1042. *Macrocyclic Compounds. Part VI.[1] Spectroscopic Studies of Bent Chromophores Built into Ring Systems; Steric Effects in the Formation of Dibutadienylbenzene Chromophores.*

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The incorporation of polyene chromophores into ring structures involves a bending whose effect on the intensity distribution in the electronic spectra is discussed.

In order to study such spectral effects, macrocyclic hydrocarbons containing the *o*-, *m*-, and *p*-dibutadienylbenzene chromophores have been synthesized by alkali-isomerization of corresponding dibut-3'-ynylbenzene groupings. In analogous open-chain reference compounds the tetraenes are readily formed; each 1,3-diene grouping has the *trans,trans*-configuration and goes completely into conjugation with the aromatic ring. In macrocyclic compounds the same isomerization is more difficult and various isomers having 1,3-diene groupings not conjugated with the aromatic nucleus are also formed, especially in sterically hindered *p*-phenylene compounds. The 1,3-diene systems move around as inseparable units, they have usually the *cis,trans*-configuration, and seem to avoid the *s-cis*-conformation. When two diene systems meet, the resulting 1,3,5,7-tetraene group immediately aromatizes, except when a *p*-phenylene group and a too small ring impede the folding of the chain.

FROM the extensive spectral studies by Zechmeister and his school[2] of geometrically isomeric sets of various carotenoids and related compounds, the dependence of the

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[1] Part V, Hubert and Dale, *J.*, 1963, 4091.
[2] For a survey see Zechmeister, *Fortschritte Chem. Org. Naturstoffe*, 1960, **18**, 223.

electronic absorption spectrum on the shape of a conjugated polyene chromophore is well established and also theoretically well understood. In particular, the intensity relations of the main band (" fundamental " or one-quantum electron jump), occurring at longest wavelengths, and the *cis*-peak (" first overtone " or two-quantum electron-jump [3]) at shorter wavelengths, are determined directly by the shape of the chromophore: in the stretched linear all-*trans*-polyene the main band reaches its highest intensity and the *cis*-peak is not observed, whereas in the most V-shaped *cis*-isomers the main band is weaker and the *cis*-peak reaches its highest intensity. On the other hand, the wavelength position of the bands varies little with the shape and depends primarily on the number of conjugated double bonds.

It was considered that the back-bending of a chromophore might be carried to an extreme and its exact shape deduced or guessed with a higher degree of certainty if it were incorporated into a macrocyclic carbon skeleton. The first ring which might be assumed sufficiently large to permit correct valency angles and the accommodation of the necessary hydrogen atoms in the interior, yet so small that steric ambiguity is unlikely, is the 18-membered. Thus it was expected that a lengthening of the polyene chromophore from the diene (Fig. 1a) through the intermediates up to the octaene (Fig. 1d) would result in a progressive displacement towards the visible of both bands under discussion. In the spectra of the lowest members the main band should be more intense than the *cis*-peak; in the intermediates they should have comparable intensities; and in the last member the main band should be very weak and the *cis*-peak very strong (the intensities being roughly proportional to the square of the pointed lines in Fig. 1). Of particular interest is the question whether the transition from the polyene spectra to the " aromatic " spectrum of the electronically closed cyclo-octadecanonaene (Fig. 1e) is continuous or is accompanied by a drastic change of spectral type.

The last member has in the meantime been synthesized through macrocyclic polyacetylenes by Sondheimer and his co-workers.[4] Our attempts [5,6] to apply similar methods to the synthesis of the shorter polyenes, such as those shown in Fig. 1a—d, met with little success because of secondary reactions. Thus, cyclic alkadiynes invariably gave *o*-polymethylenebenzenes [5] instead of cyclic alkatetraenes.

It was then decided to stabilize the polyene chromophore by building a benzene ring into the middle of it. The benzene ring should most suitably be *ortho*-linked (II), as it would then be on the " outside " and not interfere with the stereochemistry of the big
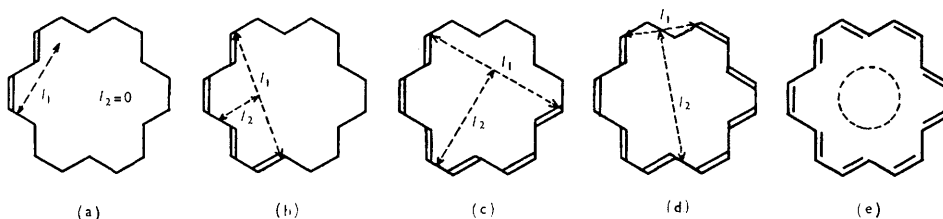

(a)   (b)   (c)   (d)   (e)

FIG. 1. The effect of increasing the size of bent polyene chromophores on the distances determining ultraviolet absorption intensities of (l_1) the main band and (l_2) the *cis*-peak. Chromophore placements have been chosen so as to keep the number of unfavourable *s-cis*-bonds a minimum.

ring itself, and it would allow through-conjugation. A *meta*-linked ring (III) would be sterically acceptable but electronically " insulating; " and a *para*-linked ring (IV), although allowing through-conjugation in principle, would give rise to steric hindrance
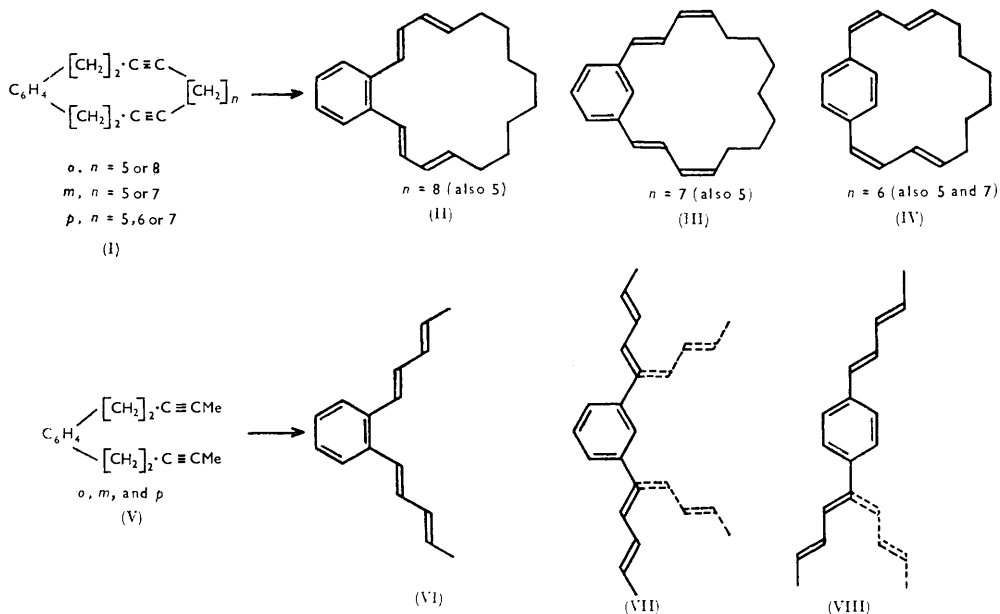
[3] Dale, *Acta Chem. Scand.*, 1954, **8**, 1235; 1957, **11**, 265.
[4] Sondheimer, Wolovsky, and Amiel, *J. Amer. Chem. Soc.*, 1962, **84**, 274.
[5] Part I, Dale, Hubert, and King, *J.*, 1963, 73.
[6] Part II, Hubert and Dale, *J.*, 1963, 86.

preventing a coplanar structure. The synthesis of acetylenic precursors for such compounds, the alkadiynylenebenzenes (I), as well as for analogous open-chain model substances (VI—VIII), the dipentynylbenzenes (V), have already been described.[6] All these compounds have the two acetylenic groups each separated from the benzene ring by two CH_2 groups, and have now been treated with potassium t-butoxide at elevated temperatures in order to produce by isomerization the respective dibutadienylbenzene chromophores.

o. n = 5 or 8
m, n = 5 or 7
p, n = 5,6 or 7

(I)

n = 8 (also 5)
(II)

n = 7 (also 5)
(III)

n = 6 (also 5 and 7)
(IV)

o, m, and p
(V)

(VI)   (VII)   (VIII)

Arguments for the justification of treating mixed chromophores, containing through-conjugated benzene rings and ethylenic bonds, essentially as a polyene system, have already been given by one of us;[7] subsidiary short-wavelength bands are accordingly interpreted as overtone bands corresponding to integral fractions of the total chromophore and not to arbitrary partial chromophores such as the styrene-, stilbene-, or butadienyl-benzene units. In the meantime three compounds (Fig. 2) containing the o-divinyl-benzene chromophore have been synthesized by Wittig and his co-workers;[8] their spectra

(a)   (b)   (c)

λ_1 (mμ): 257 (ε 14,000)   255 (ε 8000)   ~257 (ε 5000)
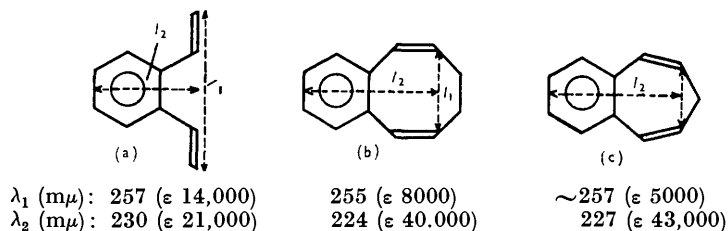λ_2 (mμ): 230 (ε 21,000)   224 (ε 40.000)   227 (ε 43,000)

FIG. 2. The spectral effect of the change in shape of the o-divinylbenzene chromophore imposed by a ring system; (a) probable conformation of o-divinylbenzene itself; (b) benzocyclo-octa-1,3,7-triene; (c) benzocyclohepta-1,3,6-triene.

may serve here as an illustration both of the validity of this overtone interpretation and of the consequences for the spectral-intensity distribution when a change in chromophore shape is imposed by incorporation into a (small) ring system. From Fig. 2 it can be seen

[7] Dale, *Acta Chem. Scand.*, 1957, **11**, 650, 971.
[8] Wittig, Eggers, and Duffner, *Annalen*, 1958, **619**, 10.

that the ends of the chromophore are drawn together in the cyclic compounds, and accordingly the intensity of the main band (at 257 mμ) decreases. On the other hand, the lateral dimension increases, and as a consequence the *cis*-peak (at 225—230 mμ) becomes much more intense. It is of particular interest that neither of these bands coincides with the main band of the only reasonable partial chromopore, styrene [7] (or 1-phenylpropene [9]), which absorbs at 240—250 mμ, just between them.

Two very recent examples of a simpler bent chromophore, the tetraenal system built into an azulene skeleton, are even more clear-cut. Whereas a corresponding open-chain system, decatetraenal,[10] shows a strong main band and a weak *cis*-peak (Fig. 3a), the two completely back-bent systems, 1-ethoxy-3-oxo-3a-phenyl-3,3a-dihydroazulene [11,12] and 3-oxo-3,3a-dihydrogaiazulene, [13] have the intensity of the two bands reversed

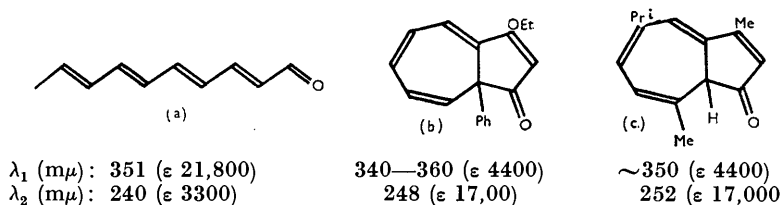|		
(a)	(b)	(c)
λ_1 (mμ): 351 (ε 21,800)	340—360 (ε 4400)	~350 (ε 4400)
λ_2 (mμ): 240 (ε 3300)	248 (ε 17,00)	252 (ε 17,000)

FIG. 3. The spectral effect of changing the shape of the tetraenal chromophore.

(Fig. 3b and c). For the former case (b), an interpretation of the strong band in terms of a partial chromophore has been proposed; [11] the weakness of the long-wavelength band was considered to be a consequence of steric hindrance. The identical intensity distribution in the latter unhindered compound (c) speaks strongly against such an interpretation.

Finally, vitamin B_{12} provides another example of a bent chromophore, although of a more complex type. Its macroheterocyclic part contains a conjugated cyanine-like system of 14 π-electrons distributed over 13 atoms. In the ultraviolet spectrum [14] there is a weak long-wavelength band and a much stronger short-wavelength band (Fig. 4b) which have already been interpreted by Kuhn [15] as the main band and the *cis*-peak, respectively. The electronically analogous open-chain system of the anion in Fig. 4a has indeed the two bands in closely similar positions, but with the inverse intensity ratio.[16] The position of the *cis*-peak (365 mμ) is predictable by a rule similar to that found for polyenes; [3] it should correspond to the position of the main band of a seven-π-electron ion, and falls in fact just between the band of a 6-electron aliphatic cyanine [17] (309 mμ) and that of an 8-electron cyanine [17] (409 mμ).

Open-chain Reference Compounds.—The isomerization of the dipentynylbenzenes (V) was followed by ultraviolet spectroscopy in order to determine the time necessary for preparative experiments. At 110° the isomerization proceeded cleanly and with no difficulty to completion within about 40 hours, whereafter the spectra remained unchanged for at least another 80 hours. Each side-chain being free to occupy its best conformation, no tendency to form incompletely conjugated isomers was observed.

The spectral development during isomerization is especially clear and instructive in

[9] Mixer, Heck, Winstein, and Young, *J. Amer. Chem. Soc.*, 1953, **75**, 4094.
[10] Blout and Fields, *J. Amer. Chem. Soc.*, 1948, **70**, 189.
[11] Druey, Jenny, Schenker, and Woodward, *Helv. Chim. Acta*, 1962, **45**, 600.
[12] Barton, Gardner, Petterson, and Stamm, *J.*, 1962, 2708.
[13] Fuks and Chiurdoglu, I.U.P.A.C. Congress on Natural Products, Brussels, 1962; cf. *Ind. Chim. Belge*, 1962, **27**, 541.
[14] Bonnet *et al.*, *J.*, 1957, 1148, 1158.
[15] Kuhn, *Fortschritte Chem. org. Naturstoffe*, 1959, **17**, 404.
[16] Schwarzenbach, Lutz, and Felder, *Helv. Chim. Acta*, 1944, **27**, 576.
[17] Simpson, *J. Chem. Phys.*, 1948, **16**, 1124.

λ_1 (mμ): 5500 (ε 112,000) 540, 581 ($E\sim1$)
λ_2 (mμ) 365 (ε 5000) 368 ($E\sim3$)
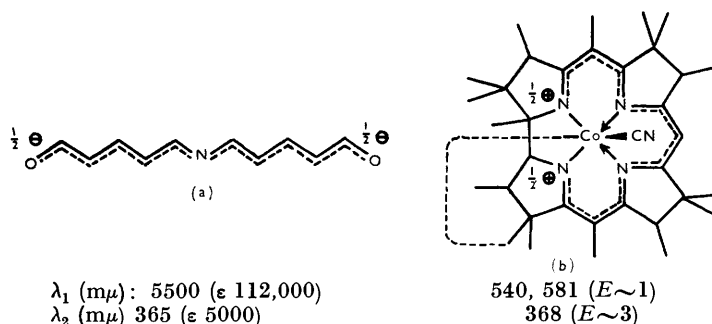
FIG. 4. The bent vitamin B_{12} chromophore (b) compared with an open-chain electronic analogue (a).

these cases (Fig. 5). The transient appearance of a band at 277 mμ for the *ortho*-isomer, and at 292 mμ for the *para*-isomer, is ascribed to the intermediate singly isomerized compound having a phenylbutadiene chromophore;[18] its absence in the fully developed chromophore of the doubly isomerized compound represents another argument against
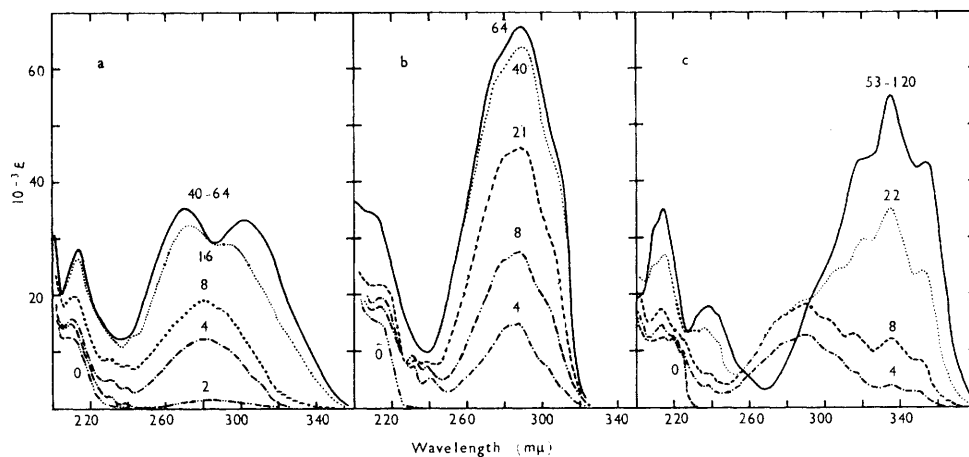

FIG. 5. Spectral development in the ultraviolet region during alkali-isomerisation at 110° of dipent-3'-ynylbenzenes (ether as solvent); (a) *ortho*-isomer; (b) *meta*-isomer; (c) *para*-isomer. Reaction times in hours are marked on the curves.

the idea of partial-chromophore bands in polyene spectra and supports an interpretation in terms of overtone bands. Thus, for the *ortho*-isomer (VI) the 303 mμ band is taken as the main band and the 269 mμ band (wavelength position corresponding to half the chromophore) as the *cis*-peak, strong because of the bent shape; the separation of the two bands is too large to be explained as a vibrational spacing.* Similarly, the *para*-isomer (VIII) has a strong main band with structure at 336 mμ; it shows no absorption in the region ($\sim$270 mμ) expected for the *cis*-peak (half-chromophore), which presumably is forbidden because the molecule is straight (full lines in VIII), but shows a weak band at a wavelength (240 mμ) corresponding well with that expected for the always allowed second overtone (third-chromophore). The *meta*-isomer (VII) shows a completely different behaviour as no intermediate band is observed. This is not unexpected considering

* The lack of structure, as well as the relatively low wavelength position of the main band (and of the band of the mono-isomerized product), are ascribed to some steric hindrance caused by the α-hydrogen atoms.

[18] Walborsky and Pendleton, *J. Amer. Chem. Soc.*, 1960, **82**, 1405.

that no through-conjugation is possible, and that similar Dewar-cross-conjugated [19] systems absorb at the same wavelength as each of the two " overlapping " real partial chromophores [7] of which it consists. In fact, the doubly isomerized product absorbs in the same region (~280 mμ) as the phenylbutadiene chromophore,[18] but with greater intensity.

The air-sensitive dipenta-1′,3′-dienylbenzenes could be isolated by crystallization. Their ultraviolet spectra are given in Fig. 6 and are essentially the same as those of the crude products. The infrared spectra show the unique strong band at 10·14 μ typical of
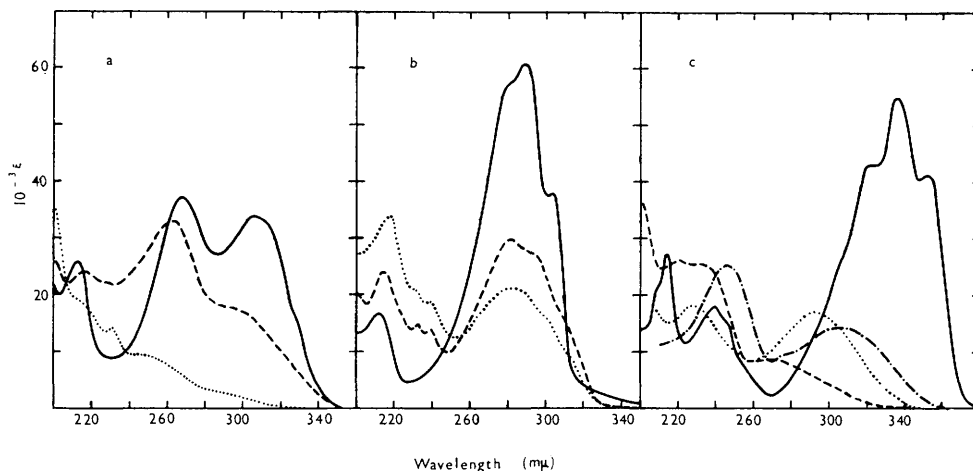

FIG. 6. Ultraviolet spectra in n-hexane (or cyclohexane for VI and VIII) of hydro-carbons containing dibutadienylbenzene chromophores; (a) *ortho*-isomers; (b) *meta*-isomers; (c) *para*-isomers. Full lines represent crystallized open-chain compounds (VI—VIII); broken lines best liquid tetraene fractions obtained by isomerization of 18-membered macrocyclic compounds (I; *o, n* = 8; *m, n* = 7; *p, n* = 6); dotted lines of a 15-membered *ortho*-ring (I; *n* = 5) and a 16-membered *meta*-ring (I; *n* = 5). The 17-, 18-, and 19-membered cyclic *para*-compounds (*n* = 5, 6, 7) gave closely similar spectra. Dotted and dash-dotted curves in (c) represent the crystalline cyclic *para*-compounds (XV) and (XIIIa, *n* = 7), respectively.

trans,trans-dienes,[20] and bands for the methyl group; these prove the configurations to be those given (VI—VIII). The positions of the double bonds were also confirmed by ozonolysis, the method [21] used involving borohydride reduction to alcohols. Further proof for the *trans,trans*-configuration was obtained by the formation of double adducts with maleic anhydride, in yields increasing in the order *ortho* < *meta* < *para*, indicative of a simple steric effect. The adducts were all stable high-melting solids, the *meta*-isomer having the lowest melting point, as was also the case for the hydrocarbons themselves. Finally, hydrogenation gave the expected dipentylbenzenes as liquids.

Cyclic Compounds.—The isomerization was much less clear-cut in the case of the cyclic compounds (I), and usually a temperature of 125° was needed for reasonable reaction times. Destruction of the doubly isomerized product set in while there remained still much of the starting material and the singly isomerized product. The transient appearance of intermediate dienynes was therefore less readily noted, and the extent of formation of the final tetraenes could be followed only with difficulty; hence, in preparative experiments the reaction had to be stopped when the total ultraviolet intensity reached

[19] Dewar, *J.*, 1952, 3544.
[20] Jackson, Paschke, Tolberg, Boyd, and Wheeler, *J. Amer. Oil Chemists' Soc.*, 1952, **29**, 229.
[21] Part IV, Hubert, *J.*, 1963, 4088.

a maximum. Chromatography on alumina gave a more or less complete separation of the mixture into doubly and singly isomerized products and starting material. Invariably, the tetraene (doubly isomerized product) was first eluted, then came the dienyne (singly isomerized product), followed by the diyne (starting material). Unfortunately, the products were practically all liquids, and each main fraction could be only incompletely separated into the various positional isomers which were present, but they were satisfactorily characterized by ultraviolet and infrared spectroscopy and by ozonolysis. Some of the tetraenes were also analysed and hydrogenated, to prove that no skeletal changes had taken palace.

As to the decomposition products, they are at least in part formed by aromatization to give a second *ortho*-phenylene unit, as observed [5] with the simple cyclic alkadiynes. Evidence for this is: the final decrease in ultraviolet absorption; the observation in some cases of a first chromatographic fraction having only aromatic ultraviolet absorption; the appearance of infrared bands for *ortho*-substituted benzene in the crude isomerization product of *para*-alkadiynylene benzenes (I); and the complete conversion into a mixture of cyclophanes and polymethylenebiphenyls under extreme conditions. Only in one case was there evidence for the intermediate formation of a 1,3,5,7-tetraene chromophore, namely, in the 17-membered *para*-compound (I; $n = 5$). With the other compounds, the two diene groupings, when they meet, seem immediately to close a six-membered ring and aromatize. A very notable feature is also that the double bonds of the 1,3-diene grouping always remain together, as shown by infrared spectroscopy and ozonolysis, although the grouping as such does not always remain in conjugation with the aromatic nucleus. The reasons for this may be in part steric, in part a tendency to avoid the unfavourable *s-cis*-conformation. The double-bond configuration is in general *cis,trans*, as shown by infrared bands [20] at 10·17 and 10·54 μ; in certain cases, when it is sterically possible, as in some singly isomerized substances, a band at 10·13 μ indicates a *trans,trans*-configuration.[20] Surprisingly, the initially formed diene, isolated in one case, has the labile *cis,cis*-configuration. No Diels–Alder adducts could be obtained.

In the following, each type of ring compound will be treated separately in more detail.

o-*Phenylene ring compounds.* Preparative experiments were carried out at 125° for 4 hours with both the 15-membered (I; $n = 5$) and the 18-membered (I; $n = 8$) o-phenylene compounds. A small chromatographic fore-fraction showed only weak ultraviolet absorption typical of o-phenylene groups and compatible with an aromatization to *ortho*-cyclophanes. The tetraene fraction was inhomogeneous: in the case of the 15-membered ring it was not well separable but contained both the fully conjugated isomer of type (II), responsible for a broad ultraviolet band (Fig. 6a) at 245 mμ (*cis*-peak) and a shoulder at ~290 mμ (fundamental band), and isolated 1,3-diene groupings responsible for a band at 241 mμ. The relative intensities indicate a very small proportion of the first isomer, and a weak *trans,trans*-band in the infrared spectrum suggests that this compound has indeed the eclipsed *s-cis*-conformation of the type (II); its inherent instability [22] must be the reason for the preference of the non-conjugated isomer(s). In the case of the 18-membered ring the tetraenes were separated into two fractions, the preponderant one eluted first being the fully conjugated isomer as shown by ozonolysis. However, it cannot have the conformation (II), as the infrared spectrum shows that the dienes are *cis,trans*. It is therefore necessary to assume that this tetraene has adopted the conformation (IX) in order to avoid being *s-cis*. Such a conformation is here geometrically possible as the polymethylene chain is longer and the two ends can be approached by a slight bending of the chromophore plane any way required to relieve α-hydrogen repulsion. The ultraviolet spectrum showed a *cis*-peak at 265 mμ and a fundamental at 290 mμ (Fig. 6a). The intensity relations, when compared with those of the corresponding open-chain compound and the smaller-ring compound, are as expected, the 18-membered ring

[22] Aston, Szasz, Woolley, and Brickwedde, *J. Chem. Phys.*, 1946, **14**, 67.

occupying an intermediate position. In addition to a shorter end-to-end distance, non-coplanarity of the ring compounds is no doubt a factor responsible for some of the loss in intensity of the main band and certainly for shifts of the maxima to shorter wavelengths. The smaller fraction eluted afterwards consisted of a tetraene having one diene grouping moved out of conjugation by one CH_2 group, as shown by ozonolysis and in accord with the ultraviolet spectrum, which had bands at 232 (1,3-diene) and 275 mμ (phenylbutadiene). The dienyne fractions (singly isomerized substances), with both ring sizes, had a main ultraviolet band at 280 mμ, indicating the phenylbutadiene chromophore and little of the isolated 1,3-dienes; they thus contain mainly conjugated isomers. However, the infrared spectra showed the smaller ring to prefer a *cis,trans*-configuration, whereas the larger ring contains mainly *trans,trans*-diene. Molecular models permit the construction of the *trans,s-trans,trans*-conformation (X) for the latter, while for the smaller ring the *trans,s-trans,cis*-conformation (XI) is better. The *trans,s-cis,trans*-conformation is, of course, the easiest to construct, but it seems to be more important to avoid a *cis*-single bond than a *cis*-double bond.


(IX)   (X)   (XI)   (XII)
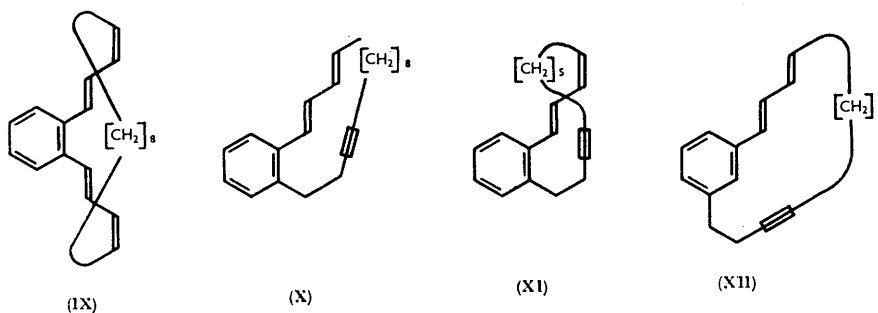
m-*Phenylene ring compounds.* The 16-membered *m*-phenylene compound (I; $n = 5$), when isomerized at 110°, reached a maximal ultraviolet absorption after about 20 hours, and this was almost constant for another 2 days. The absorption of the 18-membered homologue (I; $n = 7$) reached a maximum at 125° already after 2 hours; the intensity then decreased rapidly, suggesting a stronger tendency for aromatization.

Preparative experiments were carried out at 125°, for 8 hours with the 16-membered and for 4 hours with the 18-membered ring compound. Ozonolysis demonstrated in both cases that the tetraenes contained only ∼60% of the fully conjugated isomer (III), the non-conjugated isomers having up to three separating CH_2 groups. The reason for this deconjugation tendency is not clear. Chromatography on alumina gave tetraene fractions, and both ozonolysis and ultraviolet spectra showed that the fully conjugated isomer of the larger ring was more slowly eluted than the non-conjugated isomers, whereas this was reversed for the smaller ring. In the latter case, there was an indication of the formation of all-*cis* fully conjugated tetraenes which were eluted first (cf. the *p*-phenylene compound XV described below). The fully conjugated *cis,trans*-isomers absorb at 280 and 285 mμ, respectively, the larger ring coming closest both in position and intensity (Fig. 6b) to the open-chain compound (VII). However, its still relatively low absorption intensity remains unexplained as no steric hindrance is to be expected, and the possible shorter end-to-end distance, compared with the open-chain analogue (VII), according to simple theory, should have no influence when the benzene ring is *meta*-linked. The dienyne fraction (singly isomerized substances) of the 18-membered ring seems to be free from non-conjugated isomers; the infrared spectrum indicates a *trans,trans*-configuration (XII) and the ultraviolet maximum is at the same position as for the tetraene. This is the same behaviour as for the open-chain compound (Fig. 5b) and explicable by a lack of through-conjugation.[19]

p-*Phenylene ring compounds.* Isomerization of the 17-membered *p*-phenylene compound (I; $n = 5$) was exceptionally slow; at 110° no maximum was reached even after 120 hours, and at 125° much of the starting material could be recovered after 4 hours. At 160° the long-wavelength absorption reached a maximum after about 2 hours. The 18- and 19-membered homologues (I; $n = 6$ and 7), however, were more normal and reached maximal absorption already after 2 hours at 125°,

Preparative experiments for relatively short times (4—10 hours) at 125°, and chromatography on alumina, afforded tetraene and dienyne fractions. It transpired, however, that the conjugated tetraene (XIIIa) was present only as a minor constituent and that the product was a very complex mixture of positional isomers (XIIIa—h). The diene groupings always gave infrared spectra corresponding to the *cis,trans*-configuration, and the gas-chromatographic peaks of the ozonolysis products were rather narrow, indicating
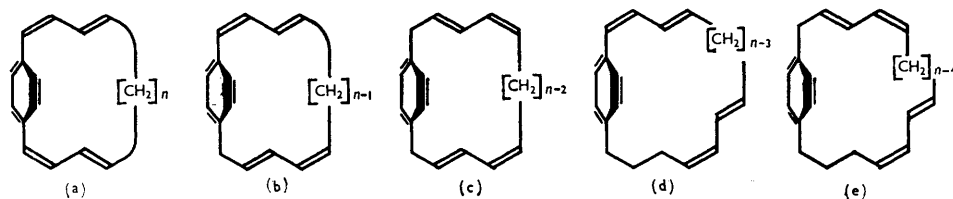

(XIII) $n = 5, 6,$ or 7 ($f : n-5,$ $g : n-6,$ $h : n-7$)

a limitation of the number of possible isomers deconjugated beyond step (b). These observations led us to postulate the principle that the diene groups avoid positions in the ring requiring the *s-cis*-conformation, which in butadiene[22] is unfavourable by 2·3 kcal. mole^{-1}. The isomers (XIIIc, d, e) should thus be preferred over other possible ones. The reason for the low tendency for conjugation is obvious; the formally conjugated isomer (XIIIa) cannot have coplanar aromatic and olefinic bonds and is therefore not effectively stabilized by mesomerism. The clear preference observed for the isomer (XIIIc) is less self-evident and is presumably caused by a conformational stability. These isomers could not in general be isolated free from the others, but the fully conjugated one is eluted somewhat more easily than those with isolated diene groupings. The ultraviolet spectra of such mixtures did not, however, permit conclusions about the spectrum of the bent *p*-dibutadienylbenzene chromophore, as the partially deconjugated isomers absorb too strongly.

Singly isomerized substances, dienynes, were also isolated in these experiments, but were absent after longer isomerization times (4 days). They seem to have a greater tendency to become conjugated, as judged from the ultraviolet absorption intensity, but this could not be checked by ozonization which, under the conditions used here, leaves triple bonds unbroken. It is surprising that the infrared spectra of the two larger rings indicate a *trans,trans*-configuration, which was not expected from a study of molecular models. The smaller ring produced the *cis,trans*-diene.

In the case of the 19-membered ring only, a small quantity of a crystalline isomeric compound, stable to air and melting at 80—85°, was eluted just in front of the usual tetraene fraction. It showed no *o*-phenylene absorption in the infrared region and no band in the 10—11 μ olefin region, yet had strong ultraviolet bands at 226 and 292 mμ (Fig. 6c); it must therefore contain only *cis*-double bonds (infrared band at 14·05 μ). The nuclear magnetic resonance (n.m.r.) spectrum confirmed the presence of olefinic protons in the correct proportion to aromatic and aliphatic protons. The double bond must be conjugated with the aromatic ring (cf. XV), as ozonolysis gave a main fragment identified as nonane-1,9-diol and another one corresponding to *p*-bishydroxymethylbenzene. The formation of the usually rather unstable *cis,cis*-diene systems is surprising, but may be the

normal primary product (cf. *cis*-but-2-ene from but-1-ene [23]) formed by protonation of the necessary intermediate allenic anion (XIV) on the assumption of attack from the least shielded side. The intermediate nature of the compound is demonstrated by its constant concentration (~3%) during the first 8 hours of reaction and its later disappearance. The insufficient length of the heptamethylene chain in its preferred stretched conformation and the steric repulsion of the aromatic hydrogen atoms both tend to twist the two terminal double bonds out of the plane, leaving the other two double bonds fairly coplanar with the aromatic ring. This would explain the ultraviolet spectrum as essentially that of a *p*-divinylbenzene chromophore with its main band at 292 mμ and the first overtone, active because of the cisoid shape, at 226 mμ. The stability to air may also be linked with the reduced conjugation. Models show that the molecule must still be quite strained, and its rigid conformation explains the high melting point. The abnormally high τ-values observed in the n.m.r. spectrum for the methylene groups reflect perhaps the strain in the too short heptamethylene chain.


(XIV)   (XV)
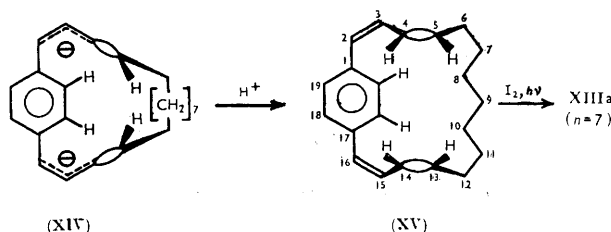
Irradiation of this all-*cis*-bicyclo[15,2,2]heneicosa-1(20),2,4,13,15,17(21),18-heptaene (XV) in hexane solution in the presence of iodine converted it within one minute into the 4,13-*trans,trans*-isomer (XIIIa; $n = 7$), as shown by the abrupt and complete change of the infrared spectrum, including the disappearance of the *cis*-absorption at 14·05 μ and appearance of the *cis,trans*-1,3-diene absorption at 10·18 and 10·56 μ. This isomer is also solid (m. p. 52—60°), and equally air-stable, indicating that the heptamethylene chain is still conformationally stable and stretched; its length should be more than sufficient and the n.m.r. signals for the methylene groups are now indeed at normal τ-values. The excessive length implies that the unsaturated system is again non-planar; the ultraviolet absorption is somewhat more intense and the bands have moved to 245 and 306 mμ (Fig. 6c), suggesting that the " terminal " double bonds have become slightly more coplanar and thus drawn more effectively into conjugation. This is supported by the relatively greater intensity of the *cis*-peak at 245 mμ with respect to the main band at 306 mμ. In spite of the non-planarity of this chromophore, obvious from a comparison with the wavelength position and intensity of the open-chain analogue (VIII) (Fig. 6c), its spectrum is nevertheless in qualitative accord with our expectations.

The final aromatization occurs to some extent at 125° in the 18- and 19-membered rings, and ultraviolet absorption at 240 mμ suggests that the main product is a non-planar biphenyl derivative [24] (XVI) rather than isomeric *ortho,para*-cyclophanes (XVII). On the other hand, the smaller 17-membered ring required treatment at 160° for 24 hours, and again the main product of the mixture seems to be a biphenyl derivative (XVI). When the reaction time (at 160°) had been very short (2—4 hours) and the ultraviolet absorption at longer wavelengths a maximum, ozonolysis showed that all four double bonds had to a great extent (more than 60%) moved into conjugation with each other. Accordingly, the infrared absorption pattern at 10—11 μ had completely changed and become more complex, with main bands at 10·20, 10·36, and 10·62 μ. The long-wavelength

[23] Schriesheim and Rowe, *Tetrahedron Letters*, 1962, 405.
[24] Beaven and Johnson, in Proc. Conf. Mol. Spectroscopy, London, 1958, Pergamon Press, 1959, p. 78; Beaven, in " Steric Effects in Conjugated Systems," Symposium, Hull, 1958, Butterworths Scientific Publns., 1958, p. 22.

position of the ultraviolet bands indicated that the chromophore might actually be that of a bent 1-phenylocta-1,3,5,7-tetraene, and the most likely configuration of the substance would be (XVIII), necessarily non-planar. This double-bond location is also in accord with the biphenyl formulation of the final aromatized substance. The reason why the

(XVI)   (XVII)   (XVIII)
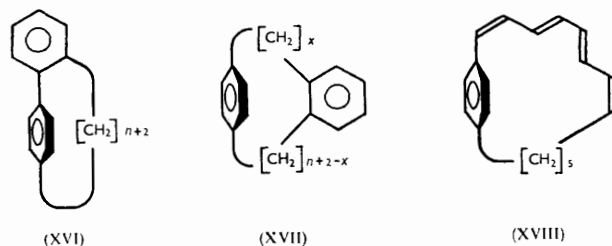
immediate precursor for the aromatization could be caught only in this case is clearly the small ring size and the *para*-phenylene group which makes it difficult for a too short chain to fold in a conformation suitable for a valency isomerization to the intermediate cyclo-hexadiene derivative:
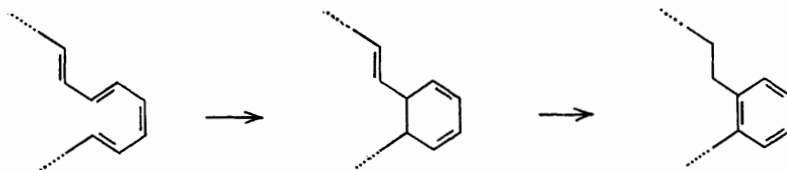
Normally, this reaction and the subsequent migration of the last double bond into the ring, appear to be extremely fast and occur as soon as the two diene systems meet.

EXPERIMENTAL

Preparation of Acetylenic Compounds.—The preparation of the dipent-3'-ynylbenzenes and the analogous cyclic diacetylenes used as starting materials have already been described.[6] One additional cyclic *para*-compound, *bicyclo*[15,2,2]*heneicosa*-1(20),17(21),18-*triene*-4,13-*diyne*, b. p. 180°/10^{-2} mm., m. p. 66°, was prepared in a similar manner from *p*-dibut-3'-ynylbenzene and 1,7-dibromoheptane in 10% yield (Found: C, 90·8; H, 9·2. $C_{21}H_{26}$ requires C, 90·6; H, 9·4%).

General Isomerization Procedure.—(a) For kinetic measurements a weighed quantity (1—2 g.) of the acetylenic compound was dissolved in a measured volume (50—100 ml.) of a solution of potassium t-butoxide, prepared by dissolution of potassium (30 g.) in t-butyl alcohol (500 ml.). Portions (∼5 ml.) were distributed in several small tubes, subsequently sealed under nitrogen. The tubes were heated in an oil-bath for the required times at the desired temperature, then cooled and opened. 2 ml. of the solution were transferred to a 10-ml. separatory funnel containing water and a little ether. After shaking, the aqueous phase was separated and the ether layer transferred to a 10-ml. volumetric flask. The funnel was rinsed and the aqueous phase washed with a little ether, which was then added to the same flask. A little sodium sulphate was added and the ultraviolet spectrum of the dry solution recorded. All these operations were carried out under nitrogen.

(b) In preparative experiments the acetylenic compound (1—2 g.) was heated with the butoxide solution (50 ml.) in a larger sealed tube (∼100 ml.) at the temperature and for the time indicated by the previous kinetic measurements as giving maximal ultraviolet absorption. The tube was then cooled and opened, and the solution poured into water. Extraction with ether and evaporation yielded the crude isomer mixture which was either crystallized from hexane at −70° (open-chain compounds) or chromatographed on alumina (cyclic compounds). The operations were carried out as far as practically possible under nitrogen as some of the fully conjugated polyenic substances are extremely autoxidizable.

8 o

Isomerization of o-*Dipent-3'-ynylbenzene* (V; *o*).—Kinetic measurements at 110° (13·1 mmoles/l.) gave the following spectral development (Fig. 5a). The ultraviolet spectrum of the starting material (λ_{max} 210 sh and 265 mμ; ε 13,100 and 140) changed into that of an intermediate product showing its characteristic features most distinctly after 8 hr. (λ_{max} 214, 232, 240, and 277 mμ; ε 20,400, 9000, 7800, and 19,000), then changed into the spectrum of the final product reaching its maximal intensity after 40 hr. (λ_{max} 214, 269, and 303 mμ; ε 28,000 35,600, and 33,600), whereafter no further change occurred except a slow intensity decrease, which even after 135 hr. amounted only to 10—15% (ε 28,400, 31,000, and 29,000).

A preparative experiment at 110° for 3 days, followed by crystallization from hexane at −70°, gave o-*dipenta*-1',3'-*dienylbenzene* (VI), m. p. 71—73° (Found: C, 91·1; H, 9·1. $C_{16}H_{18}$ requires C, 91·4; H, 8·6%). This compound, and its isomers to be described, can be kept unchanged at −70° under nitrogen for several weeks. Its ultraviolet spectrum in cyclohexane (λ_{max} 214, 268, and 305 mμ; ε 26,300, 37,300, and 34,000) is reproduced in Fig. 6a; typical infrared absorption bands of solutions in CCl_4 (2—12 μ) and CS_2 (8—15 μ) are at 6·07 and 10·13 μ (conjugated *trans,trans*-diene), at 6·26, 6·77, and 13·38 μ (o-phenylene), and at 7·24 μ (methyl). Hydrogenation over platinum dioxide in dioxan gave a liquid having the ultraviolet spectrum expected for o-dipentylbenzene. The *di-adduct* with maleic anhydride was prepared by heating the tetraene (0·23 g.) with maleic anhydride (0·3 g.) in benzene (50 ml.) at 100° for 40 hr. in a tube sealed under nitrogen. Crystals were precipitated on cooling; they were filtered off, washed with benzene, and recrystallized from much dioxan. The adduct (23%) melted with decomposition at 245° (Found: C, 71·1; H, 5·7; O, 23·8. $C_{24}H_{22}O_6$ requires C, 70·9; H, 5·5; O, 23·6%).

Isomerization of m-*Dipent-3'-ynylbenzene* (V; *m*).—Kinetic measurements at 110° (13·3 mmoles/l.) gave no evidence of an intermediate. The ultraviolet spectrum of the starting material (λ_{max} 210 and 265 mμ; ε 15,200 and 510) gave place to new absorption (Fig. 5b) increasing rapidly during the first 8 hr. (λ_{max} 214 and 288 mμ; ε 18,700 and 27,600), then more slowly to reach almost the final value after 40 hr. (λ_{max} 210 and 288 mμ; ε 34,000 and 64,000). After 64 hr. the intensity had increased only slightly further (ε 34,000 and 68,000).

A preparative experiment as above (3 days at 110°) gave m-*dipenta*-1',3'-*dienylbenzene* (VII), m. p. 50—53°, λ_{max} (in hexane) 214, 280 sh, 288, and 304 mμ (ε 16,500, 56,000, 61,000, and 37,500, Fig. 6b), λ_{max} 6·06 and 10·13 (conjugated *trans,trans*-diene), 6·26, 6·71, 12·58, and 14·57 (m-phenylene), and 7·24 μ (methyl). Hydrogenation as above gave a liquid having the ultraviolet spectrum expected for m-dipentylbenzene. The *di-adduct* with maleic anhydride was prepared as for the o-isomer (37% yield); it crystallized on addition of hexane to a solution in dioxan and melted at 200° (Found: C, 71·1; H, 5·4; O, 23·6%). From the mother-liquor a very little of another solid, m. p. 142—144°, was obtained; its composition approaches that of the *mono-adduct* (Found: C, 76·8; H, 6·2. Calc. for $C_{20}H_{20}O_3$: C, 77·9; H, 6·5%).

Isomerization of p-*Dipent-3'-ynylbenzene* (V; *p*).—Kinetic measurements at 110° (13·1 mmoles/l.) gave the following spectral development (Fig. 5c). The spectrum of the starting material (λ_{max} 220 and 265 mμ; ε 12,200 and 460) gave place to new bands belonging to an intermediate product together with, already after 8 hr., much of the final product (λ_{max} 215, 238, 292, 302, 313, 335, and 350 mμ; ε 17,500, 7300, 18,300, 15,800, 13,000, 11,200, and 8600). After 22 hr. the final product was preponderant (λ_{max} 214, 238, 295, 307, 319, 333, and 352 mμ; ε 26,000, 13,700, 19,900, 24,400, 29,400, 35,000, and 26,300) and the final spectrum was reached after 53 hr. (214, 240, 322, 336, and 352 mμ; ε 30,500, 17,500, 44,000, 55,000, and 42,800); there was only a slight general intensity reduction after 120 hr. (ε 29,800, 16,800, 43,000, 53,000, and 41,000).

A preparative experiment as above (3 days at 110°) gave p-*dipenta*-1',3'-*dienylbenzene* (VIII) as yellow flakes, m. p. 140° (Found: C, 91·0; H, 9·0%), λ_{max} (in cyclohexane) 214, 240, 322, 337, and 353 mμ (ε 27,200, 18,100, 42,800, 55,000, and 42,200; Fig. 6c), λ_{max} 6·06, 6·23, and 10·14 (conjugated *trans,trans*-diene), 6·61 and 12·17 (p-phenylene), and 7·25 μ (methyl). When the crystals were left in air, the m. p. increased; already after one day at 0° they had absorbed about 28% oxygen (Found: C, 66·5; H, 6·1%), had become insoluble, and developed an aldehydic smell. Ozonolysis and subsequent borohydride reduction [21] gave the expected fragments, p-bisdihydroxymethylbenzene and ethylene glycol. Hydrogenation as above gave p-*dipentylbenzene* as a liquid showing the expected ultraviolet absorption (Found: C, 87·8; H, 11·75. $C_{16}H_{26}$ requires C, 88·0; H, 12·0%). The *di-adduct* with maleic anhydride was prepared as for the o-isomer (70% yield) and melted at 242—244° (Found: C, 70·9; H, 5·7; O, 24·1%).

Isomerization of Benzocyclopentadec-1-ene-5,12-diyne (I, o; n = 5).—Kinetic measurements at 110° (13·1 mmoles/l.) gave the following result. In the ultraviolet spectrum of the starting material ($\lambda_{max.}$ 210 sh and 265 mμ; ε 12,200 and 270) several new bands belonging to different products developed side by side. After 4 hr. they had comparable intensities ($\lambda_{max.}$ 212, 232, 241, and 275 mμ; ε 15,500, 8150, 7700, and 7000) which were maximal after 17 hr. ($\lambda_{max.}$ 215, 232, 241, and 265 mμ; ε 18,800, 15,400, 14,500, and 10,600). Then, a general intensity decrease set in; after 135 hr. the maxima were hardly discernible ($\lambda_{max.}$ ~230, ~240, and ~270 mμ; ε 10,300, 300, and 4100).

A preparative experiment at 110° for 24 hr. gave an oil showing infrared bands at 6·25, 6·73, 10·17, 10·57, and 13·32 μ. A similar product (1 g.) was obtained at 125° (4 hr.) and was chromatographed on a 1-m. column of alumina (activity I) at 5° in the absence of daylight, with hexane, hexane–benzene mixtures, and benzene as eluents. A first fraction (265 mg.) showed broad ultraviolet maxima (Fig. 6a) at 210, 241, 245, and 290 sh mμ (ε 20,000, 14,000, 9600, and 3300) and infrared bands at 6·09, 10·24 (broad), and 10·59 μ (narrow) (conjugated *cis,trans-* and possibly *trans,trans*-diene); it must be the doubly isomerized, fully conjugated tetraene (II; n = 5) with some isolated 1,3-diene (241 mμ band). After an intermediate mixed fraction (220 mg.), containing much isolated 1,3-diene (233 and 240 mμ), came a third fraction (153 mg.) with clearer ultraviolet maxima at 215 and 280 mμ (ε 13,700 and 11,300) as well as at 233 and 240 mμ, and infrared bands at 10·19 and 10·56 μ (conjugated *cis,trans*-diene); it must contain the singly isomerized compound (XI).

All these polyenes and those described in the following sections polymerized even at 0°; insoluble solids formed after about a week.

Isomerization of Benzocyclo-octadec-1-ene-5,15-diyne (I, o; n = 8).—Kinetic measurements at 80° gave only a very slow change in the ultraviolet spectrum of the starting material ($\lambda_{max.}$ 210, 262, and 280 mμ; ε 11,300, 390, and 220); after 26 hr. the intensity at 280 mμ was 4000. At 125° the change was rapid; bands at 215 and 270 mμ had acquired most of their intensity after 2 hr. (ε 9600 and 9150), reached a maximum after 8 hr. (ε 11,800 and 12,700), then remained fairly constant (after 23 hr., ε 13,300 and 11,700). After 155 hr. general destruction had occurred, and the intensity at 270 mμ was only 3900.

A preparative experiment at 125° for 4 hr. gave an oil which was chromatographed on alumina. A small fore-run (16 mg.) had $\lambda_{max.}$ 213 and 280 mμ (ε 16,600 and 370) which indicated an aromatized product. Then came a main fraction (210 mg.) with $\lambda_{max.}$ 220, 265, and 290 mμ (ε 18,700, 30,000, and 15,700) and $\lambda_{max.}$ 6·08, 6·16, 10·17, and 10·55 μ (conjugated *cis,trans*-diene), indicating the structure to be that of the doubly isomerized fully conjugated tetraene (II; n = 8). This was confirmed by ozonolysis; [21] gas chromatography of the reduced ozonolysis products gave two main peaks identified as *o*-bishydroxymethylbenzene and decane-1,10-diol. An intermediate, not well separated, tetraene fraction (100 mg.) had $\lambda_{max.}$ 232 and 275 mμ (ε 18,700 and 11,700), indicating isolated diene and phenylbutadiene chromophores; they are separated by one CH_2 group as the ozonolysis product gave two main gas-chromatographic peaks whose retention times correspond to C_9 diols. The next main fraction (240 mg.) had $\lambda_{max.}$ 215 and 280 mμ (ε 18,000 and 17,000) and $\lambda_{max.}$ 4·50 (C≡C), 6·08, 6·16, and 10·13 μ (conjugated *trans,trans*-diene), and a weak band at 10·57 μ (some *cis,trans*-diene), indicating the singly isomerized compound (X) with a phenylbutadiene chromophore; accordingly no small fragments (diols) were obtained by ozonolysis, only higher-boiling compounds. The last main fraction (130 mg.) showed only weak ultraviolet absorption and was essentially unchanged starting material.

A preparative experiment at 125° for 8 hr. allowed chromatographic separation of a fraction of the tetraene (II; n = 8) having a somewhat higher intensity in the ultraviolet spectrum ($\lambda_{max.}$ 215, 266, and 290 mμ; ε 22,600, 33,300, and 17,700; see Fig. 6a).

No Diels–Alder adduct with maleic anhydride could be obtained. Catalytic hydrogenation on platinum oxide of the main chromatographic fractions gave liquids having $\lambda_{max.}$ 6·23, 6·32, 6·71, and 13·35 μ (*o*-phenylene). Apart from some overhydrogenation of certain fractions (reduction of the aromatic nucleus), the spectra were identical with that of the benzocyclo-octadecene obtained [6] by hydrogenation of the starting material; hence the original carbon skeleton is preserved.

Isomerization of Bicyclo[13,3,1]nonadeca-1(19),15,17-triene-4,11-diyne (I, m; n = 5).—Kinetic measurements at 110° (13·3 mmoles/l.) gave the following results. In the ultraviolet spectrum of the starting material ($\lambda_{max.}$ 210 and 263 mμ; ε 11,300 and 360) bands at 215 and

280 mμ developed quickly in the first 8 hr. (ε 16,400 and 11,100), then more slowly to reach a maximal intensity after 21 hr. (ε 25,600 and 18,000). After 40 and 64 hr. the intensity of the band at 282 mμ stayed constant (ε 16,200).

A preparative experiment at 125° for 8 hr. gave an oil (1 g.) which was separated on alumina into three strongly overlapping fractions. The first " fraction " (130 mg.) showed no infrared band (CCl_4 solution) at 10—11 μ, yet cannot be the aromatized product as it absorbed strongly in the ultraviolet region at 214 sh and 274 mμ (ε 28,000 and 14,900) and gave practically no non-fragmented products on ozonolysis. Instead, diol pairs corresponding mainly to con-jugated tetraene (*m*-bishydroxymethylbenzene and heptane-1,7-diol), but also to tetraenes deconjugated by one step (aromatic C_9 diol, aliphatic C_6 diol), by two steps (ar. C_{10} diol, al. C_5 diol), and by three steps (ar. C_{11} diol, al. C_4 diol), were observed. 1,3-Diene groupings must therefore be present and may have the *cis,cis*-configuration. The second " fraction " (250 mg.) showed the typical *cis,trans*-diene infrared bands at 6·09, 10·20, and 10·60 μ and ultraviolet bands (Fig. 6b) at 218 and 280 mμ (ε 34,000 and 21,300); a weak isolated-diene absorption appeared at 240 mμ. Ozonolysis gave the same diol pairs as above, in yields of 60, 10, 20, and 10%, respectively. The third " fraction " (200 mg.) contained also doubly isomerized products but less of the fully conjugated tetraene; the four diol pairs were now obtained in yields of 45, 15, 30, and 10%. The ultraviolet absorption was less intense at 216 and 282 mμ (ε 24,000 and 17,500) but the isolated-diene absorption at 241 mμ was somewhat stronger. The same infra-red bands were present, but the one at 10·20 μ had two shoulders; new bands appeared at 5·92 and 14·3 μ.

Isomerization of Bicyclo[15,3,1]*heneicosa*-1(21),17,19-*triene*-4,13-*diyne* (I, *m*; *n* = 7).—Kinetic measurements at 125° (66·1 mmoles/l.) gave the following result. Bands at 216 and 284 mμ were almost completely developed already after 2 hr. (ε 27,000 and 25,800), reached a maximal intensity after 4 hr. (ε 30,000 and 27,800), then started degrading; after 22 hr. the intensity of the band at 284 mμ was 16,300.

A preparative experiment at 125° for 4 hr. gave an oil which crystallized at −70° but remelted on warming. It showed infrared bands at 5·93, 6·08, 6·25, 6·36, 6·74, 10·12 sh, 10·19, and 10·57 μ, indicating some conjugated *trans,trans*-diene with the *cis,trans*-diene. Ozonolysis gave both non-fragmented products and pairs of diols arising from doubly isomerized compounds; the main constituent of these latter was the pair *m*-bishydroxymethylbenzene and nonane-1,9-diol, corresponding to a fully conjugated tetraene (estimated 62%). The tetraene deconjugated by one step (aromatic C_9 diol, aliphatic C_8 diol) constituted about 25%; tetraene(s) deconjugated by two steps (ar. C_{10} diol, al. C_7 diol) constituted about 13%; by three steps (ar. C_{11} diol, al. C_6 diol) only traces.

Chromatography of the oil (1 g.) on alumina gave a first main fraction (280 mg.) having the typical infrared bands for a conjugated *cis,trans*-diene. There were ultraviolet bands at 215 and 285 mμ whose intensities indicated less conjugated isomers in the first subfractions (ε 32,500 and 22,800) than in the later ones (ε 24,000 and 30,000); on the other hand, bands at 233 and 241 mμ (conjugated diene) were stronger at first and weaker later (Fig. 6b). Thus, among these doubly isomerized products the non-conjugated tetraenes seem to be somewhat more easily eluted than the fully conjugated tetraene (III; *n* = 7); this was substantiated by ozonolysis which gave all four diol pairs in the first subfractions and decreasing quantities of the minor ones in the later subfractions. A second main fraction (220 mg.) contained the singly isomerized product as the ultraviolet absorption was less intense (ε 19,500 and 23,700) and the ozonolysis gave non-fragmented products; infrared absorption at 10·12 μ indicates a *trans,trans*-con-figuration. However, it also contained large amounts of doubly isomerized product, but only as the fully conjugated isomer, shown by the presence of only one diol pair (ar. C_8 diol, al. C_9 diol) among the ozonolysis products. A third main fraction (160 mg.) proved to be the starting material with the constituents of the previous fraction as impurities, as shown by ozonolysis.

Isomerization of Bicyclo[13,2,2]*nonadeca*-1(18),15(19),16-*triene*-4,11-*diyne* (I, *p*; *n* = 5).—Kinetic measurements at 110° (13·1 mmoles/l.) gave the following result. The ultraviolet spectrum of the starting material ($\lambda_{max.}$ 220 and 265 mμ; ε 10,000 and 320) changed slowly and continuously with time; after 4 hr. there were maxima at 221, 238, and 265 mμ (ε 14,700, 6660, and 2580), after 22 hr. at 210, 235, and 265 mμ (ε 21,800, 14,900, and 3800), after 53 hr. at 221, 238, and 315 mμ (ε 23,200, 14,900, and 5150), and after 120 hr. at 220, 253 sb, 316 sh mμ (ε 24,000, 11,400, and 10,000). At 160° this final type of spectrum had developed after 1 hr. ($\lambda_{max.}$ 222, 274, 286, and 310 mμ; ε 26,000, 7700, 7400, and 6500) and reached a maximum

after 2 hr. ($\lambda_{max.}$ 220, 254, 290, and 315 mμ; ε 19,700, 10,500, 8300, and 8400); the intensity stayed constant after 4 hr., then the long-wavelength bands started to disappear (ε 4000 after 14 hr., 400 after 24 hr., 0 after 48 hr.).

A preparative experiment at 125° for 4 hr. gave an oil (1·5 g.) which by chromatography was separated into two first fractions (60 and 140 mg.), similar to those described in the next experiment, and a fraction containing unchanged starting material, of which about 0·7 g. was recovered by crystallization. A second experiment at 125° for 10 hr. yielded an oil (1 g.) which was also chromatographed on alumina. A first main fraction (450 mg.) showed infrared bands at 6·05, 6·20, 10·17, and 10·55 μ (conjugated *cis,trans*-diene) and ultraviolet bands at 219, 233, and 278 mμ with higher intensity in the first subfractions (ε 28,800, 26,800, and 7000) than in the later (ε 25,000, 23,500, and $\sim$5000). The 278 mμ band may partly be caused by doubly isomerized monoconjugated tetraenes (phenylbutadiene chromophore) as ozonolysis showed that very little of the fully conjugated isomer (IV; $n = 5$) was present and only in the first subfractions. Six pairs of aromatic/aliphatic diols were in fact observed, and even when several isomeric aromatic diols are conceivable, the gas-chromatographic peaks were sharp enough to represent just one and to suggest a limitation of the number on the principle that *s-cis*-conformations in the 1,3-diene systems are avoided (XIII; $n = 5$). The isomer distribution (%) (XIII; a—f) in the subfractions is on this basis roughly:

Isomer	a	b	c	d	e	f
First fraction	11	7	75	2	1	4
Middle ,,	2	33	57	3	0	5
Last ,,	0	17	31	13	33	6

The next main fraction (260 mg.) showed similar infrared bands at 6·05, 6·20, 10·18, and 10·53 μ (conjugated *cis,trans*-diene), as well as at 7·48 μ (C≡C·CH$_2$) in the later subfractions. An ultraviolet maximum was found at 222 mμ (ε 28,000) and further absorption falling off slowly towards longer wavelengths. The ozonolysis gave here a variety of diols which, however, did not fit properly together in pairs; a singly isomerized product may be involved which gives fission of a (strained?) triple bond.

A preparative experiment at 160° for 3 hr. gave an oil having $\lambda_{max.}$ 220, 254, 290, and 315, falling to 380 mμ (ε 15,700, 8400, 6800, and 6600), and $\lambda_{max.}$ 6·62 (*p*-phenylene) and 3·31, 6·10, 6·20, 10·08 sh, 10·20, 10·36, 10·62, and 10·75 sh μ (olefinic bands), indicating a 1,3,5,7-tetraene chromophore. This was confirmed by ozonolysis which showed main chromatographic peaks with retention times corresponding to an aromatic C$_{13}$ diol and ethylene glycol, but also other weaker peaks; the distribution of the isomers (XIII; $n = 5$) was roughly 10% c, 20% d, 10% e, 60% f.

Chromatography (1 g.) on alumina gave a first fraction (80 mg.) with no ultraviolet maxima, only shoulders at 232 and 270 mμ (ε 25,000 and 2300); infrared bands were at 6·62 (*p*-phenylene) 6·78 (*o*-phenylene), and (very weak) at 10·62 μ. It gave no clear ozonolysis products and must therefore contain aromatized products. The next fraction (390 mg.) showed no infrared *o*-phenylene bands, but bands at 10·07 (only a shoulder in the last subfractions), at 10·20 and 10·62 (stronger in the last subfractions) and at 10·35 μ (strong through all fractions). The ultraviolet spectra showed bands at 254 and 262 mμ, which were strongest (ε 15,600 and 15,300) in the earlier subfractions, and at 220, 303 sh, 315, 331 sh, and 347 sh mμ, which were strongest in the later subfractions (ε 25,000, 12,500, 13,300, 11,000, and 6000). Ozonolysis gave one main diol fragment, and this fraction must therefore contain the 1-phenyl-1,3,5,7-tetraene chromophore, possibly in different geometrical-isomeric forms (main band about 315 mμ, first overtone at 260 mμ, second overtone at 220 mμ). A last fraction (40 mg.) had a similar infrared spectrum (10·08 μ band absent) and an ultraviolet band at 290 mμ (ε 11,000) together with a stronger band at 220 mμ (now first overtone). Ozonolysis gave several new close-lying fragments; hence this fraction may contain tetraene systems not conjugated with the benzene ring.

Another run at 160°, but for 24 hr., gave a viscous oil which dissolved partially in pentane, leaving a residue soluble in benzene. The fractions had similar infrared spectra: there were no bands typical of olefins, but a band at 6·62 and a group of bands at 12—12·5 μ (*p*-phenylene), as well as bands at 6·20 and 6·77, and a group of bands at 13—13·6 μ (*o*-phenylene), indicating a mixture of aromatized products ("*ortho-para*-cyclophanes"). That the isomer having one single saturated chain, the 2,4'-heptamethylenebiphenyl, was also present, is indicated by the

ultraviolet spectrum, which shows a distinct shoulder at 235 mμ (ε ∼7000), reasonable for a non-planar biphenyl.[24]

Isomerization of Bicyclo[14,2,2]eicosa-1(19),16(20),17-triene-4,12-diyne (I, *p*; *n* = 6).— Kinetic measurements at 125° (66·0 mmoles/l.) gave the following result. Broad absorption in the region 260—350 mμ (λ_max. 268 mμ) stayed practically constant from 2 to 22 hr. (ε 7000—8000). A band at 222 mμ (ε 27,000 after 2 hr.) reached its maximal intensity (ε 35,000) after 4 hr., then decreased slightly (ε 28,000 after 22 hr.).

A preparative experiment at 125° for 4 hr. gave an oil whose infrared spectrum (CCl₄ solution) showed weak bands at 4·35 and 4·47 μ (C≡C) and strong bands at 6·04, 10·18, and 10·52 μ (conjugated *cis,trans*-diene); there were also bands at 6·60 (*p*-phenylene) and 6·74 μ (*o*-phenylene). Ozonolysis gave, besides some non-fragmented products, six pairs of aromatic/aliphatic diols; the gas-chromatographic peaks of the aromatic diols were again sharp, and the irregular increments in retention times can best be understood if it is assumed that only the positional isomers (XIII; *n* = 6) allowing the *s-trans*-conformation of the 1,3-diene groupings, were formed. The quantities were roughly 10% a, 10% b, 40% c, 20% d, 20% e, no f, and a few percent of g.

Chromatography of the oil (1 g.) on alumina gave a first main fraction (280 mg.), λ_max. 10·21 and 10·56 μ (conjugated *cis,trans*-diene). The earlier subfractions showed stronger ultraviolet absorption (Fig. 6c) at 270 mμ (ε 8500) than the later subfractions (ε 4000—5000); for a band at 220—230 mμ it was opposite (ε 27,000 and 30,000—35,000). This indication that the conjugated tetraene (IV; *n* = 6) is eluted before the non-conjugated tetraenes was confirmed by ozonolysis, which gave the following distribution (%) of the isomers (XIII; *n* = 6):

Isomer	a	b	c	d	e
First fraction	40	20	30	10	0
Last ,, ...	12	17	50	14	7

A second main fraction (150 mg.) had a somewhat stronger infrared band at 10·15 μ (conjugated *trans,trans*-diene?), indicating a singly isomerized product, but it seems to contain mainly non-conjugated doubly isomerized products (tetraenes), the last subfractions showing no absorption at 270 mμ but strong absorption at 225 mμ (ε 38,500) (Fig. 6c). A last main fraction (110 mg.) gave no lower diols on ozonolysis, hence must contain singly or non-isomerized substances.

Isomerization of Bicyclo[15,2,2]heneicosa-1(20),17(21),18-triene-4,13-diyne (I, *p*; *n* = 7).— Kinetic measurements at 125° (45·5 mmoles/l.) showed a rapid development of an ultraviolet band at 270 mμ which reached a maximal intensity (ε 12,000) after 2 hr.; it was then gradually displaced to 282 mμ and slowly lost intensity (ε 10,000 after 30 hr.). A band developed more slowly at 220 mμ (ε 18,600 after 2 hr.), to reach a maximum after 13 hr. (225 mμ; ε 38,000); then it diminished slowly (ε 33,000 after 30 hr.).

A preparative experiment at 125° for 8 hr. gave an oil (1 g.) which was chromatographed on alumina. A first small fraction (35 mg.) solidified, and a next fraction (70 mg.) was half-solid. The solid fraction showed only weak infrared absorption at 10—11 μ, and ultraviolet bands at 227 and 290 mμ (ε 17,400 and 14,000). Recrystallization from ethanol–methanol gave an air-stable solid, m. p. 80—85° (yield 2·5%), showing no double-bond absorption at 10—11 μ, but bands at 6·62 and 12·05 μ (*p*-phenylene), 3·42, 3·51, and 6·82 (CH₂), strong bands at 14·05 (*cis*-double bond) and 15·1 μ, as well as several other bands between 11·5 and 14·0 μ. The ultraviolet spectrum (Fig. 6c) showed two structureless bands at 226 and 292 mμ (ε 18,100 and 16,800), and analysis showed it to be isomeric with the starting material (Found: C, 90·6; H, 9·5. C₂₁H₂₆ requires C, 90·6; H, 9·4%). The n.m.r. spectrum in CS₂ (low solubility) showed a sharp line for aromatic protons at τ 2·8, a group of lines for olefinic protons at τ 3·5—3·7, and lines at τ 8·2 for α-methylene and at τ 9·1 for the other methylene groups. The relative intensities were 4·0 : 7·3 : 3·7 : 10·9 (required for XV, 4 : 8 : 4 : 10). Ozonolysis gave two gas-chromatographic peaks, identified as those of *p*-bishydroxymethylbenzene and nonane-1,9-diol. This product is therefore *all*-cis-*bicyclo[15,2,2]heneicosa-1(20),2,4,13,15,17(21),18-heptaene* (XV).

Further elution yielded oily fractions forming a first main fraction (300 mg.) overlapping with the solid-producing fractions; there were infrared bands at 6·07, 6·22, 10·18, and 10·55 μ (conjugated *cis,trans*-diene), and no band at 7·5 μ (C≡C·CH₂), showing that it contained doubly isomerized products (tetraenes). Ozonolysis demonstrated that the fully conjugated tetraene (IV; *n* = 7) was concentrated in the first subfractions, and non-conjugated isomers in the later

subfractions; again six pairs of aromatic/aliphatic diols were obtained whose sharp gas-chromatographic peaks and irregular retention time increments indicate a limitation of possible isomers (XIII; $n = 7$). The isomer distributions (%) in the subfractions were roughly:

Isomer	a	b	c	d	e	f
First fraction	30	20	37	4	7	2
Middle ,,	12	20	40	12	13	3
Last ,,	6	18	55	15	4	3

The ultraviolet spectra confirm this; a strong band at about 225 mμ (ε 27,000—35,000) is attributed to isolated 1,3-dienes, and a weaker band at about 280 mμ (ε 8800—9800) to mono-conjugated isomers (phenylbutadiene chromophore) and fully conjugated tetraenes. All the subfractions deposited an insoluble polymer on storage.

A second main fraction (140 mg.) had the same olefinic infrared bands at 6·08, 6·22, 10·18, and 10·55 μ, but also C≡C·CH$_2$ absorption at 7·5 μ; the product was therefore singly isomerized. In accordance therewith, no lower diol was obtained by ozonolysis. Weaker ultraviolet absorption than for the first main fraction at 220 mμ (ε 17,700) and stronger at 270 mμ (ε 11,700) indicate that a relatively larger proportion of the conjugated isomer is present (phenylbutadiene chromophore). No precipitate of polymer was obtained on storage.

When the reaction time was longer, only traces of the crystalline compound were isolated from the first fractions (10 hr.: <1%; 4 days: ~0). When it was shorter, the quantity remained constant (5 hr.: 2·5%; 3 hr.: 3·0%). Ultraviolet irradiation of a hexane solution of this compound in the presence of iodine produced spectral changes which came to an end after 1 min.; after this time a general decrease in ultraviolet absorption intensity indicated destruction. Evaporation of a sample after irradiation for 2 min. yielded an air-stable oil which crystallized slowly (m. p. 52—60°). It had infrared bands at 6·64 and 12·25 (*p*-phenylene), 6·07, 6·22, 10·18, and 10·56 (*cis,trans*-diene), a strong band at 11·60, and no absorption at 14 μ. The ultraviolet spectrum (Fig. 6c) showed two structureless bands at 245 and 306 mμ (ε 25,100 and 14,400). The n.m.r. spectrum in CS$_2$ showed a sharp line for aromatic protons at τ 2·9, olefinic absorption around τ 3·8, and lines at τ 7·9 for α-methylene and at τ 8·6 for the other methylene groups. Relative intensities agree qualitatively with structure (XIIa; $n = 7$) but could not be measured accurately as some bands were broad and over-lapping.

A run for 4 days at 125° also gave an oil (1 g.), which was chromatographed on alumina. A first main fraction (200 mg.) was eluted abnormally easily; the presence of infrared bands at 6·63 and 6·75 μ (*p*- and *o*-phenylene), together with the absence of strong olefinic absorption at 10—11 μ, indicate aromatization, and an ultraviolet band at 241 mμ (ε 10,700) suggests a non-planar biphenyl system [24] although a shoulder at 270 mμ (ε 5000) cannot be explained. Ozonolysis confirmed this; no lower diols were formed. An intermediate fraction (100 mg.) followed, and then came a second main fraction (250 mg.) with no *o*-phenylene absorption in the infrared region but strong bands at 10·18 and 10·55 μ (conjugated *cis,trans*-diene). Ultraviolet maxima at 227 and 275 mμ (ε 24,000—27,000, 6000—7000) indicated isolated 1,3-diene and phenylbutadiene chromophores, and ozonolysis showed the isomer distribution (XIII; $n = 7$) to be rather similar in all subfractions, namely about 10% a, 15% b, 30% c, 20% d, 25% e, and 3% f, and there was no higher-boiling product. No singly isomerized substances or starting material could be eluted.

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