Structure and Conformation of Photosynthetic Pigments and Related Compounds
3. Crystal Structure of β-Carotene*

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The crystal structure of the title compound ($C_{40}H_{56}$, $M_w = 536.8$) has been redetermined by X-ray diffraction methods in order to achieve a structure at higher resolution suitable for theoretical calculations. The crystal system is monoclinic, $P2_1/n$, $a = 7.656(2)$, $b = 9.445(5)$, $c = 23.536(15)$ Å, $\beta = 93.41(2)°$, $V = 1698.8(15)$ Å^3, $Z = 2$, $D = 1.050$ mg/m^3, 130 K. $R = 0.071$, $R_w = 0.076$.

Introduction

Carotenoids are widely distributed and function in several roles in the photosynthetic complex [1]. They serve as accessory pigments by absorbing light and transfer the excitation energy to other pigments, they protect the photosynthetic organism from photodynamic damage by singlet oxygen, have a structural role in assembling the photosystems [2] and might be involved in the electron transfer reactions [3].

After initial work by Mackinney [4] and Taylor [5] the crystal structure of β-carotene, the most widely distributed carotenoid in photosynthesis, was determined first by Sterling in 1964 [6], the publication being of considerable importance for the understanding of this type of compounds. With the recent interest in the function of carotenoids in electron transfer [3, 7] and their role in triplet-triplet energy transfer, high precision structures suitable for theoretical calculations of electron transfer and optical properties are needed. The original structure by Sterling [6], while being of special importance for the advancement of carotenoid research, is not suited for this purpose, as estimated standard deviations in the bond lengths were in the range of 0.03–0.04 Å, larger than 2° in the bond angles and refinement converged at an R-value of 19%. We have therefore redetermined this structure at low temperature.

Experimental

Dark-red parallelpipeds of β-carotene were prepared by slow diffusion of a concentrated solution in methylene chloride into petrol ether (40–60 °C fraction). A number of different samples were tested for their crystal quality. Although numerous crystallization attempts were performed, only very small red plates were obtained, neither of those diffracting above $2\theta = 52°$, thus limiting the resolution obtainable in the subsequent refinement steps. A single crystal (0.45 × 0.41 × 0.12 mm, $D_x = 1.050$ mg/m^3) was mounted on a Siemens $P2_1$ automatic diffractometer with a graphite monochromator and equipped with a locally modified Syntex LT-I device. MoK_α radiation ($\lambda = 0.71069$ Å) was used. Cell parameters were determined from 20 reflections in the range $2\theta = 20–25°$. The axis setting of space group $P2_1/n$ was chosen for refinement. $a = 7.656(2)$ Å, $b = 9.445(5)$ Å, $c = 23.536(15)$ Å, $\beta = 93.41(2)°$, $Z = 2$. F(000) = 592, $\mu = 0.054$ mm^{-1}. The intensities were measured in the range $2\theta = 0–52°$ at 130 K using a ω-scan technique; index ranges $-9 \leq h \leq 9$, $0 \leq k \leq 12$, $0 \leq l \leq 30$. The data collection was performed using a constant scan speed of 14.65°/min in ω and a scan range of 1.10°. Two standard reflections were measured every 198 reflections and showed no significant variation of intensity during the data collection. Of the 3956 collected reflections 3848 were independent and out of these, 1671 were considered as observed with $I > 2.50\,\sigma(I)$. The intensities were corrected for Lorenz and polarization effects. An absorption correction was applied using the Program XABS [9], extinction was disregarded.

The structure was solved with direct methods using the SHELXTL PLUS program system version 5 [10]. The refinement was carried out by full-matrix least-squares on F using the same program system. The function minimized was $\Sigma w(F_o - F_c)^2$. The H-atoms were located in subsequent difference maps and refined with a riding model (C–H distance 0.96 Å, $U_{iso} = 0.04$). Calculations were

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carried out on a Vaxstation 3200. The atom form factors were taken from the International Tables for X-Ray Crystallography [11]. The final cycle of refinement on |F| included 203 variable parameters and converged with $R = 0.071$, $wR = 0.076$ and $S = 1.80$. All non-hydrogen atoms were refined anisotropically. The weighting scheme used was $w^{-1} = \sigma^2(F) + 0.0003\,F^2$. Largest Δ/σ 0.002, largest difference peak 0.25 eÅ^{-3}, largest difference hole −0.25 eÅ^{-3}. The atomic coordinates and equivalent isotropic temperatures factors of the non-hydrogen atoms with their estimated standard deviations are listed in Table I*.

Results and Discussion

Fig. 1 gives a view of the molecular structure. Interatomic distances and bond angles are summarized in Table II. The overall structure, *i.e.* the *s-cis* orientation of the β-ionone ring about the C(6)−C(7) bond was found to be in agreement with the structure described by Sterling [6]. More pronounced differences were found in the β-ionone ring itself. The present structure showed a disordering of the C(2) and C(3) atoms over two positions with 0.52:0.48 relative probability for C(2) and 0.51:0.49 for C(3), determined by free refined split positions. The refinement resulted in estimated standard deviations for the bond lengths of 0.005−0.007 Å (0.009−0.013 Å for the disordered region) and in the bond angles of 0.3 to 0.5°, compared to 0.03−0.04Å and >2° in the publication of Sterling [6]. The disordering of the β-ionone ring might be one of the reasons for the high *R*-value reported by Sterling [6]. The isotropic temperature factors given for C(2) and C(3) in his paper are nearly two times as high as those of the other atoms. A comparison of the bond lengths in both structures showed larger differences in some cases. *E.g.* C(13)−C(14) 1.444(5) Å (this work) compared to 1.54(3) Å [6] or C(1)−C(1 B) 1.528(6) Å *versus* 1.65(3) Å, C(4)−C(5) 1.523(5) Å *versus* 1.62(3) Å. The higher resolved structure of β-carotene should allow a more detailed investigation of the optical and physical properties of these molecules. Studies of electron distribution and the calculation of optical spectra are currently in progress. Data with higher precision are also needed for the refinement of caroteno-proteins, which are of special importance in revealing the role of caro-

Table I. Atomic coordinates [× 10^4] and equivalent isotropic displacement coefficients [Å^2 × 10^3] for β-carotene.

	x	y	z	U_{eq}*
C(1)	0.6780(5)	1.6676(3)	0.1829(1)	41(2)
C(1 A)	0.8336(6)	1.5940(6)	0.1577(3)	83(3)
C(1 B)	0.6207(7)	1.7875(5)	0.1423(2)	68(2)
C(2)	0.7023(14)	1.7576(7)	0.2368(2)	39(3)
C(2′)	0.7723(10)	1.6959(12)	0.2408(2)	41(4)
C(3)	0.7014(7)	1.6701(9)	0.2913(3)	44(3)
C(3′)	0.6345(12)	1.7411(7)	0.2815(5)	36(4)
C(4)	0.5135(5)	1.6164(5)	0.2920(2)	44(2)
C(5)	0.4444(5)	1.5473(4)	0.2367(1)	35(1)
C(5 A)	0.2823(5)	1.4609(5)	0.2438(2)	48(2)
C(6)	0.5275(5)	1.5626(4)	0.1880(1)	33(1)
C(7)	0.4767(5)	1.4837(3)	0.1369(2)	33(1)
C(8)	0.4332(5)	1.3450(3)	0.1336(2)	33(1)
C(9)	0.3920(5)	1.2635(3)	0.0826(1)	32(1)
C(10)	0.4114(6)	1.3322(4)	0.0259(2)	38(2)
C(11)	0.3388(5)	1.1277(3)	0.0875(2)	32(1)
C(12)	0.2864(5)	1.0317(3)	0.0420(2)	33(1)
C(13)	0.2226(5)	0.9007(3)	0.0512(2)	34(1)
C(14)	0.1572(5)	0.8024(3)	0.0080(1)	33(1)
C(15)	0.1578(5)	0.8456(4)	−0.0533(2)	39(1)
C(16)	0.0975(5)	0.6752(3)	0.0248(2)	37(2)
C(17)	0.0255(5)	0.5624(4)	−0.0105(2)	38(2)

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

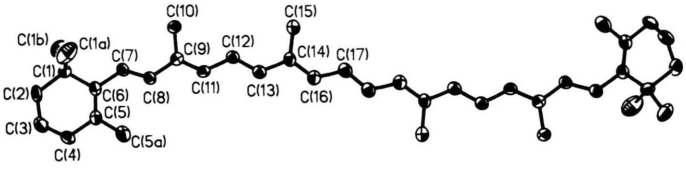

Fig. 1. A perspective view of the molecule with atom labelling. The ellipsoids show 50% of the electron probability. Hydrogen atoms have been omitted for clarity.

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* Details of the crystal structure determination can be obtained on request from the Fachinformationszentrum Energie, Physik, Mathematik GmbH, D-W-7514 Eggenstein-Leopoldshafen, by quoting the deposit number CSD-561421, the authors and the journal citation.

Table II. Bond lengths [Å] and bond angles [°] in β-carotene.

C(1)−C(1 A)	1.529(6)	C(1)−C(1 B)	1.528(6)
C(1)−C(2)	1.529(6)	C(1)−C(2′)	1.528(7)
C(1)−C(6)	1.531(5)	C(2)−C(3)	1.526(9)
C(2)−C(3′)	1.210(13)	C(2′)−C(3′)	1.527(13)
C(3)−C(4)	1.526(7)	C(3′)−C(4)	1.528(9)
C(4)−C(5)	1.523(5)	C(5)−C(5 A)	1.502(6)
C(5)−C(6)	1.351(5)	C(6)−C(7)	1.449(5)
C(7)−C(8)	1.352(5)	C(8)−C(9)	1.445(5)
C(9)−C(10)	1.500(5)	C(9)−C(11)	1.352(5)
C(11)−C(12)	1.442(5)	C(12)−C(13)	1.352(5)
C(13)−C(14)	1.444(5)	C(14)−C(15)	1.500(5)
C(14)−C(16)	1.353(5)	C(16)−C(17)	1.441(5)
C(17)−C(17 A)	1.346(8)		
C(1 A)−C(1)−C(1 B)	107.2(4)	C(1 A)−C(1)−C(2)	121.0(5)
C(1 B)−C(1)−C(2)	97.0(4)	C(1 A)−C(1)−C(2′)	95.0(4)
C(1 B)−C(1)−C(2′)	122.0(5)	C(1 A)−C(1)−C(6)	110.1(3)
C(1 B)−C(1)−C(6)	109.9(3)	C(2)−C(1)−C(6)	110.5(4)
C(2′)−C(1)−C(6)	111.1(4)	C(1)−C(2)−C(3)	112.9(5)
C(1)−C(2)−C(3′)	127.7(7)	C(1)−C(2′)−C(3)	123.8(7)
C(1)−C(2′)−C(3′)	107.5(6)	C(2)−C(3)−C(4)	104.0(5)
C(2′)−C(3)−C(4)	119.8(6)	C(2)−C(3′)−C(4)	122.4(8)
C(2′)−C(3′)−C(4)	109.6(6)	C(3)−C(4)−C(5)	114.4(4)
C(3′)−C(4)−C(5)	112.0(5)	C(4)−C(5)−C(5 A)	112.7(3)
C(4)−C(5)−C(6)	121.5(3)	C(5 A)−C(5)−C(6)	125.9(3)
C(1)−C(6)−C(5)	122.1(3)	C(1)−C(6)−C(7)	115.7(3)
C(5)−C(6)−C(7)	122.2(3)	C(6)−C(7)−C(8)	126.7(3)
C(7)−C(8)−C(9)	127.2(3)	C(8)−C(9)−C(10)	118.7(3)
C(8)−C(9)−C(11)	119.1(3)	C(10)−C(9)−C(11)	122.2(3)
C(9)−C(11)−C(12)	127.3(3)	C(11)−C(12)−C(13)	123.0(3)
C(12)−C(13)−C(14)	126.1(4)	C(13)−C(14)−C(15)	118.8(3)
C(13)−C(14)−C(16)	117.7(4)	C(15)−C(14)−C(16)	122.9(3)
C(14)−C(16)−C(17)	127.7(4)	C(16)−C(17)−C(17 A)	123.0(5)

tenoids in photosynthesis more clearly. Only detailed studies of the chromophore-protein interactions in pigment-protein complexes can answer the fundamental questions concerning exciton transfer and photoprotection in light-harvesting systems.

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[1] D. Siefermann-Harms, Biochim. Biophys. Acta **811,** 325 (1985).
[2] K. Humbeck, S. Römer, and H. Senger, Planta **108,** 242 (1989).
[3] P. Mathis and C. C. Schenck, in: Carotenoid Chemistry & Biochemistry (G. Brittin and T. W. Goodwin, eds.), pp. 339−351, Pergamon Press, Oxford 1982.
[4] G. Mackinney, J. Am. Chem. Soc. **56,** 488 (1934).
[5] W. H. Taylor, Z. Kristallogr. **96,** 150 (1937).
[6] C. Sterling, Acta Cryst. **17,** 1224 (1964).
[7] R. B. Veltky, FEBS Lett. **126,** 272 (1981).
[8] C. Kramer and P. Mathis, Biochim. Biophys. Acta **593,** 319 (1981).
[9] H. Hope and B. Moezzi, Program XABS, University of California, Davis. The program obtains an absorption tensor from $F_o - F_c$ differences, B. Moezzi, Ph.D. thesis, 1987.
[10] G. M. Sheldrick, SHELXTLPLUS, program for crystal structure solution, Universität Göttingen, Germany (1989).
[11] D. T. Cromer and J. T. Waber, International Tables for X-Ray Crystallography, **Vol. IV,** Birmingham Kynoch Press (present distributor Kluwer Academic Publ., Dordrecht) 1974.