129. The Non-planarity of the Bicyclo[2.2.1]hept-2-ene Double Bond. Crystal Structures of Bicyclo[2.2.2]oct-2-ene, Bicyclo[2.2.1]hept-2-ene, and Bicyclo[2.1.1]hex-2-ene Systems[1])

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Summary

The crystal structures of (1*R*,4*R*,5*S*,8*S*)-9,10-dimethylidenetricyclo[6.2.1.$0^{2,7}$]undec-2(7)-ene-4,5-dicarboxylic anhydride (**3**), (1*R*,4*R*,5*S*,8*S*)-11-isopropylidene-9,10-dimethylidenetricyclo[6.2.1.$0^{2,7}$]undec-2(7)-ene-4,5-dicarboxylic anhydride (**6**), (1*R*,4*R*,5*S*,8*S*)-9,10-dimethylidenetricyclo[6.2.2.$0^{2,7}$]dodec-2(7)-ene-4,5-dicarboxylic anhydride (**9**), (1*R*,4*R*,5*S*,8*S*)-tricyclo[6.2.2.$0^{2,7}$]dodeca-2(7), 9-diene-4,5-dicarboxylic anhydride (**12**) and (4*R*,5*S*)-tricyclo[6.1.1.$0^{2,7}$]dec-2(7)-ene-4,5-dicarboxylic acid (**16**) were established by X-ray diffraction. The alkyl substituents onto the endocyclic bicyclo[2.2.1]hept-2-ene double bond deviate from the C(1), C(2), C(3), C(4) plane by 13.5° in **3** and by 13.9° in **6**, leaning toward the *endo*-face. No such out-of-plane deformations were observed with the bicyclo[2.2.2]oct-2-ene derivatives **9** and **12**. The exocyclic *s-cis*-butadiene moieties in **3**, **6** and **9** do not deviate significantly from planarity. The deviation from planarity of the double bond in bicyclo[2.2.1]hept-2-ene derivatives and planarity in bicyclo[2.2.2]oct-2-ene analogues is shown to be general by analysis of all known structures in the *Cambridge Crystallographic Data File*. The non-planarity of the bicyclo[2.2.1]hept-2-ene double bond cannot be attributed only to bond-angle deformations which would favour rehybridization of the olefinic C-atoms since the double bond in the more strained bicyclo[2.1.1]hex-2-ene derivative **16** deviates from planarity by less than 4°.

Introduction. – The exceptional reactivity [1] and *exo*-stereoselectivity of the bicyclo[2.2.1]hept-2-ene double bond [2–4] have been attributed to torsional effects [5], to secondary interactions between the reactants [6], to rehybridization of the C-atoms [7] [8], to an antiperiplanar effect involving the σ(C(1),C(6)) and σ(C(4),C(5)) bonds [9] and to repulsive hyperconjugative effects between the π-electrons and the CH_2(7) methylene bridge [3a] [10]. Calculations revealed the non-planarity of the π-system [9] [11] in

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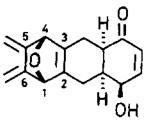
[1]) Part of this work has been presented at the meeting of the 'Société Suisse de chimie', in Bern, Oct. 15, 1982.

[2]) Parts of Ph. D. dissertations of *J.-L. Birbaum* (EPFL, 1984) and *L. Schwager* (University of Lausanne, Nov. 14, 1983).

agreement with qualitative predictions [7] [8] and X-ray data (see *e.g.*: crystallographic data on bicyclo[2.2.1]hept-2-ene [12] and sesquinorbornene (= tetracyclo-[6.2.1.1^{3,6}.0^{2,7}]dodec-2(7)-ene) derivatives [13–15]).

Recently, we have reported the X-ray structure of the 5,6-dimethylidene-7-oxabicyclo[2.2.1]hept-2-ene derivative **1** which showed (1) a deviation towards the *endo*-face of 10° for the alkyl substituents on the C(2),C(3) endocyclic double bond, whereas (2) an insignificant deviation of 2.6° was measured for the exocyclic *s-cis*-butadiene moiety at C(5),C(6). Furthermore, (3) the O-bridge of **1** tilts away from the endocyclic double bond, suggesting a larger O(7)↔π(2,3) than O(7)↔π(5,6) electron repulsion [16].



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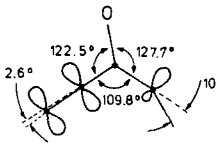
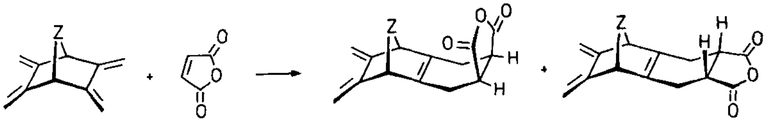


We wish to report X-ray diffraction data that demonstrate that the structural features (1)-(3) described for **1** are also present in 5,6-dimethylidenebicyclo[2.2.1]hept-2-ene and 7-isopropylidene-5,6-dimethylidenebicyclo[2.2.1]hept-2-ene systems. They are specific to the bicyclo[2.2.1]hept-2-ene skeleton since related bicyclo[2.2.2]oct-2-ene and bicyclo[2.1.1]hex-2-ene derivatives do not show the same structural deformations.

Synthesis of the *Diels-Alder* adducts. – When heated (in toluene, 80°C, 5 h) with one mol-equiv. of maleic anhydride, the 2,3,5,6-tetramethylidenebicyclo[2.2.1]heptane (**2**) [17] yielded the monoadduct **3** in 96% yield. As already observed [16] with 2,3,5,6-tetramethylidene-7-oxabicyclo[2.2.1]heptane [18], the *Diels-Alder* addition of the tetraene was highly stereoselective[3]) as no trace of the isomeric adduct **4** could be detected. Moreover, less than 1% of the corresponding bis-adduct was formed under these conditions.



Z = CH_2:	**2**	**3**	**4**
$C{=}C(CH_3)_2$:	**5**	**6**	**7**
CH_2-CH_2:	**8**	**9**	**10**

The 7,7-dimethyl[2.2.1]hericene (**5**) [20] added to maleic anhydride giving the monoadduct **6** and **7** in a ratio better than 95:5. In this case again, less than 1% of the corresponding bis-adduct was formed when only one mol-equiv. of dienophile was used. The 2,3,5,6-tetramethylidenebicyclo[2.2.2]octane (**8**) added to maleic anhydride yielding a mixture of monoadducts **9** and **10** in a ratio of *ca.* 2:1. The corresponding bis-adducts were also formed competitively, confirming that, contrary to the *Diels-Alder* reactivity of the tetraene grafted onto bicyclo[2.2.1]heptane skeletons, the additions

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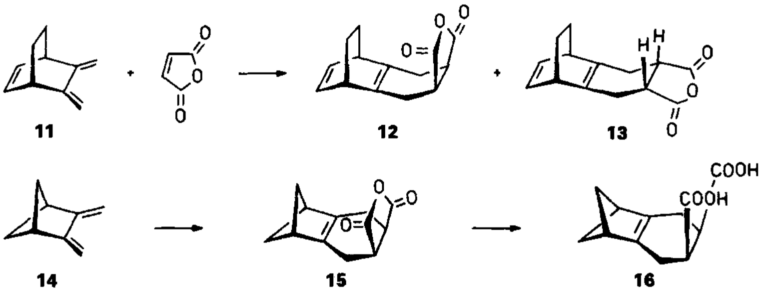
[3]) This result does not tell whether the cycloaddition was *exo*- or *endo*-face selective, see *e.g.* [19].



of the first and second equivalent of dienophile have comparable rates [21] [22]. When using an excess of tetraene **8**, the monoadduct **9** could be obtained in pure form after several recrystallizations.

The cycloaddition of triene **11** to maleic anhydride has already been discussed in detail [23]. It furnishes a 3:2 mixture of adducts **12** and **13**; **12** was obtained pure by fractional recrystallization.

Diels-Alder additions to 2,3-dimethylidenebicyclo[2.1.1]hexane (**14**) [24] serve to generate bicyclo[2.1.1]hex-2-ene systems. With maleic anhydride, the adduct **15** was formed whose crystallization failed to give suitable crystals for X-ray diffraction analysis. Hydration of **15** (acetone, H_2O, trace of acid) furnished the corresponding diacid **16** which yielded suitable crystals more easily.

X-Ray Crystal and Molecular Structures. – All crystals were grown from solution at low temperature (–20 °C). The solvents used were: AcOEt for **6**, **9**, and **12** and CH_2Cl_2/AcOEt/acetone 1:1:1 for **16**. For **3**, the initially grown crystals proved suitable for structure determination. Compound **6** crystallizes as plates, invariably twinned; a single domaine was cleaved from a larger plate. Adduct **9** crystallizes as needles, and the crystal used was cleaved from a longer needle. Adduct **12** crystallizes as thin plates, and a small crystal was cleaved from a larger plate. Compound **16** crystallizes as irregularly shaped microcrystals; the largest single crystal found was hence used for data collection.

X-ray intensity data collection was carried out at room temperature with a *Syntex P2₁* automatic diffractometer for **9** and **12**, and initially for **6**. For **3**, intensity data was obtained at room temperature with an *Enraf-Nonius-CAD-4* diffractometer. The data for **16** and a second data set for **6** were also obtained with the *CAD-4* at 120 K and 115 K, respectively. With the *Syntex* machine, niobium-filtered Mo radiation was used, and the backgrounds were obtained from analysis of the scan profile [25]. The *CAD-4* was furnished with a graphite monochromator, and the backgrounds were obtained in the usual way. The measured intensities were corrected for absorption as described previously [26].

The crystal data, intensity collection, structure solution, and refinement methods are summarized in *Table 1*. The variances of the intensities were derived from counting statistics and the fluctuations of three periodically measured check reflections.

The computer programs used for data reduction and structure solution were taken from the 'XRAY-72' program system [27]. The scattering factors for the neutral non-H-atoms were taken from *Cromer & Mann* [28] and for the H-atoms from *Stewart et al.* [29]. Starting phases were generated by the program MULTAN [30] for **6** using the room temperature data, and for **16** using only low order data ($\sin\theta/\lambda < 0.45$), the subsequent E-maps revealing all the non-H-atoms. Refinement by full matrix least squares followed by difference *Fourier* syntheses revealed all the H-atoms. In the last cycles of least squares the non-H-atoms were refined anisotropically, and the H-atoms isotropically. For **16** all H-atoms were constrained to have the same isotropic temperature factor.

Table 1. *Summary of Crystal Data, Intensity Measurements, Structure Solution, and Refinement*[a])

Compound	**3**	**6**	**6**	**9**	**12**	**16**
Temperature	300 K	300 K	115 K	300 K	300 K	120 K
Formula	$C_{15}H_{14}O_3$	$C_{18}H_{18}O_3$	$C_{18}H_{18}O_3$	$C_{16}H_{16}O_3$	$C_{14}H_{14}O_3$	$C_{12}H_{14}O_4$
Molecular weight	242.3	282.3	282.3	256.3	230.3	222.2
Crystal dimensions [mm]	0.35 × 0.24 × 0.21	0.14 × 0.16 × 0.31		0.29 × 0.24 × 0.10	0.26 × 0.28 × 0.06	0.14 × 0.12 × 0.04
Crystal system	monoclinic	orthorhombic		triclinic	monoclinic	triclinic
a [Å]	10.915(2)	6.871(1)	6.792(1)	6.552(1)	5.790(1)	6.683(2)
b [Å]	8.879(1)	13.240(2)	13.073(2)	10.525(2)	11.508(2)	7.993(3)
c [Å]	13.517(3)	32.199(5)	31.824(6)	11.042(2)	8.400(2)	10.739(6)
α [°]				115.11(1)		79.71(4)
β [°]	106.43(1)			94.98(1)	101.84(2)	75.75(4)
γ [°]				106.99(1)		76.08(3)
U [Å^3]	1228.2	2929.3	2825.6	639.6	547.8	535.3
Z	4	8	8	2	2	2
$d_{\text{calc.}}$ [g · cm^{-3}]	1.28	1.28	1.33	1.33	1.40	1.38
$d_{\text{obs.}}$ [g · cm^{-3}]					1.39	
F_{000}	512	1200	1200	272	244	216
Space group	$P2_1/a$	$Pbc2_1$	$Pbc2_1$	$P\bar{1}$	$P2_1/m$	$P\bar{1}$
μ [cm^{-1}]	0.8	0.9	0.9	1.0	1.1	1.0
$(\sin\theta/\lambda)_{\max}$	0.66	0.60	0.66	0.59	0.65	0.60
No of unique reflections	2576	2650	2819	2251	1328	1878
No of reflections $< 3\sigma$	899	1807	1035	1720	628	1025
No of observations/No of variables	11.8(10.2[b]))	6.5(4.6[b]))	6.9(6.3[b]))	9.5(7.3[b]))	12.4(9.3[b]))	9.99(7.38[b]))
Refinement method[c])	blocked matrix least squares		blocked matrix least squares		full matrix least squares	
R	0.041	0.059	0.049	0.036	0.038	0.090
R_w	0.037	0.045	0.046	0.026	0.030	0.105
Goodness of fit	1.80	1.55	2.02	1.53	1.78	1.41

[a]) Radiation: MoK_α $\lambda = 0.71069$ Å; scan method: 2θ–θ; structure solution: MULTAN [29] and *Fourier*.

[b]) Only those reflections with $I < 3\sigma$ with $|F_c| > |F_o|$ were included in the refinement.

[c]) Function minimized: $\Sigma w\,(|F_o| - |F_c|)^2$, $w = 1/\sigma^2$.

For **6**, although the room temperature data was refined to $R = 0.06$, the low number of reflections with $I > 3\sigma$ gave a large spread of values for equivalent bond lengths with poor standard deviations. Hence, the structure was rerefined with the low temperature data. In the final cycles, the non-H-atoms were refined anisotropically. The H-atoms bond to C-atoms with close to ideal geometry were constrained to be ideal (C-H = 0.97 Å). Those bound to non-ideal C-atoms C(1), C(4), C(5), and C(8) were refined without positional constraints. All H-atoms of the same type were constrained to have the same isotropic temperature factor.

The structure of **6** was solved in the acentric space group $Pbc2_1$, however, there are two molecules in the asymmetric unit. The structure of **12** was solved in the centric space group $P2_1/m$ and the molecule has crystallographic m symmetry.

The final atomic coordinates are reported in *Tables 2* (**3**), *3* (**6**), *4* (**9**), *5* (**12**), and *6* (**16**). Calculated bond lengths and angles are reported in *Tables 7–11*. Perspective drawings of the molecules prepared by the program ORTEP [31] are shown in *Figures 1a–5a* and projections looking down the endocyclic double bond in *Figures 1b–5b*. In the latter, angles between mean planes of the bicyclic skeleton C-atoms and those between the mean planes C(1),C(3),C(7),C(8) and C(2),C(3),C(6),C(7) are reported.

Table 2. *Final Atomic Coordinates for* **3** *($C_{15}H_{14}O_3$)*

Atom a)	x	y	z	Atom b)	x	y	z
C(1)	0.4471(2)	−0.2761(2)	0.3604(2)	H(1)	0.443(2)	−0.267(2)	0.430(1)
C(2)	0.4685(2)	−0.1267(2)	0.3078(1)	H(2)	0.637(2)	−0.008(2)	0.378(1)
C(3)	0.5406(2)	0.0113(2)	0.3573(1)	H(3)	0.517(2)	0.042(2)	0.421(1)
C(4)	0.5113(2)	0.1475(2)	0.2829(1)	H(4)	0.573(1)	0.228(2)	0.307(1)
C(5)	0.4976(2)	0.1167(2)	0.1682(1)	H(5)	0.573(1)	0.152(2)	0.150(1)
C(6)	0.4672(3)	−0.0507(2)	0.1305(2)	H(6)	0.544(2)	−0.092(3)	0.112(2)
C(7)	0.4356(2)	−0.1520(2)	0.2074(1)	H(7)	0.402(2)	−0.050(2)	0.067(1)
C(8)	0.3918(2)	−0.3190(2)	0.1901(2)	H(8)	0.346(2)	−0.345(2)	0.121(1)
C(9)	0.5160(2)	−0.4086(2)	0.2318(1)	H(9)	0.254(2)	−0.278(2)	0.269(1)
C(10)	0.5498(2)	−0.3846(2)	0.3446(1)	H(10)	0.314(2)	−0.451(2)	0.292(1)
C(11)	0.3309(2)	−0.3391(2)	0.2782(2)	H(11)	0.664(2)	−0.533(2)	0.213(1)
C(12)	0.5811(2)	−0.4828(2)	0.1778(2)	H(12)	0.545(2)	−0.486(2)	0.102(1)
C(13)	0.6456(2)	−0.4443(3)	0.4170(2)	H(13)	0.659(2)	−0.416(2)	0.489(2)
C(14)	0.3865(2)	0.2224(2)	0.2805(2)	H(14)	0.711(2)	−0.517(2)	0.398(1)
C(15)	0.3893(2)	0.2179(2)	0.1139(2)				
O(1)	0.3401(1)	0.2446(2)	0.3490(1)				
O(2)	0.3235(1)	0.2683(1)	0.1816(1)				
O(3)	0.3531(2)	0.2533(2)	0.0255(1)				

a) C-atom numbering, see *Fig. 1a*.

b) H-atom numbering does not follow IUPAC conventions.

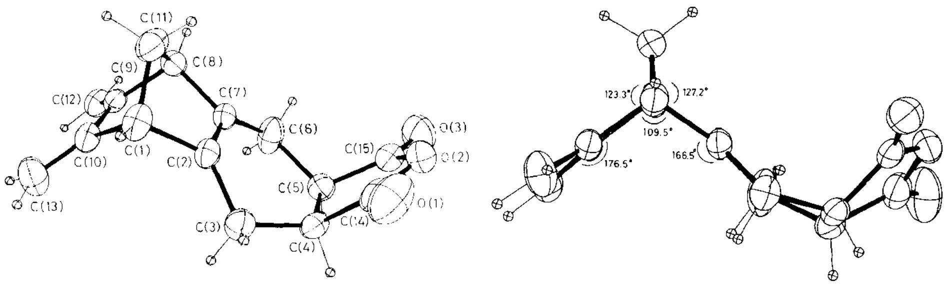


Fig. 1. *ORTEP representations of anhydride* **3**

For **3**, **6**, and **9**, the angles between the mean planes of C(1),C(8),C(9),C(10) and $CH_2 = C(9)\text{-}C(10) = CH_2$ are shown in *Fig. 1b, 2b* and *3b*, respectively. The H-atoms in all cases are represented as spheres with an isotropic temperature factor artificially fixed at 0.004 Å^2 for clarity. Lists of the observed and calculated structure factors as well as tables of temperature factors are available as supplementary material.

Table 3. *Final Atomic Coordinates for* **6** *($C_{18}H_{18}O_3$)*. Low-temperature Data[a])

Atom[b])	*x*	*y*	*z*	Atom[c])	*x*	*y*	*z*
C(1A)	0.2709(8)	1.0279(4)	0.8380(2)	H(1A)	−0.27(1)	0.883(5)	0.857(2)
C(1B)	0.2750(9)	0.8745(4)	0.6324(2)	H(1B)	0.74(1)	0.683(5)	0.664(2)
C(2A)	0.3357(8)	1.0260(4)	0.8837(1)	H(2A)	−0.13(1)	0.779(5)	0.869(3)
C(2B)	0.1980(8)	0.8088(4)	0.5956(2)	H(2B)	0.56(1)	0.595(6)	0.674(3)
C(3A)	0.3729(9)	1.1144(3)	0.9122(2)	H(3A)	−0.23(1)	1.058(6)	0.832(3)
C(3B)	0.2017(8)	0.8299(4)	0.5495(1)	H(3B)	0.78(1)	0.859(5)	0.641(2)
C(4A)	0.4982(7)	1.0800(4)	0.9517(2)	H(4A)	−0.06(1)	1.142(5)	0.817(2)
C(4B)	0.0391(9)	0.7678(4)	0.5291(2)	H(4B)	0.64(1)	0.958(5)	0.623(2)
C(5A)	0.4730(8)	0.9688(4)	0.9669(2)	H(5A)	0.309(7)	1.085(3)	0.819(1)
C(5B)	0.0110(9)	0.6568(4)	0.5454(2)	H(5B)	0.264(7)	0.948(3)	0.630(1)
C(6A)	0.3170(8)	0.9041(3)	0.9434(2)	H(6A)	0.251(7)	0.787(3)	0.863(1)
C(6B)	0.1350(9)	0.6249(4)	0.5819(2)	H(6B)	0.188(7)	0.655(3)	0.673(1)
C(7A)	0.3130(8)	0.9299(4)	0.8977(1)	H(7A)	0.46(1)	1.023(6)	0.764(3)
C(7B)	0.1721(8)	0.7139(4)	0.6104(2)	H(7B)	0.09(1)	0.991(6)	0.733(3)
C(8A)	0.2329(8)	0.8651(4)	0.8622(2)	H(8A)	0.66(1)	0.963(5)	0.766(2)
C(8B)	0.2361(8)	0.7136(4)	0.6569(2)	H(8B)	0.08(1)	1.007(6)	0.684(2)
C(9A)	0.0212(8)	0.9027(4)	0.8565(2)	H(9A)	0.50(1)	0.930(6)	0.733(4)
C(9B)	0.4608(8)	0.7302(4)	0.6562(2)	H(9B)	−0.11(1)	0.977(5)	0.710(2)
C(10A)	0.0427(8)	1.0116(4)	0.8408(2)	H(10A)	0.40(1)	0.734(5)	0.807(2)
C(10B)	0.4872(8)	0.8359(4)	0.6412(1)	H(10B)	0.04(1)	0.720(7)	0.733(3)
C(11A)	0.3328(8)	0.9204(4)	0.8241(2)	H(11A)	0.44(1)	0.750(6)	0.758(3)
C(11B)	0.1723(8)	0.8226(4)	0.6683(2)	H(11B)	−0.15(1)	0.788(5)	0.734(2)
C(12A)	0.4338(8)	0.8865(4)	0.7917(2)	H(12A)	0.62(1)	0.760(6)	0.792(2)
C(12B)	0.0713(8)	0.8562(4)	0.7017(2)	H(12B)	0.03(1)	0.817(5)	0.763(3)
C(13A)	0.5186(9)	0.9562(4)	0.7612(2)	H(13A)	0.44(1)	1.167(6)	0.897(2)
C(13B)	0.0264(8)	0.9676(3)	0.7077(2)	H(13B)	0.18(1)	0.902(5)	0.545(2)
C(14A)	0.4782(8)	0.7722(4)	0.7865(2)	H(14A)	0.25(1)	1.141(5)	0.922(2)
C(14B)	−0.0121(7)	0.7894(4)	0.7361(2)	H(14B)	0.33(1)	0.811(5)	0.538(2)
C(15A)	−0.1406(8)	0.8506(4)	0.8615(2)	H(15A)	0.35(1)	0.832(5)	0.947(2)
C(15B)	0.5978(8)	0.6639(4)	0.6655(2)	H(15B)	0.07(1)	0.572(6)	0.597(2)
C(16A)	−0.0944(9)	1.0766(4)	0.8288(2)	H(16A)	0.19(1)	0.918(5)	0.955(2)
C(16B)	0.6491(9)	0.8889(4)	0.6346(2)	H(16B)	0.26(1)	0.598(4)	0.572(2)
C(17A)	0.7173(8)	1.0884(4)	0.9410(2)	H(17A)	0.477(8)	1.129(4)	0.976(2)
C(17B)	−0.1573(9)	0.8176(4)	0.5350(2)	H(17B)	0.053(8)	0.771(4)	0.495(2)
C(18A)	0.6734(9)	0.9218(4)	0.9599(2)	H(18A)	0.457(8)	0.966(4)	0.997(2)
C(18B)	−0.2054(9)	0.6533(4)	0.5548(2)	H(18B)	0.029(8)	0.612(4)	0.529(2)
O(1A)	0.8098(6)	1.1599(3)	0.9292(1)				
O(1B)	−0.2024(6)	0.9056(2)	0.5286(1)				
O(2A)	0.8100(6)	0.9958(3)	0.9487				
O(2B)	−0.2936(5)	0.7489(2)	0.5495(1)				
O(3A)	0.7241(6)	0.8355(3)	0.9646(1)				
O(3B)	−0.3064(6)	0.5833(3)	0.5653(1)				

[a]) A and B refer to the two independent molecules in the asymmetric unit.

[b]) C-atom numbering, see *Fig. 2a*.

[c]) H-atom numbering does not follow IUPAC conventions.

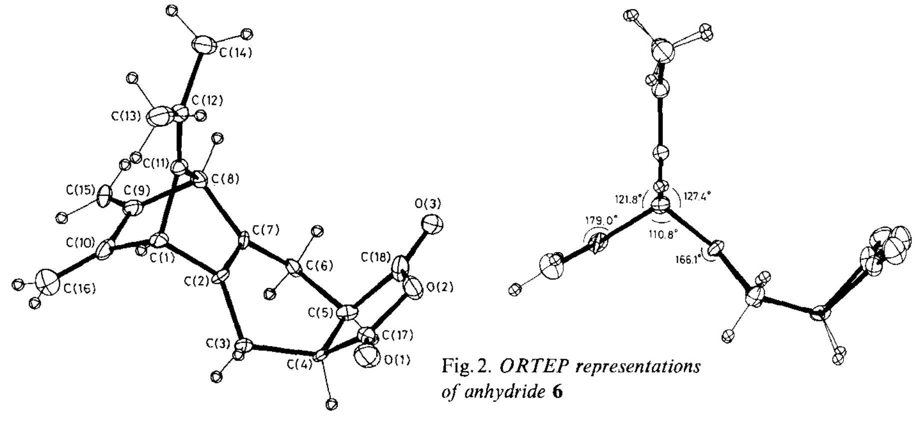


Fig. 2. *ORTEP representations of anhydride* **6**

Table 4. *Final Atomic Coordinates for* **9** *($C_{16}H_{16}O_3$)*

Atom[a])	x	y	z	Atom[b])	x	y	z
C(1)	0.2944(3)	0.6128(2)	0.2528(2)	H(1)	0.141(3)	0.574(2)	0.208(1)
C(2)	0.4426(3)	0.6673(2)	0.1739(2)	H(3N)	0.383(3)	0.578(2)	−0.036(2)
C(3)	0.3659(4)	0.6640(2)	0.0405(2)	H(3X)	0.213(3)	0.656(2)	0.026(2)
C(4)	0.5099(3)	0.8053(2)	0.0343(2)	H(4)	0.497(2)	0.784(1)	−0.060(1)
C(5)	0.7502(3)	0.8730(2)	0.1144(2)	H(5)	0.843(3)	0.897(2)	0.062(2)
C(6)	0.8248(4)	0.7772(3)	0.1676(2)	H(6N)	0.842(3)	0.696(2)	0.090(2)
C(7)	0.6556(3)	0.7174(2)	0.2318(2)	H(6X)	0.965(3)	0.842(2)	0.233(2)
C(8)	0.7042(3)	0.7091(2)	0.3639(2)	H(8)	0.860(3)	0.745(2)	0.405(1)
C(9)	0.5913(3)	0.5472(2)	0.3330(2)	H(11A)	0.253(3)	0.714(2)	0.455(2)
C(10)	0.3545(3)	0.4916(2)	0.2693(2)	H(11S)	0.311(3)	0.827(2)	0.391(2)
C(11)	0.3481(4)	0.7459(3)	0.3989(2)	H(12A)	0.620(3)	0.797(2)	0.549(2)
C(12)	0.5951(4)	0.8045(3)	0.4650(2)	H(12S)	0.670(3)	0.912(2)	0.483(2)
C(13)	0.2074(4)	0.3563(3)	0.2331(2)	H(13E)	0.045(3)	0.322(2)	0.189(2)
C(14)	0.6975(5)	0.4702(3)	0.3634(2)	H(13Z)	0.251(3)	0.282(2)	0.250(2)
C(15)	0.4262(4)	0.9305(2)	0.0982(2)	H(14E)	0.860(3)	0.523(2)	0.406(2)
O(1)	0.2544(2)	0.9381(2)	0.0624(2)	H(14Z)	0.615(3)	0.365(2)	0.342(2)
O(2)	0.5785(2)	1.0494(1)	0.2144(1)				
O(3)	0.9143(3)	1.1046(2)	0.3322(1)				

[a]) C-atom numbering, see *Fig. 3a*.

[b]) H-atom numbering follows C-atom numbering, N refers to *endo*, X to *exo*, with respect to the bicyclo[2.2.2]oct-2-ene skeleton; S refers to *syn*, A to *anti*, with respect to the double bond C(2),C(7); E means *trans* and Z *cis* with respect to the bond C(9)–C(10).

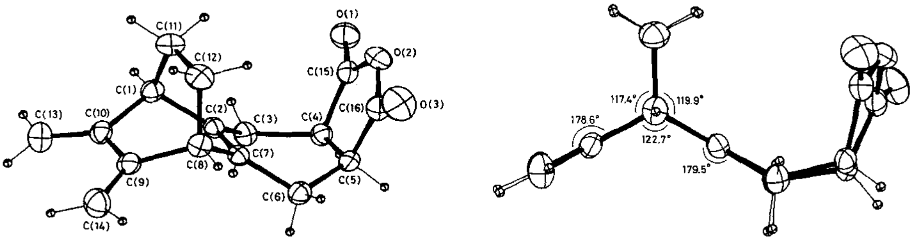


Fig. 3. *ORTEP representations of anhydride* **9**

Table 5. *Final Atomic Coordinates for* **12** *($C_{14}H_{14}O_3$)*

Atom[a])	*x*	*y*	*z*	Atom[b])	*x*	*y*	*z*
C(1)	0.7733(3)	0.8606(1)	0.4090(2)	H(1)	0.769(2)	0.945(1)	0.407(2)
C(2)	0.7268(3)	0.8074(1)	0.5644(2)	H(3N)	0.516(3)	0.873(1)	0.720(2)
C(3)	0.6896(4)	0.8735(2)	0.7108(2)	H(3X)	0.739(3)	0.954(1)	0.707(2)
C(4)	0.8304(3)	0.8166(1)	0.8667(2)	H(4)	0.780(3)	0.849(1)	0.957(2)
C(10)	0.6062(3)	0.8073(1)	0.2663(2)	H(10)	0.524(3)	0.859(1)	0.181(2)
C(12)	1.0228(4)	0.8169(2)	0.3941(3)	H(12A)	1.059(3)	0.850(1)	0.293(2)
C(13)	1.0852(4)	0.8491(2)	0.8884(2)	H(12S)	1.146(3)	0.847(1)	0.493(2)
O(1)	1.1770(2)	0.9421(1)	0.8903(2)				
O(2)	1.2259(3)	0.75	0.9043(2)				

[a]) C-atom numbering, see *Fig. 4a*.

[b]) H-atom numbering follows C-atom numbering, N refers to *endo*, X to *exo* with respect to the bicyclo[2.2.2]octa-2,5-diene skeleton; A means *anti* and S *syn* with respect to the double bond C(2),C(7).

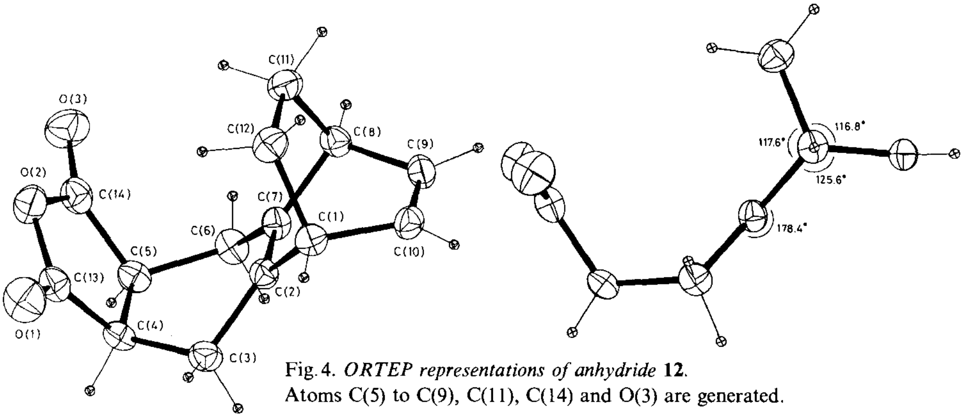


Fig. 4. *ORTEP representations of anhydride* **12**. Atoms C(5) to C(9), C(11), C(14) and O(3) are generated.

Table 6. *Final Atomic Coordinates for* **16** *($C_{12}H_{14}O_4$)*

Atom[a])	*x*	*y*	*z*	Atom[b])	*x*	*y*	*z*
C(1)	0.394(1)	0.7079(9)	0.8192(6)	H(1)	0.52(1)	0.746(8)	0.821(6)
C(2)	0.430(1)	0.5474(8)	0.7498(6)	H(3C)	0.71(1)	0.383(8)	0.731(6)
C(3)	0.628(1)	0.4385(9)	0.6841(7)	H(3T)	0.71(1)	0.522(8)	0.616(6)
C(4)	0.573(1)	0.2991(8)	0.6273(6)	H(4)	0.54(1)	0.362(8)	0.542(6)
C(5)	0.389(1)	0.2218(8)	0.7124(6)	H(5)	0.38(1)	0.138(8)	0.667(6)
C(6)	0.188(1)	0.3620(9)	0.7338(8)	H(6C)	0.09(1)	0.309(8)	0.796(6)
C(7)	0.238(1)	0.5124(8)	0.7737(6)	H(6T)	0.14(1)	0.389(8)	0.662(6)
C(8)	0.097(1)	0.6591(9)	0.8525(6)	H(8)	−0.06(1)	0.641(8)	0.900(6)
C(9)	0.191(1)	0.8167(9)	0.7748(7)	H(9A)	0.12(1)	0.928(8)	0.820(5)
C(10)	0.240(1)	0.657(1)	0.9469(7)	H(9S)	0.22(1)	0.839(7)	0.673(6)
C(11)	0.765(1)	0.1613(9)	0.5812(6)	H(10A)	0.18(1)	0.752(8)	1.000(6)
C(12)	0.442(1)	0.1323(8)	0.8423(6)	H(10S)	0.33(1)	0.533(8)	0.995(6)
O(1)	0.942(1)	0.1968(7)	0.5503(5)	H(11)	0.88(1)	−0.067(7)	0.505(6)
O(2)	0.726(1)	0.0151(7)	0.5650(5)	H(12)	0.23(1)	0.044(9)	0.933(7)
O(3)	0.6304(9)	0.0757(6)	0.8500(4)				
O(4)	0.2869(9)	0.1118(6)	0.9377(5)				

[a]) C-atom numbering, see *Fig. 5a*.

[b]) H-atom numbering follows C-atom numbering; C means *cis* and T *trans* with respect to the adjacent carboxylic group; A refers to *anti* and S to *syn* with respect to the double bond C(2),C(7).

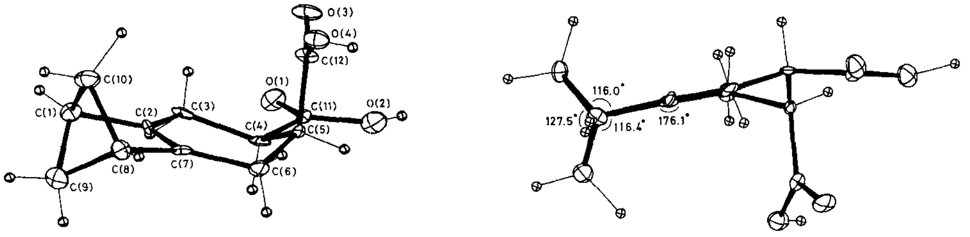


Fig. 5. *ORTEP representations of diacid* **16**

Table 7. *Bond Lengths* (Å) *and Angles* (°) *for* **3** (Fig. 1) *with Estimated Standard Deviations in Parentheses*[a])

Distances				Angles			
C(13)–C(10)	1.319(3)	C(12)–C(9)	1.321(3)	C(13)–C(10)–C(9)	128.6(2)	C(12)–C(9)–C(10)	128.5(2)
C(10)–C(1)	1.524(3)	C(9)–C(8)	1.525(2)	C(13)–C(10)–C(1)	126.8(2)	C(12)–C(9)–C(8)	127.2(2)
C(1)–C(11)	1.532(3)	C(8)–C(11)	1.529(4)	C(9)–C(10)–C(1)	104.6(1)	C(10)–C(9)–C(8)	104.2(2)
C(1)–C(2)	1.528(3)	C(8)–C(7)	1.523(2)	C(10)–C(1)–C(2)	104.1(2)	C(9)–C(8)–C(7)	102.8(1)
C(2)–C(3)	1.485(2)	C(7)–C(6)	1.474(3)	C(10)–C(1)–C(11)	99.7(2)	C(9)–C(8)–C(11)	101.0(2)
C(3)–C(4)	1.526(2)	C(6)–C(5)	1.544(3)	C(11)–C(1)–C(2)	99.7(1)	C(11)–C(8)–C(7)	100.1(2)
C(4)–C(14)	1.501(3)	C(5)–C(15)	1.489(3)	C(1)–C(2)–C(3)	127.3(1)	C(8)–C(7)–C(6)	125.8(2)
C(14)–O(1)	1.189(3)	C(15)–O(3)	1.188(3)	C(1)–C(2)–C(7)	107.7(1)	C(8)–C(7)–C(2)	107.3(2)
C(14)–O(2)	1.378(2)	C(15)–O(2)	1.384(3)	C(7)–C(2)–C(3)	123.6(2)	C(2)–C(7)–C(6)	125.1(2)
C(2)–C(7)	1.320(2)	C(9)–C(10)	1.479(2)	C(2)–C(3)–C(4)	110.0(1)	C(7)–C(6)–C(5)	113.6(2)
C(4)–C(5)	1.538(3)			C(3)–C(4)–C(14)	111.6(2)	C(6)–C(5)–C(15)	109.0(2)
				C(3)–C(4)–C(5)	118.2(1)	C(6)–C(5)–C(4)	116.5(2)
				C(5)–C(4)–C(14)	103.0(1)	C(4)–C(5)–C(15)	103.4(2)
				C(4)–C(14)–O(2)	110.3(2)	C(5)–C(15)–O(2)	110.4(2)
				C(4)–C(14)–O(1)	129.6(2)	C(5)–C(15)–O(3)	129.8(2)
				O(1)–C(14)–O(2)	120.1(2)	O(3)–C(15)–O(2)	119.8(2)
				C(14)–O(2)–C(15)	109.9(1)	C(1)–C(11)–C(8)	94.1(2)

[a]) Chemically equivalent distances or angles are reported on the same line.

Discussion. – A computer-assisted analysis of data in the *Cambridge Crystallographic Data File* showed that the bicyclo[2.2.1]hept-2-ene double bond is not planar. The substituents at C(2) and/or C(3) deviate from the C(1),C(2),C(3),C(4) mean plane towards the *endo*-face. An average out-of-plane deformation α of *ca.* 7° was calculated for 43 examples of substituted bicyclo[2.2.1]hept-2-ene derivatives (see *Fig. 6*)[4]). This value is significantly larger than that calculated recently for bicyclo[2.2.1]hept-2-ene by *ab initio* (STO 3G) MO techniques [32]. Even larger out-of-plane deviations of 10.4, 13.5, and 13.9° were observed for the 5,6-dimethylidenebicyclo[2.2.1]hept-2-ene systems **1** [16], **3**, and **6**, respectively[5]). Since the endocyclic double bond π(C(2),C(3)) of the

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[4]) All structures whose substitution introduces specific skeleton deformations ('tortured' molecules, see *e.g.* [33]) were excluded from the statistics.

[5]) For 21 bicyclo[2.2.1]hept-2-ene derivatives unsubstituted on the double bond, an average α value of 7.5° was found.

Table 8. *Bond Lengths and Angles for* **6** (Fig. 2) *with Estimated Standard Deviations in Parentheses*[a])

Distances							
C(16A)–C(10A)	1.316(8)	C(15A)–C(9A)	1.302(8)	C(16B)–C(10B)	1.317(8)	C(15B)–C(9B)	1.305(8)
C(10A)–C(9A)	1.517(8)			C(10B)–C(9B)	1.473(7)		
C(10A)–C(1A)	1.567(8)	C(9A)–C(8A)	1.530(8)	C(10B)–C(1B)	1.552(8)	C(9B)–C(8B)	1.542(8)
C(1A)–C(11A)	1.531(7)	C(8A)–C(11A)	1.566(7)	C(1B)–C(11B)	1.501(8)	C(8B)–C(11B)	1.534(7)
C(11A)–C(12A)	1.316(7)			C(11B)–C(12B)	1.338(7)		
C(12A)–C(13A)	1.452(8)	C(12A)–C(14A)	1.533(7)	C(12B)–C(13B)	1.501(7)	C(12B)–C(14B)	1.512(7)
C(1A)–C(2A)	1.522(7)	C(8A)–C(7A)	1.514(7)	C(1B)–C(2B)	1.545(8)	C(8B)–C(7B)	1.543(8)
C(2A)–C(7A)	1.342(7)			C(2B)–C(7B)	1.339(7)		
C(2A)–C(3A)	1.489(7)	C(7A)–C(6A)	1.492(7)	C(2B)–C(3B)	1.493(7)	C(7B)–C(6B)	1.496(7)
C(3A)–C(4A)	1.583(7)	C(6A)–C(5A)	1.549(7)	C(3B)–C(4B)	1.516(8)	C(6B)–C(5B)	1.495(8)
C(4A)–C(5A)	1.541(7)			C(4B)–C(5B)	1.552(7)		
C(4A)–C(17A)	1.531(8)	C(5A)–C(18A)	1.510(8)	C(4B)–C(17B)	1.496(8)	C(5B)–C(18B)	1.500(9)
C(17A)–O(1A)	1.188(6)	C(18A)–O(3A)	1.189(6)	C(17B)–O(1B)	1.208(6)	C(18B)–O(3B)	1.193(7)
C(17A)–O(2A)	1.386(6)	C(18A)–O(2A)	1.386(7)	C(17B)–O(2B)	1.369(7)	C(18B)–O(2B)	1.396(6)
Angles							
C(16A)–C(10A)–C(9A)	129.2(5)	C(15A)–C(9A)–C(10A)	127.8(5)	C(16B)–C(10B)–C(9B)	130.3(5)	C(15B)–C(9B)–C(10B)	127.6(5)
C(16A)–C(10A)–C(1A)	126.6(5)	C(15A)–C(9A)–C(8A)	127.6(5)	C(16B)–C(10B)–C(1B)	125.1(5)	C(15B)–C(9B)–C(8B)	127.5(5)
C(9A)–C(10A)–C(1A)	104.0(4)	C(10A)–C(9A)–C(8A)	104.4(4)	C(9B)–C(10B)–C(1B)	104.5(4)	C(10B)–C(9B)–C(8B)	104.9(4)
C(10A)–C(1A)–C(11A)	99.4(4)	C(9A)–C(8A)–C(11A)	99.7(4)	C(10B)–C(1B)–C(11B)	98.5(4)	C(9B)–C(8B)–C(11B)	98.8(4)
C(10A)–C(1A)–C(2A)	103.2(4)	C(9A)–C(8A)–C(7A)	104.2(4)	C(10B)–C(1B)–C(2B)	105.6(4)	C(9B)–C(8B)–C(7B)	105.3(4)
C(11A)–C(1A)–C(2A)	100.5(4)	C(11A)–C(8A)–C(7A)	99.4(4)	C(11B)–C(1B)–C(2B)	99.8(4)	C(11B)–C(8B)–C(7B)	98.3(4)
C(1A)–C(11A)–C(8A)	94.7(4)			C(1B)–C(11B)–C(8B)	96.2(4)		
C(1A)–C(11A)–C(12A)	132.7(5)	C(8A)–C(11A)–C(12A)	132.6(4)	C(1B)–C(11B)–C(12B)	134.0(5)	C(8B)–C(11B)–C(12B)	129.6(5)
C(11A)–C(12A)–C(13A)	121.3(5)	C(11A)–C(12A)–C(14A)	121.1(5)	C(11B)–C(12B)–C(13B)	121.5(5)	C(11B)–C(12B)–C(14B)	125.3(5)
C(13A)–C(12A)–C(14A)	117.5(5)			C(13B)–C(12B)–C(14B)	113.1(4)		
C(1A)–C(2A)–C(3A)	128.2(4)	C(8A)–C(7A)–C(6A)	127.4(4)	C(1B)–C(2B)–C(3B)	129.6(4)	C(8B)–C(7B)–C(6B)	128.8(4)
C(1A)–C(2A)–C(7A)	107.4(4)	C(8A)–C(7A)–C(2A)	108.5(4)	C(1B)–C(2B)–C(7B)	106.9(4)	C(8B)–C(7B)–C(2B)	107.7(4)
C(7A)–C(2A)–C(3A)	123.0(4)	C(2A)–C(7A)–C(6A)	122.2(4)	C(7B)–C(2B)–C(3B)	121.4(5)	C(2B)–C(7B)–C(6B)	121.9(5)
C(2A)–C(3A)–C(4A)	110.7(4)	C(7A)–C(6A)–C(5A)	111.0(4)	C(2B)–C(3B)–C(4B)	108.0(4)	C(7B)–C(6B)–C(5B)	110.4(4)
C(3A)–C(4A)–C(5A)	117.2(4)	C(6A)–C(5A)–C(4A)	116.1(4)	C(3B)–C(4B)–C(5B)	116.6(5)	C(6B)–C(5B)–C(4B)	116.8(5)
C(3A)–C(4A)–C(17A)	109.0(4)	C(6A)–C(5A)–C(18A)	108.9(4)	C(3B)–C(4B)–C(17B)	111.3(4)	C(6B)–C(5B)–C(18B)	112.8(5)
C(5A)–C(4A)–C(17A)	104.2(4)	C(4A)–C(5A)–C(18A)	103.8(4)	C(5B)–C(4B)–C(17B)	104.8(5)	C(4B)–C(5B)–C(18B)	102.5(4)
C(4A)–C(17A)–O(1A)	129.9(5)	C(5A)–C(18A)–O(3A)	129.0(5)	C(4B)–C(17B)–O(1B)	128.2(5)	C(5B)–C(18B)–O(3B)	130.1(5)
C(4A)–C(17A)–O(2A)	109.8(4)	C(5A)–C(18A)–O(2A)	110.9(4)	C(4B)–C(17B)–O(2B)	111.1(4)	C(5B)–C(18B)–O(2B)	111.6(4)
O(1A)–C(17A)–O(2A)	120.2(5)	O(3A)–C(18A)–O(2A)	120.0(5)	O(1B)–C(17B)–O(2B)	120.6(5)	O(3B)–C(18B)–O(2B)	118.3(5)
C(17A)–O(2A)–C(18A)	110.5(4)			C(17B)–O(2B)–C(18B)	109.7(4)		

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[a]) Chemically equivalent distances and angles in the two molecules are reported on the same line.

Table 9. *Bond Lengths* (Å) *and Angles* (°) *for* **9** (Fig. 3) *with Estimated Standard Deviations in Parentheses*[a])

Distances				Angles			
C(10)–C(13)	1.328(3)	C(9)–C(14)	1.331(4)	C(1)–C(10)–C(13)	122.9(2)	C(8)–C(9)–C(14)	122.7(2)
C(1)–C(10)	1.515(4)	C(8)–C(9)	1.514(3)	C(1)–C(10)–C(9)	110.7(2)	C(8)–C(9)–C(10)	111.1(2)
C(1)–C(2)	1.509(3)	C(7)–C(8)	1.511(3)	C(9)–C(10)–C(13)	126.4(2)	C(10)–C(9)–C(14)	126.2(2)
C(2)–C(3)	1.496(3)	C(6)–C(7)	1.495(3)	C(2)–C(1)–C(10)	108.2(2)	C(7)–C(8)–C(9)	107.9(1)
C(3)–C(4)	1.545(3)	C(5)–C(6)	1.531(4)	C(2)–C(1)–C(11)	107.5(2)	C(7)–C(8)–C(12)	107.0(2)
C(4)–C(15)	1.495(3)	C(5)–C(16)	1.495(3)	C(10)–C(1)–C(11)	106.9(2)	C(9)–C(8)–C(12)	107.4(2)
C(15)–O(1)	1.196(3)	C(16)–O(3)	1.185(2)	C(1)–C(11)–C(12)	109.2(2)	C(8)–C(12)–C(11)	109.3(2)
C(15)–O(2)	1.376(2)	C(16)–O(2)	1.397(3)	C(1)–C(2)–C(3)	125.2(2)	C(6)–C(7)–C(8)	125.2(2)
C(9)–C(10)	1.475(3)	C(11)–C(12)	1.537(3)	C(1)–C(2)–C(7)	113.8(2)	C(2)–C(7)–C(8)	114.2(2)
C(2)–C(7)	1.328(3)	C(4)–C(5)	1.529(3)	C(3)–C(2)–C(7)	121.0(2)	C(2)–C(7)–C(6)	120.6(2)
				C(2)–C(3)–C(4)	111.6(1)	C(5)–C(6)–C(7)	109.3(2)
				C(3)–C(4)–C(5)	115.1(2)	C(4)–C(5)–C(6)	115.7(2)
				C(3)–C(4)–C(15)	110.3(2)	C(6)–C(5)–C(16)	110.1(2)
				C(5)–C(4)–C(15)	104.0(1)	C(4)–C(5)–C(16)	104.0(2)
				C(4)–C(15)–O(1)	129.4(1)	C(5)–C(16)–O(3)	130.2(2)
				C(4)–C(15)–O(2)	110.8(2)	C(5)–C(16)–O(2)	110.2(2)
				O(1)–C(15)–O(2)	119.7(2)	O(3)–C(16)–O(2)	119.6(2)
				C(15)–O(2)–C(16)	109.8(2)		

[a]) Chemically equivalent distances or angles are reported on the same line.

Table 10. *Bond Lengths* (Å) *and Angles* (°) *for* **12** (Fig. 4) *with Estimated Standard Deviations in Parentheses*[a])

Distances				Angles			
C(10)–C(10')	1.320(2)	C(2)–C(3)	1.499(3)	C(1)–C(10)–C(10')	114.0(1)	C(2)–C(3)–C(4)	110.0(2)
C(1)–C(10)	1.507(2)	C(3)–C(4)	1.540(2)	C(10)–C(1)–C(12)	105.1(1)	C(3)–C(4)–C(4')	115.2(1)
C(1)–C(2)	1.514(2)	C(4)–C(13)	1.496(3)	C(10)–C(1)–C(2)	108.8(1)	C(3)–C(4)–C(13)	109.5(2)
C(1)–C(12)	1.558(3)	C(4)–C(4')	1.533(2)	C(12)–C(1)–C(2)	105.7(1)	C(4')–C(4)–C(13)	104.5(1)
C(12)–C(12')	1.541(2)	C(13)–O(1)	1.193(2)	C(1)–C(12)–C(12')	108.8(2)	C(4)–C(13)–O(1)	130.6(2)
C(2)–C(2')	1.321(2)	C(13)–O(2)	1.392(2)	C(1)–C(2)–C(2')	113.8(1)	C(4)–C(13)–O(2)	110.5(2)
				C(1)–C(2)–C(3)	125.7(1)	O(1)–C(13)–O(2)	118.9(2)
				C(2')–C(2)–C(3)	120.5(2)	C(13)–O(2)–C(13')	110.0(2)

[a]) Primed atoms are generated by reflection in a crystallographic mirror plane; they correspond to: 10' = 9, 12' = 11, 2' = 7, 4' = 5, 13' = 14 in *Fig. 4a*.

Table 11. *Bond Lengths* (Å) *and Angles* (°) *for* **16** (Fig. 5) *with Estimated Standard Deviations in Parentheses*[a])

Distances				Angles			
C(1)–C(10)	1.55(1)	C(8)–C(10)	1.55(1)	C(1)–C(9)–C(8)	82.1(5)	C(1)–C(10)–C(8)	82.4(6)
C(1)–C(9)	1.55(1)	C(8)–C(9)	1.56(1)	C(9)–C(1)–C(10)	85.0(6)	C(9)–C(8)–C(10)	85.0(7)
C(1)–C(2)	1.54(1)	C(8)–C(7)	1.553(9)	C(9)–C(1)–C(2)	99.9(7)	C(9)–C(8)–C(7)	99.7(5)
C(2)–C(3)	1.484(9)	C(7)–C(6)	1.48(1)	C(10)–C(1)–C(2)	100.8(6)	C(10)–C(8)–C(7)	99.2(6)
C(3)–C(4)	1.52(1)	C(6)–C(5)	1.53(1)	C(1)–C(2)–C(7)	103.0(6)	C(8)–C(7)–C(2)	103.6(7)
C(4)–C(11)	1.522(9)	C(5)–C(12)	1.53(1)	C(1)–C(2)–C(3)	131.1(8)	C(8)–C(7)–C(6)	131.4(7)
C(11)–O(1)	1.23(1)	C(12)–O(3)	1.25(1)	C(7)–C(2)–C(3)	125.5(7)	C(2)–C(7)–C(6)	125.1(6)
C(11)–O(2)	1.31(1)	C(12)–O(4)	1.283(8)	C(2)–C(3)–C(4)	109.2(7)	C(7)–C(6)–C(5)	108.2(7)
C(2)–C(7)	1.33(1)	C(4)–C(5)	1.53(1)	C(3)–C(4)–C(5)	114.3(5)	C(6)–C(5)–C(4)	110.7(5)
				C(3)–C(4)–C(11)	112.4(7)	C(6)–C(5)–C(12)	110.5(5)
				C(5)–C(4)–C(11)	112.9(5)	C(4)–C(5)–C(12)	110.8(7)
				C(4)–C(11)–O(1)	120.0(7)	C(5)–C(12)–O(3)	119.5(6)
				C(4)–C(11)–O(2)	115.6(7)	C(5)–C(12)–O(4)	117.6(7)
				O(1)–C(11)–O(2)	124.1(6)	O(3)–C(12)–O(4)	122.9(6)

[a]) Chemically equivalent distances or angles are reported on the same line.

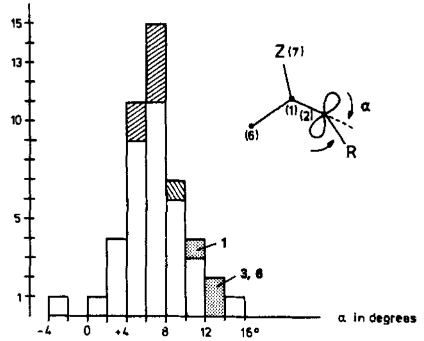


Fig. 6. *Histogram of the out-of-plane deviations of 2-substituted and 2,3-disubstituted bicyclo[2.2.1]hept-2-ene and bicyclo[2.2.1]hept-2-ene-7-one derivatives*4) *(sesquinorbornenes are not included), version of Oct. 25, 1983, 36 cases* □5). *Values of α for* **17–21** [12b] *and* **22–23** [12c], *7 cases* ▨. *Values of α for 5,6-dimethylidenebicyclo[2.2.1]hept-2-ene derivatives* **1**, **3**, *and* **6** ▩.

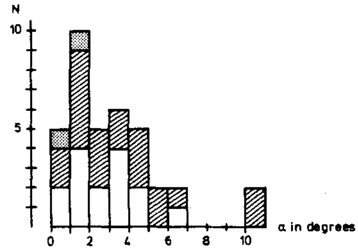
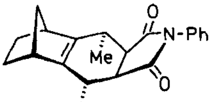
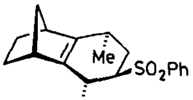


Fig. 7. *Histogram of the out-of-plane deviations of the C(2),C(3) double bond in 2-substituted and 2,3-disubstituted bicyclo[2.2.2]oct-2-ene derivatives*4), *version of Oct. 25, 1983, 15 cases* □. *Unsubstituted double bond derivatives: 20 cases* ▨. *Anhydrides* **9** *and* **12** ▩.

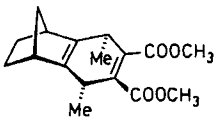
5,6-dimethylidenebicyclo[2.2.2]oct-2-ene derivative **9** was found to be essentially planar, one cannot invoke a possible homoconjugative (bis-homoaromatic character) interaction between the exocyclic *s-cis*-butadiene and ethylene moieties as being responsible for part of the pyramidalization of the endocyclic double bond in **1**, **3**, and **6**. Cyclohexene-ring annulation of the bicyclo[2.2.1]hept-2-ene cannot be considered to contribute significantly to the double-bond pyramidalization as data reported recently for derivatives **17–23** [12b] [12c] showed significantly smaller out-of-plane deviations than for **1**, **3**, and **6** (see *Fig. 6*). It is noteworthy that the π-tilting does not vary in a significant fashion when the $CH_2(7)$ bridge in **3** is replaced by an isopropylidene group (**6**). However, it is somewhat reduced upon introduction of an O(7) oxa bridge, as shown by the comparison of structures of **1** and **3**.



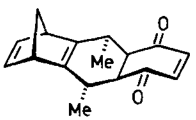
(α = 6.3°)
17



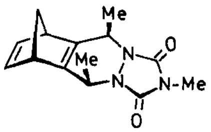
(α = 4.5°)
18



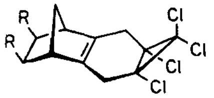
(α = 6.9°)
19



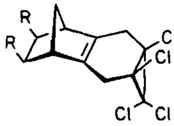
(α = 4.8°)
20



(α = 8.1°)
21



(α = 7.8°)
22



(α = 6.3°)
23

In contrast, the exocyclic diene moieties in **1**, **3**, **6**, and **9** did not deviate significantly from planarity (see *Fig. 1b–3b* and [16]). This was predicted by force-field calculations (see below) and by *ab initio* MO calculations [34].

It has been proposed that bond-angle deformations of an olefin could favour its pyramidalization [15b] [32] [35] [36]. The crystal and molecular structure of the bicyclo[2.1.1]hex-2-ene derivative **16** allows us to critically examine this proposal for the first time[6]). The out-of-plane deviation $\alpha \approx 4°$ observed for the diacid **16** shows that the double bond of this system does not deviate significantly from planarity. In fact it is not significantly larger than the out-of-plane deviations of the endocyclic double bond of the less strained bicyclo[2.2.2]octenes **9** *(Fig. 3b)*, **12** *(Fig. 4b)*, and of that of other derivatives found in the *Cambridge Crystallographic Data File* (see *Fig. 7*). The C(1)-C(2)-C(7) bond angle in **16** (103°, see *Table 11*) is definitively smaller than in the bicyclo[2.2.2]oct-2-enes **9** (114°, see *Table 9*) and **12** (113.8°, see *Table 10*). Average bond-angle values of 105.8° [16], 107.5° (see *Table 7*), and 107.6° (see *Table 8*) were found for the bicyclo[2.2.1]hept-2-ene derivatives **1**, **3**, and **6**, respectively. Our data definitively show that the double-bond pyramidalization in these latter systems cannot be attributed to bond-angle deformations.

The oxa bridge in **1** [16], the methano bridge in **3**, and the isopropylidenemethano bridge in **6** are tilted towards the exocyclic diene (see *Fig. 1b* and *2b*). This structural feature is not specific to 5,6-dimethylidenebicyclo[2.2.1]hept-2-ene systems only. What appears to be a double-bond/C(7)-bridge repulsion effect is visible in a larger number of other bicyclo[2.2.1]hept-2-ene and sesquinorbornene derivatives, as shown by a search of the *Cambridge Crystallographic Data File*, see *Fig. 8*.

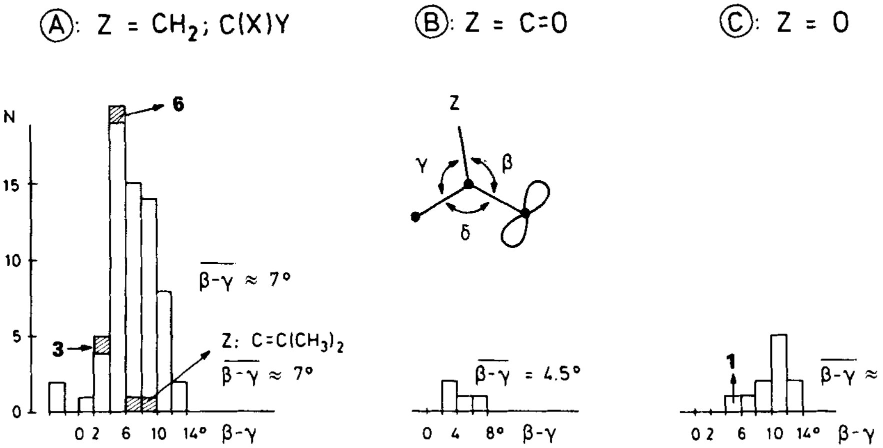


Fig. 8. *Histograms of the differences between mean dihedral angles β–γ for bicyclo[2.2.1]hept-2-ene and sesquinorbornene derivatives (* Ⓐ*, 67 cases), bicyclo[2.2.1]hept-2-ene-7-ones (* Ⓑ*, 4 cases), and 7-oxabicyclo[2.2.1]hept-2-enes (* Ⓒ*, 11 cases)*

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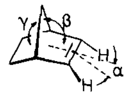
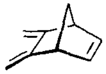
[6]) Incomplete X-ray single crystal data have been reported for hexamethylbicyclo[2.1.1]hex-2-ene-5,6-diol [37]. To our knowledge, there has been no other example of a bicyclo[2.1.1]hex-2-ene structure reported in the literature.

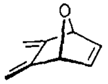
The larger value observed for the angle β (between plane C(1),C(4),Z(7), and mean plane C(1),C(2),C(3),C(4)) than for the angle γ (between plane C(1),C(4),Z(7) and mean plane C(1),C(4),C(5),C(6)) (bicyclo[2.2.1]hept-2-ene numbering) can be attributed to the difference in bond length between the π(C(2),C(3)) and σ(C(5),C(6)) bonds. The puckering of the C(1),C(4),C(5),C(6),C(7) five-membered ring is expected to increase (smaller γ values) by shortening the C(2),C(3) bond, *i.e.* when going from a single to a double bond. The histograms in *Fig. 8* suggest that the β-γ value is a function of the nature of the bridge Z (average β-γ values: *ca.* 7° for $Z = CH_2$, C(X)Y, and $C = C(CH_3)_2$; *ca.* 4.5° for $Z = C{=}O$; *ca.* 10° for $Z = O$). When replacing the methano CH_2(7) bridge by an oxa O(7) bridge [14] [16] [38], the value of β-γ is increased perhaps because of a repulsive n(O)$\leftrightarrow\pi$(C(2),C(3)) interaction. Nevertheless, this hypothesis appears to be a fragile one as we do not observe significantly larger β-γ values for the 7-isopropylidene-substituted derivative [39] than for the unsubstituted analogues (see *Fig. 8*). The *ab initio* STO 3G calculations reproduce this trend in a strongly attenuated fashion [34]. Interestingly, the X-ray structures of the bicyclo[2.2.1]hept-2-ene-7-one derivatives reported in the litterature [40] show an average β-γ value somewhat smaller than that found in other bicyclo[2.2.1]hept-2-ene systems. This suggests a possible stabilizing π^*(CO)$\leftrightarrow\pi$(C(2),C(3)) interaction [41] which would tend to reduce angle β. One should note also that the bond angles C(1)-C(11)-C(8) in **3** and **6** and C(1)-O(7)-C(4) in **1** are practically the same (95° in **1** [16], 94.1° in **3** *(Table 7)*, 94.7° in **6** *(Table 8)*). The possible interpretations given above will be tested by *ab initio* MO calculations in a forthcoming paper [34]. We report below the calculated (completely optimized) geometries for the model molecules **24–31** as obtained by force-field calculations, using *Allinger*'s MMPI1 technique [42].



	24	**25**	**26**	**27**
α :	6.7°	6.4°	6.4°	6.2°
β :	124.8°	123.6°	126.5°	124.3°
γ :	123.0°	123.6°	121.5°	124.3°
β-γ:	1.8°	0°	5°	0°

Our calculations reproduce the out-of-plane deformation of the endocyclic double bond of the bicyclo[2.2.1]hept-2-ene and 7-oxabicyclo[2.2.1]hept-2-ene systems (**24–27**), and the planarity of the exocyclic *s-cis*-butadiene moieties in the 2,3-dimethylidenebicyclo[2.2.1]heptanes (see also [21]) and 2,3-dimethylidene-7-oxabicyclo[2.2.1]heptanes (**28–31**). However, contrary to our X-ray data, the force-field calculations do





	28	**29**	**30**	**31**
α :	–	6.5°	–	6.3°
α' :	0.1°	0.0°	0.0°	0.2°
β :	124.4°	125.5°	122.9°	126.0°
γ :	124.2°	123.2°	125.6°	123.6°
β-γ:	0.2°	2.3°	−2.7°	2.4°

not reproduce an enhanced out-of-plane deformation of the bicyclo[2.2.1]hept-2-enes upon introduction of a homoconjugated, exocyclic *s-cis*-butadiene moiety at C(5),C(6). Practically, the same values of α are calculated for the pairs **24/29** and **26/31**. The introduction of a homoconjugated, endocyclic double bond does not affect the calculated pyramidalizations either (compare the pairs of dienes **24/25** and **26/27**). The methano bridges in **24** and **29**, as well as the oxa bridges in **26** and **31** are calculated to be tilted away from the endocyclic double bond. The calculated tilt β-γ is somewhat smaller than that found experimentally for crystalline derivatives (see *Fig. 8*). Nevertheless, the larger value of β-γ observed for simple 7-oxabicyclo[2.2.1]hept-2-enes (*ca.* 10°) than for bicyclo[2.2.1]hept-2-enes (*ca.* 7°) is predicted by the MMPI1-minimized geometries of model compounds **24** and **26**. The calculations, however, do not show any significant differences between the geometries of **29** and **31**. Thus, the force-field technique used here is not capable of reproducing the differences observed between the structures of the 5,6-dimethylidene-7-oxabicyclo[2.2.1]hept-2-ene and 5,6-dimethylidenebicyclo[2.2.1]hept-2-ene derivatives **1** and **3**, respectively, and the differences observed between the latter compounds and the structures of simpler bicyclo[2.2.1]hept-2-enes (see *Fig. 6* and *8*).

Conclusion. – The *Diels-Alder* additions of maleic anhydride to 2,3,5,6-tetramethylidenebicyclo[2.2.1]heptane (**2**) and to 7-isopropylidene-2,3,5,6-tetramethylidenebicyclo[2.2.1]heptane (**5**) are highly stereoselective[3]) and give (1*R*,4*R*,5*S*,8*S*)-9,10-dimethylidenetricyclo[6.2.1.$0^{2,7}$]undec-2(7)-ene-4,5-dicarboxylic anhydride (**3**) and (1*R*,4*R*,5*S*,8*S*)-11-isopropylidene-9,10-dimethylidenetricyclo[6.2.1.$0^{2,7}$]undec-2(7)-ene-4,5-dicarboxylic anhydride (**6**) (β,β-anhydrides), respectively. The addition of the first equivalent of dienophile is much faster than that of the second equivalent. Such selectivities are not observed for the addition of maleic anhydride to 2,3,5,6-tetramethylidenebicyclo[2.2.2]octane (**8**) which lead to a mixture of two mono-adducts **9** and **10** and three bis-adducts. The X-ray crystal structures of adducts **3** and **6** show relatively large out-of-plane deformation of the endocyclic double bond of the bicyclo[2.2.1]hept-2-ene systems, the annulated cyclohexene ring leaning towards the *endo*-face by 13–14°. This is not due to a hypothetical homoconjugative interaction between the exocyclic *s-cis*-butadiene and ethylene moieties in **3** and **6**. Cyclohexene ring annulation as well as bicyclic ring strain (bond-angle deformations) cannot be considered responsible either. Confirmations are given by the X-ray crystal structures of **9**, of the maleic anhydride adduct **12** to 5,6-dimethylidenebicyclo[2.2.2]oct-2-ene, and of (4*R*,5*S*)-tricyclo[6.1.1.$0^{2,7}$]dec-2(7)-ene-4,5-dicarboxylic acid (**16**).

We thank *Hoffmann-La Roche & Co. AG*, Basel, the *Swiss National Science Foundation*, the *Fonds Herbette*, Lausanne, and *La Commission Fédérale des Bourses*, Fribourg, for generous support. We are grateful also to Miss *F. Berchier*, Mr. *O. Giordano* and Mr. *Ch. Debonneville* for their technical assistance.

Experimental Part

General Remarks. Melting points (m.p.; not corrected), *Tottoli* apparatus; IR spectra (ν[cm^{-1}]), *Beckman IR-4230* spectrometer; UV spectra, *Phillips Pye-Unicam SP 8/100* (λ_{max}[nm] (ε[dm^{3}mol^{-1}cm^{-1}])). ^{1}H-NMR spectra, *Bruker WP-80 CW* (80 MHz), ^{13}C-NMR spectra, *Bruker WP 60FT* (15.08 MHz, spectral width: 3750 Hz, 4096 points, deuterium signal of $CDCl_3$ as lock signal, δ_C of $CDCl_3$ at 76.9 ppm as internal reference (δ[ppm], apparent multiplicity, apparent coupling constants, tentative attribution)); *s* = singlet, *d* = doublet, *t* = triplet, *q* = quadruplet, *m* = multiplet, br. = broad. Mass spectra (MS) in electron-ionization mode, *Finnigan 1020* (*m/z*[amu](% base peak)). Elemental analysis, *Ilse Beetz* in Kronach (Germany).

(1R,4R,5S,8S)-9,10-Dimethylidenetricyclo[6.2.1.0^{2,7}]undec-2(7)-ene-4,5-dicarboxylic Anhydride (**3**). A mixture of 2,3,5,6-tetramethylidenebicyclo[2.2.1]heptane (**2**) [17] (0.627 g, 4.35 mmol), freshly sublimed maleic anhydride (0.422 g, 4.35 mmol), and hydroquinone (5 mg) in anh. toluene (20 ml) was heated under N_2 to 80° for 5 h. After solvent evaporation *in vacuo*, the crude adduct was recrystallized from AcOEt, yielding 1 g (96%) of colourless crystals, m.p. 131-3°. UV (EtOH 96%): 223 (8400), 232 (8600), 240 (8900), 248 (6600). IR (KBr): 3010, 2990, 2950, 2920, 2860, 1850, 1780, 1650, 1630, 1450, 1310, 1250, 1240, 1190, 1170, 1100, 1080, 1015, 985, 970. ^{1}H-NMR ($CDCl_3$): 5.14 (*s*, 2 H, *H*CH=C(9) and *H*CH=C(10) *cis* to C(9),C(10)); 4.93 (*s*, 2 H, *H*CH=C(9) and *H*CH=C(10) *trans* to C(9),C(10)); 3.34 (*m*, 2 H, H–C(4), H–C(5)); 3.16 (*s*, 2 H, H–C(1), H–C(8)); 2.71 (*d*, *J*=17, 2 H, Hβ of CH_2(3) and CH_2(6)); 2.39 (*dm*, *J*=17, 2 H, Hα of CH_2(3) and CH_2(6)); 1.78 (*d*, *J*=8.5, 1 H, H–C(11) *syn* to C(2),C(7)); 1.59 (*d*, *J*=8.5, 1 H, H–C(11) *anti* to C(2),C(7)). ^{13}C-NMR($CDCl_3$): 173.7 (*s*); 147.9 (*s*); 138.8 (*s*); 101.2 (*t*, $^1J_{C,H}$=161); 53.7 (*d*, $^1J_{C,H}$=153, C(1),C(8));48.5 (*dd*, $^1J_{C,H}$=137, 144, CH_2(11)); 38.3 (*dm*, $^1J_{C,H}$=138, C(4),C(5)); 21.8 (*t*, $^1J_{C,H}$=134, C(3),C(6)). MS (70eV): 243 (10), 242 (61, M^+), 214 (22), 199 (4), 169 (100), 155 (28), 141 (33), 128 (21), 117 (40), 91 (31). Anal. calc. for $C_{15}H_{14}O_3$ (242.28): C 74.36, H 5.82; found: C 74.24, H 5.86.

(1R,4R,5S,8S)-11-Isopropylidene-9,10-dimethylidenetricyclo[6.2.1.0^{2,7}]undec-2(7)-ene-4,5-dicarboxylic Anhydride (**6**). A mixture of 7-isopropylidene-2,3,5,6-tetramethylidenebicyclo[2.2.1]heptane (**5** [20]; 0.7 g, 3.8 mmol) and maleic anhydride (0.376 g, 3.84 mmol) in anh. benzene (6 ml) was heated under N_2 to 70° for 5 h. After solvent evaporation *in vacuo*, the crude adduct (> 95% pure) was recrystallized 3 × from AcOEt yielding 0.719 g (67%) of colourless crystals, m.p. 189–191°. UV (MeCN): 195 (13 300), 238 (11 650), 244 (11 700), 253 (sh, 9300). UV (dioxane): 239 (sh, 11 500), 246 (11 800), 253 (sh, 9 600). IR (KBr): 2990, 2940, 2860, 1850, 1770, 1440, 1240, 1020, 950. ^{1}H-NMR ($CDCl_3$): 5.08 (*s*, 2 H); 4.90 (*s*, 2 H); 3.6 (br. *s*, 2 H); 3.4 (*m*, 2 H); 2.7 (*m*, 2 H); 2.48 (*m*, 2 H); 1.58 (*s*, 6 H). MS (70eV): 283 (14), 282 (76, M^+), 268 (18), 267 (100), 234 (11), 239 (60), 209 (24), 202 (14), 195 (25), 194 (18), 193 (52), 187 (19), 179 (28), 167 (27), 165 (33), 157 (50), 141 (35), 128 (33), 115 (43), 91 (26), 77 (23). Anal. calc. for $C_{18}H_{18}O_3$ (282.343): C 76.57, H 6.42; found: C 76.58, H 6.59.

(1R,4R,5S,8S)-9,10-Dimethylidenetricyclo[6.2.2.0^{2,7}]dodec-2(7)-ene-4,5-dicarboxylic Anhydride (**9**). A mixture of 2,3,5,6-tetramethylidenebicyclo[2.2.2]octane (**8** [22]; 0.55 g, 3.48 mmol) and maleic anhydride (0.3 g, 3.06 mmol) in anh. benzene (10 ml) were shaken at 20° for 2 h. After solvent evaporation *in vacuo*, the crude adduct mixture was recrystallized from acetone to remove the bis-adducts. Then, the residue was recrystallized 5 × from AcOEt yielding 0.130 g (15%) of colourless crystals, m.p. 140° (dec.). UV (EtOH): 247 (8240), 201 (8690). UV (isooctane): 260 (4590), 250 (8100), 243 (8400), 195 (9270). IR ($CHCl_3$): 3040, 3020, 2960, 1850, 1790, 1430, 1240, 1060, 960, 880. ^{1}H-NMR ($CDCl_3$): 5.08 (*s*, 2 H); 4.88 (*s*, 2 H); 3.27 (*m*, 2 H); 3.02 (br. *s*, 2 H); 2.78 (*m*, 4 H); 1.31 (*m*, 2 H); 1.18 (*m*, 2 H). MS (70eV): 257 (3), 256 (M^+, 30); 220 (100); 201 (40). Anal. calc. for $C_{16}H_{16}O_3$ (256.303): C 74.98, H 6.29; found: C 75.0, H 6.46.

(4R,5S)-Tricyclo[6.1.1.0^{2,7}]dec-2(7)-ene-4,5-dicarboxylic Acid (**16**). Freshly sublimed maleic anhydride (25 mg, 0.26 mmol), 2,3-dimethylidenebicyclo[2.1.1]hexane (**14**, 54 mg, 0.51 mmol [24]) and wet acetone (0.8 ml) were heated to 100° for 86 h in a pyrex tube sealed *in vacuo*. After cooling to 20°, the tube was opened and the solvent evaporated *in vacuo*. The crude **16** was recrystallized from CH_2Cl_2/acetone/hexane 1:1:1 at –20° yielding 56 mg (99% based on maleic anhydride) of colourless crystals, m.p. 177° (dec.). UV (MeCN): 200 (4100), 215 (sh, 3600). IR (KBr): 3400, 3000, 2980, 2920, 1705, 1260. ^{1}H-NMR (CD_3COCD_3): 6.13–4.65 (*m*, 2 H, 2 OH); 3.11 (*m*, 2 H, H–C(1), H–C(8)); 2.68 (*m*, 6 H, CH_2(3), CH_2(6), H–C(5), H–C(6)); 2.43 (*m*, 2 H, H–C(9) and H–C(10) *syn* to C(2),C(7)); 2.25 (*m*, 2 H, H–C(9) and H–C(10) *anti* to C(2),C(7)). MS (70eV): 223 (2.5), 222 (2.8 M^+), 204 (4), 176 (7.5), 131 (100), 130 (58), 91 (95). Anal calc. for $C_{12}H_{14}O_4$ (222.24): C 64.85, H 6.35; found: C 64.61, H 6.15.

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