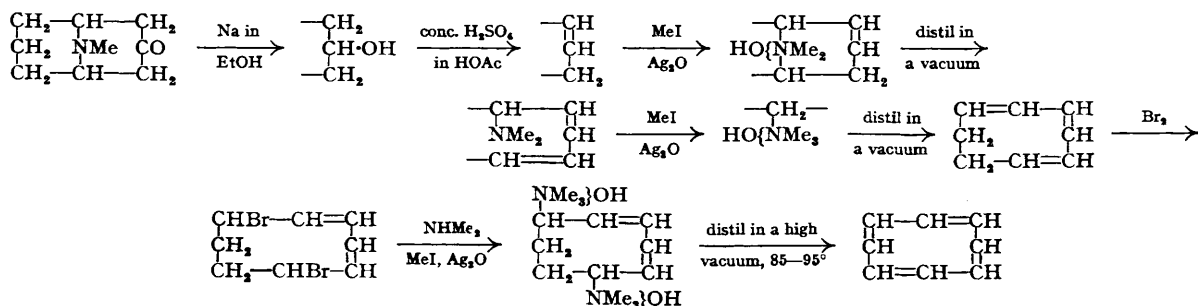
The final step, the thermal decomposition of the quaternary hydroxide derived from the diamine, was carried out at low pressure and gave the hydrocarbon in 10—20% yield as a pale yellow liquid, b. p. 42·2—42·4°/17 mm., the three analyses of which agreed well with the formula C$_8$H$_8$. It was instable on exposure to the air and deposited amorphous flocks (Willstätter and Waser) or resinified (Willstätter and Heidelberger), and, curiously, it exhibited a limited degree of unsaturation. In dilute chloroform solution at −20° it combined with bromine, giving a crystalline dibromide, C$_8$H$_8$Br$_2$, which, by the further action of bromine, gave by substitution a
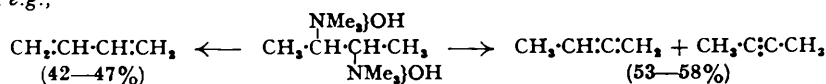
solid, incompletely characterised bromo–dibromide, $C_8H_7Br_3$. With hydrogen bromide it gave a liquid hydro-bromide, $C_8H_9Br$, which did not combine with bromine. Both the hydrocarbon and its dibromide reduced potassium permanganate energetically.

Reduction of the *cyclo*octatetraene with hydrogen and an active platinum catalyst resulted in the slow absorption of four molecules of hydrogen and formation of a hydrocarbon $C_8H_{16}$, b. p. 39—42°/15 mm., which solidified on cooling and became completely fluid at 6·5°. With the same catalyst and under the same conditions benzene was completely reduced, though slightly more rapidly. The hydrocarbon $C_8H_{16}$ was considered to be *cyclo*octane (m. p. 14°) because on oxidation with nitric acid it gave suberic acid, $HO_2C \cdot [CH_2]_6 \cdot CO_2H$, but details of this important experiment are lacking.

Although many chemists may have wondered if Willstätter's hydrocarbon really was *cyclo*octatetraene, not until 1939 was the validity of his conclusions challenged in print. In that year Vincent, Thompson, and Smith (*J. Org. Chem.*, 1939, **3**, 603) drew attention to the " striking similarity in chemical and physical properties between Willstätter's compound and its derivatives and styrene and its derivatives." This similarity to styrene was again emphasised by Goldwasser and Taylor (*J. Amer. Chem. Soc.*, 1939, **61**, 1260), who stated that styrene had the same specific gravity and showed chemical properties identical with those reported by Will-stätter for *cyclo*octatetraene. The widespread interest in *cyclo*octatetraene, undoubtedly stimulated by this suggestion, is shown by the number of independent publications dealing with the subject. In addition to those investigators whose work is specifically mentioned, preliminary experiments have been recorded by Wawzonek (*J. Amer. Chem. Soc.*, 1943, **65**, 859), Bachmann and Hoaglin (*J. Org. Chem.*, 1943, **8**, 300), and Cook, McGinnis, and Mitchell (J., 1944, 290), and Horning (*Chem. Rev.*, 1943, **33**, 96) has suggested that an intermediate in the final step of the synthesis leading to styrene is the benzene derivative $Ph \cdot CH(NMe_3 \cdot OH) \cdot CH_3$. Although the chemical properties of styrene are undoubtedly very similar to the recorded properties of *cyclo*octatetraene, the physical properties (see Table) are not, in fact, in close agreement, except for the boiling point.

|  | cyclo*Octatetraene.* |  | *Styrene.* |
|---|---|---|---|
| B. p. | 42·2—42·4°/17 mm. | B. p. | 43°/17 mm. |
| M. p. | −27° | M. p. | −33° |
| $d_4^{0°}$ | 0·943 | $d_4^{0°}$ | 0·925 |
| $d_4^{20°}$ | 0·925 | $d_4^{20°}$ | 0·907 |
| $n_D^{20°}$ | 1·5394 | $n_D^{21°}$ | 1·5446 |
| Dibromide, m. p. | 70—71·5° | Dibromide, m. p. | 74° |

A different approach was that of Hurd and Drake (*J. Amer. Chem. Soc.*, 1939, **61**, 1943), who criticised several of the assumptions which were made as to the nature of the intermediate products in the conversion of $\psi$-pelletierine into *cyclo*octatetraene. For example, both the diene and the triene were assumed to be conjugated, the addition of bromine to the triene was regarded as a 1 : 6-addition, and the derived bis-quaternary ammonium hydroxide was again supposed to give the conjugated tetraene. It is now known that bromine does not always add terminally to conjugated systems, and with regard to the decomposition of bis-quaternary ammonium hydroxides, cases investigated by Hurd and Drake showed that conjugated systems by no means always resulted, *e.g.*,

$$CH_2 \text{:} CH \cdot CH \text{:} CH_2 \longleftarrow \underset{NMe_3\}OH}{\overset{NMe_3\}OH}{CH_3 \cdot CH \cdot CH \cdot CH_3}} \longrightarrow CH_3 \cdot CH \text{:} C \text{:} CH_2 + CH_3 \cdot C \text{:} C \cdot CH_3$$
$$(42\text{—}47\%) \qquad\qquad\qquad\qquad\qquad (53\text{—}58\%)$$

The evidence available makes it impossible to come to any definite conclusion as to the nature of Will-stätter's hydrocarbon. On the one hand, its boiling point, ability to resinify, and the formation and properties of the dibromide and hydrobromide, which behave as saturated compounds towards bromine, suggest that it was styrene. It must indeed be assumed that the dibromide and hydrobromide are derivatives of benzene, because on no other reasonable ground can their saturated nature be explained, and of the possible benzenoid compounds the styrene derivatives are by far the most likely.[*] On the other hand, its physical properties, apart from the boiling point, and the recorded energetic reaction of the dibromide with potassium permanganate indicate that it is not styrene, and the formation of an octahydro-derivative oxidisable to suberic acid is con-sistent only with the presence of at least some *cyclo*octane derivative, either the conjugated *cyclo*octatetraene or, much less likely owing to strain, a *cyclo*octatetraene containing an allene group. This conflicting evidence might be partly harmonised if *cyclo*octatetraene could yield styrene derivatives by rearrangement during the addition of bromine or hydrogen bromide. This suggestion recalls the somewhat similar conversion of *cyclo*-heptatriene (tropilidene) (II) (Willstätter, *Annalen*, 1901, **317**, 204; Conn, Kistiakowsky, and Smith, *J. Amer. Chem. Soc.*, 1939, **61**, 1868; Kohler, Tischler, Potter, and Thompson, *ibid.*, p. 1057) into benzyl bromide (10% yield), by heating its dibromide on the water-bath (Merling, *Ber.*, 1891, **24**, 3122).

It is clear that in the present state of our knowledge no useful purpose can be served by contrasting either the chemical or physical properties of Willstätter's *cyclo*octatetraene with those of benzene, though it is certainly also clear that the *cyclo*octatetraene ring system is much less easy to produce than that of benzene.

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[*] A dibromide or a hydrobromide of a structure such as that of the cyclic fulvene derivative shown, or its four possible isomerides with various positions of the double bonds, is excluded if it be accepted that reduction of Willstätter's *cyclo*octatetraene gave *cyclo*octane (Barrett and Linstead, J., 1936, 611, find no conversion of 0 : 3 : 3-*bicyclo*octanes into *cyclo*octanes by reduction).

Derivatives of *cyclo*octatetraene do not occur naturally, nor have they been produced by simple reactions in the laboratory, as has benzene and a very large number of its derivatives. That this is due to something more than the usual difficulty of closing an eight-membered ring is shown by experiments with compounds in which the *cyclo*octane structure is already present. For example, Goldwasser and Taylor (*loc. cit.*) attempted the catalytic dehydrogenation of *cyclo*octene over a chromium oxide catalyst at 425°, and obtained in the liquid distillate a 93% yield of styrene, and no trace of any other system absorbing in the ultra-violet region of the spectrum.
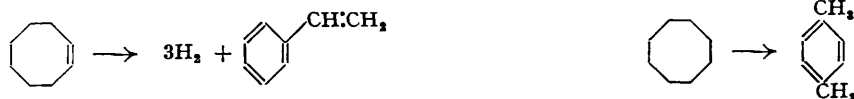


Again Ruzicka and Seidel (*Helv. Chim. Acta*, 1936, **19**, 424) showed that *cyclo*octane and *cyclo*heptane at 440° gave *p*-xylene and toluene respectively, and even in the saturated series eight- and also seven-membered rings rearrange to *cyclo*hexanes. Thus *cyclo*octane at 210° in hydrogen over nickel gave 1 : 1-dimethyl*cyclo*hexane (Willstätter and Kametaka, *Ber.*, 1907, **40**, 957), and *cyclo*heptane at 230° in hydrogen over nickel gave methyl*cyclo*hexane (Ruzicka, *Helv. Chim. Acta*, 1926, **9**, 499).

*Derivatives of* cyclo*octatetraene.* Compounds supposed to be derivatives of *cyclo*octatetraene were prepared by Fries and Pfaffendorf (*Ber.*, 1910, **43**, 212; 1911, **44**, 114) by the self-condensation of coumaranones (IX), the structures, as (X), assigned to them being based on the fact that they were produced by further condensation of dimolecular products.



(IX.)          (X.)          (XI.)
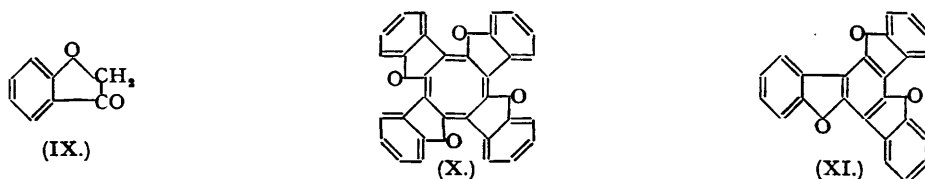
It was shown, however, by Baker and Banks (*J.*, 1939, 279) that in the case of the strictly analogous 5-methyl-coumaranone the final product had a molecular weight corresponding to that required for a triple condensation product of the simple coumaranone, and hence it must be a derivative of benzene (XI) rather than of *cyclo*octatetraene. There can be no doubt that the similar compounds described by Fries and Pfaffendorf are also tris-coumaronobenzenes. Again, the supposed benz*cyclo*octadienediones prepared by dehydration of δ-benzylidenelævulic acids with acetic anhydride (Sen and Roy, *J. Indian Chem. Soc.*, 1930, **7**, 401) have been shown (Rapson and Shuttleworth, *J.*, 1942, 33) to be otherwise constituted and are almost certainly 2-keto-5-styryl-2 : 3-dihydrofurans. A compound, $C_{48}H_{22}Br_2$, obtained by the action of bromine upon fluorocyclen (probably tetranaphthylene*cyclo*octadiene; Dziewonski and Suknarowski, *Ber.*, 1918, **51**, 457), has been formulated as a derivative of *cyclo*octatetraene (Dziewonski and Susko, *Ber.*, 1925, **58**, 725), but the experimental evidence is insufficient to establish the proposed structure.

The only known cases of genuine *cyclo*octatetraenes are certain benzo-derivatives which have recently been prepared by Rapson and Shuttleworth and their collaborators (Rapson, Shuttleworth, and Niekerk, *J.*, 1943, 326; Shuttleworth, Rapson, and Stewart, *J.*, 1944, 71). Tetraphenylene (1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-tetrabenz-$\Delta^{1:3:5:7}$-*cyclo*octatetraene) was obtained in 16% yield by the action of anhydrous cupric chloride in boiling ethereal solution upon the Grignard reagent derived from 2 : 2'-dibromodiphenyl (XIII), and is a solid, m. p. 233°, which shows the remarkable property of crystallising with half a molecule of solvent of crystallisation from chloroform, carbon tetrachloride, acetone, dioxan, benzene, and pyridine. It is oxidised by chromic acid to tribenz*cyclo*octatetraenedicarboxylic anhydride (XIV), pyrolysis of which with barium hydroxide gives 1 : 2 : 3 : 4 : 5 : 6-tribenz-$\Delta^{1:3:5:7}$-*cyclo*octatetraene (XV).



(XIII.)          (XII.)          (XIV.)          (XV.)
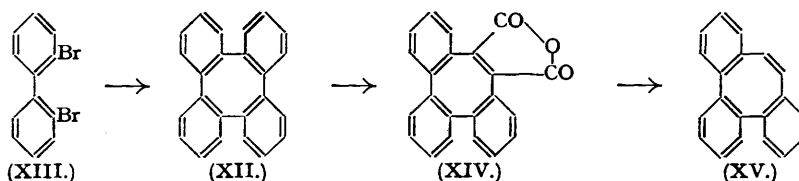
There are two points of general interest about these derivatives of *cyclo*octatetraene, one in connection with their absorption spectra and the other with their molecular geometry (Rapson, Schwartz, and Stewart, *J.*, 1944, 73). The absorption spectrum of tetraphenylene (XII) is extremely similar to that of 2 : 2'-diphenyldiphenyl (XVI), and also to that of tribenz*cyclo*octatetraene (XV). Hence in passing from (XVI) to (XII) the closing of the *cyclo*octatetraene ring causes no marked difference in the absorption spectra, and it may be concluded that no characteristic absorbing system is present in tetraphenylene except that due to the four benzene rings. In marked contrast is the difference between the absorption spectra of 2-phenyldiphenyl

(XVII) and triphenylene (XVIII), where the closure of the six-membered ring causes a completely new type of absorption to appear.



(XVI.)   (XVII.)   (XVIII.)   (XIX.)
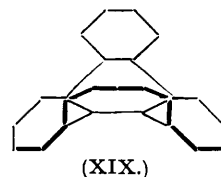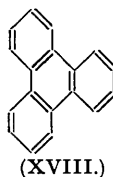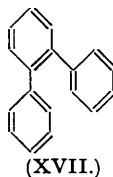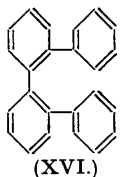
Preliminary examination by *X*-ray analysis and electron diffraction has shown that the molecule of tetraphenylene is not flat. This is to be expected from a molecular model, which when strainless takes the form shown in (XIX), being of a more generally cubic than a planar shape. In the compound itself resonance between the benzene rings will tend to make the molecule somewhat more flat, and a balance will be struck between the increased stability due to such resonance and the decreased stability due to angular deformation of the valencies. The central *cyclo*octatetraene ring is clearly far from being planar, and this may be one of the reasons why it does not show any characteristic aromatic absorption. Indeed the eight-membered ring appears to be merely a space enclosed by the four benzene nuclei, quite unlike the central six-membered ring in the (presumably) planar molecule of triphenylene (XVIII).*

These considerations have some bearing on the possible existence of *cyclo*octatetraene itself. If the molecule is to be a stable aromatic compound behaving as a saturated rather than as an unsaturated compound, then there must be resonance interaction between the bonds, and this is only possible if the molecule is planar, since the structures which contribute to the hybrid can differ only in distribution of the valency electrons and not in the relative positions of the atoms concerned. In passing from one *cyclo*octatetraene structure to the other when the positions of the carbon–carbon double and single bonds are reversed (as in the two Kekulé structures of benzene), considerable movement of the atoms is involved in the least strained structures, so that, if the molecule is to be stabilised by resonance, it must be flat, and automatically becomes to a certain extent rendered instable by strain. To what extent these two effects neutralise each other it is impossible to say, but the molecule would show some tendency to behave like an olefin rather than like the stable molecule of benzene (see Pauling, " Nature of the Chemical Bond," Cornell Univ. Press, 1939, p. 133, footnote; Penney, *Proc. Roy. Soc.*, 1934, *A*, **146**, 223, suggests that the angular strain is enough " to counteract the stabilising influence of resonance ").

The natural angle between a double and a single bond for a tetrahedral carbon atom is 125°, so that the angular distortion of the valencies in the planar benzene molecule is only 5° for each carbon atom, whereas for the planar *cyclo*octatetraene molecule (internal angle of 135°) the angular distortion is 10° per carbon atom. The total strain will, therefore, be considerably greater than in benzene, where the angular distortions are obviously of extremely little significance. It must be conceded, however, that stable molecules are known which have some of their valency angles bent very considerably from the normal. Familiar examples amongst alicyclic compounds are *cyclo*propane, *cyclo*propene, *cyclo*butane, and *cyclo*butene, in which, however, the rings are easily broken, and in the aromatic series may be mentioned fluorene (XX) and acenaphthylene (XXI)



(XX.)   (XXI.)   (XXII.)
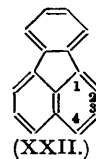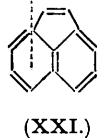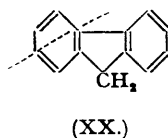
In the case of fluorene (see Hughes, Le Fèvre, and Le Fèvre, *J.*, 1937, 203, and references there cited) the two benzene rings must be inclined at an angle because of the non-identity of the dipole moments of fluorene and certain 2 : 7-disubstituted fluorenes, and even if the molecule is not completely planar the angular strain is probably of the order of 10°. The molecule of acenaphthylene is even more strained, and yet it is an exceedingly stable substance, being formed, for example, by the passage of the vapour of its dihydro-derivative, acenaphthene, over red-hot lead oxide. If the olefinic link has its normal length, the bonds joining this CH:CH group to the naphthalene system must be distorted through an angle of not less than 20°, and the same considerations apply to fluoranthene (XXII), whose structure has been established by synthesis (von Braun and Anton, *Ber.*, 1929, **62**, 145; Fieser and Seligman, *J. Amer. Chem. Soc.*, 1935, **57**, 2174), and which is also so stable as to be produced from its 1 : 2 : 3 : 4-tetrahydro-derivative by oxidation over red-hot lead oxide. These examples make it doubtful if the instability, or even the non-existence, of *cyclo*octatetraene can be explained on the grounds of strain alone.

* Since this lecture was delivered a paper has appeared by Karle and Brockway (*J. Amer. Chem. Soc.*, 1944, **66**, 1974) describing an electron diffraction examination of tetraphenylene. The molecule, models of which are illustrated, is found to be best represented by the form suggested in the lecture, with the centres of the benzene rings lying at the corners of a regular tetrahedron, and with a non-planar eight-membered ring. In a footnote to this paper it is reported that Fieser and Pechet have prepared 1 : 2 : 5 : 6-dibenz-$\Delta^{1:3:5:7}$-*cyclo*octatetraene, and that the two double bonds in the *cyclo*octatetraene ring which are not shared with the benzene rings are olefinic in character.

*Fulvenes.*—Before leaving the possible monocyclic non-benzenoid aromatic types, mention may be made of the fulvenes (XXIII), whose conjugation, though not completely cyclic, is more perfect than that in *cyclo*heptatriene. The fulvenes, which are generally orange or red, are prepared from *cyclo*pentadiene or derivatives either by condensation with aldehydes or ketones in presence of alkali, or by treatment with a Grignard reagent, giving the magnesium derivative (XXIV), followed by reaction with an aldehyde or ketone to give the tertiary alcohol (XXV) and dehydration over alumina at 250° to give the fulvene (XXIII).

|  |  |  |  |  |
|---|---|---|---|---|
| CRR′ | MgX | CRR′·OH | CH₂ | CH₂ |
| (XXIII.) | (XXIV.) | (XXV.) | (XXVI.) | (XXVII.) |
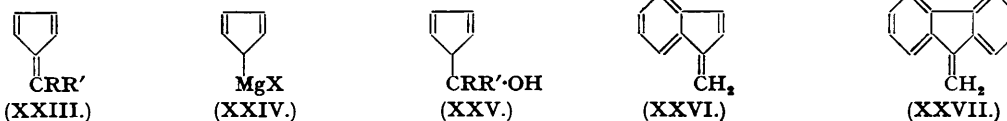
Although the fulvenes are chemically reactive, they do not rearrange to the isomeric benzene derivatives; thus benzfulvene (XXVI) does not rearrange to naphthalene at 250° over alumina, and dibenzfulvene (XXVII) has shown no tendency to rearrange to phenanthrene (Wieland, Reindel, and Ferrer, *Ber.*, 1922, **55**, 3317). These facts suggest that such molecules possess moderate resonance energy, but no determination of the value of this energy in a fulvene has been recorded.

*Pentalene.*—This is the simplest bicyclic aromatic system which might exist, if derivatives of *cyclo*butadiene are excluded. It consists of two fused five-membered fulvene rings, a structure in which two arrangements of the double bonds are possible, (XXVIII) and (XXIX), but the central bond remains single.

|  |  |  |  |
|---|---|---|---|
| (XXVIII.) | (XXIX.) | (XXX.) | (XXXI.) =CHPh |

This compound was first postulated as a possible aromatic type by Armit and Robinson (*J.*, 1922, **121**, 828), and the name " pentalene " is suggested for it in Patterson and Capell's " The Ring Index " (1940, p. 110). In view of its similarity to naphthalene attempts were made by Barrett and Linstead (*J.*, 1936, 612) to obtain this hydrocarbon by dehydrogenation of *cis*-0 : 3 : 3-*bicyclo*octane (XXX) in the vapour phase over platinum, but the compound was recovered unchanged under conditions which resulted in the dehydrogenation of decalin to naphthalene. An attempt was also made to dehydrogenate 2-benzylidene-*cis*-0 : 3 : 3-*bicyclo*octane (XXXI) to a derivative of pentalene by means of selenium at 300—330°, but it was partly unchanged and partly decomposed, although in control experiments 2-benzyl-*trans*-octalin was smoothly converted into 2-benzyl-naphthalene. Barrett and Linstead conclude that " these results, although negative, provide some experimental support for the view that naphthalene is a unique dicyclic hydrocarbon and that the *bicyclo*octatetraene (XXVIII) does not possess aromatic characteristics."

The little evidence available certainly indicates that pentalene is not a stable aromatic system, and it is difficult to suggest adequate reasons for this. Attention may be drawn, however, to three considerations. First, in pentalene there are only four electrons not necessarily involved in co-valency formation in each ring, whereas in typical benzenoid compounds there are six. Secondly, pentalene is a derivative of fulvene, and the fulvenes as a class are instable, showing a marked tendency to polymerise and to undergo autoxidation. Thirdly, on the simple strain theory based on the tetrahedral carbon atom pentalene should be a moderately strained molecule (internal angles of 108° for a *regular* pentagon, instead of 125° for the angle between a double and a single bond about a carbon atom, although the latter value might be slightly reduced because one angle in each pentagon should be 110°), but recent work on heats of hydrogenation has made it very doubtful if such considerations apply in the case of monocyclic five- and six-membered ring compounds. Classical theory predicts that introduction of one or two double bonds into *cyclo*pentane should result in a more strained and less stable molecule than when the double bonds are introduced into the molecule of *cyclo*hexane, and that in consequence the heats of hydrogenation of *cyclo*pentene and *cyclo*pentadiene should be greater than those of *cyclo*hexene and $\Delta^{1:3}$-*cyclo*hexadiene respectively. Direct measurements of the heats of hydrogenation by Kistiakowsky and his collaborators (*J. Amer. Chem. Soc.*, 1935, **57**, 65,876; 1936, **58**, 137,146; 1937, **59**, 831; see also Taylor, *Ann. Reports*, 1937, **34**, 214) have shown that, although the differences in values for the five- and six-membered rings are not great, the values themselves are unmistakably larger in the case of the hexane derivatives, and it must be concluded that the five-membered ring becomes more stable with increasing unsaturation.

A few complex molecules containing the dibenzopentalene system have been made by Brand (*Ber.*, 1912, **45**, 3071; Brand and Ludwig, *ibid.*, 1920, **53**, 809; Brand and Hoffmann, *ibid.*, p. 815; Brand and Müller, *ibid.*, 1922, **55**, 601; Brand, Gabel, and Ott, *ibid.*, 1936, **69**, 2504; Wawzonek, *J. Amer. Chem. Soc.*, 1940, **62**, 745). These are diphensuccindadienes of type (XXXII; R = Ph or Cl), brown substances obtained from diphensuccindandione either by treatment with aryl Grignard reagents and dehydration of the resulting diertiary alcohols, or by treatment with phosphorus pentachloride and elimination of two molecules of hydrogen chloride.

The aromatic system consisting of fused five- and seven-membered rings (XXXIII) is found in the azulenes, and may be regarded as the next aromatic homologue of pentalene. The azulenes are compounds of considerable stability, which is in marked contrast with the apparent instability of pentalene. Two points may be

made in this connection; first, the azulene molecule may be in part less strained than that of pentalene because the internal angles of a regular heptagon are 128·6°, which is very close to 125°, and secondly, the seven-membered



(XXXII.)                     (XXXIII.)                     (XXXIV.)
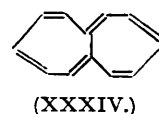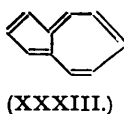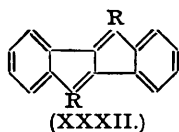
ring contains three pairs of doubly bound carbon atoms and, therefore, has six " free " electrons. It follows that, if these two points are valid, then the system consisting of two fused seven-membered rings containing six double bonds (XXXIV) should show aromatic stability, but as yet compounds of this type are unknown.

*Azulenes.*—The azulenes contain the fused five- and seven-membered ring aromatic system (XXXIII), and are isomeric with the naphthalenes. They are sufficiently well known not to require detailed description here; two reviews are available, one by Haworth (*Ann. Reports*, 1937, **34**, 393) and the other by Arnold (*Die Chemie*, 1943, **56**, 7).

The azulenes are blue, violet, or green hydrocarbons present in certain essential oils or obtained from them by high-temperature dehydrogenation, and are separated from the resulting mixtures by taking advantage of their solubility in concentrated aqueous phosphoric acid, from which solutions they separate on dilution with water (Sherndal, *J. Amer. Chem. Soc.*, 1915, **37**, 167, 1537). They form picrates and complexes with *s.*-trinitrobenzene. Their structure has been established largely by the work of St. Pfau and Plattner (*Helv. Chim. Acta*, 1936, **19**, 858; 1937, **20**, 224, 469; 1939, **22**, 202; Plattner and Wyss, *ibid.*, 1940, **23**, 907; 1941, **24**, 483) both by synthetical and degradative studies. Some simple azulenes were synthesised from octalin by ozonolysis to the diketone (XXXV) (Hückel, Gercke, and Gross, *Ber.*, 1933, **66**, 563), cyclisation to the *cyclo*penteno*cyclo*heptenone (XXXVI) (Hückel and Schnitzspahn, *Annalen*, 1933, **505**, 274), reaction with a Grignard reagent, and dehydrogenation to the azulene (XXXVII) (St. Pfau and Plattner, *Helv. Chim. Acta*, 1936, **19**, 858).



(XXXV.)                     (XXXVI.)                     (XXXVII.)
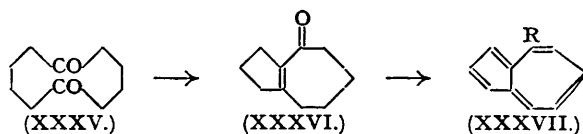
Several alkylated azulenes have also been prepared by another ingenious method due to St. Pfau and Plattner (*locc. cit.*; also Wagner-Jauregg and Hippchen, *Ber.*, 1943, **76**, 694). Hydrindene or an alkylated hydrindene is heated with diazoacetic ester, a pseudophenylacetic ester (XXXVIII) thereby being obtained. This is hydrolysed and then simultaneously decarboxylated, dehydrogenated and rearranged by heating with palladium–charcoal, and the resulting azulene (XXXIX) purified by chromatographic adsorption on alumina.



(XXXVIII.)                     (XXXIX.)
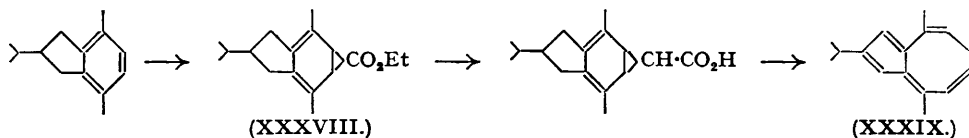
The fused five- and seven-membered ring system has been proved to be present in the naturally occurring reduced azulene derivative β-vetivone (XL), which yields vetivazulene (XXXIX) on dehydration and dehydrogenation. Controlled degradation processes have yielded on the one hand a derivative of *cyclo*pentane (XLI), and on the other hand a derivative of *cyclo*heptane (XLII) (St. Pfau and Plattner, *Helv. Chim. Acta*, 1940, **23**, 768).



(XLI.)                     (XL.)                     (XLII.)
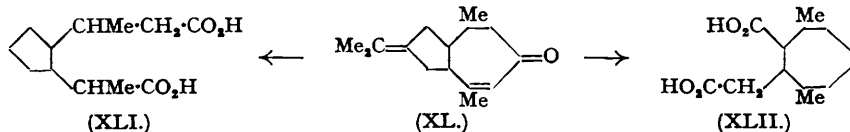
The azulenes are compounds of considerable stability, as is evident from their usual method of formation, and there is, as yet, no clear evidence that they may be converted into the isomeric naphthalenes. Nevertheless the azulenes appear to be physically less stable than the isomeric naphthalenes. Perrottet, Taub, and Briner (*Helv. Chim. Acta*, 1940, **23**, 1260) have determined the heats of combustion of the two isomeric compounds cadalene (XLIII), and guaiacazulene (XLIV), and find that the former value is 29·5 kg.-cals. per g.-mol. lower than the latter. From this it has been calculated that the total bonding energy of azulene itself is 8% less than the total bonding energy of naphthalene, and that the resonance energy of azulene is of the order of 45 kg.-cals. per g.-mol., compared with the resonance energy of naphthalene, which is 75 kg.-cals. per g.-mol.

In view of this fact it is curious that the tricyclic terpene ledol (Komppa and Nyman, *Compt. rend. Trav. Lab. Carlsberg*, 1938, **22**, 272) (XLV), which contains the carbon skeletons of both cadalene (XLIII) and guaiacazulene (XLIV), should be dehydrogenated with rupture of the *cyclo*propane ring to give mainly guaiac-

azulene and relatively little cadalene. A similar case is afforded by aromadendrene (XLVI) (Radcliffe and Short, J., 1938, 1200; Naves and Perrottet, *Helv. Chim. Acta*, 1940, **23**, 912), which is dehydrogenated to give guaiac-azulene and not a derivative of naphthalene.
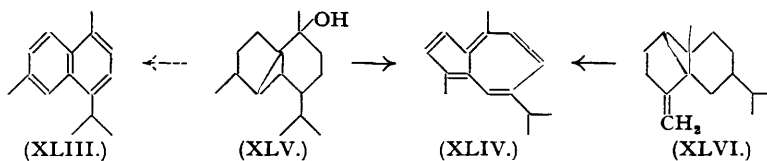


" *Diphenylene.*"—Diphenylene (also called biphenylene and *cyclo*butadibenzene) is the tricyclic hydrocarbon (XLVII), isomeric with acenaphthylene, which has been regarded for a long time as a possible aromatic type. Five arrangements of the bonds are possible, four dibenzenoid in character, and one doubly ortho-quinonoid.

The hydrocarbon has an interesting history. Hosaeus in 1893 (*Monatsh.*, **14**, 323) attempted to prepare it by the action of sodium on *o*-dibromobenzene, but obtained instead a trace of benzene, a little diphenyl and a mixture of complex products. Niementowski (*Ber.*, 1901, **34**, 3331) treated the diazonium salt derived from 2 : 2'-diaminodiphenyl with copper powder, but the product was carbazole. The dehydration of 2-hydroxy-diphenyl to diphenylene was unsuccessfully attempted by Cullinane, Morgan, and Plummer (*Rec. Trav. chim.*, 1937, **56**, 627). The preparation of diphenylene from 2 : 2'-dibromodiphenyl in almost theoretical amount by the action of sodium in boiling ether was claimed by Dobbie, Fox, and Gauge (J., 1911, **99**, 683; 1913, **103**, 36). It was described as closely resembling diphenyl but had a higher melting point (74·5—75°; diphenyl, 70·5°); it was extremely volatile and concordant results for the analyses were only obtained by carrying out the combustions under abnormally vigorous conditions. The three selected analyses and the molecular weight determinations are in fair agreement with the formula $C_{12}H_8$. The hydrocarbon was not attacked by cold alkaline permanganate, but hot chromic acid mixture gave phthalic and benzoic acids. Bromination gave 2 : 2'-dibromo-diphenyl and a dibromodiphenylene giving *p*-bromobenzoic acid on oxidation. The nature of this hydrocarbon remains obscure, and its preparation has not been successfully repeated in spite of many attempts. Complete failure has been reported by Mascarelli and Gatti (*Gazzetta*, 1933, **63**, 661), by Rapson and Shuttleworth (J., 1941, 487), and by Lothrop (*J. Amer. Chem. Soc.*, 1941, **63**, 1187), although a variety of experimental conditions was used, including the replacement of sodium by potassium, and the dibromodiphenyl by the corresponding dichloro- and di-iodo-derivatives.
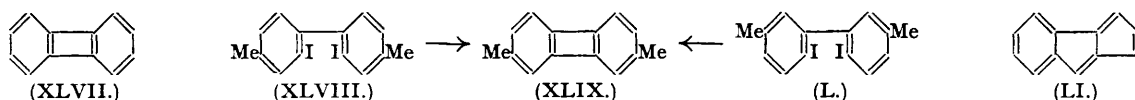


Lothrop (*loc. cit.*), having failed to repeat the earlier claim, finally succeeded in preparing a compound $C_{12}H_8$ in 5% yield by distilling 2 : 2'-dibromodiphenyl or, better, 2 : 2'-di-iododiphenyl with cuprous oxide, steam-distilling the product, and purifying the substance as its scarlet picrate. The hydrocarbon was finally liberated from the picrate by sublimation at 100°, and öbtained in light-yellow prisms, m. p. 110°, which was shown by analysis and molecular weight determination to be undoubtedly $C_{12}H_8$. The substance is not identical with the compound described in 1911, nor with acenaphthylene, and is claimed by Lothrop as diphenylene (XLVII). Oxidation with chromic acid gave some phthalic acid (yield unstated), and by passage as a vapour with hydrogen over hot copper it was one-third converted into diphenyl and two-thirds unchanged. The stability and colour of its picrate are consistent with a tricyclic aromatic hydrocarbon (see Basil and Hauber, *J. Amer. Chem. Soc.*, 1931, **53**, 1090), as is also its absorption spectrum (Carr, Pickett, and Voris, *ibid.*, 1941, **63**, 3231). Lothrop also brought forward evidence in favour of the symmetrical structure of the molecule. 2 : 2'-Di-iodo-4 : 4'-dimethyldiphenyl (XLVIII) and 2 : 2'-di-iodo-5 : 5'-dimethyldiphenyl (L) were each converted into a " diphenylene," and the products from both reactions were identical, being regarded as 2 : 7-di-methyldiphenylene (XLIX). A later paper by the same author (*J. Amer. Chem. Soc.*, 1942, **64**, 1698) described two other diphenylenes, the 1 : 8-dimethyl- and the 2 : 7-dimethoxy-derivatives.

Two novel features are involved in the diphenylene formulæ for these compounds. First, they may be regarded as derivatives of the unknown substance *cyclo*butadiene, and secondly they contain a four-membered ring fused to a benzene nucleus. With regard to the first point there is evidence to suggest that the *cyclo*-butadiene ring may be stabilised by fusion with the benzene nuclei. The second point is more difficult, because there appears to be no established case in chemical literature of a compound containing fused aromatic and four-membered rings, a subject which is discussed in a separate section (p. 266). Such molecules would have bonds attached to the aromatic nucleus strained through angles of 30°; in the case of diphenylene (XLVII) four bonds would be strained to this large extent and it might be expected that the resulting strain would confer a considerable degree of instability upon the molecule, whereas the actual " diphenylenes " are very stable, being formed by high temperature reactions, and behaving as typical aromatic compounds.

The preparation of the hydrocarbon $C_{12}H_8$ by Lothrop's method has been confirmed (Baker, Grice, and Donne, unpublished observations; Baker, *Nature*, 1942, **150**, 210) and it was reported that mild catalytic

reduction resulted in the uptake of approximately three molecules of hydrogen, giving a volatile oil, and that it behaved as a saturated compound and exhibited no acetylenic properties. The same hydrocarbon has also been prepared in 4% yield by Rapson, Shuttleworth, and Niekerk (*loc. cit.*; Rapson and Shuttleworth, *loc. cit.*) by treating the Grignard reagent prepared from 2 : 2'-dibromodiphenyl with dry cupric chloride (method due to Krizewsky and Turner, J., 1919, **115**, 560), a reaction which simultaneously yields tetraphenylene (see p. 261).

Apart from the diphenylene structure (XLVII) there appears to be only one alternative for a hydrocarbon $C_{12}H_8$ possessing the properties described and capable of yielding phthalic acid on oxidation. This is the structure (LI), the benzo-derivative of pentalene which has been called *cyclo*pentindene (Patterson and Capell, "The Ring Index," 1940). The suggestion that Lothrop's diphenylene might be *cyclo*pentindene was made in 1942 (Baker, *loc. cit.*), thus avoiding the two difficulties inherent in the diphenylene formula which have already been mentioned. On general grounds (LI), for which three arrangements of the bonds are possible, two benzenoid and one ortho-quinonoid, would be expected to be a stable, almost strainless molecule of aromatic type. Coulson (*Nature*, 1942, **150**, 577) has calculated that the resonance energies of diphenylene and *cyclo*pentindene differ by only about 4 kg.-cals., the former being the greater, but that diphenylene possesses a strain energy of possibly 100 kg.-cals., whereas the strain energy of *cyclo*pentindene is only a few kg.-cals., and concludes that *cyclo*pentindene should be considerably more stable than diphenylene.

At the time when the *cyclo*pentindene structure was put forward as an alternative to the diphenylene formula all the known facts were capable of explanation on the basis of either structure. Even the production of the same dimethyl derivative from structurally isomeric di-iododiphenyls may be accounted for by assuming that under the vigorous conditions of the reaction one of the benzene rings undergoes rupture at the bond common to the benzene and the four-membered ring (Baker, *loc. cit.*). More recently, however, three pieces of evidence have become available which give strong support to the diphenylene structure. Waser and Schomaker (*J. Amer. Chem. Soc.*, 1943, **65**, 1451), in an electron diffraction investigation of diphenylene, find inter-atomic distances of 1·42 A. (very strong), 2·44 A. (strong), 2·78 A. (strong), corresponding to the average bonded C–C distances, the *meta*- and *para*-distances in the benzene ring respectively, and 2·1 A. (very weak) regarded as the diagonals of the four-membered ring. These authors state that the *cyclo*pentindene structure is definitely excluded, because there are no C–C distances of 2·30 A. corresponding to the calculated diagonals of two regular pentagons. The validity of this assertion rests upon assumptions as to the dimensions of the two five-membered rings. These will not be regular, because, for example, the bond common to the two is wholly single, so that some of the diagonals may equal the distance between *meta*-carbon atoms in the benzene ring. The absence of any indication of a distance of the order of 2·30 A. is, however, scarcely consistent with the *cyclo*pentindene structure. A preliminary note of an incomplete X-ray crystallographical investigation of Lothrop's hydrocarbon by Chia-Si Lu (included in the paper by Waser and Schomaker, *loc. cit.*) shows a complex unit cell containing six molecules. Provisionally it has been suggested that two of these molecules may have a centre of symmetry, but this evidence has yet to be confirmed.*

The third piece of evidence concerns the reduction of diphenylene. It was suggested by Baker (*loc. cit.*) that a molecule possessing the diphenylene structure should undergo ready catalytic reduction with rupture of the strained four-membered ring to give diphenyl, and it was stated that in fact the compound combines with approximately three molecules of hydrogen. This statement was based on catalytic reduction experiments in acetic acid at room temperature in presence of a palladium–charcoal catalyst, and these experiments have since been confirmed. It has been found, however (unpublished experiments), that the course of the reduction is quite different when hydrogenation is effected in alcoholic solution in presence of Raney nickel; the uptake of hydrogen is rapid and ceases after little more than one molecule of hydrogen is absorbed, and an 85% yield of pure diphenyl can be isolated from the product. It is difficult to imagine how *cyclo*pentindene could so readily yield diphenyl, as the reaction involves the breaking of two presumably strainless C–C links and the formation of a new C–C link.

The balance of evidence is thus definitely in favour of the original diphenylene structure for Lothrop's hydrocarbon. If future work confirms this conclusion, diphenylene will have to be regarded as a unique type of molecule, in which the butadiene structure is stabilised by fusion with the two benzene rings, just as the *cyclo*octatetraene structure may be stabilised by fusion with three or four benzene rings, and in which the expected instability due to strain is compensated by increased stability due to resonance. It is probably also the only type of molecule in which it is possible to have an aromatic nucleus fused to a four-membered ring.

*Non-existence of Compounds containing a Four-membered Ring fused to an Aromatic Nucleus.*—Many formulæ are to be found in chemical literature in which an aromatic nucleus is shown fused to a four-membered ring. These fall broadly into three types, (1) tricyclic benzenoid compounds such as anthracene, acridine, phenazine, etc., (2) bicyclic compounds containing nitrogen with a bridged five-membered ring fused to a benzene ring, such as anthranil, 2-alkylindazoles, etc., and (3) a number of compounds of quite unrelated types. It would not be profitable to discuss these individual cases in the last category; most of the suggested four-membered ring structures are advanced without experimental justification, and in some cases the work is of doubtful value and a knowledge of the molecular weight of the compound is lacking. Sometimes a dipolar molecule is represented as completely covalent, and in one instance the four-membered ring is only made possible by the

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* Note added, April 30th, 1945. The complete X-ray crystallographical analysis of diphenylene has now become available (Waser and Chia-Si Lu, *J. Amer. Chem. Soc.*, 1944, **66**, 2035). The results establish conclusively the structure of the compound as (XLVII).
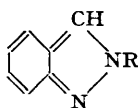
inclusion in the formula of two quinquevalent carbon atoms. In all these cases the onus of proof rests with those who suggest the formulæ.
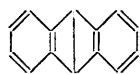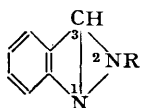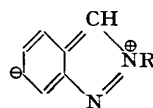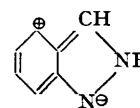


(LII.)    (LIII.)    (LIV.)    (LV.)    (LVI.)

With regard to type (1), anthracene, acridine, and related molecules were at one time written with long covalent links joining the central atoms of the system, thus making two four-membered rings as in (LII). The $X$-ray investigation of anthracene crystals by Robertson (*Proc. Roy. Soc.*, 1933, *A*, **140**, 79) has shown that the three hexagons are completely regular, so that the central atoms cannot be covalently linked. Further evidence on this point is that if the structure of anthracene were (LII), then its resonance energy would be simply that due to the two isolated benzene rings, namely $2 \times 39 = 78$ kg.-cals., whereas it is actually but little less than three times the value for benzene, namely, 105 kg.-cals. These molecules are clearly hybrid and may be written with four arrangements of the double bonds corresponding to the most stable structures which contribute to the normal state of the molecule (see Pauling, " The Nature of the Chemical Bond," Cornell University Press, 1939). It has thus rightly become customary to write these anthracene-like molecules without the central bond.

Bicyclic compounds of type (2) have been represented as containing either a four-membered ring as shown in formula (LIII) for a 2-substituted indazole, or else as being ortho-quinonoid in structure as shown in formula (LIV). The 2-alkyl- or 2-aryl-indazoles do not appear to possess the characteristics of genuine ortho-quinonoid compounds, such as colour and ability to add two molecules of bromine, and there can be little doubt that the molecules are resonance hybrids composed of the neutral orthoquinonoid form and not less than thirty-six additional dipolar forms, of which two are shown in formulæ (LV) and (LVI). If for simplicity it is assumed that these dipolar forms all contribute equally to the hybrid, the distribution of the charges is found to be such that the nitrogen atom in position 2 bears a certain positive charge, nitrogen atom 1 and carbon atoms 3 each bear one-fifth, and the six carbon atoms of the benzene nucleus each bear one-tenth of the corresponding negative charge. The result is that the molecule is stabilised by resonance to such an extent that it shows aromatic stability, and there is no need to assume the presence of the four-membered ring. As in the case of anthracene, the real state of the molecule cannot be represented by a single formula, and the determination of the actual resonance energy of such molecules and of the interatomic distances in the five-membered rings would be of very considerable interest.
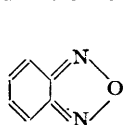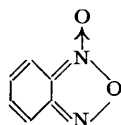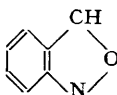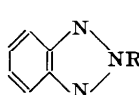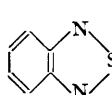


(LVII.)    (LVIII.)    (LIX.)    (LX.)    (LXI.)

There is evidence that certain molecules of this kind, all of which possess the same resonance possibilities, are much closer to genuine ortho-quinonoid types than others. This is the case with benzfurazan (LVII) and benzfurazan oxide (LVIII), which were at one time written with four-membered rings. These compounds behave like *o*-quinones in that they combine additively with two molecules of bromine, addition occurring at the olefinic bonds of the six-membered ring, and are, therefore, best represented by the formulæ shown (Hammick, Edwardes, and Steiner, J., 1931, 3308), but the rather slow rate of addition indicates some departure from the fixed ortho-quinonoid structure. The majority of molecules of this type which have been written with four-membered rings are, however, of a more hybrid character; they include anthranil (LIX; in this and the two succeeding formulæ no attempt is made to indicate the distribution of the valency electrons in the five-membered rings, and the benzene nucleus is shown as aromatic), *C*-methylanthranil, and anthranilcarboxylic acid (anthroxanic acid), thioanthranil, 2-substituted benztriazoles (LX), piazthiole (LXI), and piazselenole.

Further evidence which shows that compounds possessing a four-membered ring fused to an aromatic nucleus are at least not easy to prepare is to be found in a study of reactions where such a ring system might be produced. For example, dehydration of salicylic acid does not give a four-membered ring anhydride, but disalicylide containing an eight-membered ring, tetrasalicylide containing a sixteen-membered ring, and polysalicylides; some derivatives of salicylic acid are known to behave similarly. Phenol-*o*-sulphonic acids give not intramolecular but intermolecular anhydrides; anthranilic acid yields only intermolecular amides, and similar cases could be cited. The action of sodium on *o*-xylylene dibromide (Baker, Banks, Lyon, and Mann, J., 1945, 27) gives the centro-symmetric form of $1 : 2 : 4 : 5$-dibenz-$\Delta^{1:5}$-*cyclo*octadiene, $1 : 2 : 5 : 6 : 9 : 10$-tribenz-$\Delta^{1:5:9}$-*cyclo*dodecatriene, and polymeric products.