5. Nucleophilic Addition to C, C-Double Bonds. VII[1]). Study of Proximity Effects in Olefinic Alcohols and Amines by Photoelectron Spectroscopy

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Summary

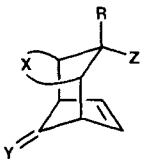
The influence of steric compression on electronic structure in polycyclic olefinic alcohols and amines is studied by PE. spectroscopy.

The unsubstituted alcohol **2** and amine **7** show PE.-spectroscopic properties that can be reconciled by postulating a predominance of intramolecularly H-bonded species in the gas phase.

For the alkylated derivatives **5** and **9**, in which H-bonding is precluded, distinct, but only moderate lone-pair double-bond interactions are observed.

In recent communications[1]) we discussed the ability of polycyclic olefinic alcohols and amines of type **a** to undergo intramolecular cyclization by nucleophilic attack of the heteroatom on the unactivated C, C-double bond (bearing no electron-attracting groups). This very uncommon reactivity can be ascribed to the structurally enforced close proximity of the reacting centers. Distances of 2.6–2.7 Å between the heteroatom and the midpoint of the C, C-double bond have been

Scheme 1



a

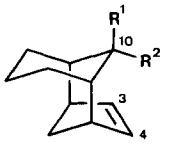
R = H or alkyl
X = CH_2–CH_2, CH_2–CH_2–CH_2, CH=CH
Y = O, H, H
Z = OH, NH_2

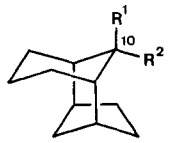
[1]) For Part VI, see [1].

[2]) New address: *F. Hoffmann-La Roche & Co. AG*, CH-4002 Basel.

determined by X-ray structure analyses of several compounds of this type [2–4]. In order to assess the influence of steric compression on electronic structure, we studied compounds **1–10** *(Scheme 2)* by photoelectron (PE.) spectroscopy. The interpretation of their PE. spectra (*Fig. 1* and *2*) was guided by both correlation of ionization potentials (IP.) and PRDDO-SCF [5] model calculations.

Scheme 2



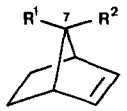


	R^1	R^2	
1	H	H	
2	H	OH	**3**
4	CH_3	OH	
5	H	OCH_3	**6**
7	H	NH_2	**8**
9	H	NC_4H_8	**10**

The unsaturated hydrocarbon **1** serves as reference for the tricyclic olefinic alcohols and amines. Its first IP. band appears at 8.68 eV *(Fig. 1)* and can be safely assigned to ionization from the π-dominated orbital. This ionization energy is approx. 0.3 eV smaller than that of norbornene[3]) (**11**: IP. (1) = 8.97 eV [6]).

The PE. spectrum of **2** *(Fig. 1)* shows two IP. bands at 8.82 and 9.37 eV, well-separated from the strongly overlapping bands at higher energies. They can be

Scheme 3



	R^1	R^2
11	H	H
12	H	OH
13	OH	H
14	H	OCH_3
15	OCH_3	H

[3]) According to IUPAC, norbornene is now called '8,9,10-trinorborn-2-ene'.

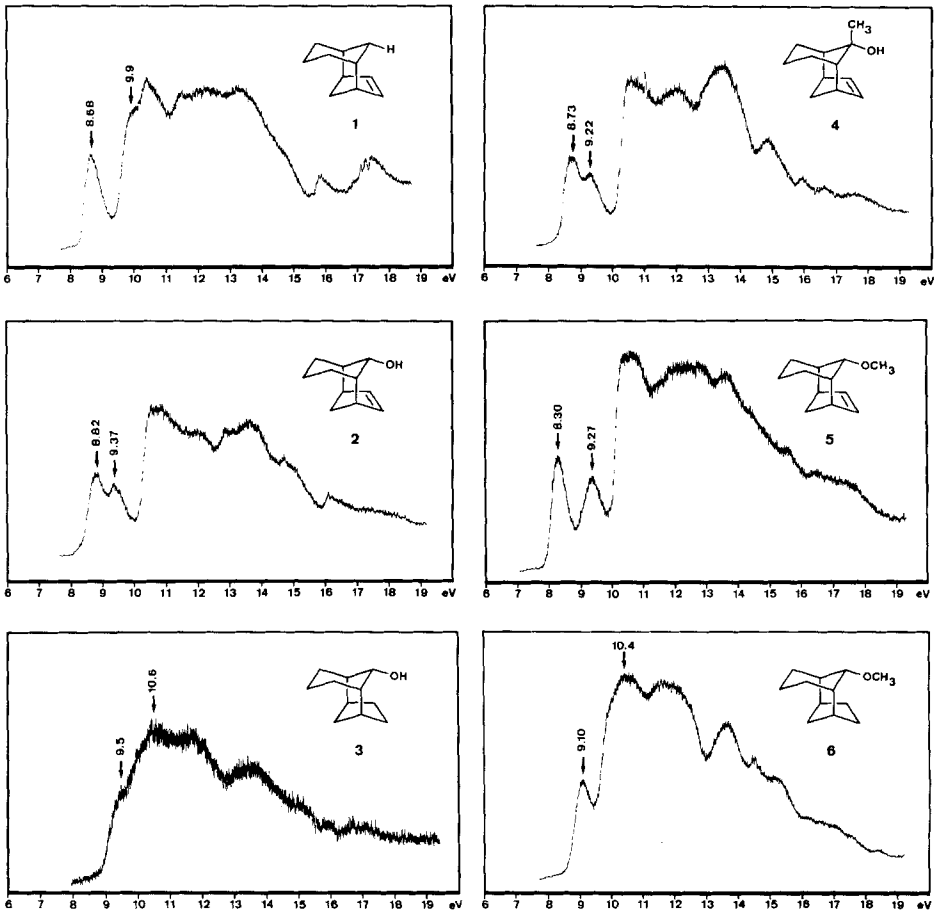


Figure 1. *He(1a)-PE. spectra of compounds* **1–6** (IP. values refer to average IP. band maxima from five Ar/Xe-calibrated spectra)

attributed to ionizations from π- and n-dominated orbitals, respectively. Hence, the π-system is stabilized by 0.1–0.2 eV upon introduction of a hydroxy group *syn* to the double bond. A similar, if somewhat larger, effect was observed by *Brown* [7] by PE.-spectroscopic comparison of *syn*-norbornenol **12** and *anti*-norbornenol **13**. Correlation of the second IP. of **2** (9.37 eV) with IP.(n) of the saturated alcohol **3** (9.5 eV) *(Fig. 1)* reveals a slight destabilization of the lone-pair system due to its interaction with the double bond, in qualitative agreement with predictions based on *ab initio* calculations by *Morokuma & Wipff* [8] for H-bonded *syn*-norbornenol **12**. These findings are reconcilable with a conformation in which the hydroxy group is H-bonded to the C,C-double bond (τ near 0°, *Fig. 3*), as recently demonstrated by IR. and NMR. spectroscopy as well as X-ray structure analysis [2].

A methyl group at C(10) in the *exo*-position leads to a substantial increase in reactivity. Compound **4** cyclizes approx. 10 times faster than **2**. However, corresponding

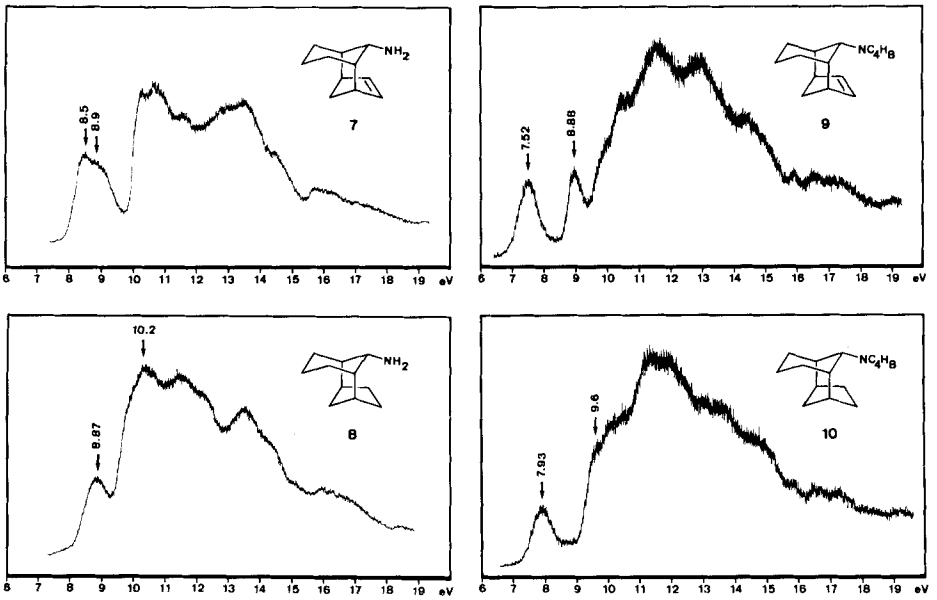


Figure 2. *He(Ia)-PE. spectra of amines* **7**–**10** (IP. values refer to average IP. band maxima from five Ar/Xe-calibrated spectra)

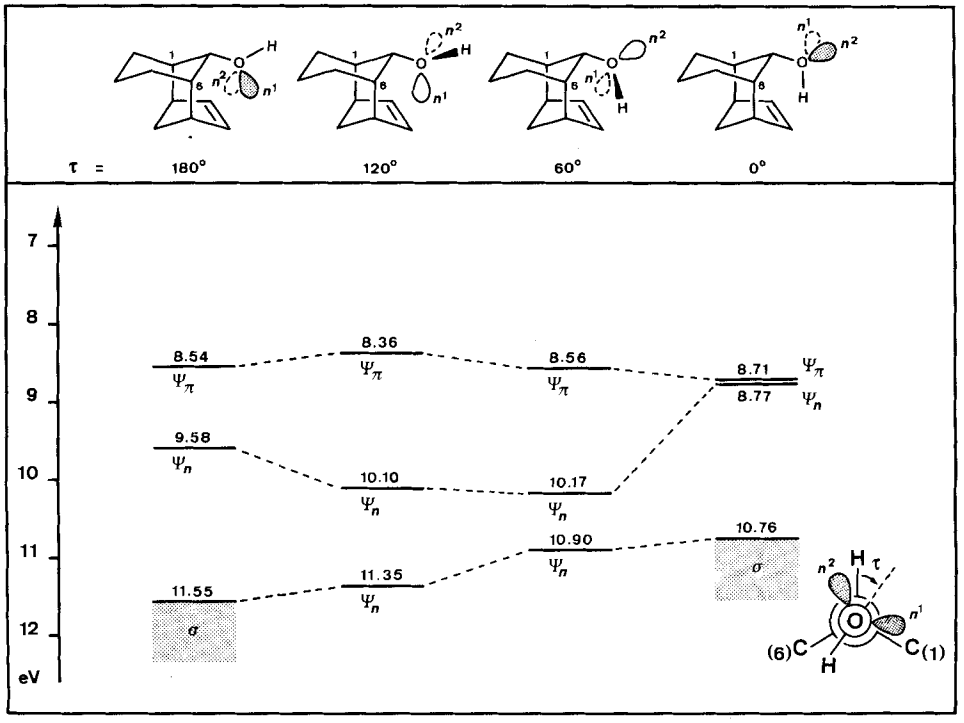


Figure 3. *Negative PRDDO SCF orbital energies for highest occupied and two subjacent MO's of alcohol* **2** *as a function of torsion angle* τ

changes in electronic structures are marginal as seen by comparison of the PE. spectra of the two compounds *(Fig. 1)*.

In compound **5** the lone-pair π-interaction should be more pronounced. Substitution of OH by OCH_3 eliminates both H-bonding and conformations with $\tau \approx 0°$. Indeed, quite a large energy gap between the first two IP.'s, $\Delta IP.(1,2) \approx 1$ eV, is observed for **5**. This contrasts with the virtual absence of such an effect in 7-methoxynorbornenes **14** and **15** [7] and may be a consequence of enhanced steric compression in **5**. The distance between the O-atom and the midpoint of the C,C-double bond in *syn*-norbornenol **12** was calculated by *Morokuma & Wipff* to be 2.89 Å [8]. However, in **5** it is likely to be at least 0.2 Å smaller based on X-ray structural analysis [2–4].

In compounds **7**–**10** the hydroxy group is replaced by an amino group. From the stronger nucleophilicity and the higher donor strength of an amine N-atom, we expected the PE. spectra of **7** and **9** to show pronounced effects. Surprisingly however, they are quite similar to those observed for the O-substituted derivatives **2** and **5**. The PE. spectrum of the amine **7** *(Fig. 2)* shows two strongly overlapping bands at 8.5 and 8.9 eV[4]). Although IR. and NMR. spectra of **7** do not give sup-

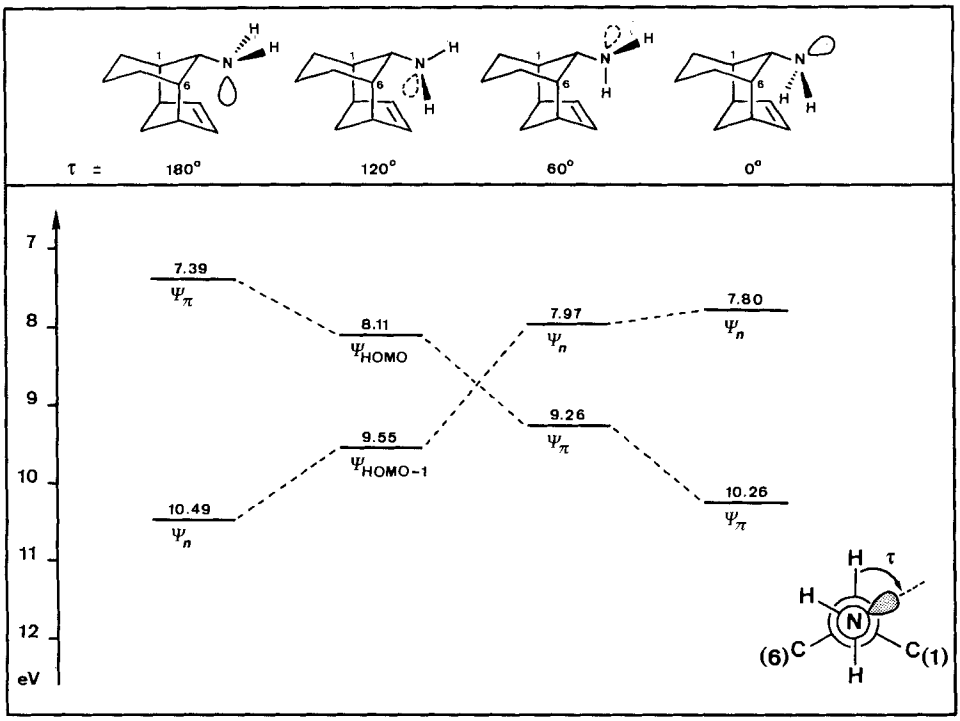


Figure 4. *Negative PRDDO SCF orbital energies for highest occupied and subjacent MO's of amine* **7** *as a function of torsion angle* τ

[4]) IP.(1) of the saturated analog **8** appears at 8.87 eV *(Fig. 2)*.

porting evidence, the small ΔIP.(1,2) of 0.4 eV may be indicative of a nonsymmetrical intramolecular H-bonded species, according to PRDDO-calculated energy levels for various conformers of **7** *(Fig. 4)*[5]). Replacement of the amino by the 1-pyrrolidinyl group, see **9** *(Fig. 2)*, eliminates the possibility of H-bonding and

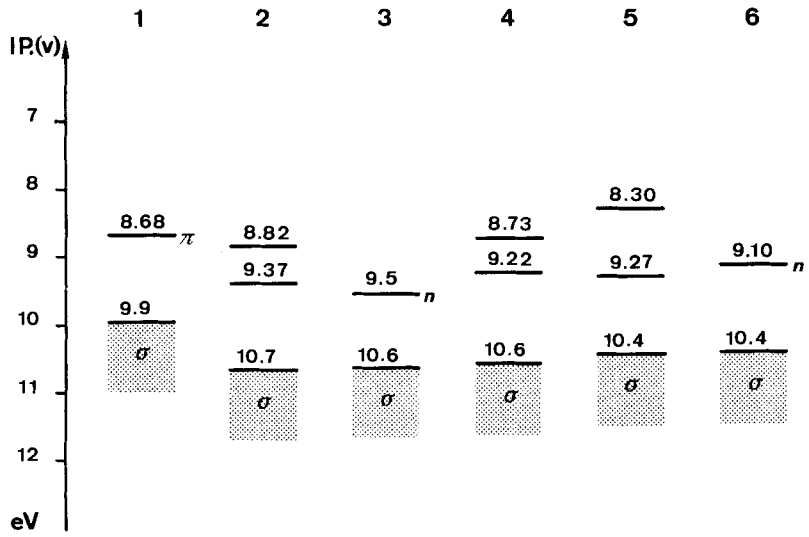


Figure 5. *Vertical ionization potentials in the range of 8–11 eV for compounds* **1–6**

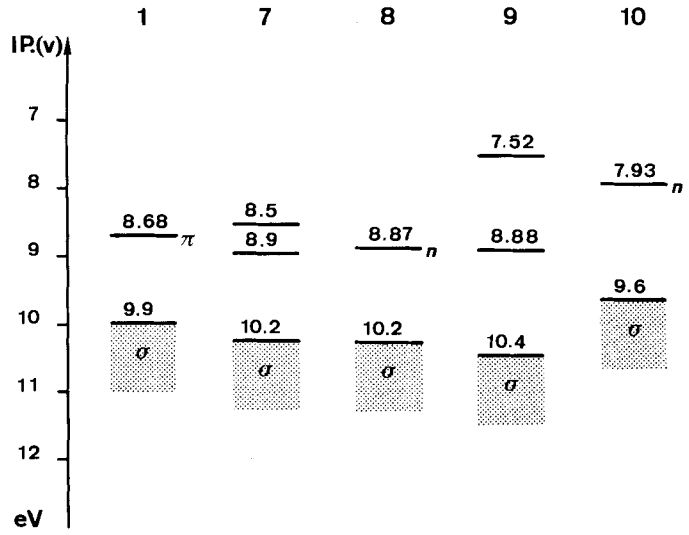


Figure 6. *Vertical ionization potentials in the range of 8–11 eV for compounds* **1, 7–10**

[5]) An intramolecular (N–H · · · π)-interaction in **7** · HCl is confirmed by X-ray structure analysis (to be published).

constrains the system to conformations with τ near 180°. Correlation of the first two IP.'s of **9** with the first IP.'s of **1** and **10** reveals IP. shifts (−0.4 eV, +0.2 eV) that are quite comparable to those obtained by correlating IP.'s of **5**, **1** and **6** (*Fig. 5* and *6*).

Thus, the PE. spectra of both the ether **5** and the amine **9** show distinct lone-pair double-bond interactions. However, these interactions are less dramatic than might have been anticipated from the close proximity of the functional groups. There is a striking resemblance of the PE. spectra of **10** and **9** *(Fig. 2)* with those of 1-azabicyclo[4.4.4]tetradecan (**16**) and 1-azabicyclo[4.4.4]tetradec-5-ene (**17**) [9] *(Scheme 4)*, respectively. Simplified LCBO-type analysis [9] provided an estimate of considerably less than 1 eV for the n-π-interaction in **17**, in support of our conclusion of a distinct, but moderate through-space interaction between the amino group and the double bond in **9**.

Scheme 4

16 **17**

IP.(1) = 7.85 eV IP.(1) ◻ 7.30 eV

IP.(2) = 8.60 eV

Synthesis of compounds *1–10.* – The compounds **1**–**10** were all synthesized from the common intermediate **18** [10], either directly (→**9** and **10**) or from the corresponding ketone **19** [11] (→**1**–**8**). The olefin **1** was obtained (30%)[6]) by reductive cleavage of the methanesulfonate **20** with sodium in liquid ammonia. The latter was prepared from **2** [11] with mesyl chloride in ethyl ether containing an equivalent amount of triethylamine and was used without further purification. The saturated alcohol **3** was obtained in quantitative yield[7]) by reduction of **21** with lithium aluminum hydride in ethyl ether at room temperature. The tertiary alcohol **4** was synthesized (91%) by treatment of **19** [10] with methyllithium in ethyl ether at 0°. Reaction of the alcohols **2** and **3**, each with excess of trimethyloxonium tetrafluoroborate and *N,N,N′,N′*-Tetramethyl-1,8-naphthalenediamine [12] in methylene chloride at room temperature afforded the methyl ethers **5** (90%) and **6** (90%), respectively. The amines **7** and **8** have already been reported [1]. The

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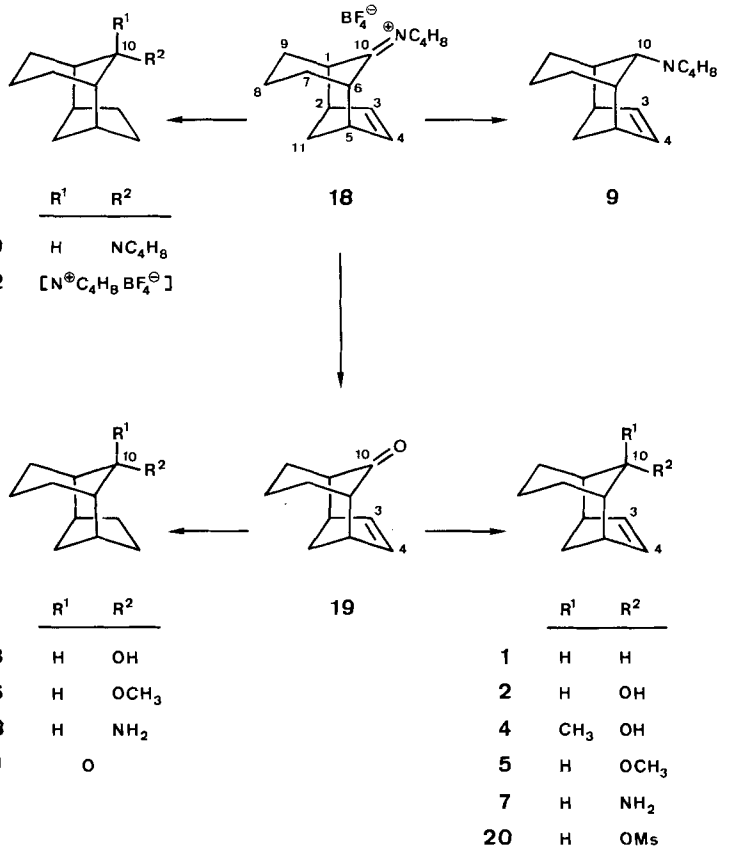
[6]) Isolated by preparative GLC. (column 250× 1 cm, packed with 10% *NGPS* on *Chromosorb W 80/100 A W-DMCS*, temp. 190°).

[7]) Yields are given, if not otherwise specified, for isolated material after column chromatography on silica gel *60 Merck* (70–230 mesh ASTM).

Scheme 5



unsaturated pyrrolidinyl compound **9** was obtained (60%) by reduction of **18** [10] with sodium borohydride in methanol at room temperature. Analogous treatment of **22**, obtained by hydrogenation of **18** [10] in ethyl acetate/methanol 4:1 at 1 atm and room temperature using 10% Pd/C as catalyst, yielded (80%) of the corresponding saturated derivative **10**.

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Experimental Part

Analytical and spectral data. – *General.* See [1]. He(Iα)-PE. spectra were recorded on a *Perkin-Elmer-PS-18* photoelectron spectrometer using an Ar/Xe-mixture for *in situ* calibration. Reported ionization potentials are average IP. band maxima from five spectra, obtained after pumping samples for at least 1 h to constancy of spectral appearance. Reproducibility was better than ±0.005 eV.

anti^{10,11}-*Tricyclo[4.3.1.1^{2,5}]undec-3-ene* (**1**). – IR.: 3055*m*, 3035*w*, 1497*w*, 1467*m*, 1458*w*, 1415*w*, 1385*w*, 1344*m*, 1302*w*, 1287*w*, 1260*m*, 1245*w*, 1087*w*, 1052*w*, 1048*w*, 978*w*, 955*w*, 912*w*. – ^{1}H-NMR. (300 MHz): 1.21 (*d*×*m*, *J*(*gem*) = 12.5, $w_{1/2}$ each ≈ 5, H_{endo}–C(10)); 1.44 (*d*×*t*, *J*(*gem*) = 11, *J*(2,11*exo*) = *J*(5,11*exo*) = 4.5, further *J*'s ≤ 1.5, H_{exo}–C(11)); 1.5–1.7 and 1.7–2.0 (2*m*, 4 H and 5 H); 2.35–2.5 (*m*, $w_{1/2}$ ≈ 16, H–C(1) and H–C(6)); 2.42 (*d*, *J*(*gem*) = 11, H_{endo}–C(11)); 6.03 (*m*, $w_{1/2}$ ≈ 4, H–C(3) and H–C(4)). – MS.: 148 (27, M^+, $C_{11}H_{16}$), 133 (5), 120 (8), 119 (9), 107 (5), 106 (9), 105 (17), 93 (13), 92 (29), 91 (27), 83 (8), 82 (7), 81 (21), 80 (29), 79 (30), 78 (11), 77 (17), 67 (35), 66 (100), 55 (15), 41 (19), 39 (16), 28 (17), 27 (8).

anti^{10,11}-*Tricyclo[4.3.1.1^{2,5}]undecan-11*endo-*ol* (**3**). M.p. 110°. – IR.: 3620*m*, 3022*w*, 1488*w*, 1465*w*, 1444*w*, 1362*w*, 1305*w*, 1223*w*, 1172*w*, 1095*w*, 1073*m*, 1056*m*, 1033*w*, 927*w*. – ^{1}H-NMR. (100 MHz): 0.97 (*d*×*m*, *J*(*gem*) = 11, *J*(2,11*exo*) = *J*(5,11*exo*) = 3.5, further *J*'s ≤ 1.5, H_{exo}–C(11)); 1.2–2.4 (*m*, 15 H); 1.47 (*s*, HO_{endo}–C(10)); 3.73 (*m*, $w_{1/2}$ ≈ 5, H_{exo}–C(10)). – MS.: 166 (< 1, M^+, $C_{11}H_{18}O$), 148 (42), 133 (16), 120 (27), 119 (43), 109 (9), 108 (5), 106 (19), 105 (22), 97 (8), 95 (15), 94 (39), 93 (21), 92 (25), 91 (39), 83 (8), 82 (14), 81 (57), 80 (75), 79 (89), 78 (48), 77 (20), 70 (11), 69 (10), 68 (10), 67 (79), 66 (100), 65 (11), 57 (14), 55 (23), 54 (9), 53 (15), 43 (10), 41 (42), 39 (23).

*10*exo-*Methyl*-anti^{10,11}-*tricyclo[4.3.1.1^{2,5}]undec-3-en-10*endo-*ol* (**4**). M.p. 147° after sublimation at 90°/12 Torr. – IR.: 3602*s*, 3032*m*, 1488*w*, 1469*m*, 1443*m*, 1379*m*, 1366*s*, 1342*m*, 1316*m*, 1263*m*, 1130*s*, 1061*m*, 1049*w*, 1030*m*, 977*w*, 953*m*, 929*m*, 907*w*, 658*w*. – ^{1}H-NMR. (100 MHz): 1.18 (*d*, *J*(H_3C_{exo}–C(10),HO_{endo}–C(10)) = 1.5, H_3C_{exo}–C(10)); 1.4–2.4 (*m*, 9 H); 2.50 (*d*, *J*(*gem*) = 11, H_{endo}–C(11)); 2.60 (*m*, $w_{1/2}$ ≈ 10, H–C(2) and H–C(5)); 4.13 (*qa*, *J*(H_3C_{exo}–C(10),HO_{endo}–C(10)) = 1.5, HO_{endo}–C(10)); 6.51 (*m*, $w_{1/2}$ ≈ 4, H–C(3) and H–C(4)). – MS.: 178 (14, M^+, $C_{12}H_{18}O$), 163 (9), 160 (68), 145 (39), 131 (27), 117 (29), 109 (23), 95 (68), 94 (100), 91 (46), 79 (54), 67 (36), 55 (18), 53 (14), 43 (50).

*10*endo-*Methoxy*-anti^{10,11}-*tricyclo[4.3.1.1^{2,5}]undec-3-ene* (**5**). – IR.: 3062*m*, 3030*w*, 2808*m*, 2775*w*, 1485*w*, 1460*m*, 1449*m*, 1404*m*, 1358*m*, 1342*m*, 1294*w*, 1278*w*, 1244*m*, 1238*m*, 1193*m*, 1108*s*, 1085*m*, 1052*m*, 1005*m*, 978*w*, 952*w*, 915*m*, 610*w*, 598*w*. – ^{1}H-NMR. (80 MHz): 1.2–2.25 (*m*, 9 H); 2.3–2.75 (*m*, H–C(2), H–C(5) and H_{endo}–C(11)); 3.15 (*s*, CH_3O_{endo}–C(10)); 3.32 (*m*, $w_{1/2}$ ≈ 4, H_{exo}–C(10)); 6.07 (*m*, $w_{1/2}$ ≈ 4, H–C(3) and H–C(4)). – MS.: 178 (39, M^+, $C_{12}H_{18}O$), 143 (13), 146 (100), 145 (10), 131 (44), 118 (39), 117 (47), 112 (21), 111 (24), 105 (32), 104 (26), 97 (54), 96 (11), 92 (26), 91 (48), 84 (41), 81 (59), 80 (47), 79 (55), 78 (25), 77 (38), 71 (27), 67 (26), 66 (30), 65 (19), 53 (19), 45 (19), 41 (52), 39 (30).

*10*endo-*Methoxy*-anti^{10,11}-*tricyclo[4.3.1.1^{2,5}]undecan* (**6**). – IR.: 3024*w*, 2812*m*, 1492*w*, 1469*m*, 1449*w*, 1442*w*, 1403*m*, 1366*w*, 1340*w*, 1318*w*, 1306*w*, 1280*w*, 1260*w*, 1194*m*, 1178*w*, 1106*s*, 1038*w*, 1014*m*, 921*m*. – ^{1}H-NMR. (80 MHz): 0.96 (*d*×*m*, *J*(*gem*) = 11, $w_{1/2}$ each ≈ 10, H_{exo}–C(11)); 1.1–2.5 (*m*, 15 H); 3.15 (*m*, $w_{1/2}$ ≈ 4, H_{exo}–C(10)); 3.28 (*s*, CH_3O_{endo}–C(10)). – MS.: 180 (9, M^+, $C_{12}H_{20}O$), 149 (16), 148 (84), 133 (16), 123 (21), 120 (34), 119 (50), 107 (78), 106 (17), 105 (23), 94 (31), 93 (24), 92 (24), 91 (40), 81 (49), 80 (100), 79 (86), 78 (36), 77 (17), 71 (19), 67 (62), 66 (77), 41 (38), 39 (15).

N-(anti^{10,11}-*Tricyclo[4.3.1.1^{2,5}]undec-3-en-10*endo-*yl)pyrrolidine* (**9**). M.p. 37–39°. – IR. (KBr): 3054*w*, 3015*w*, 2745*s*, 1480*w*, 1458*m*, 1449*w*, 1404*m*, 1361*w*, 1341*m*, 1277*w*, 1251*m*, 1192*w*, 1140*w*, 1120*w*, 1110*w*, 1048*w*, 1052*w*, 934*w*, 912*w*, 890*w*, 712*m*, 700*w*, 646*w*. – MS.: 217 (61, M^+, $C_{15}H_{23}N$), 216 (100), 202 (9), 189 (15), 188 (20), 176 (19), 174 (20), 162 (9), 160 (17), 150 (15), 148 (13), 146 (18), 137 (13), 136 (79), 134 (21), 123 (21), 120 (39), 108 (23), 97 (16), 96 (24), 91 (18), 84 (12), 81 (17), 80 (15), 79 (19), 77 (15), 70 (37), 67 (17), 41 (24).

9 · *HCl*. M.p. > 160° (dec.) after recrystallization from Et_2O/CH_3OH. – ^{1}H-NMR. (300 MHz): 1.68 (*d*×*t*, *J*(*gem*) = 11, *J*(2,11*exo*) = *J*(5,11*exo*) = 4.5, H_{exo}–C(11)); 1.7–2.2 (*m*, 8 H); 2.28 (*m*, $w_{1/2}$ ≈ 12, H–C(1) and H–C(6)); 2.4–2.6 (*m*, 2 H); 2.54 (*d*, *J*(*gem*) = 11, H_{endo}–C(11)); 2.67 (*m*, $w_{1/2}$ ≈ 10, H–C(2) and H–C(5)); 2.75–2.9 (*m*, 2 H); 2.84 (*d*, *J*(10*exo*,HN^+) = 11, H_{exo}–C(10)); 4.01 (*m*, $w_{1/2}$ ≈ 22, 2 H); 6.91 (*m*, $w_{1/2}$ ≈ 4, H–C(3) and H–C(4)); 9.1–9.5 (*m*, HN^+_{endo}–C(10)).

N-(anti^{10,11}-*Tricyclo[4.3.1.1^{2,5}]undec-10*endo-*yl)pyrrolidine* (**10**). – IR.: 3022*w*, 2772*m*, 2750*w*, 1490*w*, 1466*m*, 1445*w*, 1434*w*, 1400*m*, 1368*w*, 1338*w*, 1318*w*, 1266*w*, 1149*w*, 1189*w*, 1137*s*, 1095*w*, 1079*w*, 1045*w*, 938*w*, 899*m*. – MS.: 219 (96, M^+, $C_{15}H_{25}N$), 218 (32), 204 (11), 191 (12), 190 (30), 178 (13), 176 (35), 163 (11), 162 (34), 150 (17), 149 (13), 148 (38), 136 (55), 134 (15), 124 (15), 123 (64), 122 (26), 110 (100), 109 (15), 108 (21), 97 (53), 91 (20), 84 (47), 81 (26), 80 (15), 79 (30), 77 (19), 72 (27), 71 (36), 70 (72), 67 (34), 55 (21), 53 (16), 41 (62), 39 (17).

10 · *HCl*. M.p. > 250° (dec.) after recrystallization from acetone. – ^{1}H-NMR. (300 MHz): 1.12 (*d*×*t*, *J*(*gem*) = 12, J(2,11*exo*) = *J*(5,11*exo*) = 3.5, H_{exo}–C(11)); 1.5–2.3 (*m*, 15 H); 2.34 (*d*×*m*,

$J(gem) = 12$, $w_{1/2}$ each ≈ 6, H_{endo}–C(11)); 2.59 (*m*, $w_{1/2} \approx 22$, 2 H); 2.66 (*d*, $J(10exo, HN^+) = 11$, H_{exo}–C(10)); 2.90 (*m*, $w_{1/2} \approx 22$, 2 H); 4.19 (*m*, $w_{1/2} \approx 20$, 2 H); 9.1–9.5 (*m*, HN^+_{endo}–C(10)).

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