



On infinitenes – Reliable calculation of λ_{∞} and molecular modeling of lemniscate structured carotenoids

Ana Martínez^{a,*}, Muhammad Zeeshan^b, Asma Zaidi^b, Hans-Richard Sliwka^{b,*}, K. Razi Naqvi^{c,*}, Vassilia Partali^b

^a Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, Ciudad Universitaria, CP 04510, Coyoacán, CDMX, Mexico

^b Department of Chemistry, Norwegian University of Science and Technology, 7491 Trondheim, Norway

^c Department of Physics, Norwegian University of Science and Technology, 7491 Trondheim, Norway

ARTICLE INFO

Article history:

Received 20 November 2017

Received in revised form 14 December 2017

Accepted 16 December 2017

Available online 18 December 2017

Keywords:

Carotenoids

UV/VIS spectroscopy

DFT calculation

Polyenes

ABSTRACT

The absorption limit for an “infinite” number of conjugated double bonds has been a topic of considerable interest for over seventy years. Establishing the limit (hereafter λ_{∞}) consists in collecting the spectral data of homologous polyenes (in most previous investigation with ≤ 17 double bonds), fitting the absorption values to a formula with one or more adjustable parameters, and identifying λ_{∞} by extrapolation. Here we report establishing the unsettled value of λ_{∞} by taking as basis three recently synthesized long carotenoid families culminating in 19, 23 and 27 conjugated double bonds. Excellent fits of experimental data have been obtained by using new formulas allowing a confident λ_{∞} -extrapolation to carotenoids with infinite length. UV-visible λ_{max} values of long carotenoids were also calculated by using Time Dependent Density Functional Theory (TDDFT). The theoretical results agree well with the experimental trend. Molecular modeling confirmed that accumulating “infinite” conjugated double bonds in carotenoids imparts to the molecule the shape of a lemniscate, the symbol for infinity. The name *infinitene* is proposed for a hypothetical lemniscate carotenoid.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

Although colorless on its own, the C=C bond stands for the basic chromophoric unit in organic chemistry. The relation between the color exhibited by the molecule and N (the number of double bonds) has long fascinated chemists and color scientists [1]. A pale yellow shade occurs when $N = 6$ [2]. The larger the value of N , the longer the wavelength of maximum light absorption, which will be represented by the symbol λ_{max}^N or λ_{max} , when N needs not to be specified. Successive addition of double bonds creates flamboyant carotenoid pigments. “Does the chromophoric role of the C=C unit persist or fade away by endless addition of double bonds?” is so far a moot question. Extended plain polyenes become progressively unstable, with $N = 13$ or 15 representing an upper limit [3,4], but multitudes of double bonds accumulate in methyl branched polyenes; hence the occurrence of carotenoids. Investigations of the response of a double bond assembly to light began to flourish with the marketing of commercial UV-vis spectrophotometers in 1941 [5]. A mere decade later, $N = 19$ was recognized

as the cut-off point for chain elongation [6], a boundary later reinforced by the failure of an attempt to assemble 23 double bonds [7]. The drive for synthesizing molecular wires revived the efforts to prolong polyenes, but the enthusiastically celebrated polyenes of 1100 (or even 100000) C=C bonds displayed disappointingly low values of λ_{max} , which were soon rationalized in terms of a broad distribution of isolated conjugated segments, each segment constituting an “island of conjugation” [8,9]. Consequently, the number of C=C bonds downsized to less than 50, still ignoring that the noted $\lambda_{\text{max}} \approx 550$ nm was typical of 19 double bonds [10].

When synthetic chemists, wishing to follow the trail blazed by the polyene pioneer Richard Kuhn [2], failed to come up with longer and longer conjugated molecules, several theorists took up the gauntlet and derived analytical expressions containing some adjustable parameters whose values were fixed by optimizing the fit between experiment and the predictions of the model. Besides two other Kuhns—namely, Hans K. [11] and Werner K. [12]—most noteworthy are Dewar, Huzinga & Hasino and Hirayama [13–15]. The constrained three parameter equation of Hirayama, a long chain variant of the widespread Fieser-Woodward and less prevalent Fieser-Kuhn [16] increment method (note S1), has gained a certain reputation among carotenoid

* Corresponding authors.

E-mail addresses: martina@unam.mx (A. Martínez), richard.sliwka@ntnu.no (H.-R. Sliwka), razi.naqvi@ntnu.no (K. Razi Naqvi).

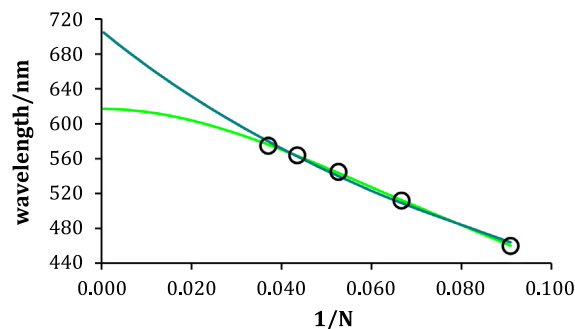


Fig. 1. Extrapolated λ_{∞} from experimental λ_{\max} of zeaxanthin isomers ($N = 11, 15, 19, 23, 27$) with the formulas of W. Kuhn (—) and H. Kuhn (—). Open circles represent the experimental values.

chemists, because it predicted $\lambda_{\max}^{[N]}$ and $\lambda_{\max}^{[N \rightarrow \infty]}$ (λ_{∞}) with tabulated compound and solvent constants at a time, when regression could not be performed in milliseconds by computer programs [17–19]. Most polyene chemists have displayed unwavering loyalty to an empirical relation when extrapolating λ_{∞} , namely a second-degree polynomials in N^{-1} . These and other equations [20,21] have not only enabled λ_{\max} -determination of yet-to-be-synthesized carotenoids, but have also tempted many scientists into locating the spectral limit by ever-increasing N . A few experimental data points can always be well fitted with inappropriate formulas to lines, but these will fan out to quite different λ_{∞} (Fig. 1, note S2, Fig. S1). A variety of λ_{∞} were calculated for carotenoids (Table S1, Fig. S2); λ_{∞} could even represent a compound-specific infinite absorption [18,19]. On the other hand, it has been argued that λ_{∞} of various carotenoids converges in a common value [22,23].

The large spread in λ_{∞} and our success in the synthesis of unprecedentedly long carotenoids [24] with $N = 23$ and $N = 27$ prompted us to return to the problem of determining the absorption limit of conjugated polyene chains with new equations, developed after a critical examination of numerous rival fitting formulas [25,26]. The exact determination of λ_{∞} is described in the first section of this account. Since synthetic polyene extensions rapidly reach its limit, we support our investigations by quantum mechanical calculations (Time Dependent Density Functional Theory, TD-DFT). TD-DFT allowed molecular modeling of successively extended carotenoids, which finally attained the structure of a lemniscate, the symbol of infinity. These results are presented in the second part of this account.

2. Computational details

All the electronic calculations were performed with the Gaussian 09 [27] package of programs. Fully optimized structures and harmonic frequencies were obtained at B3LYP/LANL2DZ level of

Table 1

Bond length alternation for the compounds reported in this investigation. Results are reported in Å.

	C–C	C=C
M06-2X	1.45–1.47	1.35–1.37
B3LYP	1.44–1.47	1.38–1.39

theory [28–32]. The absence of imaginary frequencies identified local minima. The adsorption spectra have been computed with TDDFT using the optimized geometries and M06-2x/6-311G level of theory [33–37]. Solvent effects were included by single point calculations at the M06-2x/6-311G level of theory using polarizable continuum model, specifically the integral-equation-formalism (IEF-PCM). We also optimized the structures at M06-2X/6-311G level of theory, and used these structures to obtain the adsorption spectra (see Table 2S). It was reported previously [38,39] a benchmark study concerning the central bond length alternation in eight oligomeric series of increasing size. In that investigation, authors compare DFT results with CCSD(T) values and they concluded that M06-2X is the most efficient functional with errors systematically smaller than those of B3LYP. The bond length alternation obtained in this investigation is reported in Table 1. The results are similar in all the optimized structures, but the values of λ_{\max} are different. The best agreement with the experimental results is obtained with the structures optimized at B3LYP/LANL2DZ level. For this reason, in what follows we will refer to B3LYP/LANL2DZ results.

This TD-DFT investigation is made in the so-called vertical approximation, i.e. the transition energies toward the lowest excited state are computed considering a frozen geometry (the optimal ground state structure obtained from the optimization) [40–43]. In this approximations, the vibrational degrees of freedom and hence the coupling between nuclear and electronic degrees of freedom (vibronic effects) are neglected. This approach allows us to determine the nature of different excited states but does not provide theoretical estimates that can be rigorously compared to experimental values. The obtained accuracy of the relative position of the maxima in the vibronic progression and the relative intensities of the peaks depends on the studied system [42]. To achieve accuracy, it is necessary to perform TD-DFT in its adiabatic kernel approximation. A different model might reduce the substantial discrepancy between vertical TD-DFT results and their experimental counterparts, but the overlong size of the systems precludes a realistic alternative to the vertical values.

3. Results and discussion

Carotenols (zeaxanthins CnZea:N, longest C80Zea:27), carotenoic acids (CnAcid:N, longest C45Acid:15) and carotenals (CnAld: N, longest C50Ald:19) were synthesized (Fig. 2) and the UV–vis

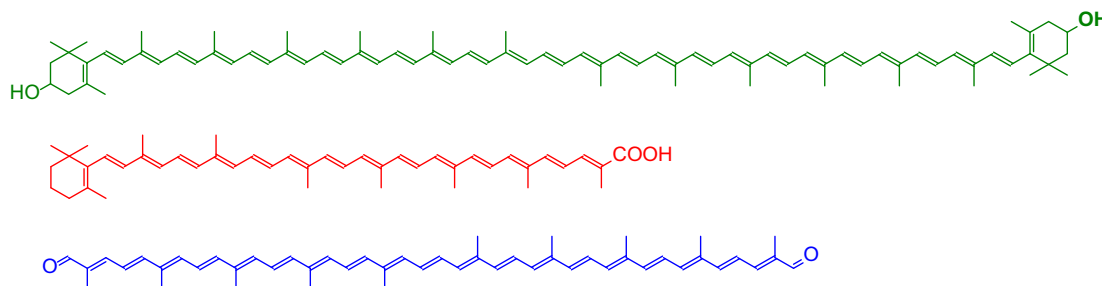


Fig. 2. Schematic representation of synthesized long carotenoids: Zeaxanthin C80Zea:27 (green), carotenoic acid C45Acid:15 (red), carotenal C50Ald:19 (blue). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

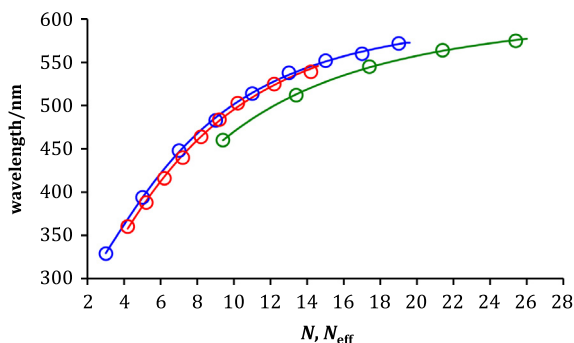


Fig. 3. Absorption (λ_{\max}) of carotenals (○, DCM, N), carotenoic acids (○, MeCN/H₂O 9:1, N_{eff}) and zeaxanthins (○, DCM, N_{eff}). Lines are fits according to Eq. (1). Solvent abbreviations: DCM = dichloromethane, MeCN = acetonitrile.

spectra recorded [24,43]. The displacement of the graphs in Fig. 3 portrays the impact of the auxochromes (–CHO, –COOH) on the increase in λ_{\max} .

The double bond in the cyclohexene end rings of the acids and zeaxanthins conjugate only to ca. 20% with the polyene chain due

to steric distortion (Fig. S3); therefore, to obtain N_{eff} , the effective number of conjugated double bonds, a deconjugation factor of 0.8 has to be subtracted from the nominal number of double bonds N , e.g. acids with one ring $N_{\text{eff}} = N - 0.8$, zeaxanthins with two rings $N_{\text{eff}} = N - 2 \times 0.8$ [15,18]. N_{eff} becomes obsolete in acquiring λ_{∞} ; values of λ_{\max} for shorter carotenoids assessed with N or N_{eff} deviate, but converge in λ_{∞} .

3.1. Optimized structures and DFT results

Full geometry optimization was performed for previously synthesized molecules. Elongation of the carotenoid polyene chain is accompanied by an increased curvature (Fig. 4). C–C and C=C bond lengths remain approximately constant. TDDFT-derived λ_{\max} -values are reported in Table 2. Identical solvents were used in experiment and calculation.

Polyene chain elongation is followed by an augmenting divergence of both TDDFT and experimental λ_{\max} (Table 2). TDDFT allocated a too elevated absorption increment for each double bond confirming prior observations [24]; thus λ_{\max} -values appear overestimated. Obviously, calculating λ_{\max} of conjugated polyenes by TDDFT remains a challenge.

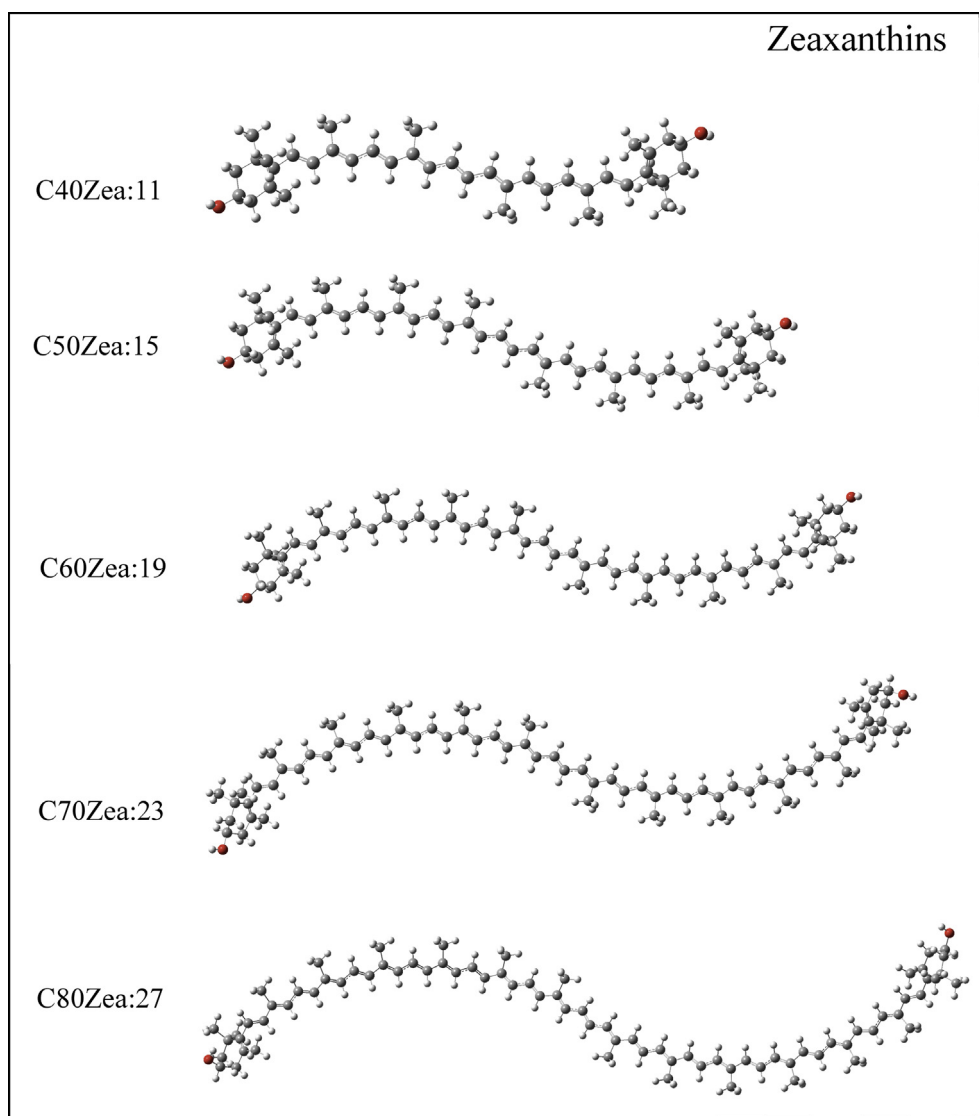


Fig. 4. Optimized structures carotenoids $C_n:N$ (n is equal to the number of C atoms, N is the number of double bonds (C=C)).

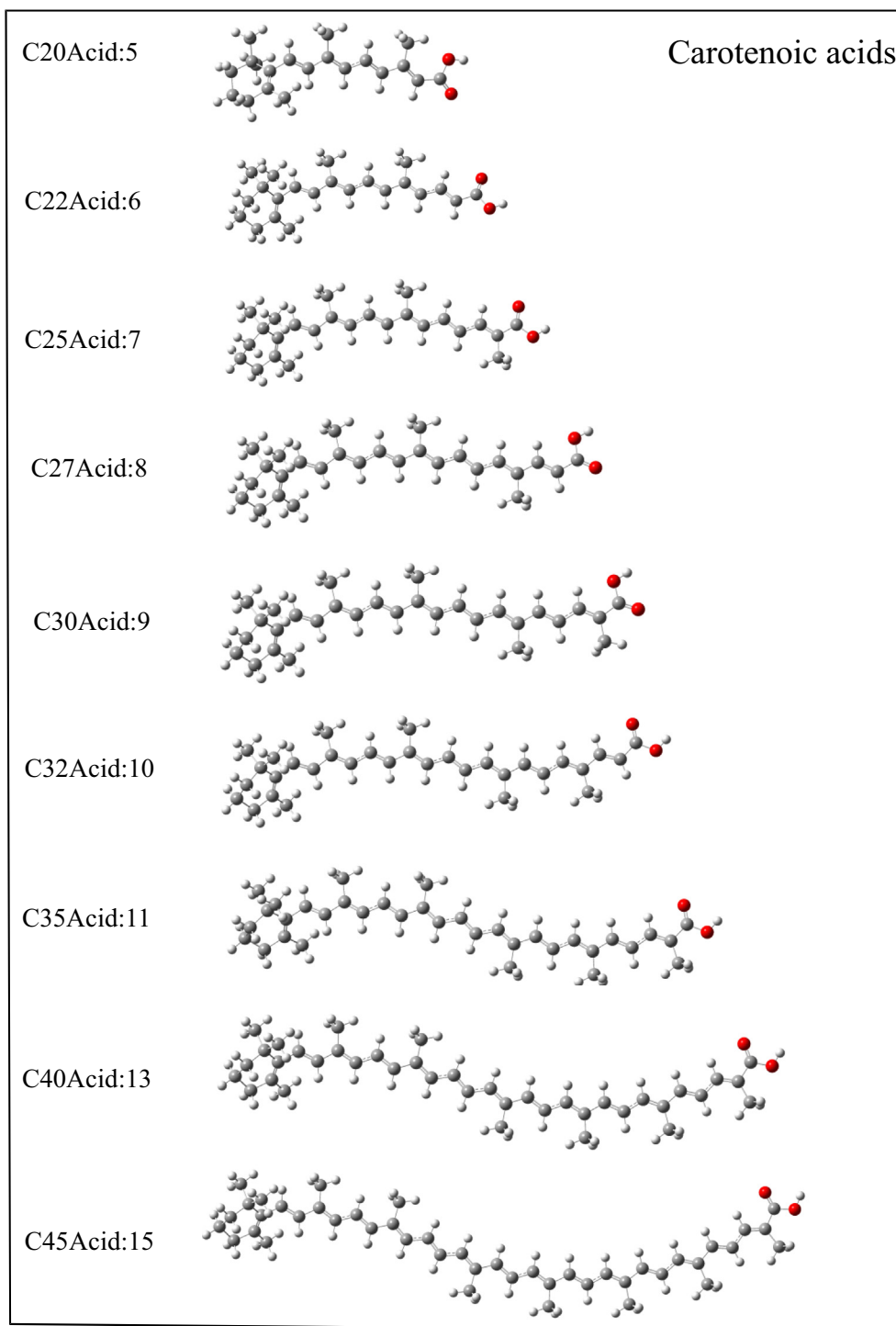


Fig. 4 (continued)

3.2. Reliable λ_∞ – extrapolation of carotenoids

We have recently demonstrated that the hitherto applied extrapolation formulas for λ_∞ are all marked with a blemish. New formulas were, therefore, developed and their quality verified. We have chosen Eq.(1), a trigonometric three parameter formula from the equations presented in Refs. [25,26] for λ_∞ -extrapolation of the three carotenoid series; fitting and extrapolation appear in Fig. 5 as a plot of λ_{\max} versus $1/N$.

$$\lambda_N = X \left[1 - A \frac{1 - \cos \frac{\pi}{N+1}}{1 - \alpha \cos \frac{\pi}{N+1}} \right] \quad (1)$$

X , A and α are constants obtained by nonlinear regression. X immediately indicates λ_∞ when $N \rightarrow \infty$ (Table 2), i.e. $C_{\infty}Zea:\infty \lambda_\infty = 615$ nm, $C_{\infty}Ald:\infty \lambda_\infty = 615$ nm, $C_{\infty}Acid:\infty \lambda_\infty = 623$ nm. Other new or amended two or three parameter formulas [25,26] gave similar results (note S3).

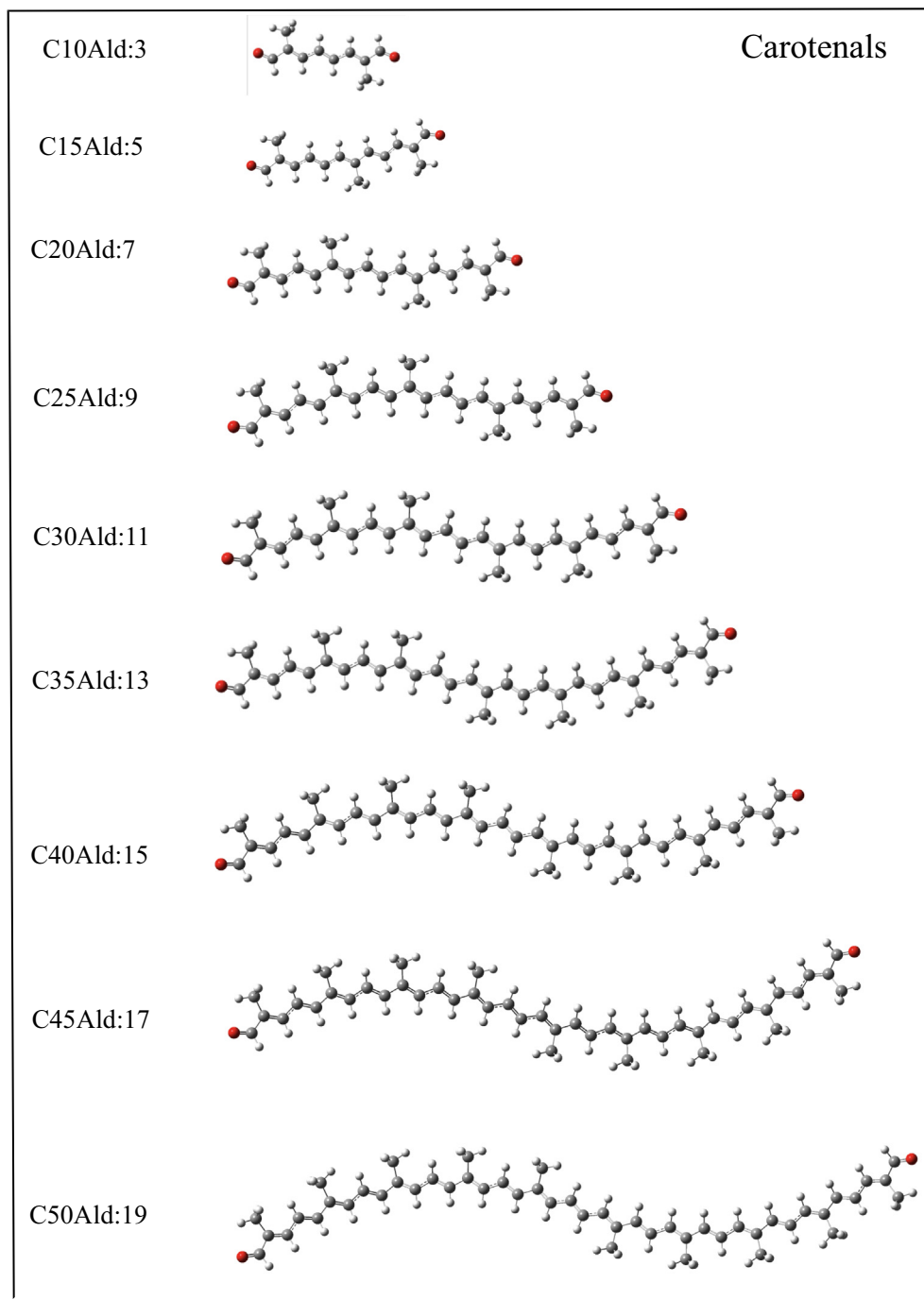


Fig. 4 (continued)

The graphs in Fig. 5, leveling off to λ_∞ imply a preceding perceptual infinite absorption λ_∞ (the symbol ∞ denotes incomplete infinity) [44]: the ophthalmic color discrimination threshold around 610 nm is limited to $\Delta\lambda \approx 2$ nm [45]; the resolution of UV-vis instruments is at best 0.1 nm. The exact λ_∞ - agreement of the zeaxanthins (no auxochrome) with the dialdehydes (two auxochrome groups) could be interpreted in favor of a finite λ_∞ for carotenoids, at least when measured in the same solvent (DCM). The acids were recorded in MeCN/H₂O 9:1.

Five carotenoid acids have been measured previously in petroleum ether [46]. Comparison of our nine compounds

series with that of five compounds illustrates again the variance in λ_∞ -extrapolation of fairly fitted experimental data, $\lambda_\infty^{[N^9 \rightarrow \infty]} = 623$ nm, $\lambda_\infty^{[N^5 \rightarrow \infty]} = 732$ nm (Fig. 5c). A reliable λ_∞ -extrapolation is, therefore, only possible with a sufficient number of long carotenoids and an optimized fitting formula. However, the difficulty in synthesizing well-defined long carotenoids for experimental verification of λ_∞ increases proportional to N . The supposed constraint of our zeaxanthin synthesis, regulated by the solubility of the reactants, can possibly stretch to 130Zea:47 or utmost to C150Zea:51 [24]. It is probably illusory to await at present an experimental λ_{\max} -verification of very

Table 2
Experimental and calculated (Eq. (1), TD-DFT) absorption λ_{\max} and λ_{∞} of zeaxantins, carotenals (both in DCM) and of carotenoic acids (in MeCN (experimental values in MeCN/H₂O 9:1)).

Zeaxanthin				Acid				Aldehyde			
	DCM	T3pU	TD-DFT		MeCN	T3pU	TD-DFT		DCM	T3pU	TD-DFT
N	λ_{\max}	λ_{\max}	λ_{\max}	N	λ_{\max}	λ_{\max}	λ_{\max}	N	λ_{\max}	λ_{\max}	λ_{\max}
11	460	460	513	5	360	358	358	3	329	329	351
15	512	513	582	6	388	390	426	5	394	393	427
19	545	544	625	7	416	418	455	7	448	446	492
23	564	563	653	8	440	443	458	9	483	486	540
27	575	576	672	9	464	464	511	11	514	515	579
∞		615		10	484	483	531	13	538	536	607
				11	503	498	546	15	552	551	630
				13	525	524	576	17	560	562	647
				15	539	543	599	19	572	571	660
				∞		623		∞		615	

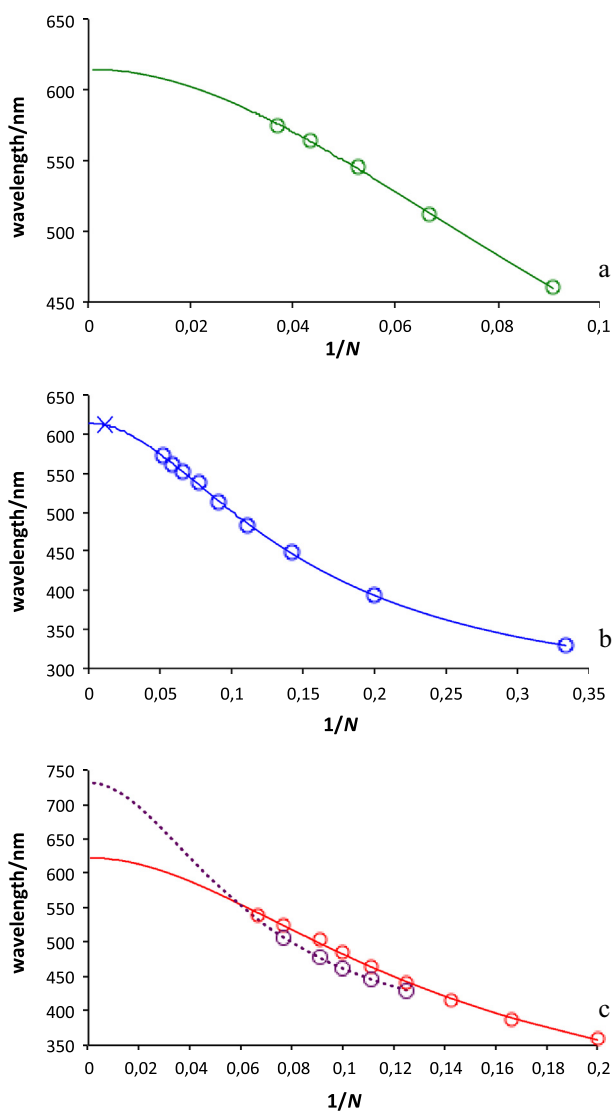


Fig. 5. Calculating λ_{∞} of carotenoids by fitting experimental data with Eq. (1); (a) zeaxanthins —, experimental \circ ; (b) polyenals —, experimental \circ , \times denotes infinitene C230Ald:91 (Fig. 6d); (c) polyenoic acids —, experimental \circ , experimental data \circ from Ref. [41].

long carotenoids. Currently, quantum chemical calculations provide the most accessible approach to an expansion of λ_{\max} -data. The problems and challenges in such calculations will be addressed in a forthcoming paper.

3.3. Molecular modeling of carotenoids

The structures of the carotenals from C10Ald:3 to C50Ald:19 were optimized (Fig. 4) and then gradually elongated beyond the experimental limit. The hypothetical molecules were analyzed by DFT. The longer the chain grew, the nearer the ends moved together (Fig. 6). DFT-calculation completed at C200Ald:79 with the available resources (Fig. 6c). Molecular Mechanics (MM)-calculation allowed attaining C230Ald:91 developing an open lemniscate symbolizing infinity (Fig. 6d). The widened curvature of the loop ends for C230Ald:91 expressed the inferior optimization by MM. The extremities of acids and zeaxanthins advanced similarly. The overall consistency of molecular modeling with X-ray diffraction measurements of carotenoids corroborates the infinite lemniscate architecture [47]. Elongated carotenoids convert to infinitenes.

Bond length equalization is a convenient conjugation probe. Conjugation in the infinity-shaped carotenals contracted the C—C bond from $l = 1.53 \text{ \AA}$ to $l = 1.45 \text{ \AA}$ and expanded C=C from $l = 1.34 \text{ \AA}$ to $l = 1.38 \text{ \AA}$ (average values) with no increased influence of conjugation on the midpoint double bond [48]. Molecule bending may influence conjugation [49], yet linear and bent β -carotene show the same λ_{\max} [50].

Only elongated *trans*-carotenoids with the characteristic methyl branched polyene chain convert to infinitenes (isotacticity of the methyl groups changes at the central double bond). In contrast, syntactic (alternate up and down) methyl branched non-carotenoid polyenes adopt a linear structure (Fig. S4).

C230Ald:91 represents an infinitene (Fig. 6d) with $\lambda_{\infty} = 615 \text{ nm}$ and a horizontal and vertical molecule dimension of $l = 80.7 \text{ \AA}$ and $l = 41.6 \text{ \AA}$. The nearly plane structure of C230Ald:91 prevents the chain-heads to overstep the central part designing an open lemniscate, the Euler symbol for infinity, Fig. 7 [51]. Carotenoid lengthening is therefore, confined by the van der Waals distance of the atoms touching the crossing point (H...O $d_w = 2.5 \text{ \AA}$) [52]. Synthetic steps by C5 units on both ends finalized extension to the ultimate Euler shaped lemniscate C230Ald:91 (indicated by \times in Fig. 5b). Nonetheless, if the encounter of the ends with the polyene chain would provoke a lateral out-of-plane bending, the edges might overcome the chain segments and the compound could by further extending adopt a reiterating ribbon like space-lemniscate with potential infinity [53], similar to particular layouts of the periodic system (Figs. S4 and S5) [54,55]. An organization of molecules to lemniscate structures has not really observed before. The loops of octaphyrins and twisted annulenes emerge too deformed to qualify for infinity [56,57].

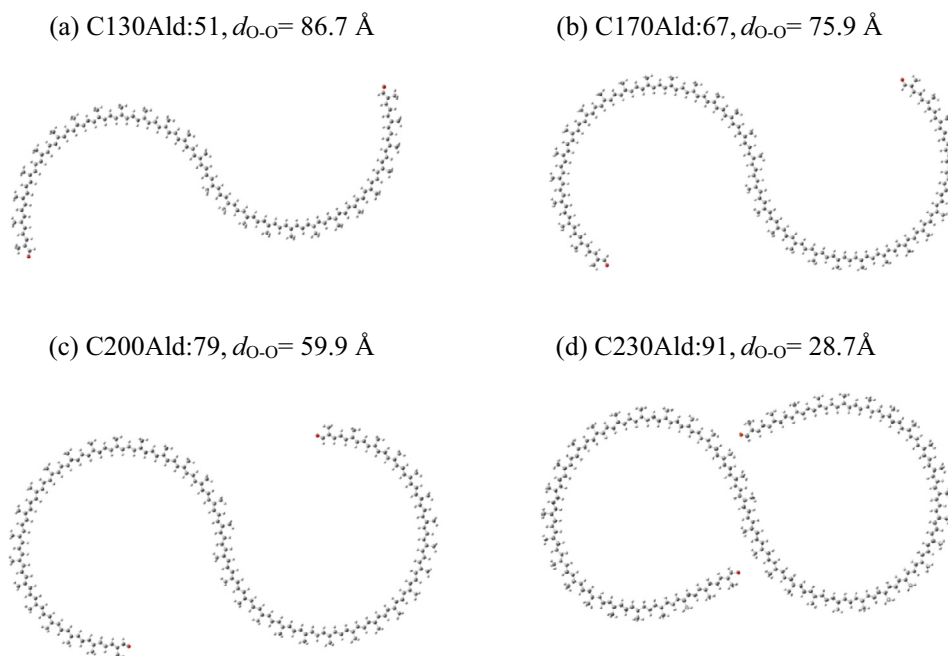


Fig. 6. Optimized structures of expanded carotenoid dialdehydes. The four molecules demonstrate the gradual rapprochement of the aldehyde oxygens (d_{O-O}) resulting finally in a lemniscate structure. The limit of DFT modeling was reached with C200Ald:79, C230Ald:91 was obtained by Molecular Mechanics.



Fig. 7. Open lemniscate (Euler symbol for infinity) [51].

4. Conclusions

Neither common UV–vis spectrophotometers nor the human eye can differentiate between λ_{∞} and λ_{∞} . The electrical wire properties of a conventional dimensioned carotenoid have been convincingly demonstrated [58,59]. However, long carotenoids arranged in lemniscates forfeit their potential as candidates for drawn-out molecular cables [59]. Infinitenes could be synthetically straightened, but blocking bending incurs steric strain and, consequently, instability [50].

Our results do not lead to a common extrapolated λ_{∞} for the three carotenoid series. Nevertheless, despite the convergence between zeaxanthins and aldehydes on the one hand, the small variance with acids on the other hand, and regardless of dissimilarities between perceptual, actual or potential infinite absorptions: the marginal variations vanish in a wider shade of blue (Fig. 8).

Extending methane, via ethane, propane and butane etc., results in $C_{390}H_{782}$, the so far terminating hydrocarbon [60]. Whether $C_{finite}H_{finite}$ or $C_{\infty}H_{\infty}$, overextended pale infinitenes stimulate only a few specialists. However, successive accumulation of conjugated C=C units, produces polyenes exhibiting the marvelous colors of the perceptible spectrum (Fig. 8). It is comforting to realize that color persists, even by expanding carotenoids to infinitenes. In an imaginary world, where carotenoids, the central natural pigments, adopt lemniscate structures by molecule extension, the Indian summer would adjust to infinite blue (Fig. S6) [61].

Acknowledgements

Muhammad Zeeshan and Asma Zaidi thank the Higher Education Commission of Pakistan for a PhD-scholarship. This study was funded by DGAPA-PAPIIT, Consejo Nacional de Ciencia y Tecnología (CONACyT), and resources provided by the Instituto de Investigaciones en Materiales (IIM). This work was carried out using a NES supercomputer, provided by Dirección General de Computo y Tecnologías de Información y Comunicación (DGTIC), Universidad Nacional Autónoma de México (UNAM). We would like to thank the DGTIC of UNAM for their excellent and free supercomputing services and Oralia L Jiménez, María Teresa Vázquez and Caín González for their technical support.



Fig. 8. Color of carotenoid acids from C20Acid:5 (retinoic acid, $\lambda_{max} = 360$ nm) to $C_{\infty}Acid:\infty$ ($\lambda_{\infty} = 623$ nm).

Appendix A. Supplementary material

A short resumé of λ_{max} -predictions, notes that refers to different λ_{∞} -extrapolations of spheroidenes, extrapolation of λ_{∞} with other recently derived formulas, different values of λ_{∞} obtained with inappropriate equations and insufficient experimental data obtained since 1952 can be found in the Supporting Material. Fig. S3 explains the partial conjugation of the ring double bond. Fig. S4 illustrates that syntactic methyl branched non-carotenoid polyenes appear with a linear chain. Reiterating ribbon like space lemniscate are illustrated in Figs. S5 and S6 with proposals to arrange the periodic systems. Supplementary data associated with this article can be found, in the online version, at <https://doi.org/10.1016/j.comptc.2017.12.006>.

References

- [1] G.N. Lewis, M. Calvin, The color of organic substances, *Chem. Rev.* 25 (1939) 273–328.
- [2] R. Kuhn, Synthesis of polyenes, *J. Chem. Soc.* (1938) 605–614.
- [3] K. Knoll, R.R. Schrock, Preparation of *tert*-butyl-capped polyenes containing up to 15 double bonds, *J. Am. Chem. Soc.* 111 (1989) 7989–8004.
- [4] D. Klein, P. Kilickiran, C. Mlynek, H. Hopf, I. Dix, P.G. Jones, A general route to fully terminally *tert*-butylated linear polyenes, *Chem. -Eur. J.* 16 (2010) 10507–10522.
- [5] R. Jarnutowski, J.R. Ferraro, D.C. Lankin, Fifty years of commercial instrumentation in absorption spectroscopy, part II, *Spectroscopy* 7 (1992) 22–35.
- [6] P. Karrer, C.H. Eugster, Carotinoidsynthesen 8. Synthese des Dodecapreno- β -carotins, *Helv. Chim. Acta* 34 (1951) 1805–1814.
- [7] G. Broszeit, F. Diepenbrock, O. Graf, D. Hecht, J. Heinze, H.D. Martin, B. Mayer, K. Schaper, A. Smie, H.H. Strehlow, Vinyllogous β -carotenes: generation, storage, and delocalization of charge in carotenoids, *Liebigs Ann.-Recl.* 11 (1997) 2205–2213.
- [8] I. Ledoux, I.D.W. Samuel, J. Zyss, S.N. Yaliraki, F.J. Schattenmann, R.R. Schrock, R.J. Silbey, Third-order microscopic nonlinearities of very long chain polyenes: saturation phenomena and conformational effects, *Chem. Phys.* 245 (1999) 1–16.
- [9] M. Tabata, M. Yasueru, T. Sugioka, Y.M. Inubishi, Cis-cis type substituted acetylene polyene and method of producing the same, *Kuraray Co.* JP2010111797, 2010.
- [10] P. Wood, I.D.W. Samuel, R. Schrock, R.L. Christensen, Conformational disorder in long polyenes, *J. Chem. Phys.* 115 (2001) 10955–10963.
- [11] H. Kuhn, A quantum-mechanical theory of light absorption of organic dyes and similar compounds, *J. Chem. Phys.* 17 (1949) 1198–1212.
- [12] W. Kuhn, Über das Absorptionsspektrum der Polyene, *Helv. Chim. Acta* 31 (1948) 1780–1799.
- [13] M.J.S. Dewar, Colour and constitution 3. Polyphenyls, polyenes, and phenylpolyenes - and the significance of cross-conjugation, *J. Chem. Soc.* (1952) 3544–3550.
- [14] S. Huzinga, T. Hasino, Electronic levels of polyene chains, *Prog. Theor. Phys.* 18 (1957) 649–660.
- [15] K. Hirayama, Absorption spectra and chemical structures 1. Conjugated polyenes and p-polyphenyls, *J. Am. Chem. Soc.* 77 (1955) 373–379.
- [16] R. Gebhard, J.T.M. Vandijk, E. Vanouwerkerk, M.V.T.J. Boza, J. Lugtenburg, Synthesis and spectroscopy of chemically modified spheroidenes, *Rec. Trav. Chim. Pays-Bas* 110 (1991) 459–469.
- [17] W. Vetter, G. Englert, N. Rigassi, U. Schwieter, Spectroscopic methods, in: O. Isler (Ed.), *Carotenoids*, Basel, Birkhäuser, 1971, p. 200.
- [18] K. Hirayama, Absorption spectra and chemical structure 2. Solvent effect, *J. Am. Chem. Soc.* 77 (1955) 379–381.
- [19] J. Szöke, Spectral investigation of linearly conjugated polyene systems. IV. Application of the Hirayama method of calculation to carotenoids of the second and third grade of oxidation, *Magyar Tudományos Akad. Kem. Tudományok Osztályának Közleményei* 16 (1961) 275–279.
- [20] J. Szöke, Linearly conjugated polyene systems III. Methods for calculation of absorption maxima of linear conjugated polyene systems, *Magyar Tudományos Akad. Kem. Tudományok Osztályának Közleményei* 14 (1960) 385–398.
- [21] J. Torras, J. Casanovas, C. Alemán, Reviewing extrapolation procedures of the electronic properties on the π -conjugated polymer limit, *J. Phys. Chem. A* 116 (2012) 7571–7583.
- [22] R.L. Christensen, M.M. Enriquez, N.L. Wagner, A.Y. Peacock-Villada, C. Scriban, R.R. Schrock, T. Polívka, H.A. Frank, R.R. Birge, Energetics and dynamics of the low-lying electronic states of constrained polyenes: implications for infinite polyenes, *J. Phys. Chem. A* 117 (2013) 1449–1465.
- [23] B.E. Kohler, Electronic structure of carotenoids, in: G. Britton, S. Liaaen-Jensen, H. Pfander (Eds.), *Carotenoids Volume 1B: Spectroscopy*, Basel, Birkhäuser, 1995, p. 7.
- [24] M. Zeeshan, H.R. Sliwka, V. Partali, A. Martínez, The longest polyene, *Org. Lett.* 14 (2012) 5496–5498.
- [25] K.R. Naqvi, Extrapolating from a homologous series of oligomers to the infinite: it's a long long way to infinity, arXiv:1512.05708 [cond-mat.mtrl-sci] 2015.
- [26] K.R. Naqvi, Least-squares is not the only yardstick for estimating the absorption limit of an infinitely long conjugated chain from spectra of oligomers, *J. Phys. Chem. Lett.* 7 (2016) 676–679.
- [27] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.J.A. Montgomery, T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, J.A. Pople, Gaussian 09, Revision A.08 Inc., Wallingford, CT, 2009.
- [28] A.D. Becke, Density-functional exchange-energy approximation with correct asymptotic behavior, *Phys. Rev. A* 38 (1988) 3098–3100.
- [29] C. Lee, W. Yang, R.G. Parr, Development of the Colic-Salvetti correlation-energy formula into a functional of the electron density, *Phys. Rev. B* 37 (1988) 785–789.
- [30] P.J. Hay, W.R. Wadt, Ab-initio effective core potentials for molecular calculations - potentials for the transition-metal atoms Sc to Hg, *J. Chem. Phys.* 82 (1985) 270–283.
- [31] W.R. Wadt, P.J. Hay, Ab-initio effective core potentials for molecular calculations - potentials for main group elements Na to Bi, *J. Chem. Phys.* 82 (1985) 284–298.
- [32] P.J. Hay, W.R. Wadt, Ab-initio effective core potentials for molecular calculations - potentials for K to Au including the outermost core orbitals, *J. Chem. Phys.* 82 (1985) 299–310.
- [33] Y. Zhao, D.G. Truhlar, The M06 suite of density functionals for main group thermochemistry, thermochemical kinetics, noncovalent interactions, excited states, and transition elements: two new functionals and systematic testing of four M06-class functionals and 12 other functionals, *Theor. Chem. Acc.* 120 (2008) 215.
- [34] G.A. Petersson, A. Bennett, T.G. Tensfeldt, M.A. Al-Laham, W.A. Shirley, J.A. Mantzaris, A complete basis set model chemistry. I. The total energies of closed-shell atoms and hydrides of the first-row atoms, *J. Chem. Phys.* 89 (1988) 2193–2198.
- [35] G.A. Petersson, M.A. Al-Laham, A complete basis set model chemistry. II. Open-shell systems and the total energies of the first-row atoms, *J. Chem. Phys.* 94 (1991) 6081–6090.
- [36] A.D. McLean, G.S. Chandler, Contracted Gaussian-basis sets for molecular calculations. 1. 2nd row atoms, $Z = 11-18$, *J. Chem. Phys.* 72 (1980) 5639–5648.
- [37] K. Raghavachari, J.S. Binkley, R. Seeger, J.A. Pople, Self-consistent molecular orbital methods. 20. Basis set for correlated wave-functions, *J. Chem. Phys.* 72 (1980) 650–654.
- [38] D. Jacquemin, C. Adamo, Bond length alternation of conjugated oligomers: wave function and DFT benchmarks, *J. Chem. Theory Comput.* 7 (2011) 369–376.
- [39] M.J.G. Peach, E.I. Tellgren, P. Sałek, T. Helgaker, D.J. Tozer, Structural and electronic properties of polyacetylene and polyene from hybrid and coulomb-attenuated density functionals, *J. Phys. Chem. A* 111 (2001) 11930–11935.
- [40] D. Jacquemin, E.A. Perpète, I. Ciofini, C. Adamo, R. Valero, Y. Zhao, D.G. Truhlar, On the performances of the M06 family of density functionals for electronic excitation energies, *J. Chem. Theory Comput.* 6 (2010) 2071–2085.
- [41] S.S. Leang, F. Zahariev, M.K. Gordon, Benchmarking the performance of time-dependent density functional methods, *J. Chem. Phys.* 136 (2012) 104101.
- [42] F. Santoro, D. Jacquemin, Going beyond the vertical approximation with time dependent density functional theory, *WIREs Comput. Mol. Sci.* 6 (2016) 460–486.
- [43] A. Zaidi, H. Li, H.R. Sliwka, V. Partali, H. Ernst, T.B. Melø, Energy and electron transfer reactions of polyenic acids with variable chain lengths, *Tetrahedron* 69 (2013) 219–227.
- [44] U+29DC, Incomplete infinity, Unicode character, Unicode 3.2.0., 2002.
- [45] L. Zhaoqing, W.S. Geisler, K.A. May, Human wavelength discrimination of monochromatic light explained by optimal wavelength decoding of light of unknown intensity, *PLoS one* 6 (2011) e19248.
- [46] O. Isler, W. Guex, R. Rüegg, G. Ryser, G. Saucy, U. Schwieter, M. Walter, A. Winterstein, Carotinoide vom Typus des Torularhodins, *Helv. Chim. Acta* 42 (1959) 864–871.
- [47] F. Mo, X-ray crystallographic studies, in: G. Britton, S. Liaaen-Jensen, H. Pfander (Eds.), *Carotenoids Vol 1B: Spectroscopy*, Basel, Birkhäuser, 1995, p. 332.
- [48] C.M. Marian, N. Gilka, Performance of the density functional theory/multireference configuration interaction method on electronic excitation of extended π -systems, *J. Chem. Theory Comput.* 4 (2008) 1501–1515.
- [49] D. Oelkrug, A. Tompert, H.J. Egelhaaf, M. Hanack, E. Steinhilber, M. Hohloch, H. Meier, U. Stalmach, Towards highly luminescent phenylene vinylene films, *Synth. Metals* 83 (1996) 231–237.

- [50] P.V. Reddy, B. Borhan, Synthesis of C15, C14'-ring locked all-*trans*- β -carotene, *Tetrahedron Lett.* 43 (2002) 3867–3869.
- [51] L. Euler, Variar observations circa series infinitas, *Comment. Acad. Sci. Petropol.* 9 (1744) 174, 188.
- [52] S. Alvarez, A cartography of the van der Waals territories, *Dalton Trans.* 42 (2013) 8617–8636.
- [53] G. Cantor, Ueber unendliche, lineare Punktmannichfaltigkeiten, *Math. Ann.* 21 (1883) 545–591.
- [54] F.A. Gooch, C.F. Walker, in: *Outlines of Inorganic Chemistry, Part II Descriptive*, Macmillan, New York, 1905, pp. 8–9.
- [55] E.G. Mazur, in: *Graphical Representation of the Periodic System During 100 Years*, University of Alabama, Tuscaloosa, 1974, p. 82.
- [56] H.S. Rzepa, The chiro-optical properties of a lemniscular octaphyrin, *Org. Lett.* 11 (2009) 3088–3091.
- [57] H. Herges, Topology in chemistry: designing Möbius molecules, *Chem. Rev.* 106 (2006) 4820–4842.
- [58] G. Leatherman, E.N. Durantini, D. Gust, T.A. Moore, A.L. Moore, S. Stone, Z. Zhou, P. Rez, Y.Z. Liu, S.M. Lindsay, Carotene as a molecular wire: conducting atomic force microscopy, *J. Phys. Chem. B.* 103 (1999) 4006–4010.
- [59] G.K. Ramachandran, J.K. Tomfohr, J. Li, O.F. Sankey, X. Zarate, A. Primak, Y. Terazono, T.A. Moore, A.L. Moore, D. Gust, L.A. Nagahara, S.M. Lindsay, Electron transport properties of a carotene molecule in a metal-(single molecule)-metal junction, *J. Phys. Chem. B* 107 (2003) 6162–6169.
- [60] G. Ungar, J. Stejny, A. Keller, I. Bidd, M.C. Whiting, The crystallization of ultralong normal paraffins - the onset of chain folding, *Science* 229 (1985) 386–389.
- [61] Color vision is stimulated in the cones of the retina by C20-polyenals (mainly 11-*cis* hydroretinal), which are generated by enzymatic (dioxygenase) cleavage of C40:11-carotenoids. If the enzyme cannot cleave long carotenoids into retinals, common vision would be impeded. If, however, the enzyme evolves in the presence of long carotenoids and the disconnecting properties of dioxygenase to C20-polyenals are maintained for carotenoids > C40:11, habitual color view is not expected to alter in a world of long carotenoids and $\lambda_{\infty} \approx \lambda_{\infty}$ will be recognized as indicated in Fig. 8. Zeaxanthin and lutein accumulate in the cones of the macula. This yellow spot in the eye may become blue with long polyenes possibly changing acuity perception.