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Cyclic Acetylenes. XIV. The Effects of Ring Strain on the Electronic Spectra of Cyclic Tolans and Cyclic Diphenyldiacetylenes

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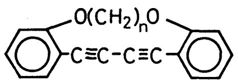
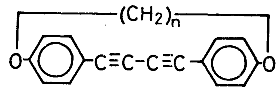
Characteristic features of the electronic spectra of *o,o'*-bridged cyclic diphenyldiacetylenes (I_n), *o,p'*-bridged cyclic tolans (II_n), *p,p'*-bridged cyclic diphenyldiacetylenes (III_n) and *p,p'*-bridged cyclic tolans (IV_n) are compared. The hyperchromism observed in the longest-wavelength absorption maxima (λ_{max}) in the higher homologues of I_n, III_n, and IV_n as compared with the absorption intensities of the respective open-chain analogues is explained in terms of the coplanarity of the chromophore system, and the marked hypochromism observed in the lower homologues of these cyclic acetylenes is attributed to ring strain. The hypochromism observed in the series of II_n is ascribed to the superposition of the effects of ring strain and the twisting of phenyl groups. The bathochromic shifts of λ_{max} with the increase of ring strain in the *p,p'*-bridged series (III_n and IV_n) are explained by the pronounced increase of the energy of the ground state of the strained molecule of this series. On the other hand, the hypsochromic shifts of λ_{max} of *o,o'*-bridged series (I_n) are regarded as the result of the minor increase of energy of the ground state along with the increase of the ring strain.

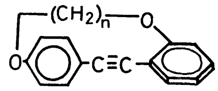
In previous papers we reported the syntheses and properties of *o,o'*-bridged cyclic diphenyldiacetylenes (I_n),[1] *o,p'*-bridged cyclic tolans (II_n),[2] *p,p'*-bridged diphenyldiacetylenes (III_n)[3] and *p,p'*-bridged cyclic tolans (IV_n).[4] In the present paper, we wish to summarize the characteristic features of the electronic



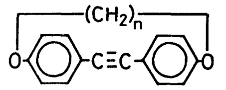
(I_n) n=3, 4, 5, 6



(III_n) n=13, 14, 15, 18



(II_n) n=7, 8, 9, 10, 11, 12



(IV_n) n=11, 12, 13, 14, 18

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[1] F. Toda and M. Nakagawa, This Bulletin, **34**, 862 (1961).

[2] M. Kataoka, T. Ando, and M. Nakagawa, *ibid.*, **44**, 177 (1971).

[3] M. Kataoka, T. Ando, and M. Nakagawa, *ibid.*, **44**, 1909 (1971).

[4] T. Ando and M. Nakagawa, *ibid.*, **44**, 172 (1971).

spectra of these four series of cyclic acetylenes.

The locations of the longest-wavelength absorption maxima (λ_{max}) and their absorption intensities (ε) of I_n, III_n, and IV_n along with those of the open-chain reference substances are summarized in Tables 1, 3, and 4. A rough molecular geometry which is revealed by an examination of the molecular models of these compounds is also shown in the Tables. Since the longest-wavelength absorption maxima of *o,p*'-bridged cyclic tolans (II_n) disappear as the ring size decreases, the wavelength of the absorption peaks at *ca.* 300 nm along with the ε-values and the molecular geometry are recorded in Table 2.

TABLE 1. MOLECULAR GEOMETRY AND ELECTRONIC SPECTRAL DATA OF *o, o*'-BRIDGED DIPHENYLDIACETYLENES (I_n)

n	Molecular geometry	λ_{max}	$\varepsilon\times10^{-2}$
3	highly strained, rigid, planar	337 nm	159
4	strained, rigid, planar,	353	199
5	rigid, planar, strain free	353	365
6	slightly flexible, strain free	349	336
o, o'-Dimethoxy-diphenyl-diacetylene		349	286

TABLE 2. MOLECULAR GEOMETRY AND ELECTRONIC SPECTRAL DATA OF *o, p*'-BRIDGED TOLANS (II_n)

n	Molecular geometry	λ_{max}	$\varepsilon\times10^{-2}$
7	highly strained, rigid, twisted	302[a)]nm	122
8	strained, rigid, twisted	301	120
9	strain free, slightly twisted	302	141
10	strain free,	302	151
11	strain free, slightly flexible	304	189
12	strain free, slightly flexible	305	208
o, p'-Dimethoxytolan		302.5	226

a) indicates the shoulder.

TABLE 3. MOLECULAR GEOMETRY AND ELECTRONIC SPECTRAL DATA OF *p, p*'-BRIDGED DIPHENYLDIACETYLENES (III_n)

n	Molecular geometry	λ_{max}	$\varepsilon\times10^{-2}$
13	highly strained, rigid, non-planar	345.5 nm	367
14	strained, rigid, non-planar	344	425
15	strain free, rigid, planar	343.5	514
18	strain free, planar	342.5	465
p, p'-Di-*n*-butoxy-diphenyl-diacetylene		340.5	407

TABLE 4. MOLECULAR GEOMETRY AND ELECTRONIC SPECTRAL DATA OF *p, p*'-BRIDGED TOLANS (IV_n)

n	Molecular geometry	λ_{max}	$\varepsilon\times10^{-2}$
11	highly strained, rigid, non-planar	318 nm	334
12	highly strained, rigid,	317	369
13	strain free, rigid, planar	317	443
14	strain free, rigid, planar	316	426
18	strain free, flexible	315	355
p, p'-Di-*n*-butoxytolan		313	319

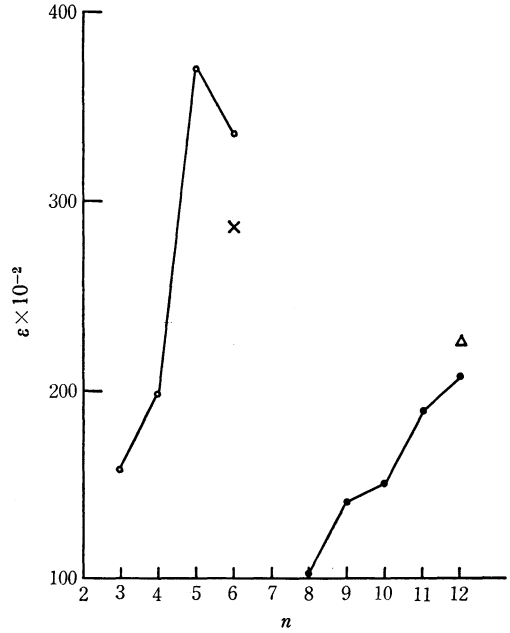


Fig. 1. The ε-values of *o,o*'-bridged diphenyldiacetylenes (I_n, ○——○), *o, p*'-bridged tolans (II_n, ●——●) and the the open-chain analogs (× =*o,o*'-dimethoxydiphenyldiacetylene; △=*o,p*'-dimethoxytolan).

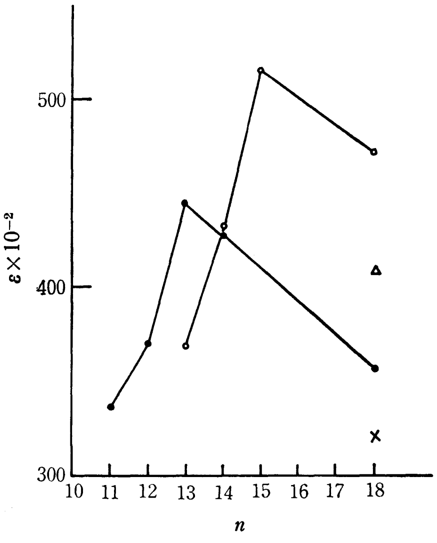


Fig. 2. The ε-values of *p,p*'-bridged diphenyldiacetylenes (III_n, ○——○), *p,p*'-bridged tolans (IV_n, ●——●) and the open-chain analogs (△=*p,p*'-di-*n*-butoxydiphenyldiacetylene; × =*p,p*'-di-*n*-butoxytolan).

The change of absorption intensities with that of the chain length is illustrated in Figs. 1 and 2. The hyperchromism of λ_{max} observed in the higher homologues of I_n, III_n, and IV_n as compared with the ε-values of the respective open-chain analogues can be reasonably ascribed to the enhanced coplanarity of the two phenyl groups as a result of the ring formation. The fact that the maximum ε-values are attained in I_5, III_{15}, and IV_{13} is consistent with the above-mentioned argument, because as indicated in Tables 1, 3, and 4, the molecular models indicate that these molecules are strain free and keep rigid and planar structures due to the presence of bridging chain of adequate length. However, the absorption intensities rapidly decrease with the decrease of chain length. The marked hypochromism of λ_{max} in the lower homologues of I_n, III_n, and IV_n should, therefore, be attributed to the increase of the ring strain.

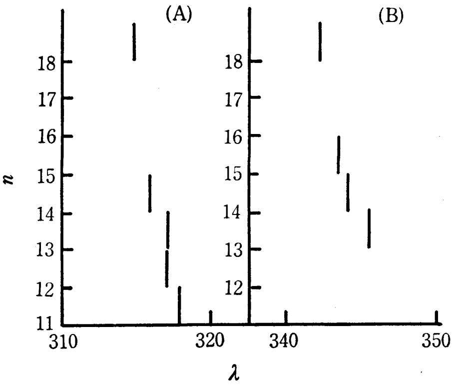


Fig. 3. The bathochromic shifts of the λ_{max} in the *p,p'*-bridged series. (A) = *p,p'*-bridged tolans (IV_n); (B) = *p,p'*-bridged diphenyldiacetylenes (III*n*).

In the case of *o,p'*-bridged cyclic tolans (II_n), the decrease of chain length should increase the twisting of the two phenyl groups, *e.g.*, the molecular model of II_7 shows that the interplanar angle of the two phenyl groups should be almost rectangular. Therefore, the hypochromism observed in II_n should be regarded as the superposition of the effect of ring strain and the effect of twisting of the two phenyl groups.

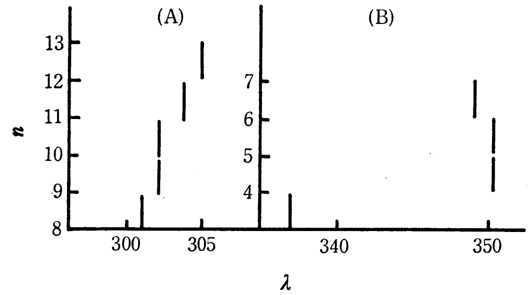
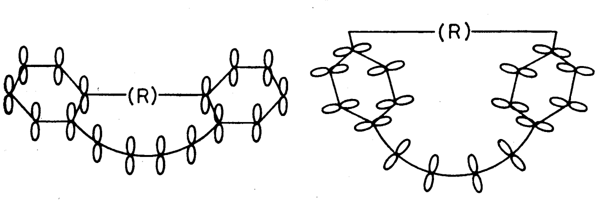


Fig. 4. The hypsochromic shifts of the λ_{max} in the *o,p'*- and *o,o'*-bridged series. (A) = *o,p'*-bridged tolans (II_n); (B) = *o,o'*-bridged diphenyldiacetylenes (I_n).

With regard to the effect of ring strain on the location of λ_{max}, the above-mentioned four series of cyclic acetylenes (I_n, II_n, III_n, and IV_n) exhibit striking contrast. As illustrated in Fig. 3, the increase of ring strain resulted in the bathochromic shifts of the λ_{max} of *p,p'*-bridged tolans (IV_n) and *p,p'*-bridged diphenyldiacetylenes (IV_n). On the contrary, as is shown in Fig. 4, the decrease of the ring size exerts hypsochromic effects on the λ_{max} of *o,o'*-bridged diphenyldiacetylenes (I_n) and that of *o,p'*-bridged tolans (II_n). The hypsochromism observed in the latter compounds (II_n) can not be ascribed only to the increase of ring strain, because the afore-mentioned twisting of the phenyl groups should also result in the increase of the transition energy of the long-wavelength bands of II_n. However, the difference in spectral behavior between the *o,o'*-series (I_n) and the *p,p'*-series (III_n and IV_n) seems to reflect the difference of the mode of ring strain in these two series of cyclic acetylenes.

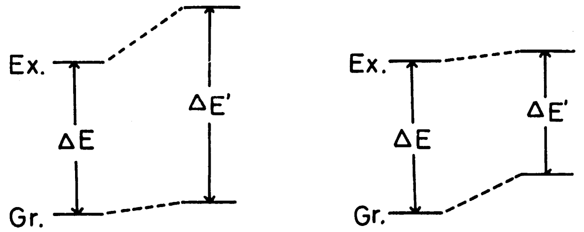


Strained *o,o'*-bridged series Strained *p,p'*-bridged series

Fig. 5. A schematic illustration of the *p*-orbitals of the strained *o,o'*- and the strained *p,p'*-bridged diphenyldiacetylenes.

The strained molecules of I_n are held in planar conformation regardless of the magnitude of the ring strain as illustrated in Fig. 5. The diacetylenic linkage in I_3 seems to be forced to bend due to the short bridging chain. However, the two phenyl nuclei should be held still in a coplanar position. Therefore, the *p*-orbitals which contribute to the conjugation of the entire chromophore system are also held in a parallel position independent of the magnitude of the ring strain.

In the *p,p'*-series (III_n and IV_n), as illustrated in Fig. 4, the two benzene nuclei should deviate from the coplanar position according to the increase of ring strain. Consequently, the *p*-orbitals which contribute to the conjugation of the entire chromophore should deviate from the parallel position in the strained members of III_n and IV_n.



Strain free Strained
$\Delta E < \Delta E'$
o,o'-Bridged series

Strain free Strained
$\Delta E > \Delta E'$
p,p'-Bridged series

Fig. 6. The transition energies of the *o,o'*-bridged and the *p,p'*-bridged cyclic acetylenes.

Thus, it seems pertinent to assume that the increase of energy of the ground state of the strained molecule of *o,o'*-series (I_n) is smaller than that of the *p,p'*-series (III_n and IV_n), whereas, the increase of energy of its excited state is larger than or almost the same as that of *p,p'*-series (III_n and IV_n). This is illustrated schematically in Fig. 6. Thus, the transition energy $\Delta E'$ of the strained *o,o'*-bridged molecule (I_n) becomes larger than that of the strain free molecule ΔE. Consequently, in the case of *o,o'*-bridged series (I_n), the increase of ring strain produces a hypsochromic shift. Inversely, the transition energy $\Delta E'$ of the strained *p,p'*-bridged molecule (III_n and IV_n) becomes smaller than that of the strain free molecule ΔE, *i.e.*, the increase of ring strain in the series of *p,p'*-bridged cyclic acetylenes (III_n and IV_n) results in a bathochromic shift.