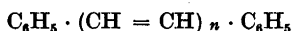


A Study of the Infrared Spectra of Some Stereoisomeric Diphenylpolyenes

K. LUNDE* and L. ZECHMEISTER

*Gates and Crellin Laboratories of Chemistry, California Institute of Technology,
Pasadena, U.S.A.*

In spite of the rapidly increasing literature on infrared spectroscopy, relatively few papers have appeared covering stereoisomeric forms of conjugated double bond systems; and these refer mostly to conjugated diene types 1-4. In the series of α,ω -diphenyl polyenes, of the general formula,



the two steric forms of diphenylethylene ⁵ ($n = 1$) and the three stereoisomeric diphenylbutadienes ⁶ ($n = 2$) have been known for some time and characterized by their ultraviolet spectra ⁷.

Recently, the present authors have isolated, out of the six theoretically possible stereoisomeric diphenylhexatrienes ($n = 3$), three *cis* forms, in the chromatographically homogeneous and ultraviolet-spectroscopically pure state ⁸. Furthermore, three *cis* isomers of diphenyloctatetraene ($n = 4$; total number of spatial forms, 10) have been obtained in collaboration with J. H. Pinckard ⁹. Some skeleton models belonging to the sets, $n = 1$ to 4, whose configurations have been assigned with reasonable reliability are shown in Figs. 1 to 4.

Our infrared curves, taken in the region 2—15 μ , are given in Figs. 7—10 while Fig. 11 represents in a comparative manner, all bands between 5—15 μ referred to in the following discussion.

In the stereoisomeric sets studied the *cis* double bonds can be subdivided into sterically "hindered" and "unhindered" types. In this series, when a "terminal" *trans* double bond, *i.e.* a double bond adjacent to the phenyl group, assumes *cis* configuration, then the overlapping of two hydrogen-atoms creates a spatial conflict.¹⁰ In the case of stilbene (Fig. 5) these are two ring-hydrogens, while in all higher homologs a ring hydrogen and an aliphatically bound H-atom would overlap (Fig. 6). Such "hindered" *cis* double bonds are contained in our models, Fig. 1 (bottom); Fig 2 (middle and bottom); Fig. 3, C; Fig. 4, C, D, and E.

* University of Oslo, Norway.

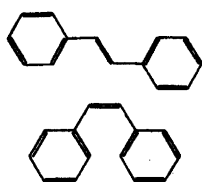


Fig. 1. Skeleton models of *trans*-stilbene (top) and *cis*-stilbene (bottom).

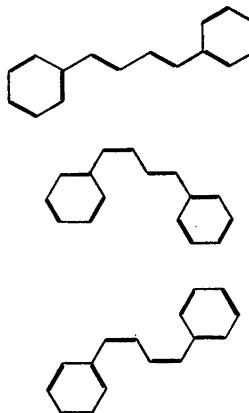


Fig. 2. Skeleton models of all-*trans*-diphenylbutadiene (top), *cis-trans* (middle), and di-*cis*-diphenylbutadiene (bottom).

No attempt has been made in the present paper to give a complete assignment of all bands observed in the region, 2—15 μ ; however, we intend to point out and discuss from the viewpoint of *cis-trans* isomerism those wave length regions in which the curves of the individual steric forms display some characteristic features.

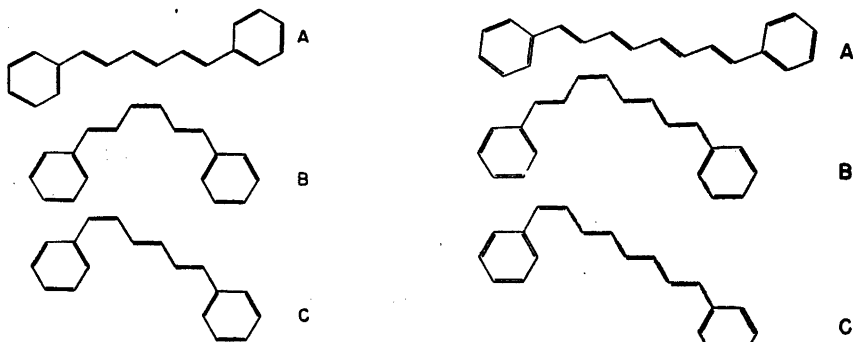


Fig. 3. Skeleton models of all-*trans*-diphenylhexatriene (A), Δ^3 -*cis*- (B), and Δ^1 -*cis*-diphenylhexatriene (C).

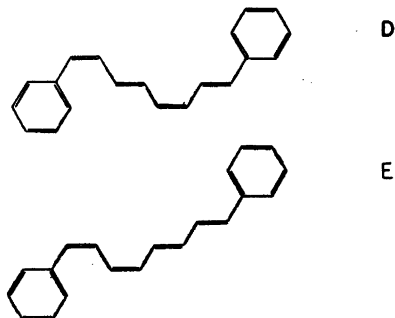


Fig. 4. Skeleton models of all-*trans*-diphenyloctatetraene (A), Δ^3 -*cis*- (B), Δ^1 -*cis*- (C), $\Delta^{1,3}$ -*di-cis*- (D), and $\Delta^{1,3}$ -*di-cis*-diphenyloctatetraene (E).

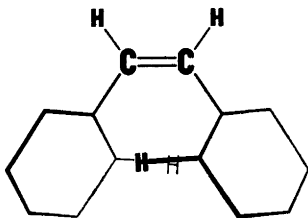


Fig. 5. Overlapping of two ortho ring-hydrogens in *cis*-stilbene (according to G.N. Lewis et al.).

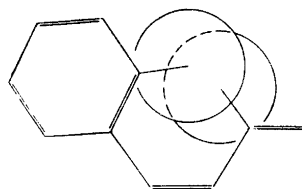


Fig. 6. Steric conflict between two hydrogen atoms in terminal-*cis* diphenylpolyenes¹⁹.

AROMATIC BANDS

Since all compounds mentioned below contain monosubstituted benzene rings, a number of bands, characteristic for such aromatic systems, appear in the curves. In most instances they are not markedly influenced by the steric configuration of the aliphatic chain and should be eliminated from discussions of spatial phenomena. This will be done in the following paragraphs.

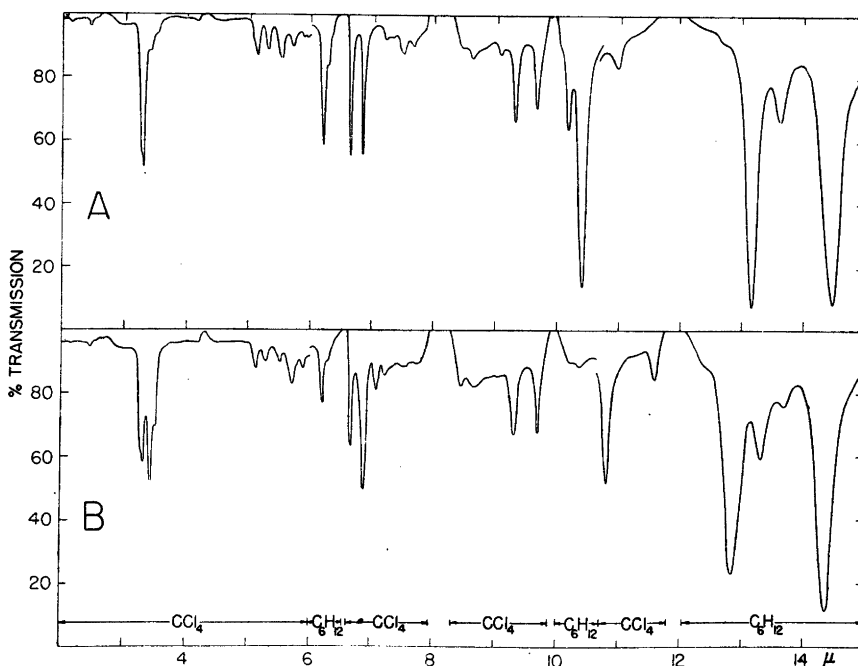


Fig. 7. Infrared curves of *trans*- (A) and *cis*-stilbene (B) in the region 2–15 μ . 1.0 % solutions in 1.0 mm cells. The curves are composed of recordings in carbon tetrachloride and cyclohexane, using the sections where the transparency of the solvents was satisfactory, as indicated below curve B.

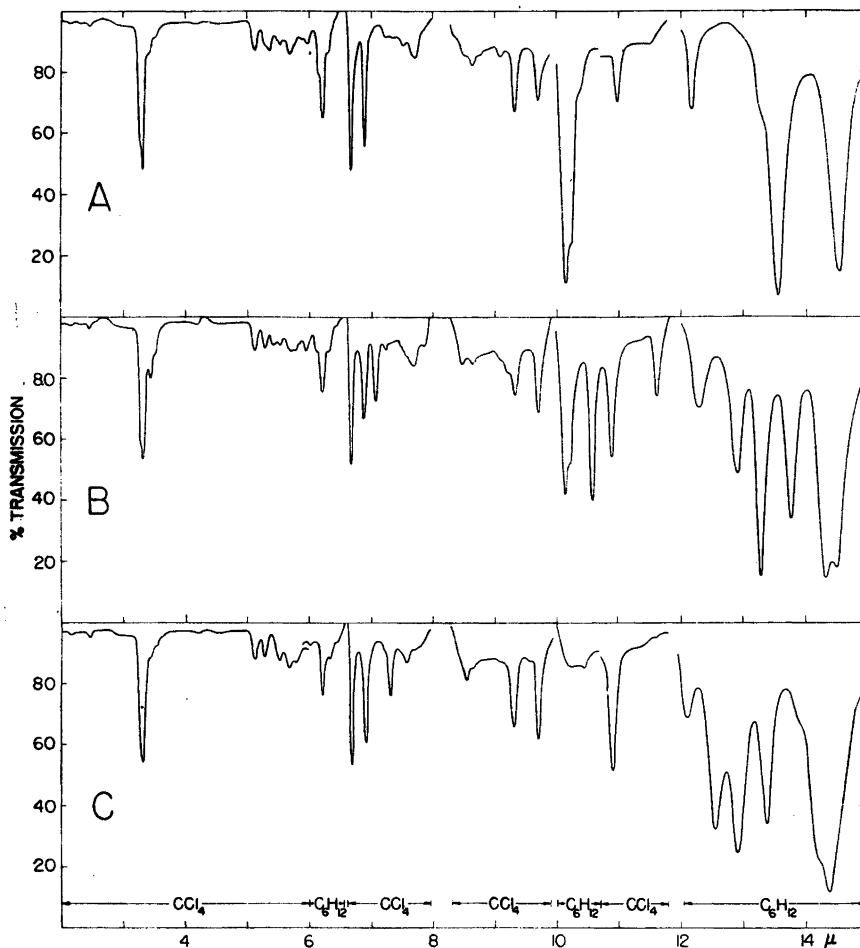


Fig. 8. Infrared curves of all-*trans*- (A), mono-*cis*- (B), and di-*cis*-diphenylbutadiene (C); cf. also Legend to Fig. 7.

In the general region of CH stretching frequencies¹⁰ there occurs a medium intensity band located at $\sim 3.30 \mu$; it undergoes splitting when some *cis* configurations are assumed but this band did not give us a sufficient basis for stereochemical conclusions.

In the region, 5–6 μ several bands are observed that are characteristic for monosubstituted benzene derivatives such as toluene or diphenyl (Fig. 11; m, n), for example. According to Ingold¹¹ they represent combination tones and overtones. The number of bands appearing in this region is subject to variations. Probably, this phenomenon does have some stereochemical significance which, however, cannot be interpreted at the present time.

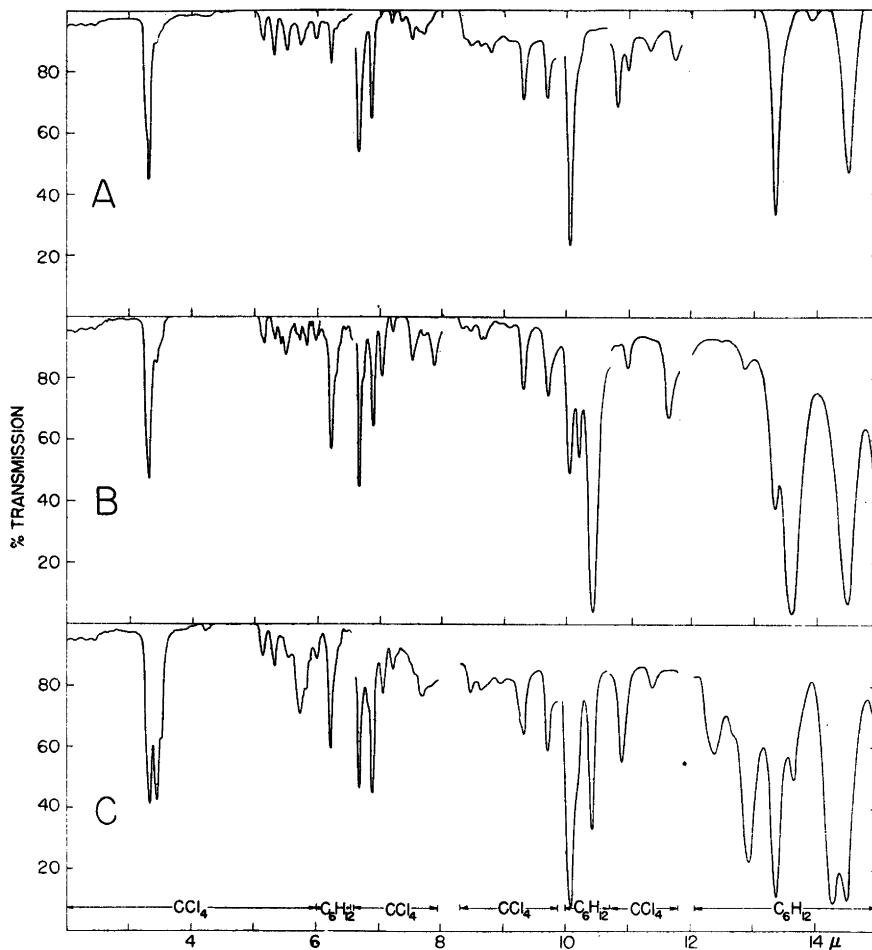


Fig. 9. Infrared curves of all-*t r a n s*- (A), Δ^3 -*c i s*- (B), and Δ^1 -*c i s*-diphenylhexatriene (C). The cyclohexane part of the spectrum of all-*t r a n s*-diphenylhexatriene was recorded in a saturated solution ($\sim 0.3\%$); cf. also Legend to Fig. 7.

As is well known, the aromatic ring exhibits a CC stretching band at $\sim 6.25 \mu$ which obscures the longer wave length C = C stretching band in an aliphatic conjugated system. The shorter wave length C = C conjugated stretching band ($\sim 6.0 \mu$) is possibly present in some (but not all) curves of our stereoisomers in accordance with some data given by Rasmussen and Brattain⁴.

According to Rasmussen¹² all other CC stretching frequencies of the aromatic ring are spread over a rather wide range, *i.e.* from 6μ to 10μ . A section of the same range is also covered by the CH bending frequencies or hydrogen in-plane vibrations in the vicinity of 7μ . There we find two modera-

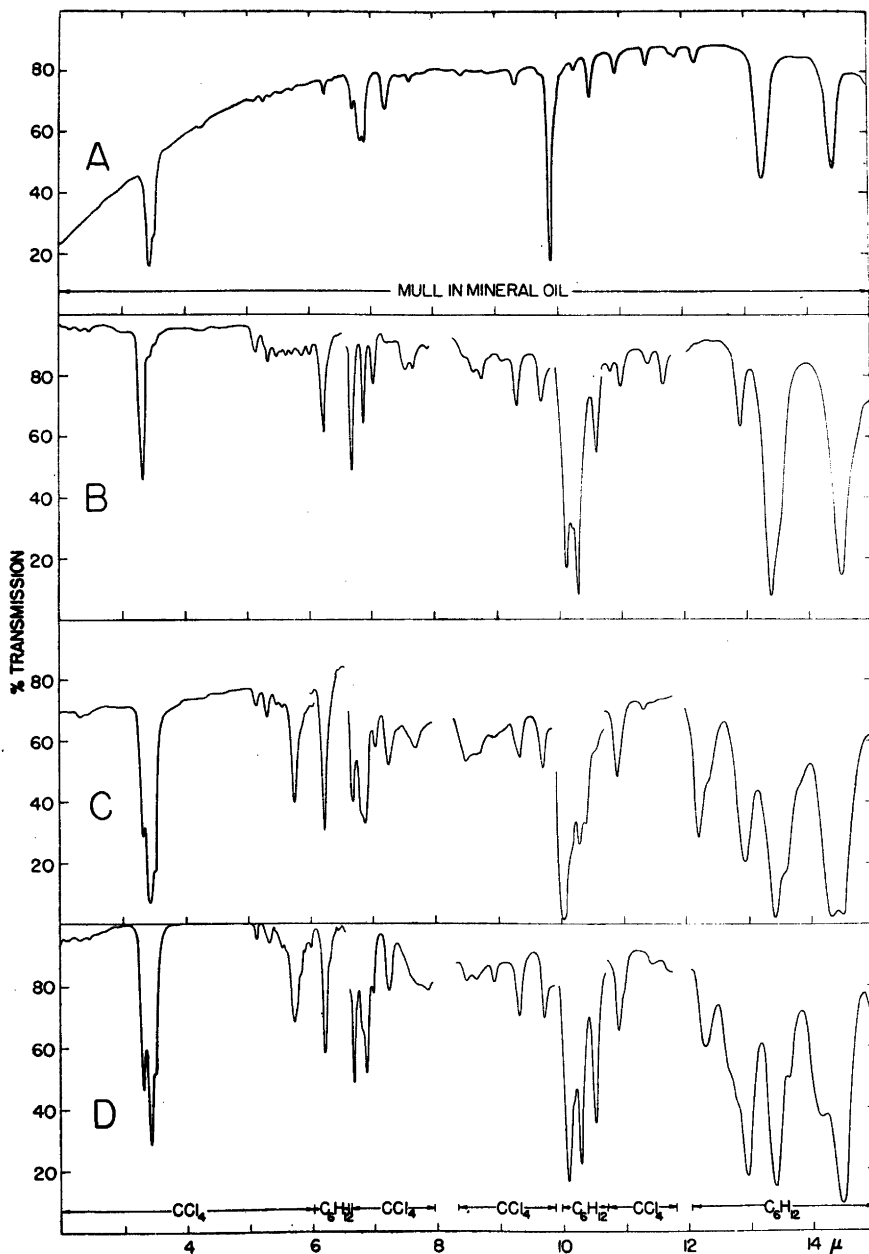


Fig. 10. Infrared curves of all-*trans*-diphenyloctatetraene (A), Δ^3 -*cis*- (B), Δ^1 -*cis*- (C), and $\Delta^{1,3}$ - or $\Delta^{1,5}$ -*di-cis*-diphenyloctatetraene. Curve A was taken on a mull; cf also Legend to Fig. 7.

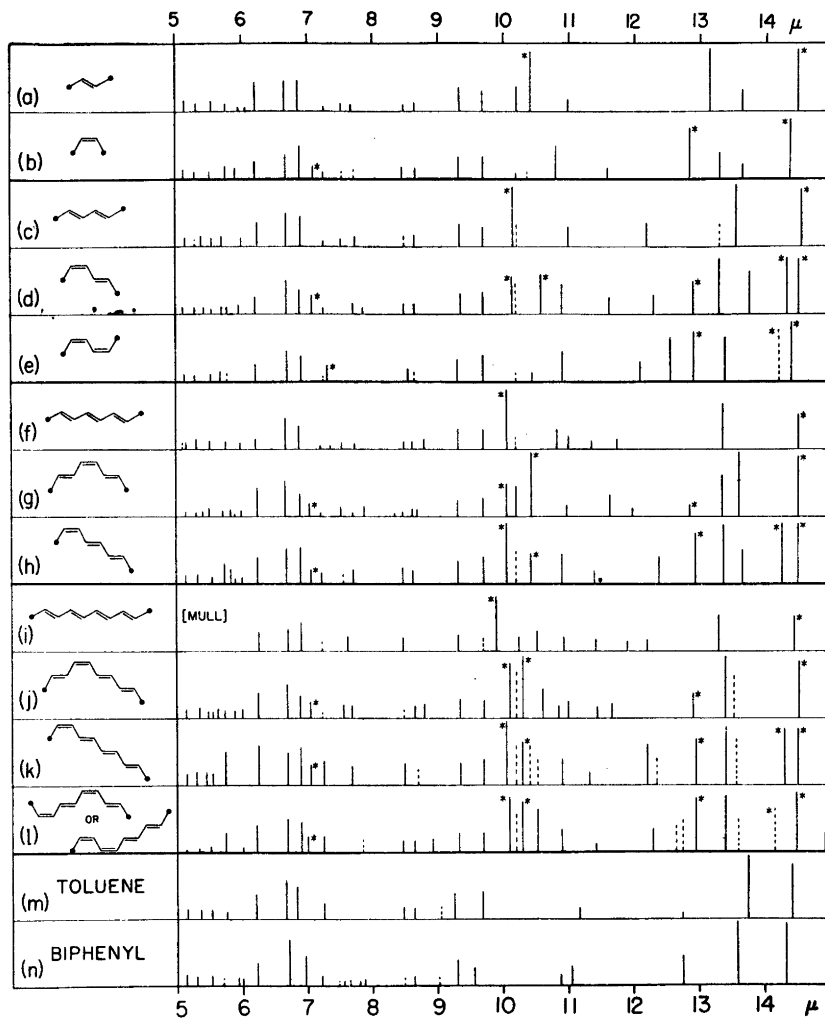


Fig. 11. General chart of the infrared bands observed between 5μ and 15μ represented as vertical lines at the band maxima; the heights designate relative intensities. The dashed lines denote unresolved bands which appear as shoulders on adjacent bands. The intensities and to a lesser degree even the positions of such bands are uncertain. Asterisk indicates a stereochemically significant band. The left column represents the stereochemical configuration of the aliphatic chain, with the terminal black dots indicating phenyl groups.

tely intense bands at remarkably constant wave lengths, viz. at $6.67 \pm 0.02 \mu$ and $6.88 \pm 0.02 \mu$. A weaker band is located at $7.23 \pm 0.02 \mu$ whose constancy allows an easy differentiation from the stereochemically significant 7.0 — 7.1μ band to be discussed below.

Between 7.5μ and 9μ there are several minor bands that evidently are sensitive to spatial rearrangements; they cannot be interpreted at the present time.

Two sharp, moderate bands characteristic for the monosubstituted benzene ring appear in all our curves at $9.30\ \mu$ and $9.70\ \mu$ and do not seem to be influenced either by the length or by the configuration of the aliphatic conjugated system.

As is well known, the $10\text{--}15\ \mu$ region is associated with the hydrogen out-of-plane rocking bands, intermixed with lower intensity carbon-carbon deformation bands, that arise from both rings and the aliphatic chain.

In this region we find, throughout all stereoisomeric sets studied, a moderate to weak band at the sharply constant wave length, $10.20\ \mu$. It appears mostly as a shoulder on the adjacent strong intensity band(s) arising from the out-of-plane rocking of hydrogen atoms attached to a *trans* double bond. Because of its constancy the band can be identified easily and does not cause difficulties in this stereochemically important region, $10.0\text{--}10.6\ \mu$ ("*trans*-band region"). Neither is a moderate to weak band at $11\ \mu$ disturbing, although, as shown in the curves, it is evidently influenced by *trans* \rightarrow *cis* rearrangements which usually shift it towards shorter wave lengths and may even split it into two distinct bands.

As demonstrated by the four all-*trans* curves (Fig. 11; a, c, f, i), the number of the bands between $11.0\ \mu$ and $12.5\ \mu$ (including that at $\sim 11.0\ \mu$) is characteristic for the number n of the aliphatic double bonds: one band for $n = 1$, two for $n = 2$, etc. Possibly, these bands are associated with the carbon-carbon deformation frequencies of the aliphatic chain. This would be in agreement with the different appearance of the individual *cis* curves in this region. However, we are unable to offer a more precise explanation at present.

The strong bands at $\sim 13.5\ \mu$ and $14.5\ \mu$ are characteristic for the monosubstituted aromatic ring and represent two modes of hydrogen out-of-plane rocking in the ring^{11,13}. The location of the former band is dependent on the nature of the substituent but no pertinent rules can yet be formulated. It is also possible that in case of certain *cis* configuration types this band would split into two, since the two rings would then be unequally substituted as a consequence of asymmetry of the aliphatic chain. The higher wave length band ($14.5\ \mu$) is influenced by a *trans* \rightarrow *cis* rearrangement of a terminal aliphatic double bond, causing a more or less extensive splitting of the band. The latter feature will be useful in the following stereochemical discussion.

STEREOCHEMICALLY SIGNIFICANT BANDS

(cf. also Table I)

Although the CH stretching bands ($\sim 3.30\ \mu$) and the CC stretching bands (between $6\ \mu$ and $10\ \mu$), as well as the CC deformation bands ($10\text{--}15\ \mu$) could be *a priori* influenced by steric changes, as mentioned above, no practical use could be made of these modes of vibrations so far. Hence, only the bands caused by the in-plane and out-of-plane vibration of hydrogen atoms attached to double bonded carbon will be considered here. The following four types of bands will have to be discussed.

1. In the CH bending region we find that the curve of each *cis* isomer studied contains a band absent from all-*trans* curves. This weak to moderate

Table 1. Stereochemically significant infrared bands in some *cis-trans* isomeric diphenylpolyene sets, listed in microns, at their absorption maxima. The figures in parentheses represent units of 10% absorption [e. g. (6) stands for 60% absorption or 40% transmittance].

Compound	Con-figuration	In-plane bending vibration of H atoms attached to <i>cis</i> double bonded carbons	Out-of-plane rocking of H atoms attached to a <i>trans</i> double bonded carbon, in conjugation with:		Out-of-pl. rocking of H atoms attached to <i>cis</i> double bonded carbons	Out-of-plane rocking of a pair of equivalent H atoms in the rings:	
			any C = C bond	a <i>cis</i> C = C bond		hindered	unhindered
Stilbene	<i>trans</i>	—	10.42(9)	—	—		14.48(9)
	<i>cis</i>	7.09(2)	—	—	12.84(8)	14.37(9)	
Diphenyl-butadiene	<i>trans</i>	—	10.15(9)	—	—		14.54(9)
	mono- <i>cis</i> di- <i>cis</i>	7.07(3) 7.31(2)	10.14(6) —	10.58(6) —	12.90(5) 12.91(7)	14.33(8) 14.20(8)	14.50(8) 14.39(9)
Diphenyl-hexatriene	<i>trans</i>	—	10.06(8)	—	—		14.50(5)
	Δ^3 - <i>cis</i>	7.03(2)	10.06(5)	10.42(10)	12.85(2)	—	14.50(9)
	Δ^1 - <i>cis</i>	7.05(2)	10.06(9)	10.42(5)	12.93(8)	14.26(9)	14.50(9)
Diphenyl-octa-tetraene	<i>trans</i>	—	9.90(9)	—	—		14.44(5)
	Δ^3 - <i>cis</i>	7.04(2)	10.11(8)	10.30(9)	12.91(4)	—	14.52(9)
	Δ^1 - <i>cis</i>	7.05(3)	10.05(10)	10.30(7)	12.95(7)	14.30(9)	14.51(9)
	$\Delta^{1,3}$ -di- <i>cis</i> or $\Delta^{1,5}$ -di- <i>cis</i>	7.00(2)	10.10(8)	10.30(8)	12.95(8)	14.15(7)	14.49(9)

band that was assigned earlier to vibrations of a hydrogen atom attached to a *cis* double bonded carbon¹⁴ is located at roughly the same wave length, 7.00—7.09 μ , in all but one of our *cis* compounds, the exception being di-*cis*-diphenylbutadiene in whose spectrum the band has been shifted to 7.31 μ . Possibly, this could be explained by the "all-hindered-*cis*" feature of this isomer, unique in the diphenylpolyene series.

2. Of the three out-of-plane rocking bands referred to in the present discussion the shortest wave length one appears at 10.0—10.6 μ . This strong band was assigned earlier to the out-of-plane rocking frequencies of hydrogen atoms attached to *trans* carbon-carbon double bonds¹⁵; a splitting of this band has been observed in the presence of a conjugated *trans-cis* diene group^{1,2}. Since the papers mentioned refer to shorter systems and hence do not mention several features needed in our discussion, the following, more detailed treatment of the 10.0—10.6 μ region seems to be justified.

According to Table 1, only the stereoisomers having at least one double bond in the *trans* configuration possess any strong absorption band(s) in this region. Since neither *cis*-stilbene nor di-*cis*-diphenylbutadiene belongs to this type, no pertinent band appears in their spectra except perhaps for traces. The presence of such trace-bands could possibly be caused by a slight *cis* \rightarrow *trans* isomerization during recording.

In the region under discussion all isomers containing both a *trans* and a *cis* double bond(s) display a doublet in contrast to the all-*trans* forms. We will tentatively formulate this as follows: a *trans* C = C bond, either isolated or in conjugation with any other bond, gives rise to a vibrational frequency of a hydrogen bonded to one of the carbon atoms. We name this band the "lower λ *trans* band". On the other hand, conjugation of a *cis* to a *trans* double bond brings about a new vibrational frequency of a hydrogen atom (linked to a *trans* C = C carbon) resulting in a "higher λ *trans* band".

Although the laws governing intensity relationships in infrared spectra are not yet well understood, our formulation seems to be in agreement with the observed relative intensities of the two *trans* bands defined above, if it is assumed that the intensities are additive. While the central *cis* double bond of diphenylhexatriene is conjugated with two *trans* double bonds, only one such possibility exists for a terminal *cis* double bond. A similar statement is valid for higher diphenylpolyenes. Consequently, the "higher λ *trans* band" should appear with lower intensity in the spectrum of a terminal mono-*cis* form than in that of non-terminal mono-*cis* forms (*cf.* the inversion of the intensity ratios of the two bands demonstrated in Fig. 11, g and h as well as j and k).

The wave length position of these two peaks is not constant from set to set. When proceeding from a to l in Fig. 11, we note that with lengthening the conjugated system the "lower λ *trans* band" migrates towards higher frequencies; it reaches approximate constancy and perhaps it is even shifted again in the opposite direction when systems containing 3—4 conjugated double bonds are reached. Analogous is the behavior of the "higher λ *trans* band" whose shift is even more extensive. Consequently, the two peaks lie more closely together in the spectra of the higher diphenylpolyenes studied than in the lower ones. Possibly, the two bands may coincide or even exchange places in still higher systems.

The tendency to shift towards higher frequencies just mentioned is also in agreement with resonance considerations. Increasing conjugation enhances the rigidity of the chain and hence its resistance to out-of-plane vibrations, which, in terms of light absorption, means a shift to higher frequencies.

While the wave length position of the "lower λ *trans* band" is constant within simpler sets, the position given in Table 1 for the all-*trans*- and Δ^1 -*cis*-diphenyloctatetraenes, *viz.* 9.90 μ and 10.05 μ respectively, are markedly lower than the corresponding data listed for the two other *cis* forms. The 9.90 μ value is explained by the circumstance that in this instance the spectrum of a solid phase (mull) had to be recorded; indeed, the curve of a saturated solution (< 0.1 %) of the all-*trans* compound shows a weak but distinct band at 10.10 μ . Similar differences between liquid and solid phase infrared spectra were observed earlier¹⁶. For the shift to the 10.05 μ position small amounts of the all-*trans* isomer were probably responsible, formed by a slight *cis* \rightarrow *trans* rearrangement as demonstrated by the appearance of a number of small all-*trans* crystals during recording of the exceptionally labile Δ^1 -*cis* isomer.

3. According to several authors^{17,18,14} the band arising from the out-of-plane rocking of hydrogen atoms attached to a *cis* carbon-carbon double bond appears over a wide range, *i.e.* between 12.0 μ and 14.5 μ . In this region

all our curves contain a variety of strong to moderate bands that makes the identification of the true "cis-band" difficult. We believe, however, that the band at 12.84—12.95 μ , present in each *cis* compound but in none of our *trans*-forms, is this "cis-band". Such assignment is also in agreement with an observation made by the authors on central mono-*cis*- β -carotene whose curve shows a sharp band at 12.84 μ , absent from the all-*trans*- β -carotene curve.

Some of the other bands appearing in this region may possibly be explained in terms of conjugation, in analogy to the splitting of the "trans-band" mentioned in Section 2. For another explanation of the richness of bands in this region, *cf.* the discussion of the $\sim 13.5 \mu$ band in the Chapter, "Aromatic Bands".

4. As mentioned above, the presence of a terminal *cis* double bond results in a splitting of the 14.5 μ aromatic band, yielding a new one at a somewhat shorter wave length. If it is assumed that the latter band is caused by the out-of-plane rocking of ring-hydrogens in *o*-position to the side-chain, this splitting becomes explainable on the basis of the spatial conflict between an aliphatic hydrogen and an *ortho* ring-hydrogen (Fig. 6). The resistance to the out-of-plane rocking of such a ring-hydrogen would require energy absorption on a higher level, *i.e.* at a lower wave length, as shown by all sterically hindered *cis* compounds studied. The new band would then become a part of a doublet since the 14.5 μ band would not be expected to disappear; it represents the normal ("unhindered") vibrations of *ortho* hydrogen atoms.

Another possible interpretation of the doublet could be formulated as follows: Upon the introduction of one terminal *cis* bond the rings will no longer be substituted equally, considering their different distances from the *cis* bond mentioned. This situation would then give rise to two (instead of one) vibrational frequencies. Such an explanation seems, however, to be in contradiction to the lack of a doublet in the Δ^3 -*cis*-diphenyloctatetraene spectrum (Fig. 9, j). The writers are in favor of the first explanation of the doublet given above.

EXPERIMENTAL

The preparation and purification of the substances used are described in References 1—4. All samples were chromatographically and U.V.-spectroscopically pure, and solutions of *cis* forms were re-checked chromatographically for possible *cis* \rightarrow *trans* isomerization after each recording. This check gave satisfactory results except for *cis*-II-diphenyloctatetraene that underwent considerable rearrangement, possibly caused by infrared illumination; as mentioned, tiny crystals of the all-*trans* compound were visible in the cell after recording. However, rapid operations (including recording) have probably reduced the extent of this rearrangement to less than 10 %.

The solvents used were, "Eastman Spectro Grade". All but two substances were recorded in 1.0 % carbon tetrachloride and cyclohexane solutions using a 1.0 mm sodium chloride cell. Some of the minor isomers were filled into a micro cell (1.0 mm). A saturated (~ 0.3 %) cyclohexane solution of all-*trans*-diphenylhexatriene was used for recording that part of the spectrum which had to be taken in this solvent. For the still less soluble all-*trans*-diphenyloctatetraene a Mineral Oil (No. 7) mull was used.

The solutions were prepared and filled into the cells in dim light, and exposure to short wave length light was avoided during the recordings.

In all experiments a Perkin-Elmer self-recording infrared spectrophotometer, Model 21 was used. The curves given in Figs. 7—10 represent combinations of the regions taken in carbon tetrachloride (2—6; 6.6—7.95; 8.30—9.90; 10.70—11.80 μ) and in cyclohexane (6—6.55; 10.00—10.70; 12.05—15.00 μ).

SUMMARY

Infrared spectra of several *cis-trans* isomeric diphenylpolyenes, $C_6H_5 \cdot (CH = CH)_n \cdot C_6H_5$, are given for the sets, $n = 1$ to 4, in the region 2 to 15 μ . The observed bands, so far as they can be interpreted at present, have been divided into two groups. The first one includes the bands caused by the presence of the aromatic ring, and the second group is characteristic for certain spatial configurations. Two "cis-absorption" regions are pointed out resulting from in-plane and out-of-plane vibrations of hydrogen atoms. As a rule, *trans* absorption bands are shown to be influenced by conjugation to a *cis* double bond, giving a doublet. An aromatic hydrogen rocking band was found to split in the presence of a terminal, *i.e.* sterically hindered *cis* double bond.

REFERENCES

1. Jackson, J. E., Paschke, R. F., Talberg, W., Boyd, H. M. and Wheeler, D. H. *J. Am. Oil Soc.* **29** (1952) 229.
2. Celmer, W. D. and Solomons, I. A. *J. Am. Chem. Soc.* **75** (1953) 3430.
3. Sheppard, N. and Simpson, D. M. *Quart. Revs. (London)* **6** (1952) 1.
4. Rasmussen, R. S. and Brattain, R. R. *J. Chem. Phys.* **15** (1947) 131.
5. Otto, R. and Stoffel, F. *Ber.* **30** (1879) 1799.
6. Straus, F. *Ann.* **342** (1905) 190.
7. Pinckard, J. H., Wille, B. and Zechmeister, L. *J. Am. Chem. Soc.* **70** (1948) 1938.
8. Lunde, K. and Zechmeister, L. *J. Am. Chem. Soc.* **76** (1954), 2308.
9. Zechmeister, L. and Pinckard, J. H. *J. Am. Chem. Soc.* **76** (1954), 4144.
10. Herzberg, G., *Infrared and Raman Spectra of Polyatomic Molecules*. Van Nostrand, New York, 1945.
11. Herzfeld, N., Ingold, C. K. and Poole, H. G. *J. Chem. Soc.* **1946** 316.
12. Rasmussen, R. S. *Fortschr. Chem. organ. Naturst.* **5** (1948) 131.
13. Gourlay, J. S. *Nature* **159** (1947) 129.
14. Colthup, N. B. *J. Opt. Soc. Am.* **40** (1950) 397.
15. Sheppard, N. and Sutherland, G. B. B. M. *Proc. Roy. Soc. A* **196** (1949) 195.
16. Szasz, G. J. and Sheppard, N. *Trans. Faraday Soc.* **49** (1953) 358.
17. Rasmussen, R. S., Brattain, R. R. and Zucco, P. S. *J. Chem. Phys.* **15** (1947) 135.
18. Hatch, L. F. and Nesbitt, S. S. *J. Am. Chem. Soc.* **72** (1950) 727.
19. Zechmeister, L. and Le Rosen, A. L. *J. Am. Chem. Soc.* **64** (1942) 2755.

Received April 6, 1954.