1239. *Macrocyclic Compounds. Part X.*[1] *Macrocyclic Hydrocarbons Containing Conjugated Diene Systems*

By A. J. Hubert and Johannes Dale

Cycloalka-1,3-dienes were isolated from isomer mixtures obtained by equilibration of non-conjugated dienes. Only the *cis,trans*-isomer is formed with ring sizes from C_{12} to C_{16}, and the chromophore has a planar transoid conformation in the 14-membered and larger rings. With ring sizes from C_{18} also the *trans,trans*-isomer is present; this chromophore can be planar transoid in 18-membered and larger rings.

Cycloalkatetraenes containing two diametrically placed conjugated *cis,cis*-diene systems were obtained by trialkylborane reduction of corresponding tetraynes (C_{16}–C_{24}). Alternation in melting point and in structure of the ultraviolet absorption band along this series reflects the expected alternation in conformational rigidity.

Normal and medium-sized conjugated cycloalkadienes have already been reported and their ultraviolet spectra discussed.[2-4] From a study of molecular models and certain relationships between intensity and wavelength, position of the absorption maximum,

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[1] Part IX, A. J. Hubert and J. Dale, *J.*, 1965, 3118.
[2] E. Pesch and S. L. Friess, *J. Amer. Chem. Soc.*, 1950, **72**, 5756.
[3] R. W. Fawcett and J. O. Harris, *J.*, 1954, 2673.
[4] A. T. Blomquist and A. Goldstein, *J. Amer. Chem. Soc.*, 1955, **77**, 998.

and the degree of coplanarity of the double bonds, Braude [5] has drawn conclusions about configuration and conformation of these diene chromophores. Thus, the 8-membered ring is said to be the largest to have a *cis,cis*-configuration as its most stable form, while the 9-membered ring requires a *cis,trans*-configuration; both chromophores are assumed to have a non-planar cisoid (s-*cis*) conformation. The most stable configuration of the 10- and 11-membered cycloalka-1,3-dienes was deduced to be *cis,trans*, and the chromophores have been assigned a non-planar transoid (s-*trans*) conformation. Later, however, a perfectly stable *cis,cis*-cyclodeca-1,3-diene was prepared [4] which has no maximum in the ultraviolet and therefore must have the double bonds in mutually perpendicular planes.

Some higher members, C_{12}, C_{13}, C_{14}, C_{16}, and C_{18}, have been reported,[6-8] but ultraviolet absorption intensities were not given and configurations not established. Furthermore, these compounds were all prepared under isomerising conditions and were all liquids. When we found [9] that the equilibrium mixture of macrocyclic alkadienes contains large amounts of non-conjugated isomers and that the isolated 14-membered conjugated isomer is a solid, it became of great interest to take a closer look at this series.

As in the case of cyclotetradeca-1,3-diene,[9] also the conjugated dienes of other ring sizes in the C_{12}–C_{22} range could be isolated, by chromatography on alumina, from the equilibrium mixture of dienes obtained by treating more easily available [9] non-conjugated isomers of the general type $\overline{\text{-CH=CH}\cdot(\text{CH}_2)_m\cdot\text{CH=CH}\cdot(\text{CH}_2)_n\text{-}}$ where $m = n$ or $n + 1$, with triethylborane. The conjugated isomers are the most strongly absorbed on alumina, and the separation was followed conveniently by infrared and ultraviolet spectroscopy. In the lower members (C_{12}–C_{16}) the conjugated isomer had in each case exclusively the *cis,trans*-configuration, as shown by the typical infrared bands at 10·17 and 10·54 μ,[10] and showed an ultraviolet absorption maximum at about 235 mμ (Figure 1). In the higher members (C_{18}, C_{20}, C_{22}) the spectra of the eluted fractions showed a striking variation; the first fractions showed more pronounced vibrational structure in the ultraviolet spectrum with a maximum at 233 mμ and an infrared band at 10·13 μ typical [10] for the *trans,trans*-1,3-dienes, while the later fractions had the same characteristics as the *cis,trans*-1,3-dienes of the lower members (Figure 1). However, the overlapping of fractions became more and more serious as the ring size increased, and the conjugated *trans,trans*-diene was always contaminated with non-conjugated isomers, as shown by an infrared band at 10·35 μ (*trans*-olefin), too low absorption intensity in the ultraviolet (Table 1 and Figure 1), and by ozonolysis.[11] On the other hand, the *cis,trans* fractions, which were eluted last, were pure. The earlier *cis,trans* fractions contained also the *trans,trans*-diene, so that the yields given in Table 1 are only approximate. All these conjugated *cis,trans*-dienes except the already reported *cis,trans*-cyclotetradeca-1,3-diene,[9] were liquid, and attempts to crystallise the impure *trans,trans*-dienes failed.

The ultraviolet spectra (Figure 1) of these dienes do not show extreme variations. The intensity maximum lies as normally on the second vibrational peak and at the same wavelength as in open-chain dienes, thus excluding drastic deviations from a planar transoid conformation. However, the 12- and 13-membered *cis,trans*-dienes show definitely lower absorption intensity, indicating some twisting. It is of particular interest that the 14-membered diene is the first one to reach the full intensity and that it shows the sharpest vibrational structure, a feature generally associated with a rigid structure. This ring is actually the smallest one for which a practically strain-free molecular model can be constructed having all single bonds staggered and the correct stereochemistry [12] about the planar

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[5] E. A. Braude, *Chem. and Ind.*, 1954, 1557.

[6] M. Stoll and A. Commarmont, *Helv. Chim. Acta*, 1948, **31**, 1077.

[7] R. B. Ingraham, D. M. MacDonald, and K. Wiesner, *Canad. J. Research*, 1950, **288**, 453.

[8] M. F. Bartlett, S. K. Figdor, and K. Wiesner, *Canad. J. Chem.*, 1952, **30**, 291.

[9] A. J. Hubert and J. Dale, *J.*, 1963, 4091.

[10] J. E. Jackson, R. F. Paschke, W. Tolberg, H. M. Boyd, and D. H. Wheeler, *J. Amer. Oil Chemists' Soc.*, 1952, **29**, 229.

[11] A. J. Hubert, *J.*, 1963, 4088.

[12] J. Dale, *J.*, 1963, 93.

cis,trans-diene grouping [Figure 2(a)]. This type of conformation becomes again possible in the 18-membered [Figure 2(b)] and the 22-membered ring, and it may be significant that the absorption intensity is here higher than in the 16- and 20-membered rings. The *trans,trans*-isomer, which in open chains is by far the dominant species in the equilibrium, makes its appearance for the first time (Figure 1) in the 18-membered ring, which interestingly is the smallest ring for which a fairly strain-free molecular model can be constructed accommodating the planar *trans,trans*-diene in the required fashion[12] in a ring with only staggered single bonds [Figure 2(c)]. The next ring for which this type becomes again possible is again the 22-membered. The relative yield of *cis,trans*- and *trans,trans*-diene in these two ring sizes (Table 1) is surprisingly in favour of *cis,trans*, although, as shown above, good models are possible for all four isomers. An explanation is suggested by the fact that conformation (c) in Figure 2 is somewhat less compact than conformation (b), and contains two more *gauche*-bonds.

TABLE 1

Conjugated cycloalkadienes isolated from the equilibrium isomer mixture

Ring atoms	Confign.	Yield (%)	ε (in hexane) at 235 mμ	Found (%) C	Found (%) H	Formula	Required (%) C	Required (%) H
12	*cis,trans*	10	17,700	—	—	$C_{12}H_{20}$	87·7	12·3
13	,,	25	18,000	87·4	12·4	$C_{13}H_{22}$	87·6	12·4
14	,,	50	22,800	87·3	12·4	$C_{14}H_{24}$	87·4	12·6
15	,,	52	23,900	86·7	12·0	$C_{15}H_{26}$	87·3	12·7
16	,,	48	22,000	87·5	12·8	$C_{16}H_{28}$	87·2	12·8
18	,,	26	24,700	87·2	13·2	$C_{18}H_{32}$	87·0	13·0
,,	*trans,trans*	19	(16,900) *	—	—	,,	,,	,,
20	*cis,trans*	14	20,000	86·3	12·8	$C_{20}H_{36}$	86·9	13·1
,,	*trans,trans*	22	(15,000) *	—	—	,,	,,	,,
22	*cis,trans*	29	22,500	86·5	13·0	$C_{22}H_{40}$	86·8	13·2
,,	*trans,trans*	16	(11,800) *	—	—	,,	,,	,,

* $\lambda_{max.}$ at 233 mμ; intensity too low because of the presence of non-conjugated isomers.

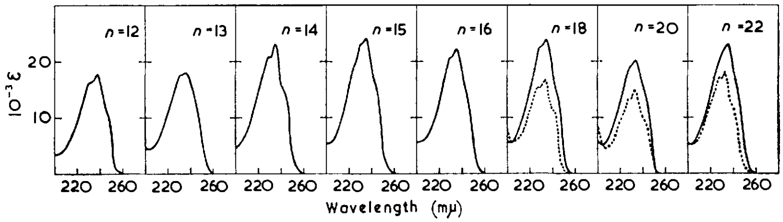


FIGURE 1. Ultraviolet spectra in n-hexane of cycloalka-1,3-dienes. Full lines represent pure *cis,trans*-isomers, broken lines *trans,trans*-isomers with some non-conjugated isomers as impurity. *n* is the number of ring (or carbon) atoms

To verify whether the very much lower absorption intensity of the medium-sized *cis,trans*-cycloalka-1,3-dienes (ε 6200[3] for C_{11}; ε 5000[3] or 7250[4] for C_{10}; ε 2500[3] for C_9) could not at least in part be due to the presence of non-conjugated isomers, the synthesis of *cis,trans*-cyclodeca-1,3-diene, according to Blomquist and Goldstein,[4] *via* a Hofmann degradation was repeated. The product obtained had the same characteristics ($\lambda_{max.}$ 222 mμ, ε 7450) and showed only one peak in the gas chromatogram, but revealed the presence of both non-conjugated isomers and cyclodecene (in all ~30%) by quantitative ozonolysis.[11] However, this corresponds to a corrected $\varepsilon_{max.}$ of no more than 10,650, so that it is still clear that the chromophore is quite twisted, and much more so than in the 12-membered and higher rings.

A conjugated *cis,cis*-diene grouping is not more easy to incorporate into a large ring structure than a *trans,trans*-diene if the preferred[13] transoid conformation is to be preserved.* It is therefore natural that no indication of *cis,cis*-isomers was found in the equilibrium mixtures. However, conjugated *cis,cis*-dienes can be obtained by partial reduction of conjugated diynes, and especially easily with trialkylboranes as described in the preceding Paper.[14] By this method a series of macrocyclic alkatetraynes (I) were reduced to all *cis*-cycloalkatetraenes (II) containing two *cis,cis*-diene groupings placed diametrically. Data for these compounds are given in Table 2; the ultraviolet spectra are reproduced in Figure 3 and compared with the spectrum of the open-chain analogue, *cis,cis*-dodeca-5,7-diene.[14]

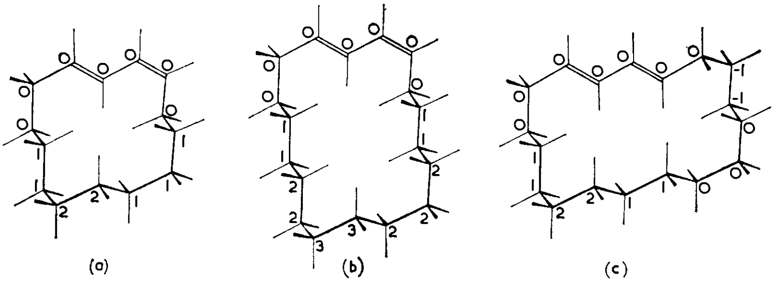
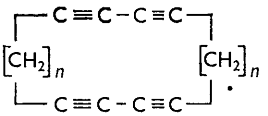
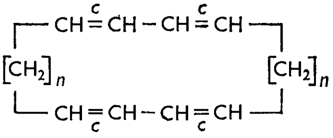


FIGURE 2. Conformations of (a) *cis,trans*-cyclotetradeca-1,3-diene, (b) *cis,trans*-, and (c) *trans,trans*-cyclo-octadeca-1,3-diene. All ring atoms marked with the same number lie in a common plane, and all these planes are parallel



(I)



(II)

The very strong melting-point alternation in this series (Table 2) resembles the alternation (high m. p. for odd *n*, low for even *n*) found in the parent cycloalkatetraynes[15] and many other homologous series,[12,15] and can be explained on the same conformational basis. Only when the number (*n*) of methylene groups in the two saturated chains is odd can an entirely strain-free carbon skeleton, such as the one shown in Figure 4, be constructed, and only in those cases is conformational homogeneity and rigidity to be expected. The ultraviolet spectra (Figure 3) strongly support this idea; the vibrational structure, which generally reflects structural rigidity, is clearly more pronounced in the cases when

TABLE 2

Conjugated cycloalkatetraenes (II) from trialkylborane reduction of cycloalkatetraynes (I)

						Found (%)			Required (%)	
n	Ring size	Yield (%)	M. p.	$\lambda_{\max.}$ (mμ) (in hexane)	ε	C	H	Formula	C	H
4	16	—	liq.	229	22,200	—	—	$C_{16}H_{24}$	88·8	11·2
5[14]	18	33	117°	229	55,000	88·4	11·6	$C_{18}H_{28}$	88·45	11·55
6	20	15	liq.	229	44,700	87·0	11·4	$C_{20}H_{32}$	88·2	11·8
7	22	23	68°	229, 235	50,000	88·2	12·2	$C_{22}H_{36}$	87·9	12·1
8	24	25	liq.	235	45,000	87·2	12·0	$C_{24}H_{40}$	87·7	12·3
(*cis-cis*-Dodeca-5,7-diene[14])				(236	24,000)					

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* In smaller rings the unstable cisoid (or gauchoid) conformation becomes of course imposed, and then a *cis,cis*-configuration is most easily incorporated.

[13] J. Dale and A. J. Hubert, *J.*, 1963, 5475.

[14] A. J. Hubert, preceding Paper.

[15] J. Dale, A. J. Hubert, and G. S. D. King, *J.*, 1963, 73.

n is 5 or 7 than when n is 4, 6, or 8. The absorption intensity shows also a slight alternation in the same sense, but only for the first member ($n = 4$) is it so low that it can be concluded on this basis that the chromophores must there be considerably twisted. Another trend (Figure 3) is a regular displacement of the intensity maximum from the third and fourth vibrational peaks in the 16-membered ring ($n = 4$), *via* the third peak ($n = 5$ and 6), and further to the second and third ($n = 7$) to end finally on the second peak in the 24-membered ring ($n = 8$), as is also normally the case in open chains. According to the Franck–Condon principle, this would mean that the central single bond undergoes a relatively larger change of double-bond character during the electronic transition $\mathrm{C{=}C{-}C{=}C} \longrightarrow {}^{\pm}\mathrm{C{-}C{=}C{-}C}^{\mp}$ in the lower than in the higher members, and so points to a gradually increasing planarity and electronic delocalisation as the series is ascended. On this basis the proposed conformation of Figure 4 has to be modified. Its unfavourable feature is evidently [12] that there is a too large open hole in the middle, a consequence of the excessive length of the diene bridges. A more compact conformation, requiring a slight twisting of the diene groupings, may therefore be a perferred compromise, although its detailed nature is hardly predictable.

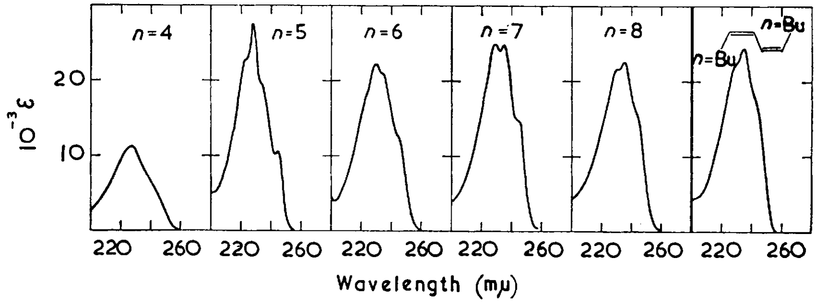

FIGURE 3. Ultraviolet spectra in n-hexane of the all-*cis*-cycloalkatetraenes (II). The extinction value is half-molar in order to permit comparison with *cis*,*cis*-dodeca-5,7-diene (to the right)

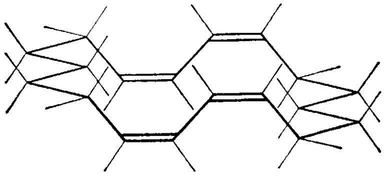

FIGURE 4. A possible strain-free but open conformation of all-*cis*-cyclo-octadeca-1,3,10,12-tetraene (II; $n = 5$)

EXPERIMENTAL

Isolation of Cycloalka-1,3-*dienes*.—The non-conjugated *cis*,*cis*-cycloalkadines described earlier [9,15] were used as starting materials. The isomerisation with triethylborane [9] was carried out at 200°. After destruction of the catalyst the mixture of isomers was chromatographed on alumina (Woelm, activity I) from hexane. Each fraction (15 ml.) was examined for ultraviolet absorption at about 235 mμ, evaporated, and weighed; infrared spectra were measured only of selected fractions. The spectral data given in Figure 1 and Table 1 refer to the most homogeneous fractions; only in one case (cyclotetradeca-1,3-diene [9]) was purification by crystallisation possible. The best fractions were also analysed (Table 1). The purity as concerns double-bond position was checked by semiquantitative ozonolysis [11] and the absence of an infrared band at 10·35 μ; for the configurational purity the infrared spectrum was consulted (see (ext).

Preparation of cis,trans-*Cyclodeca*-1,3-*diene*.—The procedure of Blomquist and Goldstein [4] was followed and gave a liquid with a structureless absorption band (in hexane) at 222 mμ (ε 7450); reported [4] 222 mμ (ε 7250). It formed a 1 : 1 *complex* with silver nitrate (Found: C, 38·3; H, 5·25; Ag, 36·4. $C_{10}H_{16},AgNO_3$ requires C, 39·2; H, 5·3; Ag, 33·9%). The liquid hydrocarbon gave one unresolved peak by gas chromatography on polyethylene glycol succinate. Ozonolysis followed by sodium borohydride reduction and acetylation [11] gave in the gas chromatogram the expected octane-1,8-diol diacetate only in about 70% yield; other peaks corresponded to heptane-1,7-diol diacetate (from cyclodeca-1,4-diene) and decane-1,10-diol diacetate (from cyclodecene).

*Preparation of all-*cis*-Cycloalkatetraenes* (II).—These compounds were prepared from the corresponding tetraynes [15] (I), as already described [14] for the case of cyclo-octadeca-1,3,10,12-tetraene ($n = 5$), by reaction with tri-isobutylborane and subsequent hydrolysis with acetic acid. In all cases the expected quantity of isobutene was evolved. Yields, spectral data, and analyses are given in Table 2; full ultraviolet spectra are in Figure 3. They all had olefinic infrared bands at 3·33, 6·25, and 14·0 μ, and no typical bands at 10—11 μ.

Our thanks are due to Mr. M. Hubert for experimental assistance.

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[*Received, May 26th,* 1965.]