

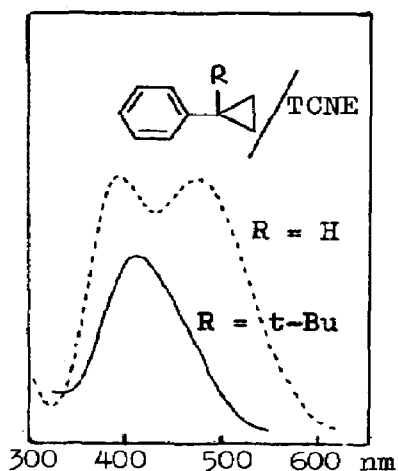
CONFORMATIONAL RELAXATION IN EXCITED CHARGE-TRANSFER COMPLEXES OF  $\alpha$ -ALKYL-ARYLCYCLOPROPANES

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Charge-transfer (CT) complexes of  $\alpha$ -alkyl-arylcyclopropanes (**1**, R = H, CH<sub>3</sub>) with electron acceptors such as tetracyanoethylene (TCNE) show double CT-absorption maxima (cf. Fig. 1)

Fig. 1



due to removal of the degeneracy of the benzene upper  $\pi$ -level by efficient hyperconjugation in a bisected conformation (cf. Fig. 2).

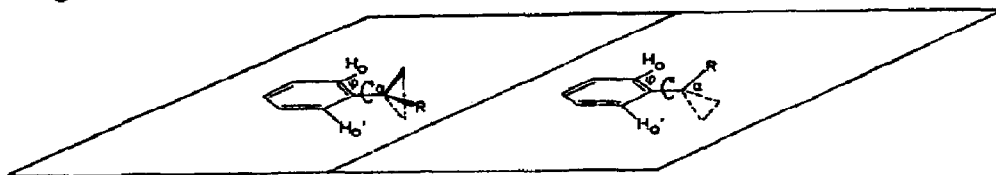


Fig. 2. The bisected ( $\phi = 0^\circ$ ) and the non-bisected ( $\phi = 90^\circ$ ) conformation of the arylcyclopropane system.

For larger R (R = Et, i-Pr, t-Bu) sterical interaction of R with H<sub>o</sub> (cf. Fig. 2) enforces a non-bisected conformation with concomitant decrease in hyperconjugation, leading to a hypsochromic shift of the first CT-absorption band.

Emission spectroscopy shows that in the relaxed -emissive- excited state of the complexes efficient cyclopropyl-aryl hyperconjugation occurs even for the larger R groups (e.g. R = Et, iPr but not for t-Bu).

This is attributed to relaxation of 1 from a non-bisected conformation in the Franck-Condon excited state to a bisected conformation in the relaxed -emissive- excited state. The driving force for this conformational relaxation being the increased electron demand of the aryl system in the excited state of the CT-complex.