172. The π-Anisotropy of the Double Bond of a *syn*-11-Oxasesquinorbornene Derivative[1]). Stereoselectivity of the *Diels-Alder* Additions of (2-Norborneno)[*c*]furan[2]). Crystal Structure of 11-oxa-*endo*-tetracyclo[6.2.1.1^{3,6}.0^{2,7}]-dodec-2(7)-ene-9,10-*exo*-dicarboxylic Anhydride

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Summary

The reaction of (2-norborneno)[*c*]furan (**4**) with maleic anhydride gave 11-oxa-*endo*-tetracyclo[6.2.1.1^{3,6}.0^{2,7}]dodec-2(7)-ene-9,10-*exo*-dicarboxylic anhydride (**5**) and, with methyl acetylenedicarboxylate, methyl 11-oxa-*endo*-tetracyclo [6.2.1.1^{3,6}.0^{2,7}]dodeca-2(7),9-diene-9,10-dicarboxylate (**7**). The *syn*-11-oxa-sesquinorbornenes **5** and **7** could be equilibrated with their cycloaddents. They are at least 2 kcal/mol more stable than the corresponding *anti*-sesquinorbornenes **6** and **8**. The structure of **7** was deduced from its spectral data, by epoxidation with air or a peracid to give the *exo*-epoxide **13** and by catalytic hydrogenation to give **14**. The structure of **5** was established by single-crystal X-ray diffraction. A dihedral angle of 163° was measured between the C(1,2,7,8) and C(2,3,6,7) planes in **5**. This important deviation from planarity for the C(2,7) double bond is attributed to (π, σ)-repulsive interactions that make the π-electron density of 2-norbornene and 7-oxa-2-norbornene derivatives preferentially polarized toward the *exo*-face. This finding is discussed in relation with the relative stability of the *syn*- and *anti*-11-oxasesquinorbornenes and with the *endo*-stereoselectivity of the cycloadditions of the norbornenofuran **4**.

Introduction. – The stereoselectivity of the *Diels-Alder* additions to 3b,4,6,6a-2*H*-tetrahydrobis(cyclopentadienylene) **1**, "isodicyclopentadiene", has been investigated by several authors [1–3]. In the cycloaddition of methyl acrylate, methyl propiolate [1b] [2], *N*-methyl-triazolinedione [3], methyl acetylenedicarboxylate, phenylvin-

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[1]) The name "sesquinorbornene" is generally used for 1,2,3,4,5,6,7,8-octahydro-1,4,5,8-dimethanonaphthalene [1]. We use the IUPAC numeration derived from tetracyclo[6.2.1.1^{3,6}.0^{2,7}]dodec-2(7)-ene.

[2]) For a preliminary communication, see [8].

[3]) Author to whom correspondence should be addressed.

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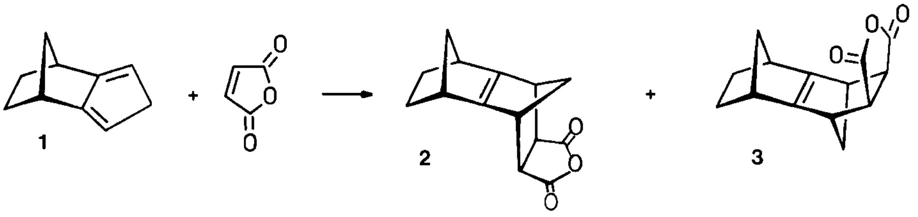
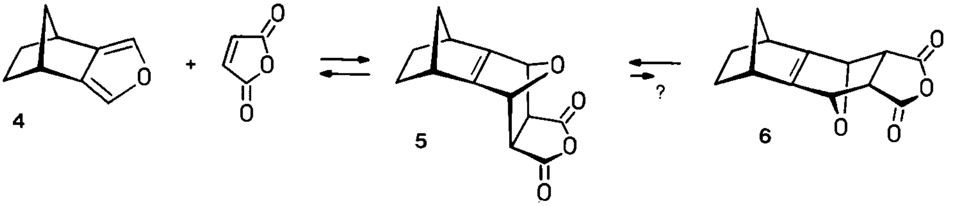
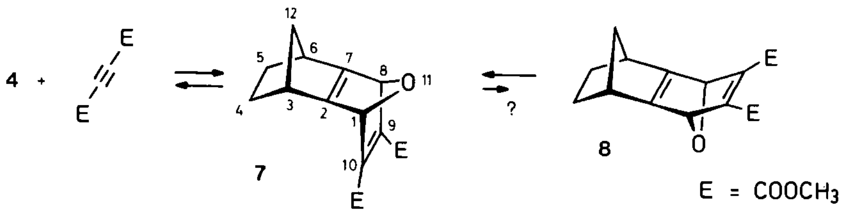
ylsulfone, benzoquinone and dehydrobenzene [1b] *endo*-attack was found to be preferred. The photooxidation of **1**, however, proceeded only with moderate *endo* stereoselectivity [4]. With maleic anhydride[4]), the *endo/exo*-selectivity (product ratio **2**/**3**) varied between 55:45 to 35:65 depending upon the temperature and the solvent [5]. *Paquette et al.* [1b] [3] [4] attributed the *endo* preference to secondary orbital interactions between the dienophiles and **1**. They assumed a kinetic stereoelectronic control that is independent of a kinetic control due to a possible stability difference between the *endo* and *exo* adducts. If the *Bell-Evans-Polanyi* principle [6] is followed, the most stable isomer would be also the fastest to be formed!



We have developed a synthesis for (2-norborneno)[c]furan (**4**), an oxa-analog of **1** [7]. Because of the aromaticity of the furan ring, **4** can be equilibrated with this cycloadducts even at room temperature when strong dienophiles are involved. This allows one, in principle, to test whether the cycloadditions give different stereoselectivities under kinetic and thermodynamic control [8]. We report the high *endo*-stereoselectivity of the *Diels-Alder* additions of **4** to maleic anhydride and methyl acetylenedicarboxylate giving the adducts **5** and **7**, respectively. In these two cases, the *endo*-adducts were found to be at least 2 kcal/mol more stable than the corresponding *exo*-isomers **6** and **8**. This is probably due to the "synergic" effect of the double bond π-anisotropy of the norbornene [9] and 7-oxanorbornene [10] systems joined together by the same double bond in the *syn*-oxasesquinorbornene derivatives **5** and **7**. The single-crystal X-ray structure of **5** confirms the hypothesis.





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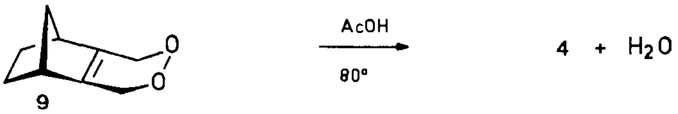
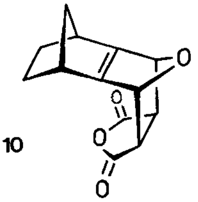
[4] We thank Professor *P. D. Bartlett* for a preprint of his recent work on the double bond deformation in two crystalline derivatives of *syn*-sesquinorbornene [5].

Results and discussion. – The (2-norborneno)[c]furan (**4**) was formed as a minor product (*ca.* 1%) during the gas phase or solution (benzene or pentane, 130°) pyrolysis of the *endo*-peroxide **9** obtained by photooxidation of 2,3-dimethylidenenorbornane [7]. However, when heated in AcOH (containing 1% Ac_2O) for 1 h at 80°, **9** furnished the norbornenofuran **4** (61% isolated yield) together with some polymeric material[5]).



A priori, four isomeric adducts **5**, **6**, **10**, and **11**, can be formed in the *Diels-Alder* addition of **4** to maleic anhydride. At –60° ($CDCl_3$) or at higher temperatures, only **5** was observed. The equilibrium constants $K_{21°} \simeq 22$ and $K_{77°} \simeq 0.6$ $lmol^{-1}$ were measured ($CDCl_3$) for the reaction **4** + maleic anhydride $\rightleftarrows$ **5** (by ^{1}H-NMR., the equilibrium was reached in a few minutes at 77°C). No trace of the other isomeric compounds **6**, **10**, or **11** (or other products) could be detected by TLC., or by ^{1}H- and ^{13}C-NMR. even after prolonged heating in $CDCl_3$ or benzene at 150° (sealed pyrex tubes, several days), thus suggesting that the kinetically formed adduct **5** is also the most stable isomer[6]). Considering a detection limit of 1% one can estimate **5** to be at least 2.5 kcal/mol more stable than any other isomer.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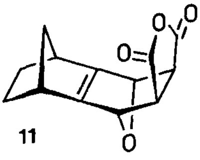
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Similarly, methyl acetylenedicarboxylate added to **4** with high *endo*-stereoselectivity giving the adduct **7**. At 21°C, the equilibrium ($K_{21°} \simeq 280$ $lmol^{-1}$ in $CDCl_3$) was reached in *ca.* 12 h. No other adduct could be detected at higher temperatures. Prolonged heating at 150° led to slow decomposition into polymeric material and some

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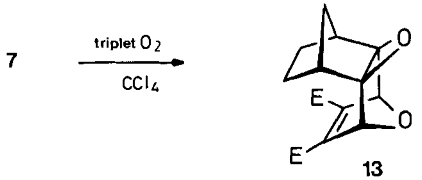
[5]) The synthesis of 2,5-diphenylfuran was achieved similarly by *Berthelot et al.* [11] by dehydrating the corresponding *endo*-peroxide in AcOH + 1% H_2SO_4. Under these conditions, **4** was rapidly polymerized. *Demole et al.* prepared the solanofuran by dehydratation of the corresponding *endo*-peroxide with basic alumina [12]. Under the latter conditions (Al_2O_3, benzene, 2 days, 25°), **9** was isomerized into *trans*-2,3-bis(formyl)norbornane. Rhodium(I) complexes promoted the *Kornblum-DeLa Mare* rearrangement [13] of **9** and allowed the isolation of the corresponding 2-formyl-3-(hydroxymethyl)-2-norbornene [7] [14]. Asymmetric induction was observed when this rearrangement was catalyzed by natural, optically pure bases [14].

[6]) Considering a rate constant $k > 1/60$ $lmol^{-1}s^{-1}$ at 77° for the *endo*-attack, we estimate a $\Delta G^{\neq} < 23.5$ $kcalmol^{-1}$ and $\Delta H^{\neq} < 13$ $kcalmol^{-1}$ assuming a $\Delta S^{\neq} = -30$ e.u. At 150° and after 10 days, we can consider $k < 1/200{*}3600$ $lmol^{-1}s^{-1}$, thus giving $\Delta G^{\neq} > 36.5$ $kcalmol^{-1}$ and $\Delta H^{\neq} > 21$ $kcalmol^{-1}$ for the *exo*-attack, if the *exo*-isomer **6** or **11** should be as stable as **5**. This is a much higher activation enthalpy than 13 kcal mol^{-1} and makes it difficult to admit that **6** or **11** had no time to be generated at 150° after 10 days. It is more reasonable to admit that the *exo*-adducts are less stable than the *endo*-adduct and because of that, they are not observed under our equilibrium conditions.

methyl 3,4-furandicarboxylate [15]. The adduct **7** was not isolated as it reacted with air yielding the epoxide **13** (40–50%) together with various oxidized oligomers (in the dark or in the light). The same epoxide **13** was formed by treatment of **7** with *m*-chloroperbenzoic acid in CH_2Cl_2. Analogous autooxidations of norbornene derivatives have been reported by *Jefford et al.* [16] and *Paquette et al.* [17]. In contrast, the maleic anhydride adduct **5** was stable toward triplet oxygen. Similar reactivity trends and selectivities (between the two double bonds in **7**) have been reported recently for sesquinorbornene derivatives [17].



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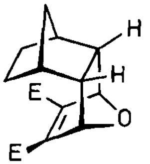
The structure of **13** was deduced from its elemental analysis and spectral data. In the ^{13}C-NMR. spectrum, a typical $\delta_C = 63.2$ ppm (triplet) was observed for the methano bridge (*cf.* [17]). The spectral data of **7** and **13** did not allow us to distinguish between **7** and **8**. However, catalytic hydrogenation of the adduct (H_2,Pd/C,acetone, 20°, 1 h) gave **14** whose structure was established from its ^{1}H- and ^{13}C-NMR.spectra. Vicinal coupling constants (^3J(H,H) $\approx$ 2–3 Hz) were measured between the bridgehead protons of the 7-oxanorbornane [18] ($\delta_H = 5.0$ ppm) and of the norbornane [19] ($\delta_H = 2.27$ ppm), and the adjacent tertiary H-atoms ($\delta_H = 2.84$ ppm), thus establishing the configuration *endo, endo* for **14** and, consequently, *endo* for **7**[7]). The structure of the adduct **5** was suggested by its spectral data. Distinctions between the isomeric pairs *endo, exo*-**5**/*exo, exo*-**6** and *endo, endo*-**10**/*exo, endo*-**11** was based on the observation of a vicinal coupling constant <0.5 Hz between the bridgehead H-atoms H–C(1,8) of the oxanorbornane ($\delta_H = 5.37$ ppm) and the H-atoms H–C(9,10) adjacent to the carboxylic groups ($\delta_H = 2.89$ ppm). Interestingly, a ^5J(H,H) $\simeq$ 1 Hz was measured between the norbornane (H–C(3,6), $\delta_H = 3.2$ ppm)[8])



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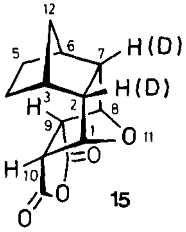

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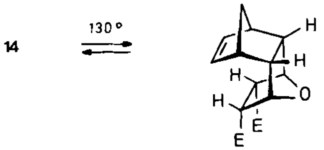
[7]) The structure of **14** was further confirmed by the observation of a thermoneutral dyotropic transfer of two H-atoms. This work is reported elsewhere [20].



[8]) Furans are known to give *exo*-adducts under thermodynamic control [21].

and the 7-oxanorbornane bridgehead protons. Catalytic hydrogenation of **5** ($H_2(D_2)$, Pd/C, acetone, –30°) gave **15** whose configuration was given unambiguously by the ^3J(H,H) coupling constants between the bridgehead and vicinal H-atoms and a NOE. of *ca.* 27% on H–C(9,10) by irradiating H–C(4,5) (80 MHz). One cannot exclude a fast equilibrium **6**$\rightleftarrows$**5** where **5** would be less stable than **6** but much more reactive than **6** under our hydrogenation conditions, even though the equilibrium **5**$\rightleftarrows$**4** + maleic anhydride was found not to be reached after 24 h at –30°. In order to eliminate this hypothetical ambiguity, we measured the X-ray single-crystal structure of the maleic anhydride adduct to **4**. This proved unequivocally the structure **5** for this adduct (see *Fig. 1, 2*).

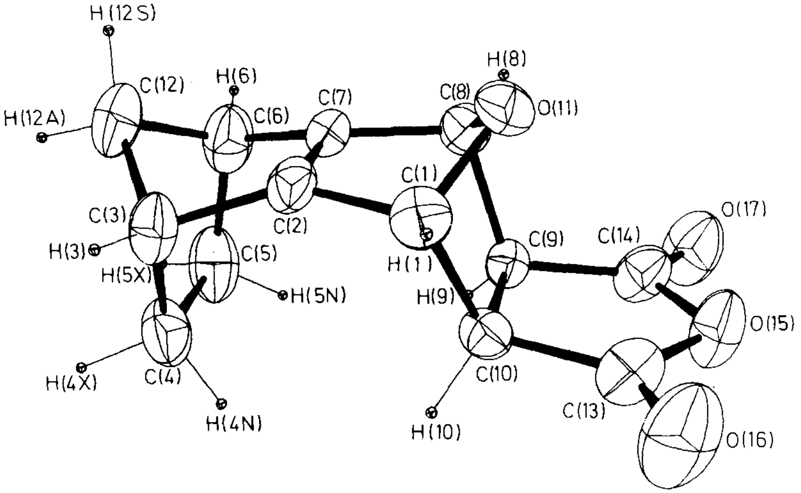


Fig. 1. *Perspective drawing of* **5** *prepared by ORTEP*

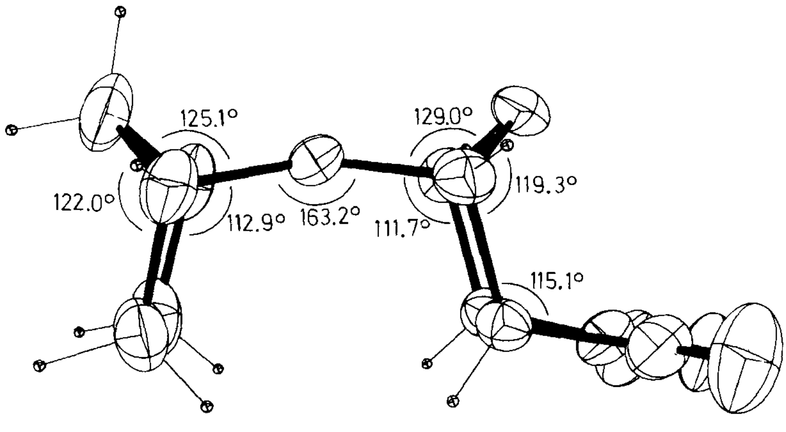
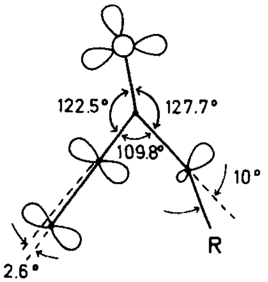


Fig. 2. *View of* **5** *down the C(2)–C(7) double bond showing interplanar angles*

Bond lengths and valence angles are given in *Tables 1* and *2*. Interplanar angles are given in *Table 3* and the shortest intermolecular contacts in *Table 4*. The C(2,7) distance of 1.335 Å in **5** is normal for an isolated double bond. Angles of 106° and 108° between the double and single bonds as well as the angles of less than 100° between the single bonds of the methano C(3)–C(12)–C(6) and oxa C(1)–O(11)–C(8) bridges and the large (142°) exocyclic angles at C(2) and C(7) correspond to the ring strain inherent in the 2-norbornene [22] and 7-oxa-2-norbornene systems [10] [23]. The interplanar angle of 163° between C(1,2,7,8) and C(3,2,7,6) indicate a significant deviation of the C(2,7) double bond from planarity. This cannot be attributed to intermolecular forces (see *Table 4*). Torsional effects between the substituents may also be ruled out. We found in the 5,6-dimethylidene-7-oxa-2-norbornene derivative **16** a deviation toward the *endo*-face of 10° for the R-substituents on the endocyclic double bond, whereas an insignificant deviation of *ca.* 2.5° was measured for the exocyclic diene [10a]. Torsional effects involving the bridgehead H-atoms as well as rehybridization of the olefinic C-atoms due to bond angle deformations would have led to similar out-of-plane distortions for both the exocyclic diene and the R-substituents. Repulsive interactions between the H-atoms H–C(4,5*endo*) and H–C(9,10*endo*) in **5** (separated by 2.35 Å) would tend to reduce the bending of the C(2,7) double bond. If one assumes a 10° deviation due to the 7-oxanorbornene subsytem [10a], a contribution of at least 7° must be attributed to the 2-norbornene subsystem in **5** to yield the observed 17° deviation from planarity of the C(2,7) double bond. These values are larger than those predicted by recent MO calculations [10b, 9c]. We feel that electronic correlation (MO calculations using extended basis sets and configuration interactions) must be considered to approach a possible rationale of our observations.



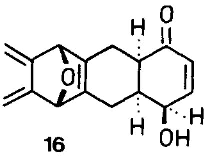


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Table 1. *Bond lengths* (Å) *with e.s.d's in parentheses for* **5**[a])

C(4)–C(5)	1.546(5)	C(10)–C(13)	1.504(5)	C(6)–C(7)	1.504(5)
C(3)–C(4)	1.553(7)	C(13)–O(15)	1.388(4)	C(7)–C(8)	1.507(5)
C(3)–C(12)	1.541(5)	C(13)–O(16)	1.187(4)	C(8)–O(11)	1.451(4)
C(2)–C(3)	1.505(5)	C(9)–C(10)	1.535(4)	C(8)–C(9)	1.574(5)
C(1)–C(2)	1.503(4)	C(2)–C(7)	1.335(4)	C(9)–C(14)	1.500(5)
C(1)–O(11)	1.448(3)	C(5)–C(6)	1.551(7)	C(14)–O(15)	1.393(4)
C(1)–C(10)	1.567(6)	C(6)–C(12)	1.551(7)	C(14)–O(17)	1.190(4)

H(4*endo*)...H(10*endo*) 2.37(4); H(5*endo*)...H(9*endo*) 2.32(4)

[a]) C–H bond lengths lie in the range 0.93(3)–1.05(4) Å.

Table 2. *Bond angles (°) with e.s.d's in parentheses for* **5**

C(3)–C(4)–C(5)	103.3(3)	C(9)–C(10)–C(13)	104.3(3)	C(5)–C(7)–C(2)	105.8(2)
C(2)–C(3)–C(4)	106.7(3)	C(10)–C(13)–O(16)	129.2(3)	C(7)–C(8)–O(11)	101.2(3)
C(4)–C(3)–C(12)	100.8(3)	C(10)–C(13)–O(15)	110.5(2)	C(7)–C(8)–C(9)	106.2(3)
C(2)–C(3)–C(12)	98.5(3)	O(15)–C(13)–O(16)	120.3(3)	C(9)–C(8)–O(11)	100.0(2)
C(3)–C(2)–C(1)	141.9(2)	C(13)–O(15)–C(14)	110.2(3)	C(8)–C(9)–C(10)	101.4(3)
C(3)–C(2)–C(7)	107.8(2)	C(1)–O(11)–C(8)	96.9(2)	C(8)–C(9)–C(14)	112.2(2)
C(1)–C(2)–C(7)	106.4(3)	C(4)–C(5)–C(6)	103.4(4)	C(10)–C(9)–C(14)	104.3(2)
C(2)–C(1)–O(11)	101.1(2)	C(5)–C(6)–C(7)	106.8(3)	C(9)–C(14)–O(17)	130.6(3)
C(2)–C(1)–C(10)	107.7(3)	C(5)–C(6)–C(12)	100.3(3)	C(9)–C(14)–O(15)	110.4(3)
C(10)–C(1)–O(11)	99.1(3)	C(7)–C(6)–C(12)	98.4(3)	O(15)–C(14)–O(17)	119.0(3)
C(1)–C(10)–C(9)	102.0(2)	C(6)–C(7)–C(8)	142.3(3)	C(3)–C(12)–C(6)	94.1(3)
C(1)–C(10)–C(13)	109.1(3)	C(6)–C(7)–C(2)	108.1(3)		

Table 3. *Angles (°) between least squares planes* a)

Plane 1	Plane 2	Angle
C(3)–C(6)–C(12)	C(3)–C(6)–C(4,5)	122.0
C(3)–C(6)–C(12)	C(3)–C(6)–C(2,7)	125.1
C(3)–C(6)–C(4,5)	C(3)–C(6)–C(2,7)	112.9
C(2)–C(7)–C(3,6)	C(2)–C(7)–C(1,8)	163.2
C(1)–C(8)–C(2,7)	C(1)–C(8)–O(11)	129.0
C(1)–C(8)–C(2,7)	C(1)–C(8)–C(9,10)	111.7
C(1)–C(8)–O(11)	C(1)–C(8)–C(9,10)	119.3
C(9)–C(10)–C(1,8)	C(9)–C(10)–C(13,14)	115.1

a) All planes have been defined by three points to obtain best torsion angles. Atoms named C(n,m) refer to the mid-point of the line C(n)–C(m).

Table 4. *Shortest intermolecular contacts* (Å)

O(15)...H(10)	2.67(3)	H(3)... H(1)	2.81(4)
O(15)...H(9)	2.66(2)	H(12*syn*)... H(1)	2.88(4)
O(16)...H(5*exo*)	2.78(3)	H(12*syn*)... H(8)	2.78(5)
O(16)...H(8)	2.41(2)	H(1)... H(1)	2.87(4)
O(17)...H(5*endo*)	2.85(3)	H(1)... H(6)	2.89(3)
O(17)...H(9)	2.67(2)	H(10)... H(6)	2.67(4)
O(17)...H(10)	2.70(2)	C(2)... H(1)	2.72(3)

Table 5. *Summary of crystal data, intensity measurements, structure solution and refinement*

Formula	$C_{13}H_{12}O_4$	λ (Å)	0.71069
Molecular weight	232.2	μ (cm^{-1})	1.2
Crystal dimensions (mm)	0.31 × 0.26 × 0.17	Scan method	2θ–θ
		Backgrounds from	Scan profile interpretation [38]
Crystal system	Monoclinic		
a (Å)	12.239(1)	$(\sin\theta/\lambda)_{max}$	0.54
b (Å)	8.0649(8)	No. of unique reflections	1408
c (Å)	12.281(1)	No. of reflections $<3\sigma$	547
β (°)	117.797(9)	No. of observations/ No. of variables	7.0 (5.6)[a])
V ($Å^3$)	1072.3(2)		
Z	4	Structure solution	MULTAN [44] and Fourier
d_{calcd} ($g–cm^3$)	1.44		
d_{obsd} ($g.cm^{-3}$)	1.44	Refinement method	Blocked least squares
F_{000}	488	Function minimised	$\Sigma w(\lvert Fo\rvert - \lvert Fc\rvert)^2$
Space group	$P2_1/n$	w	$1/\sigma^2$
Systematic absences	h0l h + l = 2n + 1	R	0.038
	0k0 k = 2n + 1	R_w	0.036
Radiation	Mo–K_α (niobium filtered)	Goodness of fit	1.99

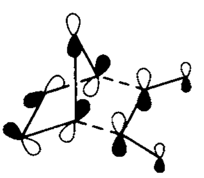
[a]) Only those "less-thans" (reflections with $I < 3\sigma$) with $\lvert Fc\rvert > \lvert Fo\rvert$ were included in the refinement.

Kawamura et al. have established the pyramidal geometry of the 2-norbornyl and 7-oxa-2-norbornyl radicals, with the H–C(2) bond tilting in the *endo* direction [24]. This deformation allows the accomodation of the relatively small C(1,2,3) bond angles (see MO calculations on deformed ethylene [25]); the pyramidalization reduces the extra ring strain introduced by a sp^2-centre. The π-polarization toward the *exo* rather than toward the *endo*-face has been attributed to orbital mixing involving the methano bridge [9]. We favour the hypothesis of an electronic repulsion between the π-electrons and those of the adjacent σ-bonds of the ethano bridge in 2-norbornene and 7-oxa-2-norbornene. The latter bonds are better aligned with the 2p-orbitals of the endocyclic double bond than are the σ-bonds of the methano or oxa bridges.

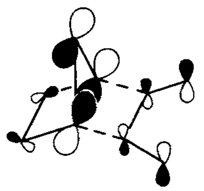
The 2-norbornene can be viewed as resulting from the interactions of a puckered cyclopentane ring with an ethylene group [26] [27]. The electron density in this cyclopentane ring is distributed between symmetric (a′) and antisymmetric (a″) MO's [28]. Because the nodal plane (the miror plane in 2-norbornene) cuts one of the σ-bonds (the σ-bond C(5,6)); the a″ MO's have their electron density polarized towards C(7) and consequently, the a′ MO's compensate that polarization by concentrating the electron density in the opposite direction, *i. e.* C(5,6) of the C(1,7,4,5,6) cyclopentane group of 2-norbornene *(cf. Fig. 3)*. The cyclopentane ring resembles the cyclopropane more than the cyclobutane ring as far as its hyperconjugating ability is concerned [27] [29]. Thus, the π-electron density in 2-norbornene is "pushed" away from the *endo*-face by the a′ MO's localized on the C(1,7,4,5,6) cyclopentane fragment, leading to the deviation from planarity observed for the π(2,7)-bond of **5** (and other 2-norbornene derivatives). In the case of a 2,3-dimethylidenenorbornane, the π-electron density of the exocyclic diene is "pushed" by two competing and opposite interactions, *i. e.* π_1(a′)↔cyclopentane a′ MO's (leading to *exo*-

Table 6. *Positional and thermal parameters for* **5** *with standard deviations in parantheses*

Atom	X	Y	Z	U11 (or U)	U22	U33	U12	U13	U23
C(1)	0.8934(3)	0.9880(4)	0.5629(3)	0.034(2)	0.037(2)	0.043(2)	0.003(2)	0.024(2)	–0.001(2)
C(2)	0.8603(3)	1.1448(4)	0.4880(3)	0.039(2)	0.034(2)	0.038(2)	–0.002(2)	0.027(2)	0.002(2)
C(3)	0.9028(3)	1.3206(4)	0.4908(3)	0.038(2)	0.043(2)	0.054(2)	–0.008(2)	0.025(2)	0.007(2)
C(4)	0.8514(3)	1.4235(5)	0.5637(4)	0.058(2)	0.030(2)	0.063(3)	–0.007(2)	0.033(2)	–0.001(2)
C(5)	0.7102(3)	1.4196(5)	0.4794(4)	0.053(2)	0.035(2)	0.084(3)	0.008(2)	0.038(2)	0.015(2)
C(6)	0.6960(3)	1.3131(5)	0.3683(4)	0.045(2)	0.051(3)	0.050(2)	–0.005(2)	0.014(2)	0.018(2)
C(7)	0.7382(3)	1.1408(4)	0.4164(3)	0.043(2)	0.033(2)	0.028(2)	–0.007(2)	0.018(2)	0.002(2)
C(8)	0.6948(3)	0.9809(4)	0.4469(3)	0.033(2)	0.040(2)	0.031(2)	–0.009(2)	0.012(2)	–0.002(2)
C(9)	0.7046(3)	1.0057(4)	0.5783(3)	0.029(2)	0.027(2)	0.030(2)	–0.001(2)	0.016(1)	0.002(2)
C(10)	0.8451(3)	1.0048(4)	0.6602(3)	0.029(2)	0.030(2)	0.031(2)	–0.003(2)	0.015(2)	–0.004(2)
C(12)	0.8117(4)	1.3699(5)	0.3576(4)	0.075(2)	0.047(3)	0.060(3)	–0.007(2)	0.038(2)	0.018(2)
C(13)	0.8700(3)	0.8458(4)	0.7319(3)	0.043(2)	0.049(2)	0.039(2)	0.006(2)	0.021(2)	0.007(2)
C(14)	0.6602(3)	0.8569(4)	0.6196(3)	0.041(2)	0.050(2)	0.037(2)	–0.001(2)	0.022(2)	0.006(2)
O(11)	0.8011(2)	0.8748(2)	0.4781(2)	0.058(1)	0.030(1)	0.044(1)	–0.003(1)	0.032(1)	–0.009(1)
O(15)	0.7601(2)	0.7651(3)	0.7045(2)	0.046(1)	0.049(2)	0.055(2)	–0.001(1)	0.024(1)	0.022(1)
O(16)	0.9660(2)	0.7859(3)	0.8017(2)	0.047(1)	0.072(2)	0.071(2)	0.018(1)	0.017(1)	0.035(2)
O(17)	0.5582(2)	0.8115(3)	0.5927(2)	0.043(1)	0.075(2)	0.065(2)	–0.016(1)	0.026(1)	0.017(1)
H(1)	0.981(2)	0.942(3)	0.601(2)	0.032(8)					
H(3)	0.986(2)	1.338(3)	0.517(2)	0.035(8)					
H(4N)	0.877(2)	1.377(3)	0.649(3)	0.05(1)					
H(4X)	0.885(3)	1.544(4)	0.575(3)	0.06(1)					
H(5N)	0.667(3)	1.372(4)	0.521(3)	0.06(1)					
H(5X)	0.675(3)	1.530(4)	0.448(3)	0.07(1)					
H(6)	0.616(2)	1.323(3)	0.295(3)	0.039(9)					
H(8)	0.620(2)	0.930(3)	0.389(2)	0.040(9)					
H(9)	0.664(2)	1.101(3)	0.584(2)	0.018(7)					
H(10)	0.879(2)	1.100(3)	0.716(2)	0.023(8)					
H(12S)	0.827(3)	1.304(4)	0.292(3)	0.07(1)					
H(12A)	0.813(2)	1.490(4)	0.343(2)	0.045(9)					



π_1(a′)



π_2(a″)

polarization of π_1) and $\pi_2(a'') \leftrightarrow$ C(1,7,4,5,6) cyclopentane a″ MO's (leading to *endo*-polarization of π_2). Consequently, an insignificant deviation from 180° for the angle between the C(1,2,3,4) plane and the exocyclic diene is expected in 2,3-dimethylidenenorbornane. This hypothesis is supported by our results on the crystal structure of **16** [10a]9).

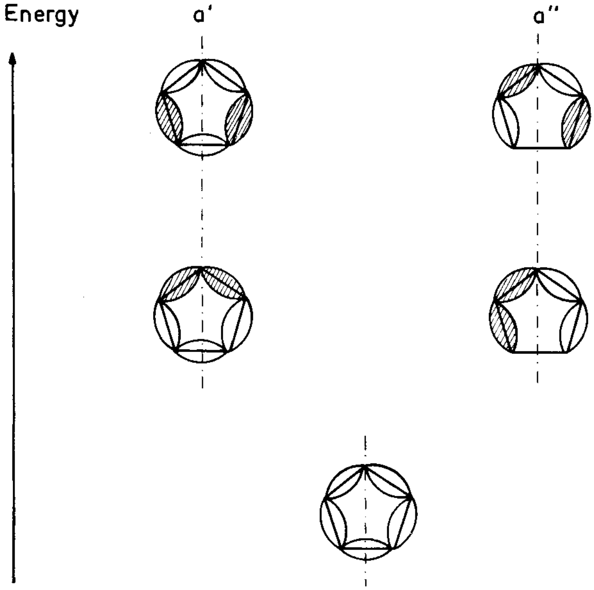


Fig. 3. *Schematic representation of the occupied MO's of a cyclopentane ring as a combination of five σ(CC)-bonds.* The contribution of the σ(CH)-bonds are ignored (*cf.* also [27] [28]).

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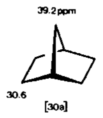
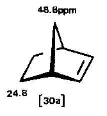
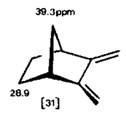
9) The endocyclic double bond in 2-norbornene derivatives exerts a remarkable downfield-shift of 10–17 ppm on the bridge C-atom C(7) chemical shift relative to the saturated analogs [30]. This positive γ-effect on C(7) is accompanied by a negative γ-effect on C(5,6). These effects are not observed in 2,3-dimethylidenenorbornanes [31], in acyclic, monocyclic hydrocarbons [32] and in the bicyclo[2.2.2]octane series [33]. It appears therefore that there is a correlation between the π-anisotropy of the endocyclic double bond and of the exocyclic diene at C(2,3) and the γ-effects on C(5,6,7) in norbornane derivatives (see also the ^{17}O-chemical shifts in the corresponding 7-oxanorbornanes [34]).







The relatively high stability of the *endo*-adducts **5** and **7** is most probably due to the "synergic" effect of the double π-anisotropy of the norbornene and 7-oxanorbornene joined together by the C(2,7) double bond in the corresponding *syn*-11-oxasesquinorbornenes. In the *exo*-isomers **6** and **8**, such an effect cannot intervene. The apparent kinetic *endo*-stereoselectivity of the cycloadditions of the furan **4** (at low temperature) parallels the relative stability of the isomeric adducts (the *Bell-Evans-Polanyi* principle might well be followed [6]!)

The high *exo*-stereoselectivity of the catalytic hydrogenations of **5**→ **15** and **7**→ **14**, as well as that of the epoxidation **7**→ **13** is easily understood in terms of the *exo*-π-anisotropy of the C(2,7) double bond in these systems. The enhanced reactivity of the C(2,7) double bond in **7** toward triplet O_2 compared to that in **5** might be due to a larger deviation from planarity of the C(2,7) bond in **7** than in **5** because of the additional polarization induced by the homoconjugated C(9,10) double bond.

The enhanced reactivity and high *exo*-stereoselectivity of 2-norbornene toward electrophilic reagents [35] is readily explained by the *exo*-π-anisotropy evidenced in this work and predicted theoretically [9].

Conclusion. – The stability of *syn*-11-oxasesquinorbornenes with respect to their *anti*-isomers is attributed to a "synergic" effect of the polarization of the double bond π-electron density in the *exo*-face of the norbornene and oxanorbornene subsystems joined together by the same C(2,7) double bond. The kinetic *endo*-stereoselectivity of the cycloadditions of the (2-norborneno)[*c*]furan (**4**) to maleic anhydride and methyl acetylenedicarboxylate is parallel to the thermodynamic stereoselectivity. Electronic repulsions involving the π-electrons of the endocyclic double bond and the σ-electrons of the hyperconjugating 5-membered rings are probably responsible for the π-anisotropy in 2-norbornenes and 7-oxa-2-norbornenes.

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Experimental Part

General remarks. See [36].

(2-Norborneno)[d]*(3,6-dihydro-1,2-dioxine)* (**9**). 2,3-dimethylidenenorbornane[37] (19 g, 0.158 mol) in freshly distilled CH_2Cl_2 (400 ml) containing *meso*-tetraphenylporphine (30 mg, 0.049 mmol) was irradiated (iodine lamp, 24V/10A, *Phillips*, pyrex vessel, 0°) while bubbling O_2 through the solution. After disappearance of the diene (*ca.* 30 min), the solvent was evaporated and the residue distilled *i. v.* (behind a protecting screen!). Yield: 18.8 g (78%), colourless liquid, b.p. 30–40°/10^{-2} Torr. – UV. (isooctane): final absorption. – IR. ($CHCl_3$): 2960, 2890, 2855, 1675, 1460, 1435, 1365, 1305, 1230, 1160, 1130, 1075, 1045, 1020, 990, 960, 950, 925, 880, 865. – ^{1}H-NMR. ($CDCl_3$, 30°): 4.74 ($d \times m$, $J = 16.1$, 2 H, H_2C–O); 4.51 ($d \times m$, $J = 16.1$, H_2C–O); 2.90 (*m*, 2 H); 1.9–0.95 (*m*, 6 H). – ^{13}C-NMR. ($CDCl_3$, 30°): 137.0 (*m*, 2 C); 69,7 (*t*, 144.0 2 CH_2–O); 46.7 (*t*, 135); 42.5 (*d*, 140); 26.0 (*t*, 135). – MS. (70 eV): 152 (20), 136 (37), 120 (29), 105 (24), 95 (35), 92 (100), 91 (63), 81 (30), 79 (72), 77 (46), 67 (77), 66 (40), 65 (34), 55 (32), 53 (35), 41 (52), 39 (65).

$C_9H_{12}O_2$ (152.18) Calc. C 71.03 H 7.95% Found C 71.17 H 7.98%

(2-Norborneno)[c]*furan* (**4**). The dioxine **9** (1 g, 6.6 mmol) was heated in AcOH (10 ml) and Ac_2O (100 mg) to 80° for 3 h. After cooling to RT., pentane (100 ml) and water (100 ml) were added. The aque-

ous solution was extracted with pentane (2 × 50 ml). The organic extracts were washed with water (2 × 100 ml), the with sat. soln. of $NaHCO_3$ (2 × 100 ml). After drying ($MgSO_4$), the solvent was removed *i. v.* and the residue distilled. Yield: 0.52 g (60%), colourless liquid, b.p. 25°/10^{-3} Torr. – UV. (isooctane): 255 (1700). – IR. ($CHCl_3$): 2975, 2960, 2930, 2880, 1670, 1570, 1470, 1450, 1360, 1300, 1265, 1155, 1120, 1080, 1000, 950, 915, 900, 870, 825. – ^{1}H-NMR. ($CDCl_3$): 7.01 (*s*, 2 H); 3.30 (*m*, 2 H); 2.07–1.17 (*m*, 6 H). – ^{13}C-NMR. ($CDCl_3$): 134.8 (*m*, 2 C), 129.6 (*d* × *d*, 202.3, $^3J = 6.0$, 2 C); 50.6 (*t* × *m*, 132, 1 C); 36.8 (*d* × *m*, 150.2, 2 C); 28.6 (*t* × m, 135, 2 C). – MS (70 eV): 134 (87.5), 129 (91), 127 (47), 106 (56), 105 (86), 91 (100), 79 (31), 78 (63), 77 (59), 51 (31).

$C_9H_{10}O$ (134.18) Calc. C 80.56 H 7.51% Found C 80.70 H 7.59%

11-Oxa-endo-*tetracyclo[6.2.1.1^{3,6}.0^{2,7}]dodec-2(7)-ene-9,10*-exo-*dicarboxylic anhydride* (maleic anhydride adduct to **4**) (**5**). The furan derivative **4** (0.5 g, 3.7 mmol) and maleic anhydride (0.363 g, 3.7 mmol) in CH_2Cl_2 (1.5 ml) were stirred under N_2 at 25° for 12 h. After the addition of hexane (1.5 ml), the mixture was cooled to –20° and the precipitate was collected and recrystallized from CH_2Cl_2/hexane 1:1. Yield: 0,713 g (83%), colourless crystals, m.p. 115–117° (dec.: *retro-Diels-Alder*). – UV. (isooctane): final absorption. – IR. ($CHCl_3$): 3000, 2990, 2880, 1875, 1835, 1785, 1315, 1220, 1130, 1120, 1080, 1040, 1010, 950, 920, 865, 855, 835. – ^{1}H-NMR. ($CDCl_3$): 5.37 (*d*, $^5J_{(1,6)} = {}^5J_{(3,8)} \approx 1$, H–C(1,8)); 3.2 (*m*, H–C(3,6)); 2.89 (*s*, H–C(9,10)); 1.58–1.93 (*m*, 3 H); 1.31 (*m* × *d*, $J = 9.0$ and 1.6, 1 H); 0.73 (*d* × *m*, 12.0, 5.0, 2.4, 2 H). – ^{13}C-NMR. (CD_3CN): 172.1 (*d*, $^3J = 1.9$, C=O); 156.4 (*m*, C(2,7)); 83.2 (*d* × *d*, 171, $^3J = 9$, C(1,8)); 51.6 (*t* × *m*, 137, $^3J = 6.5$, C(12)); 50.7 (*d*, 150.0, C(9,10)); 42.7 (*d* × *d*, 150.0, $^3J = 9$, C(3,6)); 24.9 (*t* × *m*, 133.0, C(4,5)). – MS. (70 eV): 232 (2), 187 (3), 135 (11), 134 (100), 133 (21), 132 (12), 131 (11), 119 (67), 115 (10), 106 (71), 105 (59), 104 (17), 103 (22), 91 (51), 79 (16), 78 (48), 77 (38).

$C_{13}H_{12}O_4$ (232.24) decomposes *(retro-Diels-Alder)*, see hydrogenated derivative **15**.

Methyl 11-oxa-endo-*tetracyclo[6.2.1.1^{3,6}.0^{2,7}]dodeca-2(7),9-diene-9,10-dicarboxylate* (adduct of methyl acetylenedicarboxylate to **4**) (**7**). Furan derivative **4** (0.5 g, 3.7 mmol) and methyl acetylenedicarboxylate (0.525 g, 3.7 mmol) in CD_3CN (1.5 ml) were stirred under N_2 at 25° for 12 h. Only one adduct is formed (by ^{1}H- and ^{13}C-NMR.). It could not be isolated as it was readily oxydized in the presence of air. – UV. (isooctane): 210 (3800). – IR. ($CHCl_3$): 2940, 1715, 1630, 1430, 1280, 1245, 1205, 1095, 845. – ^{1}H-NMR. ($CDCl_3$): 5.54 (*d*, $^5J_{(1,6)} = {}^5J(3,8) \simeq 1$, H–C(1,8)); 3,80 (*s*, 6 H, $COOCH_3$); 3.20 (*m*, H–C(3,6)); 1.95–1.12 (*m*, 4 H, H–C(4,5 *exo*, 12)); 0.47 (*d* × *m*, $^2J = 12.4$, $^nJ = 3.9$ and 2.3, H–C(4,5 *endo*)). – ^{13}C-NMR. ($CDCl_3$): 162.7 (*d*, $^3J = 3.7$, C=O); 159.1 (*m*, C(2,7)); 150.1 (*s*, C(9,10)); 83.8 (*d* × *d*, 173.0, $^3J = 9.1$, C(1,8)); 51.5 (*qa*, 147.4, CH_3); 47.9 (*t* × *t*, 132.8, $^3J = 6.0$, C(12)); 41.3 (*d* × *d*, 150.2, $^3J = 11.0$, C(3,6)); 21.0 (*t* × *m*, 134.5, C(4,5)).

*Methyl 2,7*exo-*epoxy-11-oxy*-endo-*tetracyclo[6.2.1.1^{3,6}.0^{2,7}]dodec-9-ene-9,10-dicarboxylate* (**13**). The furan derivative **4** (0.5 g, 3.7 mmol) and methyl acetylenedicarboxylate (0.525 g, 3.7 mmol) in CCl_4 (1.5 ml) were stirred at 25° for 12 h. Then O_2 was bubbled through the solution at 25° for 1 h. The epoxide **13** was purified by chromatography on silicagel (1 mm plates, AcOEt/hexane 1:1, Rf 0.8). Yield: 0.432 g (40%), colourless crystals, m.p. 81–82° (ether/pentane). – UV. (isooctane): 250 (6300). – IR. ($CHCl_3$): 2940, 1710, 1620, 1430, 1320, 1280, 1250, 1110, 1065, 980, 900, 845. – ^{1}H-NMR. ($CDCl_3$): 5.10 (*s*, H–C(1,8); 3.88 (*s*, CH_3); 2.80 (*m*, H–C(3,6)); 2.15 (*d* × *m*, $J = 9.6$, H(syn)–C(12); 1.75–0.95 (*m*, H–C(4,5,12 anti)). – ^{13}C-NMR. ($CDCl_3$): 162.4 (*qa*, $^3J = 4.6$, C=O); 148.5 (*d*, $^3J = 2.7$, C(9,10)); 80.9 (*d* × *d*, *174.0*, $^3J = 9.1$, C(1,8)); 63.2 (*m*, C(2,7)); 52.4 (*qa*, 148.3, CH_3); 40.2 (*t* × *m*, 138.7, C(12)); 38.0 (*d* × *d* × *m*, 148.8 $^3J = 7.8$, C(3,6)); 25.1 (*t* × *m*, 133.6, C(4,5)). – MS. (chemical ionization, CH_4): 293 (100), 265 (34), 261 (34), 247 (28), 233 (80), 147 (11), 117 (25), 75 (31). – MS. (70 eV): 263 (59), 223 (40), 195 (11), 153 (12), 146 (17), 145 (24), 144 (18), 123 (29), 119 (13), 118 (26), 117 (51), 116 (40), 115 (100), 105 (30), 103 (25), 91 (72), 89 (31), 79 (53), 78 (29), 77 (80).

$C_{15}H_{16}O_6$ (292.29) Calc. C 61.64 H 5.52% Found C 61.73 H 5.50%

The epoxide **13** was obtained also by oxidation with *m*-chloroperbenzoic acid (3 fold excess, CH_2Cl_2, $NaHCO_3$, 25°). Yield: 76%.

Methyl 11-oxa-endo,endo-*tetracyclo[6.2.1.1^{3,6}.0^{2,7}]dodec-9-ene-9,10-dicarboxylate* (**14**). The furan derivative **4** (0.5 g, 3.7 mmol) and methyl acetylenedicarboxylate (0.525 g, 3.7 mmol) in acetone (1.5 ml) were stirred under N_2 at 25° for 12 h. After addition of more acetone (3.5 ml) and 10% Pd/C (0.1 g), the mixture was hydrogenated (*ca.* 1 h); the reaction was stopped after absorption of 3.7 mmol of H_2 (control by TLC., hexane/AcOEt 7:3). The catalyst was filtered off and the solvent eliminated *i. v.* The crude **14** was purified by column chromatography on silicagel (hexane/AcOEt 85:15). Yield: 0.75 g (73%), colourless oil. – UV. (isooctane): 251 (6100). – IR. ($CHCl_3$): 2980, 2940, 2865, 1715, 1625, 1430, 1345, 1315, 1275, 1250, 1200, 1120, 1080, 1065, 965, 940, 885. – ^{1}H-NMR. ($CDCl_3$): 5.0 (*d*×*d*, 2.5, H–C(1,8)); 3.87 (*s*, CH_3); 2.84 (*m*, H–C(2,7)); 2.27 (*m*, H–C(3,6)); 2.02–0.85 (*m*, H–C(4,5,12)). – ^{13}C-NMR. ($CDCl_3$): 162.7 (*s*, CO); 144.2 (*s*, C(9,10)); 82.5 (*d*×*d*, 168.5, $^3J=8.2$, C(1,8)); 52.0 (*qa*, 147.4, CH_3); 48.9 (*d*×*m*, 136.4, C(2,7)); 47.9 (*t*×*m*, 134.6, C(12)); 37.3 (*d*×*d*×*m*, 142.8, $^3J=7.7$, C(3,6)); 25.1 (*t*×*m*, 136.4, C(4,5)). – MS. (70 eV): 256 (2), 185 (14), 153 (45), 123 (52), 115 (21), 103 (19), 91 (41), 79 (37), 77 (44), 66 (100), 59 (31). – MS. (chemical ionization, *i*-C_4H_{10}): 279 (100), 247 (64), 229 (5), 185 (7).

C_{15}-$H_{18}O_5$ (278.31) Calc. C 64.73 H 6.52% Found C 64.65 H 6.52%

11-Oxa-endo,endo-*tetracyclo[6.2.1.1^{3,6}.0^{2,7}]dodecane-9,10*-exo-*dicarboxylic anhydride* (**15**). The adduct **5** (0.5 g, 2.15 mmol) was hydrogenated (100 mg 10% Pd/C) in acetone (50 ml) at –30° (*ca.* 30 min). The catalyst was filtered off and the solvent distilled *i. v.* The residue (pure **15** by ^{1}H-NMR.) was recrystallized from MeOH. Yield: 0.46 g (92%), colourless crystals, m.p. 157–8°. – UV. (isooctane): final absorption. – IR. ($CHCl_3$): 2980, 2900, 1870, 1835, 1785, 1245, 1225, 1200, 1095, 985, 925, 880, 755, 740. – ^{1}H-NMR. ($CDCl_3$): 4.85 (*d*×*d*, 2.2 and 2.7, H–C(1,8)); 3.90 (*s*, H–C(9,10)); 2.67 (*m*, H–C(2,7); is deuteriated when D_2 was used instead of H_2); 2.47 (*m*, H–C(3,6)); 1.9–1.5 (*m*, $H_2C(4,5,12)$). – ^{13}C-NMR. ($CDCl_3$): 172.3 (*d*, $^3J=2.7$, C=O); 83.4 (*d*×*d*, 162, $^3J=9.1$, C(1,8)); 48.7 (*d*×*m*, 139.2, C(2.7)); 48.6 (*t*×*m*, 135.0, C(12)); 47.8 (*d*×*m*, 144.6, C(9,10)); 38.4 (*d*×*d*×*m*, 143.7, $^3J=7.3$, C(3,6)); 24.1 (*t*×*m*, 130.9, C(4,5)). – MS. (70 eV): 206 (5), 205 (5), 188 (6), 162 (19), 133 (21), 108 (25), 107 (19), 105 (24), 95 (22), 94 (28), 91 (56), 81 (39), 80 (77), 79 (86), 77 (73), 68 (50), 67 (74), 66 (100), 65 (48), 55 (33), 54 (35), 53 (42), 51 (45), 41 (71), 39 (100).

$C_{13}H_{14}O_4$ (234.25) Calc. C 66.66 H 6.02% Found C 66.81 H 5.88%

Crystal Structure determination of 5. – Suitable crystals for structure determination were obtained by recrystallisation from butanol/chloroform/ether 3:1:2. X-ray intensity data collection was carried out with a *Syntex* P2$_1$ automatic four-circle diffractometer. The crystal data, intensity collection, structure solution and refinement methods are summarized in *Table 5.* The crystal form was accurately measured as described previously [39], and used to apply a numerical absorption correction to the measured intensities. The computer programs used for data reduction and structure solution were taken from the "XRAY-72" program system [40]. The scattering factors for the neutral non-hydrogen atoms were taken from *Cromer & Mann* [41] and for hydrogen atoms from *Stewart et al.* [42]. Anomalous scattering coeficients were taken from *Cromer & Libermann.* Starting phases were generated by the program MULTAN [44], the subsequent E-map revealing all non-hydrogen atoms. Refinement by full matrix least squares to $R=0.12$ followed by a difference *Fourier* synthesis revealed all the hydrogen atoms. Refinement by block diagonal least squares was continued to $R=0.038$ and the final atomic coordinates are given in *Table 6.* A perspective drawing of the molecule prepared by the program ORTEP [45], is shown in *Figure 1,* the H-atoms being represented as spheres with an isotropic temperature factor artificially fixed at 0.002 Å^2 for clarity. Calculated bond lengths are reported in *Table 1,* and angles in *Table 2.* Angles between planes are given in *Table 3,* where pairs of atoms in parenthese represent a fictive atom at the midpoint of the pair. Planes were defined thus in order to obtain best dihedral angles for comparison purposes. Selected intermolecular distances are reported in *Table 4.* A list of calculated and observed structure factors is available on demand.

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