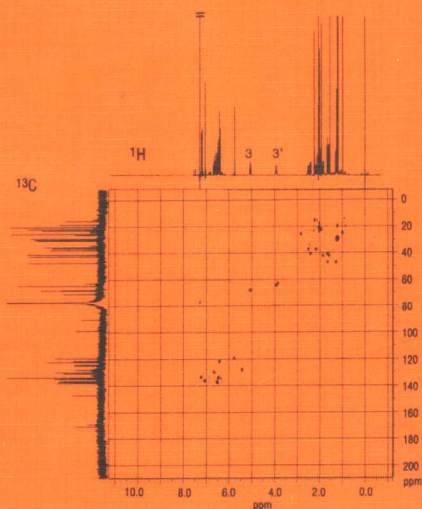


Carotenoids

Volume 1B: Spectroscopy

Edited by G. Britton
S. Liaaen-Jensen
H. Pfander



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Birkhäuser Verlag
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Preface to Volume 1B

The informed use of a range of spectroscopic methods is essential to modern analysis and structure elucidation. The application of such techniques including X-ray diffraction for the identification and structure elucidation of carotenoids is surveyed in Volume 1B. The use of spectroscopic methods for studying the location and functioning of carotenoids *in vivo* has not been covered in detail.

For all spectroscopic methods a sound understanding of the basic principles is imperative. References are therefore given to suitable general books and reviews. UV/Visible light absorption spectroscopy is a basic analytical method used by all carotenoid workers. The treatment of this technique, with more details of basic principles and procedures and structural correlations, reflects this wider use. Other physical techniques are generally more specialized and require expert knowledge and experience for many applications. A more specialized treatment is therefore given. However, major emphasis is placed throughout on practical guidance for interpretation of spectra, and on tabulated data such as NMR assignments and MS fragmentations for carotenoid end groups, identification of functional groups by IR and identification of chromophores by UV/Vis spectroscopy.

George Britton
Synnøve Liaaen-Jensen
Hanspeter Pfander

Editors' Notes on the Use of these Books: Vol. 1B

The *Carotenoids* books are planned to be used with the *Key to Carotenoids*, Second Edition. Throughout the series, whenever a known, natural carotenoid is mentioned, its number in the *Key to Carotenoids* or the *Appendix* (Vol. 1A, Chapter 8) is given in bold print. Other compounds, including purely synthetic carotenoids, that do not appear in the *Key* are numbered separately, in italics, in sequence for each Chapter, and their formulae are shown. Note that the *Key* numbers given are those in the Second Edition of the *Key to Carotenoids* (1987). The numbering of compounds in the original *Key to Carotenoids* (1976) and the list in the 1971 Isler *Carotenoids* book is different.

There is substantial cross-referencing between Volume 1A and 1B, which constitute two parts of a single volume and are intended to be used together.

Trivial names

The IUPAC semi-systematic names for all known naturally occurring carotenoids are given in the *Key to Carotenoids*, 2nd Edition, and in the *Appendix* (Vol. 1A, Chapter 8). Trivial names for many carotenoids are, however, well-established and convenient, so the practice of using these trivial names rather than the often cumbersome IUPAC semi-systematic names will, in general, be maintained in this series. An important exception is the naming of those compounds which bear the trivial name '(prefix)-carotene'. To avoid confusion caused by the use of Greek-letter prefixes that do not correspond to the series of prefixes used to designate end groups in the IUPAC system (*e.g.* ' γ -carotene' does not contain γ end groups) the old names α -carotene, β -carotene, γ -carotene, δ -carotene and ϵ -carotene are abandoned according to the IUPAC recommendation, and replaced by β,ϵ -carotene, β,β -carotene, β,ψ -carotene, ϵ,ψ -carotene and ϵ,ϵ -carotene, respectively.

References

Selective key references for major papers and review articles are given, rather than comprehensive lists of original literature sources.

Indexing

The indexes have been prepared primarily to aid the use of these books as general information and practical guides. No author index or index of biological sources of carotenoids is given. For information on individual carotenoids the *Key to Carotenoids*, which gives the trivial and semi-systematic names of each carotenoid, and references to its occurrence, isolation, spectroscopic properties, synthesis, *etc.* should be used.

The Index should be used together with the List of Contents to direct the reader to particular concepts, definitions, phenomena, techniques and procedures during the practical use of the books.

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Chapter 1

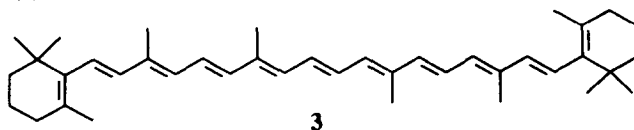
Electronic Structure of Carotenoids

Bryan E. Kohler

A. Introduction

The carotenoids play an obvious role as pigments that give many natural objects their pleasing colours. They have even more important roles as initiators and mediators of photochemistry in processes that range from photosynthesis to vision. There are several other chromophores that absorb light in the visible and near-ultraviolet regions of the spectrum, but the electronic structure of linear polyene chains is qualitatively distinct from that of other conjugated hydrocarbons such as, for example, the polyacenes. The aim of this Chapter is to communicate the picture of the electronic structure of linear polyenes that has emerged over the past 20 years. Although much of this work has concentrated on short-chain polyenes as models, it nevertheless provides a basis for understanding the spectroscopic and photochemical properties of carotenoids.

In 1972 it was discovered that the excited state responsible for the longest wavelength strong absorption band in diphenyloctatetraene was not the lowest-energy excited singlet state [1]. A previously undetected excited singlet state at lower energy rationalized fluorescence properties that had been thought to be anomalous (Fig. 1), so it was conjectured that all linear polyenes, the carotenoids included, would have a similar hidden low-lying excited singlet state [2-4]. This is now known to be true. An important goal of this Chapter is to describe this relatively newly discovered S_1 state in terms of simple molecular orbital concepts. This is critically important; since virtually all photoprocesses in linear polyenes originate in the lowest-energy excited singlet state, the importance of correctly identifying and characterizing that state cannot be overemphasized. The revised state ordering given in Fig. 1 accounts for a number of observations previously considered curious, including the provocative lack of fluorescence of β,β -carotene (3).



In the discussion that follows, some basic properties of linear conjugated molecules are reviewed, such as delocalized π -electrons, bond-length alternation, isomers and conformers. A brief outline of the simple molecular orbital concepts that apply to these molecules provides a background for the UV/Vis spectroscopy of the carotenoids.

Polyene Electronic Structure

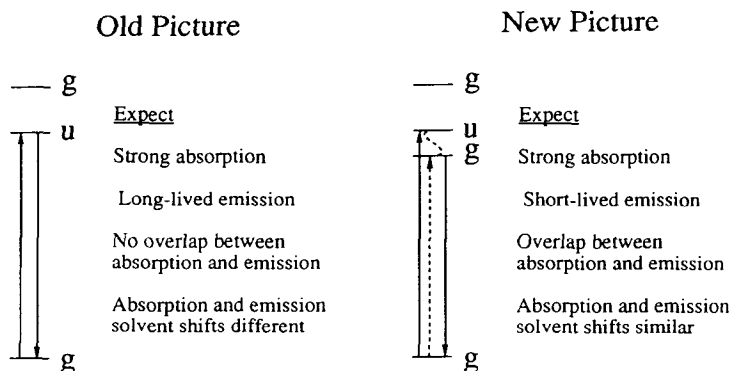


Fig. 1. Energy level diagrams for linear polyenes. The old and new pictures are presented. The expectations for the new picture correspond to what is observed, those of the old picture do not.

B. Overview of Carotenoid Electronic Structure

The key structural element of carotenoids is the conjugated polyene backbone. It is the delocalization of π -electrons along this backbone that gives carotenoids their characteristic electronic spectra and is largely responsible for the photophysical and photochemical properties of these molecules, including *cis-trans* photoisomerization.

The atoms in an unsubstituted linear polyene are arranged in a planar zigzag chain, with the formal repeating unit $-\text{CH}=\text{CH}-$. There is pronounced bond-length alternation. The length of a formal C-C single bond (1.45 Å) is shorter than that in a normal alkane (1.53 Å), although the length of a formal C=C double bond (1.34 Å) is the same as that in ethylene (1.336 Å). The shortening of the single bonds is consistent with delocalization of the π -electrons, that is that they are able to move along the polyene chain.

Carotenoids are methyl-substituted polyenes which have the formal repeating unit $-\text{CH}=\text{CH}-\text{CCH}_3=\text{CH}-$. Alternatively, they may be considered as linear polyenes in which every fourth hydrogen atom (or fifth in the central part of the molecule) has been replaced by a methyl group. X-Ray crystallography has shown that the structural consequences of this methyl substitution are relatively minor; the C-C and C=C bond lengths are nearly the same as in the unsubstituted polyenes. The C=C-C bond angles in the linear polyenes are all very close to 125°. In the carotenoids the C=C-C bond angle is also 125° if the carbon at the apex is not

methyl substituted, but averages 117° if this carbon is methyl substituted. This presumably reflects steric crowding which gives a slight bow and a barely perceptible helical twist to the zigzag backbone of the carotenoids.

The barriers to rotation about the formal double bonds in a polyene or carotenoid are sufficiently large for double-bond *cis* and *trans* isomers to be isolated as independent, distinct compounds. This is not true of *s-cis* and *s-trans* conformers.

The differences in excitation energies for *cis* and *trans* isomers of a given molecule are small compared to the change in excitation energy that is associated with adding or subtracting a conjugated double bond. The basic electronic structure is, therefore, almost independent of isomeric form.

C. The Electronic Structure of Linear Polyenes

1. Identification of the S_1 and S_2 states

The main objective in this Section is to describe the molecular orbital character of the S_1 and S_2 states of polyenes. It is useful to review briefly the essentials of a description of the electronic structure of a conjugated polyene chain by the simplest of molecular orbital theories, Hückel theory [5, 6], in order to define terms that will be used in the discussion of spectra that follows. Further details may be found in standard texts [6] or in review articles [7, 8].

Because it accounts for the excitation energy and the intensity of the lowest-energy strong absorption band of linear polyenes, the description of the π -electron states that is given by Hückel theory can be considered to be very successful. On the other hand, Hückel theory may be considered to have a serious weakness, because it incorrectly predicts that the excited state responsible for this absorption is S_1 , the lowest-energy excited singlet state (as will be seen below, it is not S_1 , it is S_2). However, LCAO-MO (linear combination of atomic orbitals-molecular orbital) theory at the Hückel level is well known and the new state ordering may be described efficiently in terms of linear combinations of Hückel configurations.

Because it is so well established, the electronic structure of the simplest conjugated model compound, butadiene, will be described. In simple Hückel theory only those electrons are considered that are not used in making the σ -bonded framework of sp^2 -hybridized carbons (Fig. 2). The problem is to find for these electrons the linear combinations of the atomic orbitals (2p orbitals that are perpendicular to the plane of the zigzag chain; also called 2p- π orbitals) that are solutions of the Schrödinger equation for the molecule. A linear polyene with n double bonds will have $2n$ 2p- π atomic orbitals which will lead to $2n$ linearly independent molecular orbitals. Hückel theory, which is a set of approximations for the molecular Schrödinger equation, generates a closed-form general solution for molecular orbital energies and gives the atomic orbital coefficients for a given molecular orbital for a polyene with an arbitrary number of double bonds in conjugation [6]. The molecular orbitals for butadiene ($n = 2$) are sketched in Fig. 3.

An electronic configuration is defined as a particular assignment of the $2n$ π -electrons to molecular orbitals. At this level of treatment, the energy of a given configuration is simply the