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THE ABSOLUTE CONFIGURATION OF (+)-1,3-DIPHENYLALLENE FROM THE ELECTRONIC ABSORPTION AND CIRCULAR DICHROISM SPECTRA.

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The synthesis of (+)-1,3-diphenylallene from (-)-trans-2,3-diphenylcyclopropane-carboxylic acid has been recently described,[1] and the stereochemical course of the conversion is analysed in the previous communication,[2] which indicates that (+)-1,3-diphenylallene has the S-configuration[3] (Fig. 1) in agreement with the results of our circular dichroism study of the isomer.

Spectroscopically 1,3-diphenylallene consists primarily of two orthogonal styrene chromophores, the allene group making only a small contribution to the total light-absorption in the quartz ultraviolet (Fig. 2). From a study[4] of crystals of trans-cinnamic acid with plane-polarized light, it is known that the electric dipole transition moment of the 2500 Å styrene absorption is orientated along the long-axis of the chromophore. Molecular orbital calculations indicate that this transition moment lies at an angle of 28° to the 1-4 axis of styrene in the sense that a parallel line through the 4-position cuts the exocyclic C=C bond. In 1,3-diphenylallene the excitation moments of the two styrene chromophores

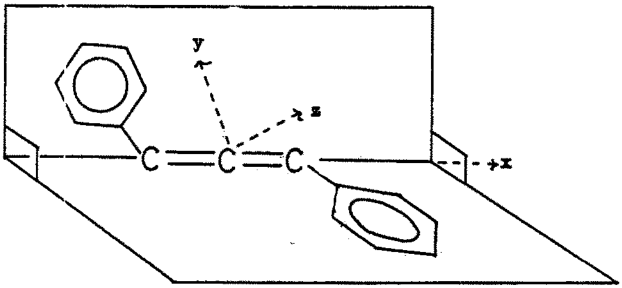

Fig. 1. The absolute configuration of (+)-1,3-diphenylallene

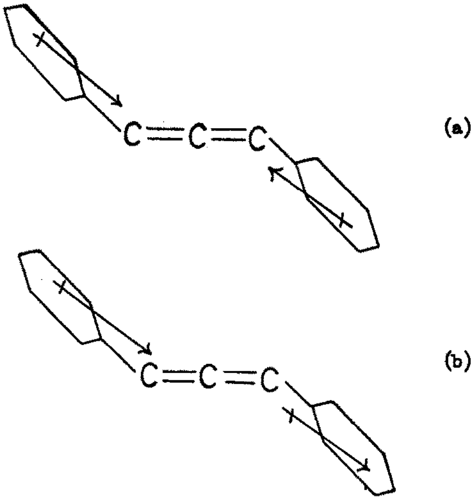

Fig. 3. The coupling modes of the styrene excitation moments in 1,3-diphenylallene, (a) in-phase, giving the resultant transition of A-symmetry, and (b) out-of-phase, giving the resultant transition with B-symmetry.

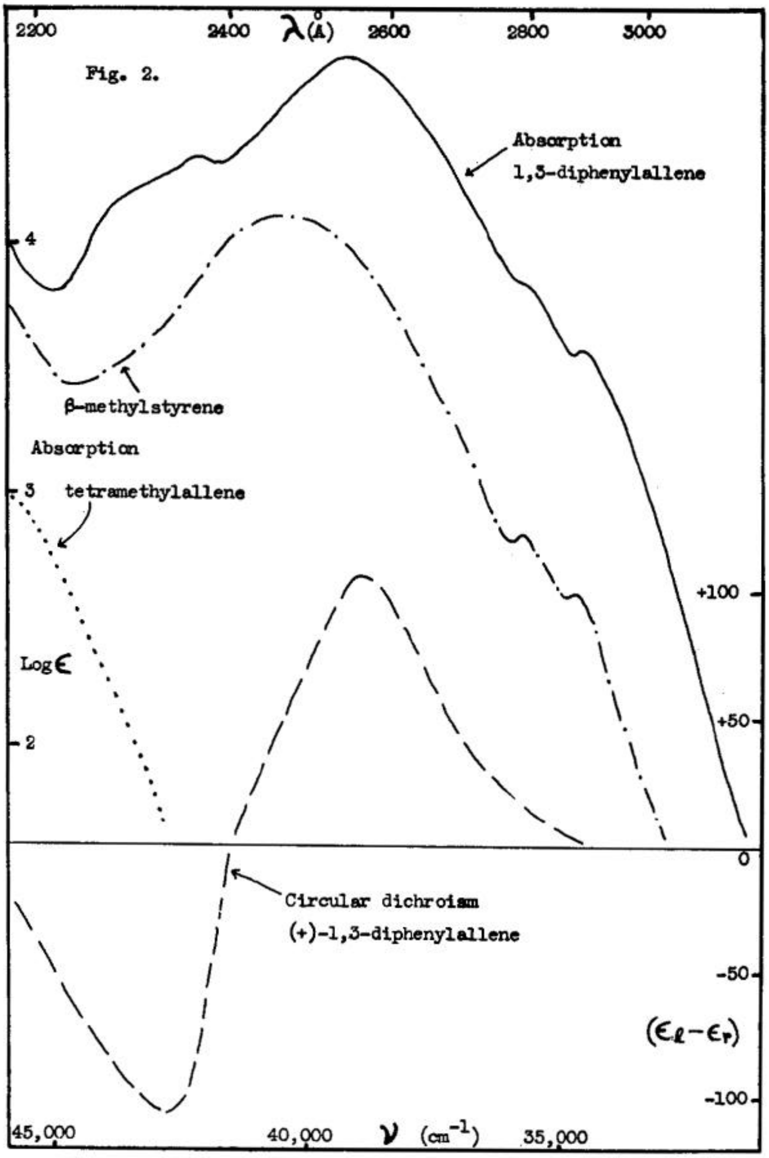

Fig. 2.

2200
2400
λ(Å)
2600
2800
3000
Absorption
1,3-diphenylallene
4
β-methylstyrene
Absorption
3
tetramethylallene
Log ε
2
+100
+50
0
Circular dichroism
(+)-1,3-diphenylallene
-50
$(\epsilon_l - \epsilon_r)$
-100
45,000
40,000
ν (cm⁻¹)
35,000

couple in-phase to give a resultant transition with A symmetry in the group C_2 of the molecule (Fig. 3a) or out-of-phase (Fig. 3b) to give a resultant transition with B-symmetry. Interactions between the two component excitation moments give the resultant A transition (Fig. 3a) a higher energy and a lower absorption intensity, and the resultant B transition (Fig. 3b) a lower energy and a higher intensity.

It is observed (Fig. 2) that the 40700 cm^{-1} styrene absorption is split in 1,3-diphenylallene into a high-intensity band at 39,300 cm^{-1} and a low-intensity band at 43,000 cm^{-1}, which are thus due to the B and to the A resultant transition, respectively (Fig. 3). For the S-configuration[3] of 1,3-diphenylallene the coupling mode giving the resultant A-transition (Fig. 3a) has the overall form of a charge displacement through a left-handed helical path along and about the z-axis (Fig. 1) which is the C_2 axis of the molecule, whereas the B-transition (Fig. 3b) has the form of a right-handed helical charge-displacement. Thus the A-transition should give a negative circular dichroism band and the B-transition a positive circular dichroism band. For the R-configuration the signs are reversed, the A- and the B-transition giving a positive and a negative circular dichroism band, respectively. It is found (Fig. 2) that the negative circular dichroism band of (+)-1,3-diphenylallene at 42800 cm^{-1} lies under the lower-intensity higher-energy absorption band, and the positive circular dichroism band at 38900 cm^{-1} under the higher-intensity lower-energy absorption band. Thus the positive and the negative circular dichroism bands given by (+)-1,3-diphenylallene in the quartz ultraviolet are due to the B (Fig. 3b) and to the A (Fig. 3a) transitions, respectively, and the isomer has the S-configuration (Fig. 1).

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