

CHIROPTICAL PROPERTIES OF LINEAR NON-PLANAR POLYENES

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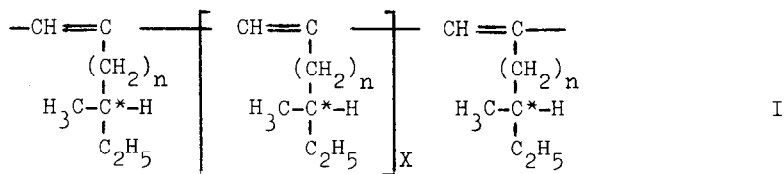
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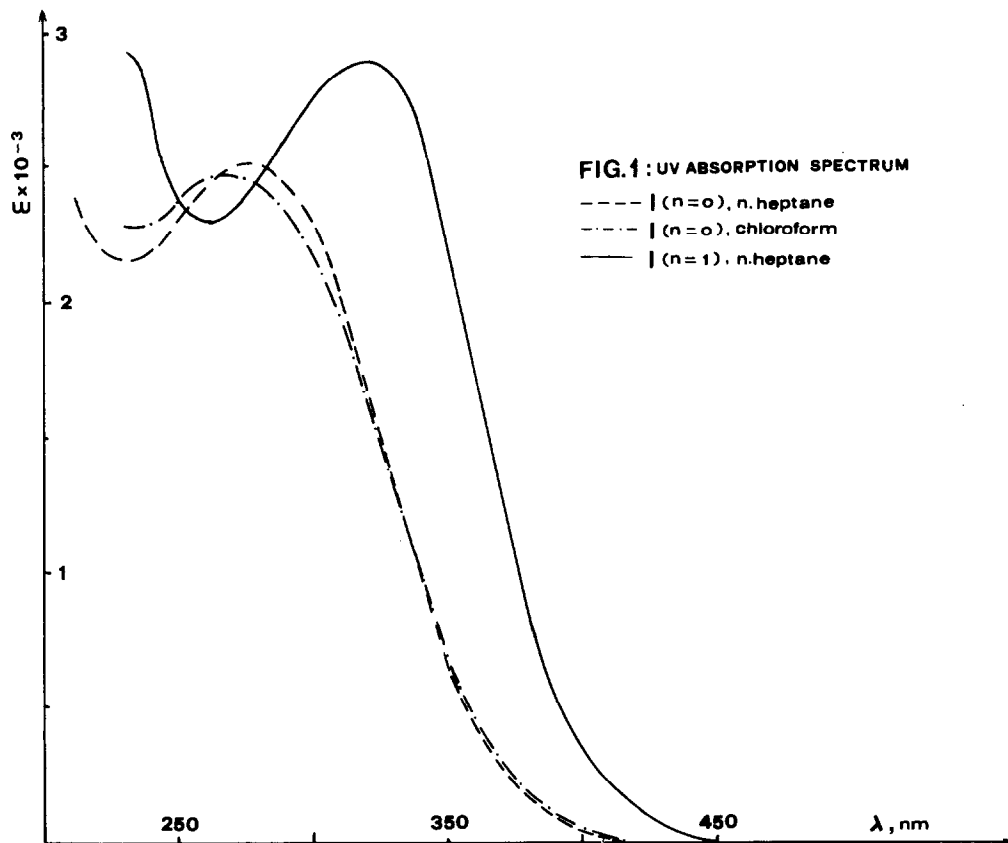
It has been shown in 1961⁽¹⁾ that a non-planar system of two alternate double bonds, when part of a rigidly fixed ring, can originate an inherently dissymmetric chromophore which in general outweighs any contributions associated with asymmetrically disposed substituents. In fact the longest wavelength transition is optically active and its rotational strength is much larger⁽²⁾ than that expected for a dissymmetrically perturbed chromophore. However some cases are reported in which the ellipticity of the band associated to the above transition is remarkably lower because of the presence of appreciable amounts of the two senses of skewness, which are in equilibrium⁽³⁾. Few examples of optically active open chain 1,3-dienes are reported in the literature^(4,5) and their chiroptical properties can be interpreted on the basis of the dissymmetric perturbation of a planar system of conjugated double bonds by the asymmetric substituent. A conjugated polyene system, perturbed by one or two chiral end-groups has been observed in carotenoids⁽⁶⁾.

We report now that a linear polyene (I) with asymmetric carbon atoms in the side chain which are in "1,3" position, exhibits chiroptical properties in agreement with the existence of a inherently dissymmetric polyene chromophore.



I(n=0) and I(n=1) have been obtained by polymerization respectively of (S)-3-methyl-pentyne and (S)-4-methyl-1-hexyne by Fe^{III} acetylacetonate/ $\text{Al}(\text{i.C}_4\text{H}_9)_3$ as reported in a previous paper⁽⁷⁾. The chemical structure of I and the enantiomeric purity (90%) have been demonstrated both by chemical (oxidative cleavage and hydrogenation) and spectroscopic methods (IR, NMR and UV). The last give also

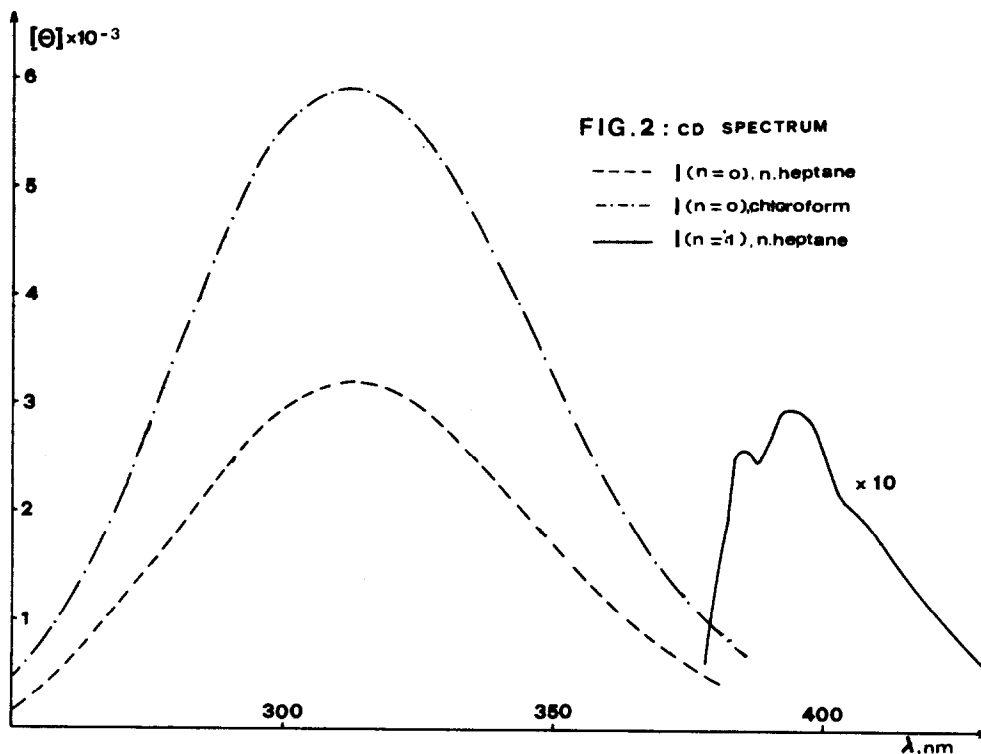
preliminary information on the secondary structure in solution. In fact in the IR spectrum a single band is present in the region of the stretching vibration of the carbon-carbon double bond and its position ($1618-1612\text{ cm}^{-1}$) is intermediate between that of isolate and of conjugated double bonds⁽⁸⁾. Accordingly the 60 MHz NMR spectrum shows a single wide band at 5.90 p.p.m. which can be assigned to the olefinic proton⁽⁹⁾. In spite of the large number (more than 100) of alternate double bonds per molecule, the UV absorption spectrum shows (Fig.1) in both I(n=0) and I(n=1) that the longest wavelength absorption maximum is at wavelengths well below that of compounds containing 5-6 conjugated double bonds, the ϵ_{max} per double bond being markedly lower than in planar conjugated polyenes⁽¹⁰⁾.



These data can be explained considering that, because of the presence of rather bulky side chains in "1,3" relative position, the main chain is forced to assume a non-planar conformation: as a consequence the conjugation of the alternate double bonds is reduced. The lower ϵ_{max} and λ_{max} of the absorption band in I(n=0) with respect to I(n=1) show that the steric inhibition to the resonance increases with decreasing distance between side chain branching and main

chain. The absorption characteristics do not change appreciably with temperature and solvent (Fig.1).

A positive band is present in the CD spectrum (Fig.2) at 314 and 393 nm in I(n=0) and I(n=1), respectively. The ellipticity per double bond is much larger in I(n=0), where it is of the same order of magnitude as in several inherently dissymmetric skewed 1,3-dienes⁽²⁾. The last data confirm the non-planar conformation of the polyene chain and show that the rotation angle between two successive double bonds has predominantly a single sense of skewness.



Taking into account that the macromolecules I consist of repeating units having the same structure, the non-planar conformation of the polyene chain must be a helix with a predominant screw sense. Both screw senses must however exist, the equilibrium being shifted more or less in one direction depending on temperature and solvent. The effect of the latter is clearly shown by the fact that going from n-heptane to chloroform the ellipticity of I(n=0) markedly increases (Fig. 2) without appreciable variation of the wavelength, in agreement with the absorption data. As a change of the absolute value of the skew angle should produce a change of position and mainly of intensity of the related band, both in

absorption⁽¹¹⁾ and CD spectra⁽¹²⁾, the solvent effect observed should consist in changing the equilibrium position between left and right handed helices, where the alternate skewed double bonds are in enantiomeric relationship. The existence of this equilibrium could explain the low ellipticity of the CD band at 394 nm in I(n=1). In fact in this case the predominance of one screw sense over the opposite one is probably lower than in I(n=0). It must be also considered that in the former case the skew angle is smaller in absolute value than in the latter⁽¹²⁾.

The reported data give clear spectroscopic evidence that the cooperative effect among chiral side chains can induce in open chain compounds a large conformational preference, that is a helical conformation with a predominant screw sense.

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REFERENCES

1. A. Moscovitz, E. Charney, U. Weiss, and H. Ziffer, *J. Amer. Chem. Soc.* **83**, 4661 (1961).
2. U. Weiss, H. Ziffer, and E. Charney, *Tetrahedron* **21**, 3105 (1965).
3. G. Snatzke, E. sz. Kovats, and G. Ohloff, *Tetrahedron Letters*, 4551 (1966).
4. R. Rossi and E. Benedetti, *Gazz. Chim. Ital.* **96**, 483 (1966).
5. Z. Janovic and D. Fles, *J. Polymer Sci. A-1*, **9**, 1103 (1971).
6. L. Bartlett, W. Klyne, W. P. Mose, P. M. Scopes, G. Galasko, A. K. Mallams, B. C. L. Weedon, J. Szabolcs, and G. Toth, *J. Chem. Soc. C* 2527 (1969).
7. F. Ciardelli, E. Benedetti, and O. Pieroni, *Makromol. Chem.* **103**, 1 (1967).
8. R. N. Jones and C. Sandorfy, in A. Weissberger, "Techniques of Organic Chemistry", Interscience **9**, 368-73 (1956).
9. M. Mousseron-Conet and J. C. Mani, *Bull. Soc. Chim. France* 3285 (1966).
10. H. H. Jaffè and M. Orchin, "Theory and Application of Ultraviolet Spectroscopy", J. Wiley & Sons, New York 1962, p. 228.
11. G. W. Wheland, "Resonance in Organic Chemistry", J. Wiley & Sons, New York 1955, p. 323.
12. E. Charney, *Tetrahedron* **21**, 3127 (1965).