Pergamon

Tetrahedron Letters, Vol. 38, No. 1, pp. 19-20, 1997
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0040-4039/97 $17.00 + 0.00

PII: S0040-4039(96)02244-7

X-Ray Crystal Structure of cis-Mini-3 (A Spiralene[3])

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Abstract. The X-ray crystal structure of the highly crowded cis isomer of the lowest member of the homologs of β-carotene has been determined at 120K. The triene chromophore exists in the postulated bis-S-cis conformation, assuming the novel spiral shape suitable for secondary 1,6-orbital interaction.

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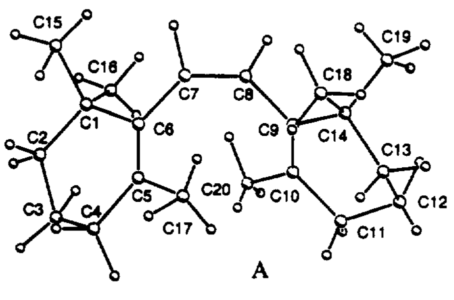
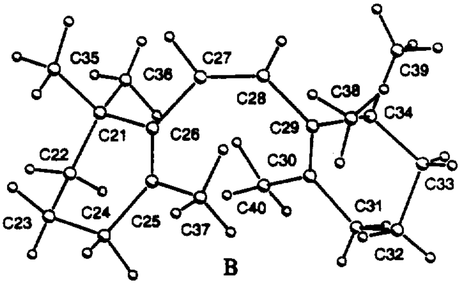
Retinoids[1] and carotenoids[2] are known to adopt the twisted S-cis ring chain conformations.[3] Thus in our study of the UV-Vis absorption properties of the Mini-3, the lowest member of double bond truncated homologs of β-carotene and related compounds,[4] we postulated that the bis-S-cis conformation is retained even in the highly crowded cis isomer. The resultant spiral conformation of the triene chromophore could account for the unusual red-shift effect of the cis isomer (λ_{max} = 254 nm in ethanol, compared to 247 nm for the trans).

We have since recrystallized the cis isomer from methanol in the form of a low melting (29-30°C) white solid. Its crystal structure determined at 120K and reported herein, substantiates the postulated spiral shape of the crowded triene. The compound crystallizes in the monoclinic space group $P2_1/c$.[5] Selected bond lengths and angles are included below.[6] The asymmetric unit of the crystal comprises two molecules with its helical triene chromophore twisted in a same sense (see below). One molecule (A) has a greater degree of disorder in the conformation of one of its rings, as indicated by the shortened C2-C3 bond length of 1.43 (3) Å. This type of disorder has been noted before for the related molecules cantaxanthin[7] and all-trans-retinal.[8] The disorder is present in only one of the two rings of A; in the other ring the C12-C13 bond length is 1.50 (2) Å. The second



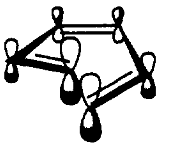
A



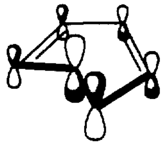
B

molecule, B, exhibits a lesser degree of disorder (C22-C23 = 1.51 (2) Å; C32-C33 = 1.51 (2) Å) and has approximate C_2 symmetry which is destroyed by the pucker of one ring: C23 puckers away from the center of the molecule while C32 puckers toward it. This disorder is even greater at 298K; both A and B have disorder in one of their rings (C2-C3 = 1.1(1) Å, C12-C13 = 1.46(4) Å, C22-C23 = 1.44(4) Å, C32-C33 = 1.27(5) Å).

The most notable feature of the triene from its crystal structure is the existence of the spiral geometry (thus, the name spiralene[3]^4). The dihedral angles of the sp^2-sp^2 single bonds fall between 40-50°, giving the chromophore a helical structure, which orientes the p-lobes of the terminal carbons in a direction for interaction between the top lobe of one and the bottom lobe of the other. In the HOMO (π_3), the interaction is antibonding that would destabilize the ground state (Figure, right) while in the LUMO (π^*_4) it is bonding that would stabilize the first excited (S_1) state. The net decrease in the energy gap between the ground and excited states produces the observed red shift.



HOMO



LUMO

This red-shifted absorption is anomalous for a cis compound which is usually blue-shifted from the trans.[9] This type of red shift has been noted previously,[10] but to our knowledge no other system has been devised in which the spiral conjugation has been sterically locked into place. The helical triene backbone in the crystal structure suggests that this is also the conformer of lowest energy. This conclusion is consistent with MMP2 (PC-Model, Sun Sparc Station) calculations which show that both the bis-s-trans and the s-cis,s-trans conformers are higher in energy (2.0 and 1.8 kcal/mole, respectively, over the bis-s-cis).[11]

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5. Cell dimensions: a = 7.541(1), b = 20.961(3), c = 21.595(7) Å, β = 96.07(3), V = 3394(1) Å^3, Z = 8, d_{calc} = 1.07 g cm^{-3}, μ = 0.6 cm^{-1}, F = 1216. X-ray diffraction data were collected at 120K, using an Enraf-Nonius CAD MACH diffractometer, MoKα radiation (0.71073 Å), θ-2θ scan mole to 2θ max = 45°. Crystal size = sphere, r = 0.50 mm. Of 4566 unique reflections collected, 1416 had $I > 2\sigma(I)$. The structure was solved using the direct methods programs in Texasan and refined by full-matrix least-squares procedure. Final values of the observed data are R = 0.080 and R_w = 0.081; S= 1.21.
6. Selected bond lengths: Molecule A: 4,5 = 1.52(2), 5,6 = 1.33(2), 5,17 = 1.52(2), 6,7 = 1.48(2), 7,8 = 1.34(2), 8,9 = 1.48(2), 9,10 = 1.31(2), 9,14 = 1.53(2), 10,11 = 1.51(2), 10,20 = 1.53(2). Molecule B: 24,25 = 1.55(2), 25,26 = 1.33(2), 25,37 = 1.52(2), 26,27 = 1.49(2), 27,28 = 1.34(2), 28,29 = 1.48(2), 29,30 = 1.33(2), 29,34 = 1.52(2). Selected torsion angles: Molecule A: 17,5,6,7 = 5(2),5,6,7,8 = 45(2), 6,7,8,9 = -6(3), 7,8,9,10 = 48(3), 8,9,10,20 = 2(2). Molecule B: 37,25,26,27 = 0(2), 25,26,27,28 = 46(2), 26,27,28,29 = 2(3), 27,28,29,30 = 40(3), 28,29,30,40 = 8(2).
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11. This project was partially supported by grants from U. S. Public Health Services (DK17806) and Army Research Office (DAAH04-96-1-0031). CJS acknowledges a grant from the Island Foundation (Polynesian Cultural Center) for the purchase of the Enraf-Nonius diffractometer.

(*Received in USA* 24 *October* 1996; *revised* 5 *November* 1996; *accepted* 8 *November* 1996)