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X-RAY CRYSTAL STRUCTURE ANALYSES OF UNSATURATED BISSECO/BISHOMO DODECAHEDRANES

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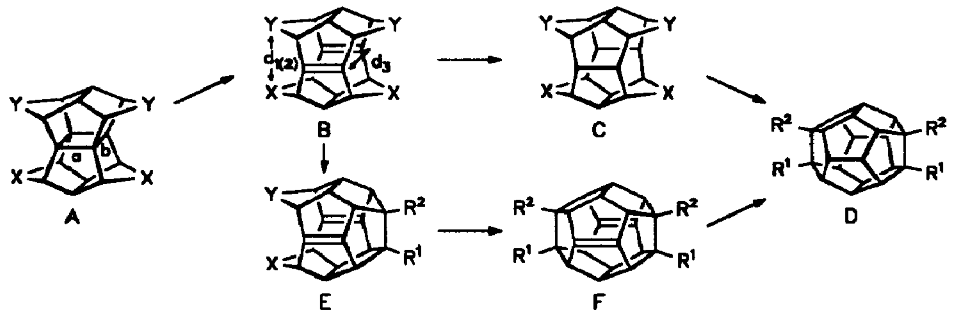
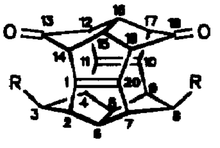
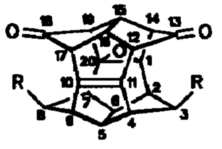
Summary. For the *syn*-periplanar C,C double bonds in the bisseco dodecahedradiene **1** and the non-pentagonal dodecahedradiene **4** unusually short π,π-distances of 2.764 and 2.81 Å, resp., are determined (olefinic pyramidalization angles Φ = 14.6-18.3°). In the epoxy (dihydro) derivatives **2** (**3**), the respective values change to 2.83 (3.07) Å (Φ = 9.6-11.0°).

The bisseco dodecahedradienes **B**, arising from the pagodane precursors **A** through scission of the lateral (b) cyclobutane bonds,[1] are instrumental intermediates on the way to dodecahedranes **D** (route B; **B** → **C** → **D**;[2] **B** → **E** → **F**→ **D**[3]). A characteristic structural feature of these caged dienes, in comparison with the (seco)dienes **E** and **F**, is the unusually proximate *syn*-periplanar positioning of the two C,C double bonds. The nature of the transannular bonding in the respective radical cations[4] and dications,[5] particularly the dependence of the σ-homoaromaticity observed for the bisseco dications B^{2+} on geometry in going to the increasingly ball-shaped dications E^{2+} and F^{2+}, are prominent subjects of experimental and theoretical studies.[6,7] In this context, precise knowledge of structural situations, particularly of transannular distances, is of utmost importance. Specifically for the bisseco dienes **B** with their strong π,π-interaction, MM2 calculations[8] - otherwise well reproducing the experimental structures of pagodanes[9], dodecahedranes[10] and secodienes[11] - had to be expected to underestimate the transannular π,π-distances (d_3).[12] X-ray structural analyses presented in this letter for bisseco 13,18-diketo-3,8-diester-diene **1**, its epoxy (**2**) and dihydro (**3**) derivatives[13] as well as for the non-pentagonal dodecahedradiene **4**[14] provide essential data,[15] even though in three cases crystal disorder had to be faced. The substitution patterns were generally established by the synthetic route.



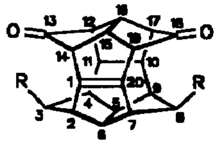


1

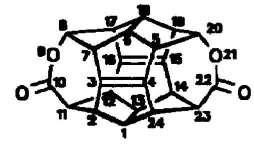


2

R = CO_2CH_3

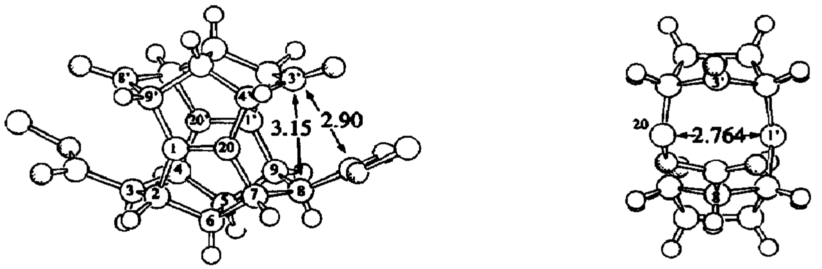


3



4

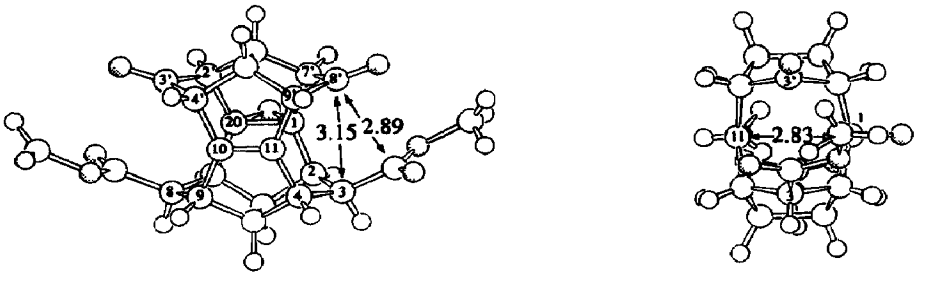
Bissecodiene **1** crystallized from CH_2Cl_2 in small prisms[16] and was found to be centrosymmetrically disordered with the 3,8-diketo-13,18-diester substitution pattern being superimposed. Hence, the C-C bond lengths and bond angles are average values, the thermal displacement parameters of the substituents are relative large. Still, the most important data, the distance (d_3) between the perfectly *syn*-periplanar π-bonds (interorbital angle 180°) and the transcaveal ($d_{1(2)}$) distances are unequivocal. The d_3 distance, with 2.764 Å one of the shortest of this type experimentally corroborated,[17] is significantly longer than calculated (MM2) for the parent hydrocarbon **B** (2.62 Å, X = Y = CH_2), but only slightly so than calculated for the 3,8-diketone **B** (2.70 Å, X = C=O, Y = CH_2). In good agreement with the calculations are also the pyramidalization angles of the olefinic carbons (13.4° for the diketone). The length of the ridge-bonds (C5-C6) and the range of bond angles around the olefinic carbon atoms are expressions of the high molecular strain.[12]



C1-C20	1.333	C2-C1-C9'/C4'-C20-C7	132.4	Φ_{C1} = 15.3
C5-C6	1.606	C2-C1-C20-C4'/C7-C20-C1-C9'	167.0	Φ_{C20} = 14.6
		(Ψ = 13.0)		

Figure 1. SCHAKAL[18] plots and selected X-ray structural data (bond lengths, through space distances (Å), bond, torsional, and pyramidalization (Ψ, Φ) angles (°)) for diene **1** (centrosymmetrical disorder).

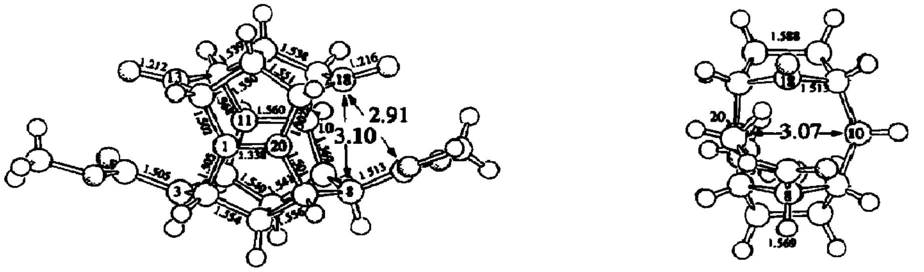
Epoxyene **2** was crystallized from CH_2Cl_2/ethyl acetate[16] and was found to be disordered about a molecular twofold axis perpendicular to the double bond C10-C11. Compared to **1**, the transannular (d_3) distance is slightly longer, the transcaveal distances ($d_{1(2)}$) are practically identical, the ridge C-C bonds (1.590 Å) again by far the longest. The pyramidalization angles at C10(11) are even (somewhat) smaller than in **1**, at C1(20) closer to those of **1** than of **3**, the epoxy side of the molecule is still rather flat.



C10-C11	1.329	C9 -C10-C4'	133.3	C9-C10-C11-C9'	171.5	Φ_{C10} = 10.6; Φ_{C11} = 9.6
C1 -C20	1.459	O21-C1 -C20	59.8	(Ψ = 8.5)		
C1 -O21	1.451	C1 -O21-C20	60.4	C2-C1-C20-C2'	156.2	Φ_{C1} = 28.9; Φ_{C20} = 27.6
		C2 -C1- C7'	133.0	(Ψ = 23.8)		

Figure 2. SCHAKAL plots and selected X-ray structural data (bond lengths, through space distances (Å), bond, torsional, and pyramidalization (Ψ, Φ) angles (°)) for epoxyene **2** (twofold disorder).

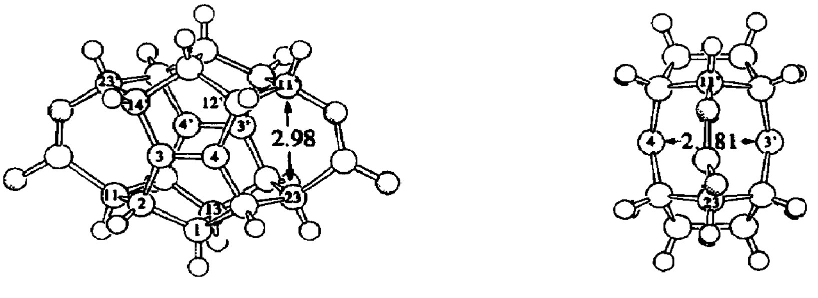
Monoene **3** crystallized from CH_2Cl_2/ethyl acetate in form of colorless prisms.[16] As a consequence of the large pyramidalization angles at C10(11) - yet still much smaller than for saturated dodecahedrane ($C_{20}H_{20}$, 57.8°) - the d_3 distance is significantly enlarged; the transcaveal distances, however, are only insignificantly changed. The increase in strain tied to the hydrogenative saturation of one of the hyperstable C,C bonds in **1** is inter alia manifested in the average length (1.567 Å) of the bonds starting out from C10(11) and the large outer valence angles at the central carbons.



C2 -C3 -C4	105.3	C2 -C1 -C20	113.2	C9-C10-C11-C12	138.5	C14-C1-C20-C7	171.4
C7 -C8 -C9	104.5	C14-C1 -C20	113.0	(Ψ = 41.5)		(Ψ = 8.6)	
C12-C13-C14	108.6	C9 -C10-C11	108.1	C17-C10-C11-C4	139.7		
C17-C18-C19	108.6	C9 -C10-C17	126.2	(Ψ = 40.3)		Φ_{C1} = 11.0; Φ_{C20} = 10.0	
C2 -C1 -C14	132.9	C11-C10-C17	107.5	C2-C1-C20-C19	170.5		
				(Ψ = 9.5)		Φ_{C10} = 47.5; Φ_{C11} = 47.7	

Figure 3. SCHAKAL plots and selected X-ray structural data (bond lengths, through space distances (Å), bond, torsional, and pyramidalization (Ψ, Φ) angles (°)) for monoene **3**.

9,21-Dioxa-10,22-diketo-diene **4** crystallized from CH_2Cl_2/ethyl acetate as colorlesss needles[16] and again turned out as centrosymmetrically disordered with the 10,22-dioxa-9,21-diketo form being superimposed. It is in line with calculations that the insertion of the two OCO-linkages into the skeletal periphery of the parent dodecahedradiene **F** ($d_{\pi,\pi}$ = 3.52 Å; Φ = 42.8°)[2,6] enforces a molecular curvature similar to that of **1**. In fact, at close correspondence with respect to bond lengths and angles, the olefinic pyramidalization is somewhat stronger, the distance between the once again perfectly *syn*-periplanar π-bonds therefore somewhat larger than in **1**.



C3 -C4	1 320	C2-C3-C14'	130.4	C2-C3-C4-C12'	163.8
C1 -C13	1.579			(Ψ = 18.2)	
				Φ_{C3} = 18.3; Φ_{C4} = 18.2	

Figure 4. SCHAKAL plots and selected X-ray structural data (bond lengths, through space distances (Å), bond, torsional, and pyramidalization (Ψ, Φ) angles (°)) for bislactodiene **4** (centrosymmetrical disorder).

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16) Crystal data for **1**: Dimethyl 13,18-dioxo-nonacyclo[12.6.0.0^{2,6}.0^{4,11}.0^{5,9}.0^{7,20}.0^{10,17}.0^{12,16}.0^{15,19}] icosa-1(20),10-diene-3,8-dicarboxylate, formula $C_{24}H_{20}O_6$; crystal size 0.50 x 0.25 x 0.50 mm; space group P1 (No. 2), Z = 1, a = 8.333(1), b = 8.850(1), c = 6.204(1) Å; $\alpha = 98.77(1)°$, $ß = 106.31(1)°$, $\gamma = 85.15(1)°$, V = 433.6(2) Å^3; $D_{calc.} = 1.55\ Mg{\cdot}m^{-3}$; Mo K_α; $\sin\theta/\lambda = 0.61$; unique reflections 2078, observed ($I \geq 2.5\ \sigma(I)$) 1734; R = 0.067, $R_w = 0.125$; parameters = 196.
Crystal data for **2**: Dimethyl 13,18-dioxo-21- oxadecacyclo[12.7.0.0^{1,20}.0^{2,6}.0^{4,11},0^{5,9}.0^{7,20}.0^{10,17}.0^{12,16}.0^{15,19}]henicosa-10-ene-3,8-dicarboxylate, formula $C_{24}H_{22}O_6$; crystal size 0.45 x 0.24 x 0.18 mm; space group P2$_1$/c (No. 14), Z = 4, a = 9.365(2), b = 11.563(1), c = 16.714(3) Å; $\beta = 95.24(1)°$, V = 1802.3(6) Å^3; $D_{calc.} = 1.490\ Mg{\cdot}m^{-3}$; Cu K_α; $\sin\theta/\lambda = 0.62$; unique reflections 3806, observed ($I \geq 2\ \sigma(I)$) 3149; R = 0.077, $R_w = 0.084$; parameters = 327.
Crystal data for **3**: Dimethyl 13,18-dioxo-nonacyclo[12.6.0.0^{2,6}.0^{4,11},0^{5,9}.0^{7,20}.0^{10,17}.0^{12,16}.0^{15,19}] icosa-1(20)ene-3,8-dicarboxylate, formula $C_{24}H_{20}O_7$; crystal size 0.4 x 0.2 x 0.1 mm; space group P2$_1$/c (No. 14), Z = 4, a = 8.791(2), b = 8.878(1), c = 23.27(3) Å; $\beta = 96.64(1)°$, V = 1804.3(1) Å^3; $D_{calc.} = 1.548\ Mg{\cdot}m^{-3}$; Cu K_α; $\sin\theta/\lambda = 0.6226$; unique reflections 3800, observed ($I \geq 2\ \sigma(I)$) 2822; R = 0.045, $R_w = 0.042$, parameters = 359.
Crystal data for **4**: 9,21-Dioxaundecacyclo[11.11.0.0^{2,11}.0^{3,7}.0^{4,24}.0^{5,20}.0^{6,18}.0^{8,17}.0^{12,16}.0^{14,23}.0^{15,19}]tetracosa-3,15-diene-10,22-dione, formula $C_{22}H_{16}O_4$; crystal size 0.35 x 0.14 x 0.60 mm; space group P2$_1$/n (No. 14), Z = 2, a = 8.629(3), b = 10.553(2), c = 8.751(2) Å; $ß = 113.44(1)°$, V = 731.1(2) Å^3; $D_{calc.} = 1.56\ Mg{\cdot}m^{-3}$; Cu K_α; $\sin\theta/\lambda = 0.65$, unique reflections 1669, observed ($I \geq 2\ \sigma(I)$) 1228; R = 0.087, $R_w = 0.065$; parameters = 147.
Further details of the X-ray structure analyses are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich technische Information mbH, D-76344 Eggenstein-Leopoldshafen, on quoting the depository numbers CSD-400513 (**1**), CSD-400494 (**2**), CSD-400493 (**3**), and CSD-400492 (**4**), the name of the authors, and the journal citation.
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