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MOLECULAR STRUCTURES OF A SECO-DODECAHEDRADIENE AND AN ISO-DODECAHEDRANE

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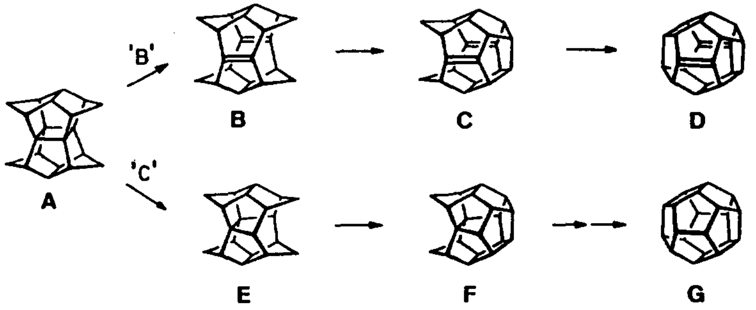
SUMMARY: The olefinic carbon atoms on the closed side of seco-dodecahedradiene **1** are strongly pyramidalized (ϕ = 35.3°). The transanular C1-C2 bond of non-pentagonal isododecahedrane **2** is one of the longest C-C bonds (1.691Å) ever measured in cage structures.

The seco-dodecahedradiene **C** and the iso-dodecahedrane **F** are intermediates on the "B" and "C"-routes from pagodanes (**A**) to dodecahedradienes (**D**)[1,2] and to dodecahedranes (**G**)[1,3], respectively. X-ray structural data for such **C**- and **F**-skeletons are of importance *inter alia* for the evaluation of theoretical concepts widely applied in the context of transanular reactivity phenomena in dienes of type **B**-**D** (bent of the C=C double bonds, "orbital steering"[4], σ-homoaromaticity[5], π-electron density distribution[6]) and of energetic consequences arising from structural modifications in **F**-polycycles (C10-C19 bridging, C1-C2 hydrogenolysis).



1 and **2**, interconvertible by addition/elimination of bromine[2], are well crystallizing, and in the case of **1** somewhat stabilized, representatives of parent structures **C** and **F**. Their structures could now be solved by direct methods[7] - what complements the picture in

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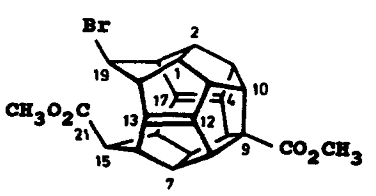
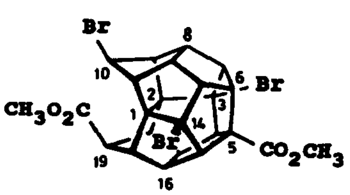
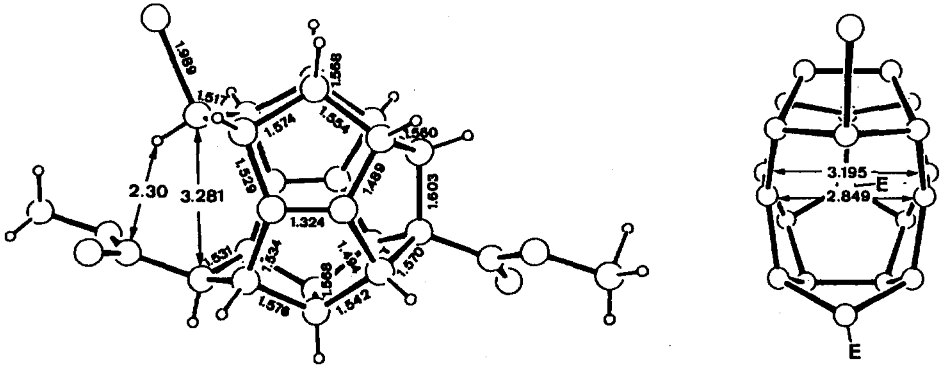




2

the saturated series **A**[3,5,8]-**G**[9,10]. Lack of suitable crystals and high oxygen sensitivity have so far prevented X-ray analyses of **B**- and **D**-structures (diepoxy derivatives have recently been analyzed[9]; data for tetrahydro-**C** compounds are available from the Paquette group[10]).

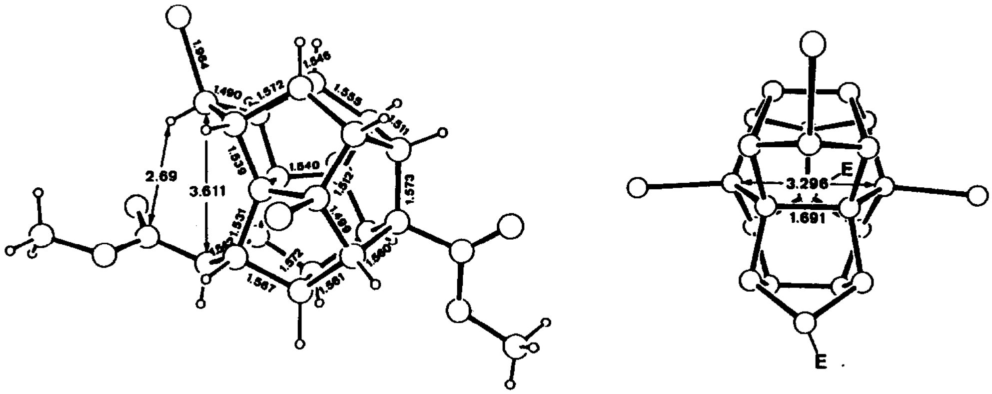
Seco-diene **c** is structurally a "Zwitter" of the nearly flat bisseco **b**- and the ballshaped **d**-skeletons, as expressed by the degree of pyramidalization at the olefinic carbons (ϕ)[2] and the transcaveal π/π distances. For **1**, the ϕ-angle at C-13(17) of 15.5° is only slightly larger than that calculated for parent diene **b** (11.7°), but approaches at C-4(12) with 35.3° that of **d** (42.9°) - what constitutes the so far largest crystallographically determined pyramidalization of olefinic carbon[6,11,12]. Consequently, the (inner-outer) bond angles at C-13(17) (110.2-137.7°) deviate much more from standard values than that at C-4(12) (114.7-117.4°). The bond length of the C=C double bonds (1.329; 1.319 Å) are practically equal to that in a highly "pyramidalized" bisspiro *syn*-sesquinorbornatriene (1.325 Å, ϕ = 32.4°)[12], being somewhat shorter than that in parent bicyclo[3.3.0]oct-1(5)-ene (1.345 Å) and other bridged derivatives thereof (1.340 Å)[13]. The transcaveal π/π distance C13···C17 of 2.849 Å on the open vs. C4···C12 of 3.195 Å on the closed side (calculated 2.9 and 3.1 Å for parent **c**[2]) have to be compared with the 2.7 (3.5) Å calculated for **b**(**d**)-derivatives[3]. The intramolecular distances H19···C21 = 2.30 Å and C15···C19 = 3.281 Å are less than the respective *van der Waals* contacts - with concomitant slight pyramidalization at C21. A good part of strain appears in the opposite C9-C10 bond, which is remarkably streched to 1.603 Å. A favorable alignment of the C19-Br bond for the transanular S_N2-substitution[2] to give the corresponding dodecahedradiene (**d**)-diester is clearly demonstrated. Typical differences for the seco and the closed side of **c** show up in the C(sp^2)-C(sp^3) bond lenghts (1.491 Å (av.) vs. 1.531 Å (av.)), in the folding of the cyclopentane units (torsional angles varying from -44.2(2)° for C7-C14-C15-C16 to -7.2(2)° for C6-C5-C9-C8) and in the H-C-C-H torsion angles around the periphery (cf. $J_{3,10}$ = 9.5, $J_{14,15}$ = 5, $J_{18,19}$ < 0.5 Hz).



C12 - C13 - C14	110.8(2)	C8 - C12 - C11	117.4(2)	H1 -C1 -C11-H11	:	11.4(3)
C12 - C13 - C20	110.2(2)	C8 - C12 - C13	114.7(2)	H7 -C7 -C8 -H8	:	-9.4(3)
C14 - C13 - C20	137.3(2)	C11 - C12 - C13	115.9(2)	H3 -C3 -C10-H10	:	9.9(3)
C4 - C17 - C16	110.4(2)	C3 - C4 - C5	117.2(2)	H10-C10-C11-H11	:	-8.9(3)
C4 - C17 - C18	110.3(2)	C3 - C4 - C17	114.9(2)	H14-C14-C15-H15	:	-50.7(2)
C16 - C17 - C18	137.7(2)	C5 - C4 - C17	115.1(2)	H15-C15-C16-H16	:	48.2(2)
				H18-C18-C19-H19	:	69.8(3)
				H19-C19-C20-H20	:	-65.4(3)

Fig.1 Selected bond lengths (averaged, ORTEP plot), transanular distances (Å), bond and torsional angles (°) of **1**. Standard deviations of the bond lengths are 0.002-0.003 Å. E = CO_2CH_3

For non-pentagonal iso-dodecahedrane **2**[7], the X-ray analysis proves the correctness of the structure based so far on spectral data. As for **1**, the salient structural feature again consists in its being a "Zwitter", here of (seco)pagodane **A**(**B**) and dodecahedrane **G** "halfes". On the **A**-side of **2**, the chemically interesting C10···C19 intramolecular distance (3.611 Å) is exactly as large as that in the 4*syn*,9*syn*-dimethyl dicarboxylate of **A** (3.611 Å[3]; 3.530 Å in parent **A**; 3.421 Å in 2,12 dimethoxy-**B**[5]) - and significantly longer than C15···C19 in **1** (3.281 Å), in line with the futility in bringing about the highly endothermic intramolecular C-C bond formation by S_N2-substitution (bisdehydrododecahedrane). Compared with the lateral cyclobutane bonds in the above **A**-derivatives (1.589 Å[3], 1.614 Å in **A**, 1.598 Å in 2,12-dimethoxy-**B**)[5] the C1-C2 bond in **2**, to be cleaved on the way to **G**, is enormously elongated (1.691 Å), representing in fact one of the longest C-C bonds found in cage structures[14]. Concentration of strain in this part of the molecule is additionally manifested by the unusual bond angles around C-1(2) ranging from 99.9 to 135.7° (100.2 to 135.2°). On the **G**-side, the transanular distance C3···C14 (3.296(8) Å) differs not much from that of C4...C12 on the **D**-side in **1** (3.195 Å). Typical discrepancies exist again between the **A**/**G**-sides with respect to the shape of the cyclopentane units (torsion angles of -5.2(6)° for C15-C5-C4-C17 and of 54.5 (5)° for C16-C20-C19-C18) and the peripheral H-C-C-H torsion angles (cf. $J_{6,7}$ = 10.5, $J_{9,10}$ = 1.5, $J_{18,19} \simeq$ 2 Hz).



C2 - C1 - C11	100.5(4)	Br2 - C14 - C1	110.3(4)	H6 -C6 -C7 -H7	: 12.8(7)
C2 - C1 - C14	121.3(5)	Br2 - C14 - C13	112.0(4)	H6 -C6 -C13-H13	: -11.4(6)
C2 - C1 - C20	101.0(4)	Br2 - C14 - C15	110.4(4)	H9 -C9 -C10-H10	: 57.3(7)
C11 - C1 - C14	101.2(4)	C1 - C14 - C13	103.7(4)	H10-C10-C11-H11	: -60.2(6)
C11 - C1 - C20	135.7(5)	C1 - C14 - C15	104.6(5)	H18-C18-C19-H19	: 57.4(7)
C14 - C1 - C20	99.9(4)	C13 - C14 - C15	115.3(5)	H19-C19-C20-H20	: -62.3(6)
C1 - C2 - C3	121.5(4)	Br3 - C3 - C2	110.3(3)	H12-C12-C13-H13	: 14.0(6)
C1 - C2 - C9	100.5(4)	Br3 - C3 - C4	110.0(4)	H15-C15-C16-H16	: -10.0(7)
C1 - C2 - C18	100.2(4)	Br3 - C3 - C7	111.8(4)		
C3 - C2 - C9	100.2(4)	C2 - C3 - C4	104.3(5)		
C3 - C2 - C18	102.0(5)	C2 - C3 - C7	105.0(5)		
C9 - C2 - C18	135.2(5)	C4 - C3 - C7	115.0(5)		

Fig.2 Selected bond lengths (averaged, ORTEP plot), transanular distances (Å), bond and torsional angles (°) of **2**. Standard deviations of the bond lengths are 0.005-0.011 Å. E = CO_2CH_3

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7) 19*anti*-Bromo-decacyclo[$9.9.0.0^{2,18}.0^{3,10}.0^{4,17}.0^{5,9}.0^{6,16}.0^{7,14}.0^{8,12}.0^{13,20}$]icosa-4(17),12-diene-9,15*syn*-dimethyl dicarboxylate (**1**), $C_{24}H_{21}BrO_4$; space group $P\bar{1}$; $Z = 2$; $a = 7.544(2)$, $b = 11.107(4)$, $c = 11.534(2)$ Å; $\alpha = 81.14(2)°$, $\beta = 77.44(2)°$, $\gamma = 84.29(3)°$, $D_{calc} = 1.62$[Mg m^{-3}]. CAD4 diffractometer (Enraf-Nonius), Mo-K_α radiation, $(\sin\theta/\lambda)_{max} = 0.66$ $Å^{-1}$, unique reflections 4440, observed ($I > 2.5\sigma$ (I) 3180; $R = 0.03$. 3,10*anti*,14-Tribromo-undecacyclo[$9.9.0.0^{1,14}.0^{2,9}.0^{2,18}.0^{3,7}.0^{4,17}.0^{5,15}.0^{6,13}.0^{8,12}.0^{16,20}$]icosane-5,19*syn*-dimethyl dicarboxylate (**2**), $C_{24}H_{21}Br_3O_4$ (**2**) crystallizes with 0.3 CH_2Cl_2; space group $P2_1/n$; $Z = 4$; $a = 8.607(2)$, $b = 9.576(2)$, $c = 26.831(10)$; $\beta = 91.62(2)°$, $D_{calc} = 2.11$[Mg m^{-3}], unique reflections 4440, observed 2986; $R = 0.04$. Further details of the X-ray structure analyses are available on request from the Director of the Cambridge Crystallographic Data Center, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, U.K. Any request should be accompanied by the full literature citation for this communication.

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