134. Control of the *Diels-Alder*-Addition Regioselectivity by Remote Olefins. Syntheses and Cycloadditions of 2,3,5-Trimethylidenebicyclo[2.2.1]heptane and 2,3,5,6,7-Pentamethylidenebicyclo[2.2.2]octane[1])[2])

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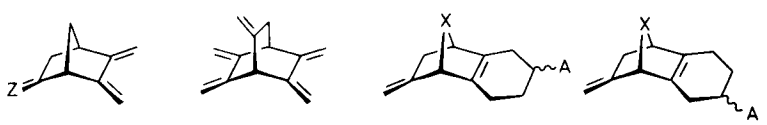
(2.VI.86)

The syntheses of 2,3,5-trimethylidenebicyclo[2.2.1]heptane (**1**) and 2,3,5,6,7-pentamethylidenebicyclo[2.2.2]-octane (**2**) are reported. The *Diels-Alder* additions of the diene moieties of these polyenes can be regioselective, probably because of a possible transannular interaction between the homoconjugated methylidene and s-*cis*-butadiene groups.

Introduction. – The *Diels-Alder* regioselectivity of an exocyclic diene[4]) grafted onto bicyclo[2.2.1]heptane and bicyclo[2.2.2]octane skeletons can be controlled by remote substitution of the bicyclic systems [3–5]. The ability of the homoconjugated methylidene group at C(5) in triene **1** to induce a *'para'*[5]) regioselectivity was used in one [4] of our doubly-convergent syntheses of anthracyclines [5] [6]. We report here on the synthesis of **1** and on its *Diels-Alder* reactivity toward several dienophiles. We report also on the synthesis of the exocyclic pentaene **2**[6]). The homoconjugative interactions invoked to



1 Z = CH_2
3 Z = O

2

'para'

'meta'

interpret the *'para'* regioselectivity of the cycloadditions of **1** must be a less important phenomenon in the case of the *Diels-Alder* additions of **2**. Indeed, while the addition of methyl propynoate to **2** was slightly *'para'*-regioselective, that of the *Lewis*-acid-catalyzed addition of butynone to **2** was *'meta'*-regioselective[5]).

Syntheses of the Polyenes. – Triene **1** was obtained by methylenation of the dienone **3** [8] using the *Oshima-Nozaki* technique [9] (CH_2Br_2, Zn, $TiCl_4$). Attempts to apply *Corey*'s

[1]) For a preliminary communication, see [1].

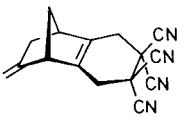
[2]) Interaction between non-conjugated chromophores, Part 26. Part 25, see [2].

[3]) Present address: *Centro Nestlé de investigación y desarrollo technologico de alimentos para America Latina, Latin Reco S.A.*, Quito, Cumbaya, Ecuador.

[4]) An exocyclic diene moiety means that each double bond is in an exocyclic position on the ring skeleton.

[5]) In this paper, *'para'* designates the 4,9-disubstituted tricyclo[6.2.1.$0^{2,7}$]undecane and 4,9-disubstituted tricyclo[6.2.2.$0^{2,7}$]dodecane derivatives, *'meta'* designates the corresponding 4,10-di-substituted derivatives.

[6]) For a synthesis of a bis(tricarbonyliron) complex of **2**, see [7].



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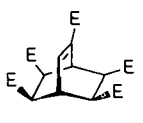
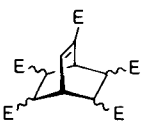
[10], *Wittig*'s [11], or *Chan*'s [12] methylenation methods failed to transform **3** into **1**. The structure of **1** was given by its spectral data. Its UV absorption spectrum was similar to that of 2,3-dimethylidenebicyclo[2.2.1]heptane [13]. Triene **1** added 1 equiv. of ethylenetetracarbonitrile (TCNE) and afforded the corresponding adduct **4**.

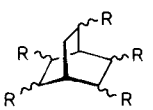
A first synthesis of pentaene **2** starts with the pentaester **5**, the starting material of our synthesis of [2.2.2]hericene [14]. On heating **5** to 110° in anh. DMF containing 1 equiv. of CsF, a mixture of the more stable pentaesters **6** (70%) was obtained. Catalytic (10% Pd/C) hydrogenation (H_2, 4.5 atm, 8 d) afforded **7** (92%) which was reduced with an excess of $LiAlH_4$ in THF to a mixture of pentols **8** (84%). Esterification with MsCl in pyridine afforded a mixture of the pentamesylates **9** (73%). On treating **9** with a base such as *t*-BuOK in DMSO or THF or CsF in DMF or DMF/HMPT, mixtures of the pentaenes **2** and **10** were obtained in which **10** was always the major compound. To avoid this problem, we developed a second synthesis of **2**, starting with the ketone **11** [15].



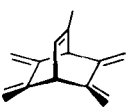
5 E = $COOCH_3$



6 E = $COOCH_3$



7 R = E = $COOCH_3$
8 R = CH_2OH
9 R = $CH_2OSO_2CH_3$



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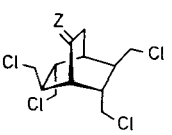


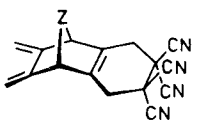
t-BuOK → **10**

CsF/DMF → **2**

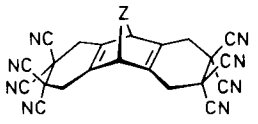
11 Z = O
12 Z = CH_2

Methylenation of **11** [9] (CH_2Br_2, Zn, $TiCl_4$) gave the tetrachloro-alkene **12** (82%). On heating **12** in anh. DMF with an excess of CsF (140°, 22 h), pure pentaene **2** was obtained in 50% yield, with no trace of the isomeric pentaene **10**. In contrast, when **12** was treated with an excess of *t*-BuOK in DMSO (20°, 22 h), the pentaene **10** was obtained in 58% yield. ^{1}H-NMR spectrum of the crude reaction mixture did not show the presence of **2**.

The structures of pentaenes **2** and **10** were deduced from their spectral data, their elemental analysis, their mode of formation and their reactions with dienophiles (see below). The UV spectra of **2** and **10** were similar to those of 2,3,5,6-tetramethylidenebicyclo[2.2.2]octane and 5,6,7,8-tetramethylidenebicyclo[2.2.2]oct-2-ene, respectively [16]. They showed features typical for transannular interactions between the homoconjugated s-*cis*-butadiene chromophores [17]. However, if there is a transannular interaction between the methylidene function at C(7) and the butadiene moieties in **2**, it is not obvious from a comparison of the UV spectrum of **2** with that of 2,3,5,6-tetramethylidenebicyclo-



13 Z = $CH_2C{=}CH_2$
15 Z = $CH{=}CCH_3$

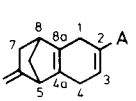


14 Z = $CH_2C{=}CH_2$
16 Z = $CH{=}CCH_3$

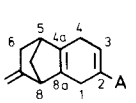
[2.2.2]octane. This is also true for the comparison of the UV spectrum of triene **1** with that of 2,3-dimethylidenebicyclo[2.2.1]heptane [13].

When **2** was allowed to react (20°, 30 min) with 1 equiv. of TCNE in benzene, a 63:22:15 mixture of the monoadduct **13**, bis-adduct **14**, and **2** was obtained. This demonstrates that the two successive cycloadditions **2** + TCNE → **13** and **13** + TCNE → **14** have similar rate constants (k_1/k_2 = 1–2). This is typical of the *Diels-Alder* reactivity of 2,3,5,6-tetramethylidenebicyclo[2.2.2]octane derivatives [14] [15], whereas 5,6,7,8-tetramethylidenebicyclo[2.2.2]oct-2-ene systems showed a large reactivity difference between the first and second cycloadditions ($k_1/k_2 \approx 250$ for TCNE) [14]. This was also the case with the TCNE additions to **10** which gave successively the mono-adduct **15** (k_1) and the bis-adduct **6** (k_2), with $k_1/k_2 > 100$.

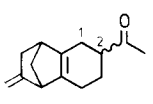
***Diels-Alder* Regioselectivities.** – When **1** was heated to 100° with an excess of methyl propynoate (1.5 h), butynone (2 h), and methyl vinyl ketone (2.5 h) in benzene in *Pyrex* tubes sealed under vacuum, a 71:29 adduct mixture **17**/**18** (99%), a 56:44 mixture **19**/**20** (95%), and a 71:29 mixture **21**/**22** (85%), respectively, were obtained. Weaker dienophiles such as 1,1-diethoxyprop-2-yne and ethoxyacetylene did not add to **1** after 15–30 d at 100°. The adduct ratios were determined by 360-MHz-^{1}H- and 90-MHz-^{13}C-NMR of the crude mixtures.



17 A = COOMe
19 A = $COCH_3$



18 A = COOMe
20 A = $COCH_3$



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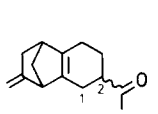

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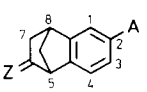
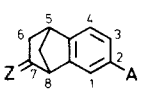


Z = CH_2, A = $COOCH_3$: **23**
Z = CH_2, A = $COCH_3$: **25**
Z = O, A = $COOCH_3$: **27**
Z = $C(CN)_2$, A = $COOCH_3$: **40**



24
26
28
41

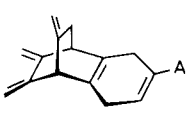
The structures of the adducts **17**–**22** were given by their ^{13}C-NMR spectra and more specifically by the chemical-shift differences measured between the two quaternary olefinic C-atoms C(4a) and C(8a) [3c]. They were confirmed chemically in the following way. On treatment of a 71:29 mixture **17**/**18** with 2 mol-equiv. of 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ = 4,5-dichloro-3,6-dioxocyclohexa-1,4-diene-1,2-dicarbonitrile) in benzene (20°, 23 h), a 73:27 mixture of the methyl benzoates **23**/**24** was obtained in 99% yield. Under similar conditions the adducts **19**/**20** and **21**/**22** were aromatized into a 57:43

and a 70:30 mixture of **25/26**, respectively. The structures of **23–26** were given unambiguously by their 360-MHz-^{1}H-NMR spectra and with the help of NOE measurements between the signals of the bridgehead protons at C(5) and C(8) and the adjacent aromatic protons at C(1) and C(4). For instance, irradiation of the signal at 7.18 ppm (*d*, ^3J = 7.8 Hz, H–C(4)) of the major methyl benzoate **23** led to NOE's at 3.56 (H–C(5)) and 8.22 ppm (*dd*, ^3J = 7.8, ^4J = 1.3 Hz, H–C(3)). Irradiation of the signal at 3.56 ppm led to NOE's at 7.18 (H–C(4)), 5.21 (H of CH_2=C(6) *cis* with respect to C(5)) and 1.55 ppm (CH_2 of the 5,8-methano bridge). Irradiation of the signal at 3.14 ppm (H–C(8)) led to NOE's at 8.23 (*d*, ^4J = 1.3 Hz, H–C(1)), 2.32 (CH_2(7)), and 1.55 ppm. The structures of the minor benzoate **24** and of the aryl methyl ketones **25/26** were determined independently in a similar way. Furthermore, a 73:27 mixture **23/24** was oxidized into a 71:29 mixture of the known ketones **27/28** [3c] in 66% yield on treatment with $NaIO_4/OsO_4$ in H_2O/t-BuOH/CH_2Cl_2 (52°, 45 min).

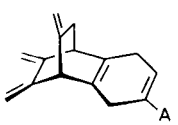
Our results showed a favoured *'para'* regioselectivity for the *Diels-Alder* additions of triene **1**. It was slightly improved on lowering the temperature of the reaction. For instance, the adducts **17/18** were obtained in a 76:24 ratio on heating **1** with methyl propynate in C_6D_6 to 60° for 60 h (95% yield). The *'para'* regioselectivity was the same when the cycloadditions were carried out in acetone, MeOH, MeCN, or DMSO. In the presence of a *Lewis* acid (*e.g.* $AlCl_3$, $SnCl_4$), the selectivity of the cycloaddition of **1** to methyl propynoate was not improved! With methyl vinyl ketone precomplexed at −82° with 0.9 equiv. of $BF_3 \cdot Et_2O$, $SnCl_4$, $AlCl_3$, or $EtAlCl_2$ (1M solutions in CH_2Cl_2, 3 equiv. of **1**), the *Diels-Alder* addition had already occurred at −82°. The fastest reaction was observed for the $BF_3 \cdot OEt_2$-catalyzed process. Under the latter conditions, however, the regioselectivity was only 70:30, not better than under thermal conditions (see above). The best *'para' vs. 'meta'* regioselectivity was obtained with the $AlCl_3$- (76:24, 42% yield; 15 min, −82°) and $EtAlCl_2$- (78:22, 80% yield; 16 h, −82°)catalyzed cycloadditions. Each regioisomeric adduct **21** and **22** was composed of a mixture of two stereoisomers (α *vs.* β position of the Ac group at C(2)). Their relative configuration could not be established unequivocably. Nevertheless, for **21** and **22**, one of the two stereoisomers dominates by more than 80%.

On heating pentaene **2** with 1.3 equiv. of butynone (C_6H_6, 50°), a mixture of mono- and bis-adducts was formed from which a 1:1 mixture **29/30** could be isolated in 43% yield by column chromatography on silica gel. When precomplexed with 1 equiv. of $BF_3 \cdot Et_2O$ in CH_2Cl_2 (−90°, 30 min), butynone added to **2** (−90°, 0.1M, 1 h) to give a 38:62 mixture **29/30** (38% yield). On heating **2** with 1.2 equiv. of methyl propynate (C_6H_6, 50°), a 65:35 mixture of the mono-adducts **31/32** was isolated after column chromatography (35%). The *'para'* regioselectivity could be improved to 75:25 when **2** was added (−90°, CH_2Cl_2) to methyl propynoate precomplexed with 1 equiv. of Me_2AlCl (0.1M, CH_2Cl_2).

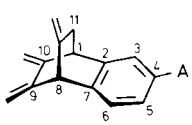
The structures of the mono-adducts **29–32** were deduced from their spectral data. On treatment of **31/32** with DDQ (20°, C_6H_6), a mixture **35/36** was obtained. As in the case of



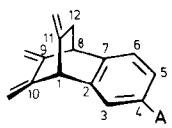
29 A = $COCH_3$
31 A = $COOCH_3$



30 A = $COCH_3$
32 A = $COOCH_3$



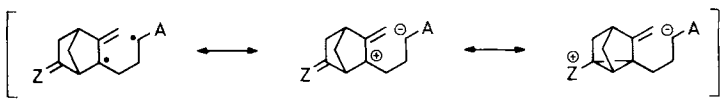
33 A = $COCH_3$
35 A = $COOCH_3$



34 A = $COCH_3$
36 A = $COOCH_3$

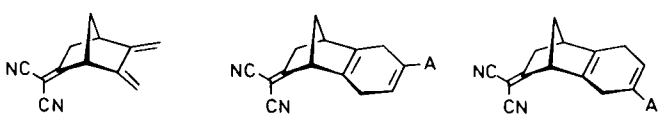
23–28, NOE measurements allowed the recognition of the bridgehead protons at C(1) and C(8) and their proximity to the aromatic protons at C(3) and C(6) in **35** and **36**, thus establishing unambiguously the reported regioselectivities. Treatment of **29/30** with DDQ led to a mixture of unstable compounds containing ketones **33/34**. Unfortunately, their detailed ^{1}H-NMR analysis was not possible.

Discussion. – The PMO theory [18] has been very successful in rationalizing *Diels-Alder* reactivity [19] [20], stereoselectivity, and regioselectivity [21]. Accordingly, and to a first approximation, the regioselectivity of the cycloaddition of **1** and **2** to strong dienophiles such as methyl propynoate, butynone and methyl vinyl ketone should be given by the shape (*p* coefficients) of the HOMO of the polyenes. MNDO, MINDO/3, CNDO/S, EHT [22], and *ab initio* STO 3G calculations [23] showed comparable *p* coefficients for the two methylidene groups of the s-*cis*-butadiene moiety in **1**. A possible homoconjugative interaction between the exocyclic diene and monoolefin chromophores did not manifest itself by the shape of the HOMO of **1** (see also the UV absorption spectra of **1** and **2**). Thus, the PMO theory would predict little regioselectivity for the *Diels-Alder* additions of **1** contrary to the experimental results reported for the cycloadditions of **1** and those of the more complex derivatives **42** and **43** (see below).



i **ii** **iii**

The *Woodward-Katz* visualization of *Diels-Alder* transition states [24] as diradicaloids [25] [26], a reasonable hypothesis [27] for the reaction of non-symmetrically substituted cycloaddends for which the two forming σ bonds may occur in a non-synchronous fashion [28], seems to be more appropriate for interpreting our results with **1** and **2**. If one writes the possible configurations **i↔ii↔iii** of a diradicaloid [27] [29] which is supposed to represent the transition state of the *'para'* mode of addition of **1** and **2** to a strong dienophile, one sees that the charge-transfer configuration **ii** with the negative charge α to the electron-withdrawing substituent A and a positive charge homoconjugated with the methylidene group (Z = CH_2) can profit from the homoconjugative stabilization **ii↔iii** [30]. This situation is not possible in the transition state of the *'meta'* mode of addition. Following this model (Z = $C(CN)_2$), we predicted 5-(dicyanomethylidene)-2,3-dimethylidenebicyclo[2.2.1]heptane (**37**) to react with dienophiles with a normal electronic

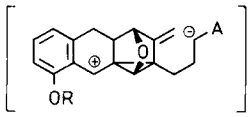


37 **38** A = $COOCH_3$ **39** A = $COOCH_3$

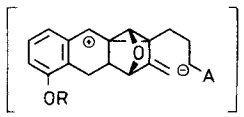
42 **43**

demand with a lesser *'para'* regioselectivity than **1**, *i.e.*, with no regioselectivity or, at the limit, with *'meta'* regioselectivity. In agreement with this hypothesis, the cycloaddition of methyl propynoate to **37** (80°, 2 h, C_6H_6) gave a 47:53 mixture of the *'para'* and *'meta'* adducts **38**/**39** (92% yield). This mixture was oxidized with DDQ (C_6H_6, 80°, 4.5 h) to a 44:56 mixture of the corresponding methyl benzoates **40**/**41** (see above; 92%) whose structures were established unambiguously by 360-MHz-^{1}H-NMR and with the help of NOE measurements.

The more complex polyenes **42** and **43** have been reported to favour the corresponding *'para'* regioisomers in their *Diels-Alder* additions to strong dienophiles [4]. With **42** (R = α-naphthoyl, R = Me) and methyl vinyl ketone precomplexed with $BF_3 \cdot Et_2O$, *'para' vs. 'meta'* regioselectivities of 84:16 and 90:10, respectively, were observed at −78° in CH_2Cl_2. Under similar conditions (−82°, CH_2Cl_2), triene **1** gave a 70:30 mixture **21**/**22**. The better regioselectivity observed with **42** and **43** (R = α-naphthoyl) [4] than with **1** is consistent with our model **i**↔**ii**↔**iii**. It implies that the contribution of the charge-transfer configuration **ii**↔**iii** should be increased on substituting the methylidene group at C(5) with electron-donating groups. This is the case for the limiting configurations **iv** and **iv'** assumed to be responsible of the good *'para'* regioselectivities of the cycloadditions of **42** and **43**, respectively.



iv



iv'

According to our transition state model **i**↔**ii**↔**iii**, we expected a lower *'para'* regioselectivity for the *Diels-Alder* addition of **2** compared with those of **1**, because the methylidene group at C(7) in **2** cannot participate as well as the methylidene group at C(5) in **1**. This is expected to be the case because the distance between the homoconjugated methylidene and s-*cis*-butadiene moieties is larger in the bicyclo[2.2.2]octane than in the bicyclo[2.2.1]heptane systems [31]. Our results are consistent with this hypothesis. However, we have not found yet a satisfactory interpretation for the preferred *'meta'* regioselectivity of the *Lewis*-acid-catalyzed cycloaddition of **2** to butynone. In terms of differences in activation enthalpies, the regioselectivities of the cycloadditions presented here are small effects. Therefore, our model for their transition-state should be considered as tentative only.

We thank *Hoffmann-La Roche & Co. AG*, Basel, the *Swiss National Science Foundation*, and the *Fonds Herbette*, Lausanne, for financial support. We are grateful to Dr. *P.-A. Carrupt* for technical assistance and for disclosure of unpublished MO calculations. We thank Prof. *M. McGlinchey* for reading the manuscript.

Experimental Part

General. See [2] [4].

2,3,5-Trimethylidenebicyclo[2.2.1]heptane (**1**). Under vigourous stirring and at 20°, CH_2Br_2 (1.95 g, 0.78 ml, 11.2 mmol) was added dropwise to powdered Zn (2.2 g, 33.6 mmol) in a flame-dried (under Ar) flask, followed by anh. THF (10 ml). A 1M soln. of $TiCl_4$ (0.9 ml, 8.2 mmol) in anh. CH_2Cl_2 (8.2 ml) was added slowly (using a syringe) to the stirred mixture at 10°. Then, the mixture was stirred at 20° for 15–20 min, and 5,6-dimethylidenebicyclo-

[2.2.1]heptan-2-one [8] (**3**; 1 g, 7.46 mmol) was added dropwise (syringe) followed by anh. THF (6 ml). The mixture was stirred at 20° for 2 h and then poured into a vigourously stirred mixture of sat. aq. $NaHCO_3$ soln. (200 ml) and CH_2Cl_2 (30 ml). The org. layer was collected, washed with sat. aq. $NaHCO_3$ soln. until neutrality. After drying, the solvent was evaporated under reflux (*Vigreux* column) and the residue filtered through *Florisil* (20 g, CH_2Cl_2/petroleum ether 1:3), yielding after solvent evaporation, 497 mg (50%) of a colourless oil, b.p. 35°/0.2 Torr. UV (isooctane): 258 (sh, 3900), 248 (5690), 242 (sh, 5230), 228 (sh, 4600). IR (film): 1675, 880. ^{1}H-NMR ($CDCl_3$): 5.15, 5.11 (2 br. *s*, 2 H); 4.94, 4.63 (2*m*, 2 H); 4.84 (*m*, 2 H); 3.25 (*m*, H–C(4)); 2.90 (*m*, H–C(1)); 2.50–1.93 (*m*, CH_2(6)); 1.50 (*m*, CH_2(7)). ^{13}C-NMR ($CDCl_3$): 151.1, 150.6, 149.6 (3*s*); 103.6, 100.9, 100.3 (3*t*, ^1J(C,H) = 156–157); 55.0, 45.2 (2*d*, ^1J(C,H) = 150); 40.0 (*t*, ^1J(C,H) = 135); 37.2 (*t*, ^1J(C,H) = 135). MS (70 eV): 132 (18, $M^{+\cdot}$) 117 (100). Anal. calc. for $C_{10}H_{12}$ (132.21): C 90.85, H 9.14; found: C 90.72, H 8.97.

5-Dicyanomethylidene-2,3-dimethylidenebicyclo[2.2.1]heptane (= *2-(5,6-Dimethylidenebicyclo[2.2.1]hept-2-ylidene)malonodinitrile*; **37**). A mixture of malonodinitrile (364 mg, 5.5 mmol), **3** (173 mg, 1.3 mmol), MeOH (10 ml), and a few drops of piperidine was stirred at 55–65° for 5 h. After solvent evaporation, the residue was purified by column chromatography on silica gel (16 g, MeOH/petroleum ether 1:9). The first fraction contained malonodinitrile (TLC (SiO_2, MeOH/$CHCl_3$ 1:99) R_f 0.36), and the 2nd fraction (R_f 0.73) **37**. After solvent evaporation, the residue was distilled (bulb-to-bulb), yielding 129 mg (55%) of a colourless oil, b.p. 130°/0.1 Torr. UV (isooctane): 284 (3230), 236 (22600). UV (96% EtOH): 284 (2570), 236 (20000). IR ($CHCl_3$): 2230, 1745, 1630. ^{1}H-NMR ($CDCl_3$): 5.36, 5.26, 5.21, 5.06 (4 br. *s*, 4 H); 4.00 (*m*, H–C(4)); 3.18 (*m*, H–C(1)); 2.80 (*dd*, *J* = 17.6, 3.6, H_{exo}–C6)); 2.50 (*dd*, *J* = 17.6, 4, H_{endo}–C(6)); 1.80 (*m*, CH_2(7)). ^{13}C-NMR ($CDCl_3$): 186.7 (*s*); 146.4, 143.1 (2*s*); 111.3 (*s*, CN); 106.8, 104.0 (2*t*, ^1J(C,H) = 159); 79.4 (*s*); 55.8, 44.1 (2*d*, ^1J(C,H) = 155); 40.4 (*t*, ^1J(C,H) = 135, CH_2(7)). MS (70 eV): 182 (100, $M^{+\cdot}$), 181 (73), 154 (83), 91 (19), 78 (79). Anal. calc. for $C_{12}H_{10}N_2$ (182.23): C 79.10, H 5.53, N 15.37; found: C 79.01, H 5.35, N 15.36.

9-Methylidenetricyclo[6.2.1.0^{2,7}]undec-2(7)-ene-4,4,5,5-tetracarbonitrile (**4**). A mixture of **1** (66 mg, 0.5 mmol), freshly sublimed TCNE (64 mg, 0.5 mmol) and anh. benzene (2 ml) was stirred at 20° for 6 h, then at 80° for 13 h. After solvent evaporation, the residue was recrystallized from CH_2Cl_2/hexane 1:1 yielding 112 mg (86%) of colourless crystals, m.p. 199–200°. UV (CH_3CN): 210 (7400). IR (KBr): 2940, 1650, 1430, 1225, 875. ^{1}H-NMR ($CDCl_3$): 5.10, 4.90 (2*m*, CH_2=C(9)); 3.20 (*m*, 5 H); 2.95 (*m*, H–C(1)); 2.40 (*dm*, *J* = 15, H_{exo}–C(10)); 1.80 (*dm*, *J* = 15, H_{endo}–C(10)); 1.65 (*m*, CH_2(11)). MS (70 eV): 260 (89, $M^{+\cdot}$), 220 (31), 132 (77), 117 (52), 92 (100), 91 (80). Anal. calc. for $C_{16}H_{12}N_4$ (260.30): C 73.83, H 4.65; found: C 73.71, H 4.62.

9-(Dicyanomethylidene)tricyclo[6.2.1.0^{2,7}]undec-2(7)-ene-4,4,5,5-tetracarbonitrile (TCNE adduct of **37**). Same procedure as for the preparation of **4**, starting with **37**. Yield 93%, pink crystals, m.p. 244–245°. UV (CH_3CN): 236 (12300), 266 (sh, 5900), IR (KBr): 2960, 2240, 1615, 1430. ^{1}H-NMR ($CDCl_3$): 4.00 (*m*, H–C(8)); 3.38 (*m*, 5 H); 2.82 (*dd*, *J* = 18, 3, H_{exo}–C(10)); 2.35 (*dd*, *J* = 18, 3.6, H_{endo}–C(10)); 2.10 (*m*, CH_2(11)). MS (70 eV): 310 (34, $M^{+\cdot}$), 256 (24), 232 (100), 182 (73), 91 (26). Anal. calc. for $C_{18}H_{10}N_6$ (310.32): C 69.67, H 3.25; found: C 69.54, H 3.33.

Pentamethyl Bicyclo[2.2.2]oct-7-ene-2,3,5,6,7-pentacarboxylates (**6**). A soln. of the pentaester **5** (10 g, 25 mmol [14]) and CsF (3.75 g, 25 mmol; dried in the flame) in anh. DMF (50 ml) was heated to 110° for 40 h. After solvent evaporation, the residue was dissolved in $CHCl_3$ (50 ml) and washed with brine (50 ml, 5 times). After drying ($MgSO_4$) and solvent evaporation, 7.15 g (70%) of a white paste was obtained. UV (CH_3CN): 215 (9200). IR ($CHCl_3$): 3040, 3010, 2970, 2860, 1740, 1630, 1440, 1270, 1175, 1090. ^{1}H-NMR ($CDCl_3$): 7.35 (*m*, H–C(8)); 4.03 (*m*, H–C(1)); 3.73, 3.68, 3.60 (3*m*, H–C(4), 5 $COOCH_3$); 3.28, 2.90 (2*m*, H–C(2), H–C(3), H–C(5), H–C(6)). ^{13}C-NMR ($CDCl_3$): 173.0, 172.8, 172.2, 172.0 (4*s*); 164.3, 163.9 (2*s*, C=C–*C*O); 143.9, 142.5 (2*d*, ^1J(C,H) = 176, C(8)); 136,4, 134.4 (2*s*, C(7)); 52.7, 52.6, 51.9 (3*q*, ^1J(C,H) = 150, $COOCH_3$); 45.4, 44.8, 44.3, 44.1, 44.0, 43.8, 42.7, 40.8, 40.6 (8*d*, ^1J(C,H) = 140, C(2), C(3), C(5), C(6)); 36.0, 35.9, 35.6, 35.3 (4*d*, ^1J(C,H) = 150, C(1), C(4)). CI-MS (CH_4): 439 (6), 428 (18), 427 (20), 400 (18), 399 (26), 398 (25, $M^{+\cdot}$), 367 (100), 339 (5). Anal. calc. for $C_{18}H_{22}O_{10}$ (398.37): C 54.27, H 5.57; found: C 54.09, H 5.56.

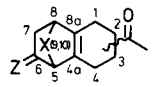
Pentamethyl Bicyclo[2.2.2]octane-2,3,5,6,7-pentacarboxylates (**7**). A degassed mixture of **6** (6 g, 15 mmol), 10% Pd/C (2 g), and acetone (250 ml) was pressurized with 4.5 atm of H_2 and shaken at 20° for 7 d (*Parr* apparatus). After filtration on *Celite* and solvent evaporation, the crude **7** was recrystallized from acetone, yielding 5.5 g (92%) of a white powder, m.p. 153–155°. UV (CH_3CN): 212 (1000). IR (KBr): 3040, 3010, 2970, 2860, 1740, 1440, 1380, 1325, 1265, 1175, 1090, 1050, 1010. ^{1}H-NMR ($CDCl_3$): 3.75, 3.65, 3.58 (3*m*, 5 $COOCH_3$); 3.29, 3.17, 3.07, 2.97, 2.90, 2.66 (6*m*, 6 H); 2.69, 2.51 (2*m*, H–C(7)); 2.11, 1.87, 1.67 (3*m*, CH_2(8)). CI-MS (CH_4): 442 (5), 441 (5), 430 (16), 429 (18), 428 (2), 401 (10), 400 (10, $M^{+\cdot}$), 370 (80), 369 (100). Anal. calc. for $C_{18}H_{24}O_{10}$ (400.39): C 54.00, H 6.04; found: C 53.91, H 6.08.

Bicyclo[2.2.2]octane-2,3,5,6,7-pentamethanols (**8**). To a stirred suspension of $LiAlH_4$ (1.1 g, 29 mmol) in anh. THF (20 ml), a soln. of **7** (3.25 g, 8.1 mmol) in anh. THF (20 ml) was added dropwise under N_2. After heating under

Table. *^{13}C-NMR Chemical Shifts* [ppm] *and* $^{1}J(C,H)$ [Hz] *for* **17**, **26**, **29**, **30**, *and* **38**–**41** ($CDCl_3$, δ(TMS) = 0.0 ppm, $J \pm 1$ Hz)[a])

	C(1)	C(2)	C(3)	C(4)	C(4a)	C(5)	C(6)	C(7)	C(8)	C(8a)	C(9)	C(10)	CO	others			
17	24.8	128.5	137.6	25.4	133.9	53.4	151.7	33.5	44.4	138.7	47.8		167.6	51.4	102.4		
	(*t*, *J* = 133)	(*s*)	(*d*, *J* = 163)	(*t*, *J* = 130)	(*s*)	(*d*, *J* = 150)	(*s*)	(*t*, *J* = 136)	(*d*, *J* = 150)	(*s*)	(*t*, *J* = 137)		(*s*)	(*q*, *J* = 150)	(*t*, *J* = 158)		
18	26.4	137.3	128.7	23.8	136.2	53.8	151.5	33.5	43.9	136.5	47.8		167.6	51.4	102.6		
	(*t*, *J* = 130)	(*d*, *J* = 163)	(*s*)	(*t*, *J* = 133)	(*s*)	(*d*, *J* = 150)	(*s*)	(*t*, *J* = 136)	(*d*, *J* = 150)	(*s*)	(*t*, *J* = 137)		(*s*)	(*q*, *J* = 150)	(*t*, *J* = 158)		
19	23.6	151.4	138.6	26.7	135.8	53.3	137.9	33.5	44.4	136.7	47.8		201.5	25.2	102.3		
	(*t*, *J* = 133)	(*s*)	(*d*, *J* = 159)	(*t*, *J* = 131)	(*s*)	(*d*, *J* = 151)	(*s*)	(*t*, *J* = 136)	(*d*, *J* = 150)	(*s*)	(*t*, *J* = 137)		(*s*)	(*q*, *J* = 130)	(*t*, *J* = 162)		
20	25.7	138.2	151.7	22.7	133.4	53.8	139.2	33.5	43.8	138.1	47.7		201.5	25.2	102.6		
	(*t*, *J* = 132)	(*d*, *J* = 159)	(*s*)	(*t*, *J* = 133)	(*s*)	(*d*, *J* = 151)	(*s*)	(*t*, *J* = 136)	(*d*, *J* = 150)	(*s*)	(*t*, *J* = 137)		(*s*)	(*q*, *J* = 130)	(*t*, *J* = 162)		
21	22.9	48.6	25.1	25.4	138.9	54.4	152.7	34.0	44.8	139.0	48.0		211.7	28.0	102.0		
	(*t*, *J* = 127)	(*d*, *J* = 128)	(*t*, *J* = 129)	(*t*, *J* = 128)	(*s*)	(*d*, *J* = 147)	(*s*)	(*t*, *J* = 134)	(*d*, *J* = 148)	(*s*)	(*t*, *J* = 135)		(*s*)	(*q*, *J* = 127)	(*t*, *J* = 157)		
22	24.4	25.0	48.9	24.1	136.4	54.4	152.4	34.1	44.8	141.4	48.0		211.7	28.0	102.0		
	(*t*, *J* = 130)	(*t*, *J* = 129)	(*d*, *J* = 128)	(*t*, *J* = 136)	(*s*)	(*d*, *J* = 147)	(*s*)	(*t*, *J* = 134)	(*d*, *J* = 148)	(*s*)	(*t*, *J* = 135)		(*s*)	(*q*, *J* = 127)	(*t*, *J* = 157)		
23	121.8	127.8	128.2	120.4	151.5	53.1	149.3	35.2	43.5	147.7	50.6		167.2	51.7	105.3		
	(*d*, *J* = 162)	(*s*)	(*d*, *J* = 162)	(*d*, *J* = 162)	(*s*)	(*d*, *J* = 149)	(*s*)	(*t*, *J* = 135)	(*d*, *J* = 149)	(*s*)	(*t*, *J* = 136)		(*s*)	(*q*, *J* = 147)	(*t*, *J* = 157)		
24	120.7	128.1	128.0	121.6	146.4	52.7	149.5	35.0	43.8	153.0	50.6	–	167.2	51.7	104.9		
	(*d*, *J* = 162)	(*d*, *J* = 162)	(*s*)	(*d*, *J* = 162)	(*s*)	(*d*, *J* = 149)	(*s*)	(*t*, *J* = 135)	(*d*, *J* = 149)	(*s*)	(*t*, *J* = 136)		(*s*)	(*q*, *J* = 147)	(*t*, *J* = 157)		
25	120.4	149.4	127.3	120.5	148.0	53.0	135.4	35.1	43.4	151.8	50.5	–	198.0	26.4	105.5		
	(*d*, *J* = 163)	(*s*)	(*d*, *J* = 162)	(*d*, *J* = 164)	(*s*)	(*d*, *J* = 154)	(*s*)	(*t*, *J* = 137)	(*d*, *J* = 151)	(*s*)	(*t*, *J* = 139)		(*s*)	(*q*, *J* = 131)	(*t*, *J* = 162)		
26	120.8	127.1	149.4	120.2	146.7	52.7	135.5	34.9	43.7	153.3	50.5		197.9	26.4	105.1		
	(*d*, *J* = 164)	(*d*, *J* = 162)	(*s*)	(*d*, *J* = 163)	(*s*)	(*d*, *J* = 154)	(*s*)	(*t*, *J* = 137)	(*d*, *J* = 151)	(*s*)	(*t*, *J* = 139)		(*s*)	(*q*, *J* = 131)	(*t*, *J* = 162)		
29	28.7	137.6	137.6	25.9	133.4	56.5	145.2	34.4	46.4	129.6	145.7	147.2	198.5	25.0	102.9	105.3	
	(*t*, *J* = 130)	(*s*)	(*d*, *J* = 158)	(*t*, *J* = 130)	(*s*)	(*d*, *J* = 139)	(*s*)	(*t*, *J* = 133)	(*d*, *J* = 140)	(*s*)	(*s*)	(*s*)	(*s*)	(*q*, *J* = 128)	(*t*, *J* = 158)	(*t*, *J* = 158)	
30	25.6	137.7	136.7	29.1	130.3	57.1	145.0	34.6	45.8	132.8	145.9	146.9	198.5	25.0	103.2	105.1	
	(*t*, *J* = 130)	(*d*, *J* = 158)	(*s*)	(*t*, *J* = 130)	(*s*)	(*d*, *J* = 139)	(*s*)	(*t*, *J* = 133)	(*d*, *J* = 140)	(*s*)	(*s*)	(*s*)	(*s*)	(*q*, *J* = 128)	(*t*, *J* = 158)	(*t*, *J* = 158)	
38	25.3	128.1	138.1	25.1	133.0	54.2	190.7	38.3	43.8	148.3	48.9		169.1	51.4	78.9	113.8	114.0
	(*t*, *J* = 126)	(*s*)	(*d*, *J* = 164)	(*t*, *J* = 133)	(*s*)	(*d*, *J* = 156)	(*s*)	(*t*, *J* = 139)	(*d*, *J* = 154)	(*s*)	(*t*, *J* = 136)		(*s*)	(*q*, *J* = 149)	(*s*)	(*s*)	(*s*)
39	26.5	137.9	128.3	23.9	135.5	55.3	190.5	38.5	43.3	146.0	49.0	–	169.0	51.4	80.9	113.7	114.1
	(*t*, *J* = 130)	(*d*, *J* = 164)	(*s*)	(*t*, *J* = 134)	(*s*)	(*d*, *J* = 156)	(*s*)	(*t*, *J* = 139)	(*d*, *J* = 154)	(*s*)	(*t*, *J* = 136)		(*s*)	(*q*, *J* = 149)	(*s*)	(*s*)	(*s*)
40	122.8	130.2	129.4	122.8	144.7	53.9	185.9	40.2	42.9	148.1	51.8	–	166.4	52.1	81.8	111.2	111.3
	(*d*, *J* = 160)	(*s*)	(*d*, *J* = 160)	(*d*, *J* = 160)	(*s*)	(*d*, *J* = 154)	(*s*)	(*t*, *J* = 138)	(*d*, *J* = 149)	(*s*)	(*t*, *J* = 138)		(*s*)	(*q*, *J* = 146)	(*s*)	(*s*)	(*s*)
41	121.8	130.3	129.8	123.9	140.1	53.6	186.0	40.0	43.1	152.0	51.8	–	166.3	52.1	81.1	111.2	111.3
	(*d*, *J* = 160)	(*d*, *J* = 163)	(*s*)	(*d*, *J* = 163)	(*s*)	(*d*, *J* = 155)	(*s*)	(*t*, *J* = 136)	(*d*, *J* = 155)	(*s*)	(*t*, *J* = 140)		(*s*)	(*q*, *J* = 148)	(*s*)	(*s*)	(*s*)

[a]) For reasons of simplicity, we use the atom numbering given in **44**; it does not necessarily correspond to the IUPAC rules.



44

reflux for 2 d, the mixture was cooled to 20° and H_2O (3 ml) was added. Hot MeOH (25 ml) was added and the mixture filtered through silica gel (10 g). The residue and the silica gel were extracted with hot MeOH (25 ml, 3 times, 15 min of heating under reflux). The extracts were combined and evaporated. The residue was dissolved in H_2O (20 ml) and filtered through an ion exchanger (*Dowex 50 W* × *8*, 100/200 mesh, 25 g). After evaporation of the solvent, 1.78 g (84%) of a white paste was obtained. UV (95% EtOH): final absorption. IR (KBr): 3300, 2940, 2920, 2880, 1470, 1380, 1210, 1100, 1040, 1020. ^{1}H-NMR (D_2O): 3.72 (*m*, 5 CH_2OH); 1.87, 1.45 (2*m*, 9 H).

Bicyclo[2.2.2]octane-2,3,5,6,7-pentamethyl Pentamethanesulfonates (**9**). A mixture of **8** (1.1 g, 4.2 mmol), methanesulfonyl chloride (4.2 ml, 51 mmol), and anh. pyridine (15 ml) was stirred at 0° for 60 h. The mixture was poured onto a stirred mixture of ice/H_2O (50 g). The paste was washed with ice-cold H_2O (50 ml, 3 times) and then dissolved in CH_2Cl_2 (40 ml). After washing with H_2O (40 ml, 5 times), the soln. was dried ($MgSO_4$) and treated with charcoal. After solvent evaporation and drying *in vacuo*, 2.0 g (73%) of a white-beige powder was obtained; m.p. 60–65°. IR (KBr): 2950, 1360, 1340, 1175, 970, 950, 820. ^{1}H-NMR (CD_2Cl_2): 4.25 (*m*, CH_2–OMs); 3.08 (15 H); 2.30, 1.95 (2*m*, 9 H). CI-MS (CH_4): 556 (3), 473 (4), 461 (12), 459 (14), 366 (15), 364 (53), 286 (27), 268 (100). Anal. calc. for $C_{18}H_{34}O_{15}S_5$ (650.78): C 33.22, H 5.27; found: C 33.49, H 5.34.

(1RS,2SR,3SR,4SR,5SR,6SR)-2,3,5,6-Tetrakis(chloromethyl)-7-methylidenebicyclo[2.2.2]octane (**12**). Under vigourous stirring and at 20°, CH_2Br_2 (17 ml, 0.3 ml) and anh. THF (150 ml) were added under Ar to powdered Zn (47.5 g, 0.73 mmol) in a flame-dried (under Ar) flask. After cooling to 0°, $TiCl_4$ (19 ml, 174 mmol) in anh. CH_2Cl_2 (115 ml) was added dropwise. After stirring at 20° for 15 min, (1*RS*,4*SR*,5*SR*,6*SR*,7*SR*,8*SR*)-5,6,7,8-tetrakis(chloromethyl)bicyclo[2.2.2]octan-2-one [15] (5 g, 16 mmol; **11**) in anh. THF (50 ml) was added. After stirring at 20° for 2 h, CH_2Cl_2 (500 ml) was added and the mixture poured onto a stirred sat. aq. $NaHCO_3$ soln. (500 ml). The org. layer was filtered through silica gel (150 g), then washed with sat. aq. $NaHCO_3$ soln. (1 l, 3 times) and with H_2O (1 l, 3 times). After drying ($MgSO_4$), the solvent was evaporated and the oily residue purified by column chromatography on silica gel (400 g, CH_2Cl_2/petroleum ether 2:3). After recrystallization from $CHCl_3$/pentane, 4.1 g (82%) of white crystals were obtained; m.p. 55–56°. UV (95% EtOH): final abs., 255 (ε < 100). IR (KBr): 2960, 2940, 2900, 1650, 1440, 1305, 1280, 1270, 1260, 1185, 1150, 900, 890, 770, 760, 750, 720, 700. ^{1}H-NMR ($CDCl_3$): 4.92 (*m*, CH_2=C(7)); 3.8–3.2 (*m*, 4 CH_2Cl); 2.62 (br. *s*, H–C(1)); 2.5–2.1, 2.0–1.3 (2*m*, 7 H). ^{13}C-NMR ($CDCl_3$): 143.8 (*s*, C(7)); 111.2 (*t*, ^1J(C,H) = 155, CH_2=C(7)); 46.6, 46.2, 45.2, 38.9 (4*t*, 4 CH_2Cl); 45.4, 45.2, 44.2, 40.6, 39.0 (5*d*, ^1J(C,H) = 128); 31.3 (*d*, ^1J(C,H) = 138, H–C(4)); 30.0 (*t*, ^1J(C,H) = 120, C(8)). MS (70 eV): 320 (1.7), 318 (8), 316 (18), 314 (12), 279 (11), 267 (10), 243 (14), 229 (14), 189 (41), 153 (65), 105 (100). Anal. calc. for $C_{13}H_{18}Cl_4$ (316.10): C 49.40, H 5.74; found: C 49.44, H 5.67.

2,3,5,6,7-Pentamethylidenebicyclo[2.2.2]octane (**2**). A mixture of **12** (3 g, 9.5 mol), CsF (12 g, 80 mmol; dried in a flame), and anh. DMF (350 ml) was heated to 140° for 22 h under Ar. After cooling to 20°, H_2O (700 ml) was added and the mixture extracted with pentane (300 ml, 6 times). After volume reduction, the pentane soln. was washed with brine (250 ml, 6 times) and dried ($MgSO_4$). After solvent evaporation, the crude liquid was purified by column chromatography on silica gel (60 g, pentane). After recrystallization from pentane at −20°, 800 mg (50%) of white crystals were obtained; m.p. 65–66°. UV (95% EtOH): 256 (sh, 9400), 243 (12500), 209 (9780). UV (isooctane): 256 (sh, 9520), 244 (12500), 239 (sh, 12250), 211 (8990). IR (KBr): 3080, 2980, 2960, 2920, 2910, 1790, 1650, 1610, 1430, 1170, 1130, 890. ^{1}H-NMR ($CDCl_3$): 5.28, 5.26 (2*s*, 4 H); 4.89 (br. *s*, 5 H); 4.67 (*m*, 1 H); 3.51 (*s*, H–C(1)); 3.20 (*t*, *J* = 3.5, H–C(4)); 2.51 (*dd*, *J* = 4, 2, CH_2(8)). ^{13}C-NMR ($CDCl_3$): 146.3, 145.9, 145.2 (3 br. *s*); 107.1, 104.9, 104.7 (3*t*, ^1J(C,H) = 158); 59.5 (*d*, ^1J(C,H) = 138, C(1)); 48.7 (*d*, ^1J(C,H) = 141, C(4)); 35.9 (*t*, 128, C(8)).

2-Methyl-5,6,7,8-tetramethylidenebicyclo[2.2.2]oct-2-ene (**10**). Freshly sublimed *t*-BuOK (0.5 g, 4.4 mmol) was added portionwise to a stirred mixture of **12** (150 mg, 0.475 mmol) and DMSO (2 ml) at 20°. After stirring at 20° for 22 h, ice was added and the mixture extracted with CH_2Cl_2 (10 ml, 5 times). The extracts were united and washed with H_2O (50 ml, 5 times). After solvent evaporation, the residue was purified by column chromatography on neutral Al_2O_3 (15 g, petroleum ether), yielding 46 mg (58%) of white crystals, m.p. 79–80°. UV (95% EtOH): 252 (10300), 237 (10900), 228 (11000), 221 (sh, 10400), 204 (12650). UV (isooctane): 251 (10600), 237 (11200), 228 (11400), 220 (sh, 10700). IR (KBr): 3090, 3040, 2980, 2960, 2940, 2920, 2870, 2850, 1790, 1650, 1610, 1440, 890, 820, 780. ^{1}H-NMR ($CDCl_3$): 5.98 (*dm*, *J* = 7, H–C(3)); 5.27, 4.96 (2 br. *s*, 8 H); 3.78 (*d*, *J* = 7, H–C(4)); 3.60 (br. *s*, H–C(1)); 1.86 (*d*, *J* = 2, CH_3–C(2)). ^{13}C-NMR ($CDCl_3$): 145.0, 144.4, 142.1 (3*s*); 124.9 (*d*, ^1J(C,H) = 170, C(3)); 103.7, 103.3 (2*t*, ^1J(C,H) = 158); 58.9 (*d*, ^1J(C,H) = 139, C(1)); 52.9 (*d*, ^1J(C,H) = 147, C(4)); 19.1 (*q*, ^1J(C,H) = 125, CH_3). MS (70 eV): 171 (9), 170 (57), 169 (13), 155 (100), 153 (31), 142 (28), 141 (37), 129 (30), 128 (46), 118 (67), 117 (79), 115 (79), 91 (70), 77 (55). Anal. calc. for $C_{13}H_{14}$ (170.26): C 91.71, H 8.29; found: C 91.87, H 8.13.

9,10,11-Trimethylidenetricyclo[6.2.2.0^{2,7}]dodec-2(7)-ene-4,4,5,5-tetracarbonitrile (**13**). A mixture of **2** (51 mg, 0.3 mmol) and TCNE (39 mg, 0.3 mmol) in anh. benzene (5 ml) was stirred at 20° for 30 min. After solvent

evaporation, the residue was recrystallized from acetone, yielding 28 mg (22%) of **14** (see below). The mother liquor was concentrated and purified by column chromatography on silica gel (1 g, CH_2Cl_2/petroleum ether 3:2). Recrystallization from CH_2Cl_2 gave 56 mg (63%) of **13** as a colourless solid, m.p. > 200° (dec.). UV (95% EtOH): 260 (sh, 4950), 248 (sh, 7800), 243 (sh, 8050). UV (dioxane): 260 (sh, 5050), 249 (sh, 7900), 243 (8100), 230 (sh, 8300), 224 (sh, 9000). IR (KBr): 3090, 2990, 2940, 2860, 2260, 1800, 1655, 1640, 1445, 1430, 1235, 1155, 900, 835, 805. ^{1}H-NMR ($CDCl_3$): 5.29, 5.27 (2*s*, 2 H); 4.93 (br. *s*, 3 H); 4.76 (*m*, 1 H); 3.48 (*s*, 1 H); 3.22 (*s*, 4 H); 3.15 (*t*, J = 3, H–C(8)); 2.37 (*m*, 2 H). MS (70 eV): 299 (14), 298 (61, $M^{+\cdot}$), 283 (10), 259 (18), 258 (87), 219 (11), 51 (100). Anal. calc. for $C_{19}H_{14}N_4$ (298.35): C 76.49, H 4.73; found: C 76.56, H 4.79.

15-Methylidenetetracyclo[6.6.2.0^{2,7}.0^{9,14}]hexadeca-2(7),9(14)-diene-4,4,5,5,11,11,12,12-octacarbonitrile (**14**). M.p. > 250° (dec.). UV (95% EtOH): final abs., 203 (ε = 7000). IR (KBr): 3080, 2950, 2860, 1715, 1600, 1440, 1360, 1240, 1220, 890. ^{1}H-NMR (CD_3COCD_3): 5.06, 4.79 (2 br. *s*, CH_2=C(15)); 4.04 (*s*, H–C(1)); 3.74 (*m*, H–C(8)); 3.62 (*m*, 8 H); 2.22 (*m*, 2 H). MS (70 eV): 427 (26), 426 (68, $M^{+\cdot}$), 399 (4), 386 (11), 372 (3), 258 (100). Anal. calc. for $C_{25}H_{14}N_8$ (426.44): C 70.41, H 3.31; found: C 70.21, H 3.46.

9-Methyl-11,12-dimethylidenetricyclo[6.2.2.0^{2,7}]dodeca-2(7),9-diene-4,4,5,5-tetracarbonitrile (**15**). A mixture of **10** (16 mg, 0.094 mmol) and TCNE (12 mg, 0.094 mmol) in anh. benzene (1 ml) was stirred at 20° for 30 min. After solvent evaporation, the residue was purified by column chromatography on silica gel (3.5 g, CH_2Cl_2). Recrystallization from CH_2Cl_2 gave 20 mg (72%) of **15** as a colourless solid, m.p. 180° (dec.). UV (CH_3CN): 271 (7800), 262 (8250), 256 (7950), 250 (sh, 6950). IR ($CHCl_3$): 3080, 3020, 2960, 2920, 2900, 2840, 2240, 1620, 1430, 880, 810. ^{1}H-NMR ($CDCl_3$): 6.04 (*dm*, J = 6, H–C(10)); 5.36, 5.22, 4.97, 4.93 (4*s*, 4 H); 3.82 (*d*, J = 6, H–C(8)); 3.66 (br. *s*, H–C(1)); 3.27 (*s*, 4 H); 1.92 (*d*, J = 2, CH_3–C(9)). MS (70 eV): 299 (8), 298 (34, $M^{+\cdot}$), 283 (15), 170 (15), 155 (41), 142 (16), 118 (30), 52 (100).

15-Methyltetracyclo[6.6.2.0^{2,7}.0^{9,14}]hexadeca-2(7),9(14),15-triene-4,4,5,5,11,11,12,12-octacarbonitrile (**16**). A mixture of **10** (11 mg, 0.065 mmol) and TCNE (18 mg, 0.14 mmol) in anh. benzene was stirred at 20° for 10 d. After solvent evaporation, the residue was recrystallized from acetone/petroleum ether, yielding 24 mg (83%) of colourless crystals, m.p. > 230° (dec.). UV (CH_3CN): 236 (4500). IR (KBr): 3060, 2980, 2950, 2920, 2260, 1440, 1250, 1230, 1220, 1150. ^{1}H-NMR ($CDCOCD_3$): 6.46 (*dm*, J = 6, H–C(16)); 4.58 (*d*, J = 6, H–C(8)); 4.48 (br. *s*, H–C(1)); 3.67 (*m*, 8 H); 1.95 (*d*, J = 2, 3 H). MS (70 eV): 427 (12), 426 (39, $M^{+\cdot}$), 399 (3), 372 (5), 298 (63), 283 (45), 278 (16), 258 (49), 252 (28), 250 (23), 170 (68), 155 (65), 115 (48), 68 (69), 52 (100).

Methyl 1,4,5,6,7,8-Hexahydro-6-methylidene-5,8-methanonaphthalene-2-carboxylate (**17**) *and Methyl 1,4,5,6,7,8-Hexahydro-7-methylidene-5,8-methanonaphthalene-2-carboxylate* (**18**). A mixture of **1** (230 mg, 1.26 mmol), methyl propynoate (744 mg, 0.74 ml, 8.8 mmol), and anh. benzene (4 ml, degassed under vacuum) was heated in a sealed *Pyrex* tube to 100° for 2 h. The solvent was evaporated and the excess of dienophile distilled off, yielding 330 mg of a 71:29 mixture **17**/**18** as a colourless oil. IR ($CHCl_3$): 2990, 1715, 1430. ^{1}H-NMR (C_6D_6) of **17**: 6.90 (*m*, H–C(3)); 4.95, 4.70 (2*m*, CH_2=C(6)); 3.47 (*s*, $COOCH_3$); 3.20–2.45 (*m*, 6 H); 2.15, 1.66 (2*dm*, ^2J = 15, CH_2(7)); 1.56, 1.31 (2*dm*, ^2J = 8, C(5)–CH_2–C(8)). ^{1}H-NMR (C_6D_6) of **18**: 6.90 (*m*, H–C(3)); 4.95, 4.70 (2*m*, CH_2=C(7)); 3.47 (*s*, CH_3); 3.20–2.45 (*m*, 6 H); 2.15, 1.66 (2*m*, ^2J = 15, CH_2(6)); 1.56, 1.31 (2*dm*, ^2J = 8, C(5)–CH_2–C(8)). ^{13}C-NMR of **17** and **18**: see the *Table*. MS (70 eV): 216 (80, $M^{+\cdot}$), 157 (100), 142 (49), 129 (66), 115 (60), 91 (21).

1,4,5,6,7,8-Hexahydro-6-methylidene-5,8-methanonaphth-2-yl Methyl Ketone (**19**) *and 1,4,5,6,7,8-Hexahydro-7-methylidene-5,8-methanonaphth-2-yl Methyl Ketone* (**20**). A mixture of **1** (130 mg, 0.98 mmol), but-3-yn-2-one (496 mg, 0.54 ml, 6.89 mmol) and anh. benzene (1.6 ml) was degassed under vacuum and heated to 100° for 2 h in a *Pyrex* tube sealed under vacuum. After cooling to 20°, the soln. was evaporated, yielding 188 mg (95%) of a 56:44 mixture **19**/**20**. GC (methyl silicone, 25 m, 150°–200°): t_R of **19**, 4'48", and of **20**, 4'42". IR ($CHCl_3$): 2980, 1670, 1630, 1240, 875. ^{1}H-NMR ($CDCl_3$): 6.91 (*m*, H–C(3)); 4.95, 4.68 (2*m*, CH_2=C); 2.95 (*m*, 4 H); 2.79, 2.18 (2*m*, H–C(5), H–C(8)); 2.30 (*s*, CH_3); 1.88–1.35 (*m*, 4 H). MS (70 eV) of **19**: 200 (78, $M^{+\cdot}$), 185 (31), 157 (53), 142 (62), 129 (100). MS (70 eV) of **20**: 200 (38, $M^{+\cdot}$), 185 (69), 157 (76), 142 (57), 129 (92), 115 (100).

1,2,3,4,5,6,7,8-Octahydro-6-methylidene-5,8-methanonaphth-2-yl Methyl Ketone (**21**) *and 1,2,3,4,5,6,7,8-Octahydro-7-methylidene-5,8-methanonaphth-2-yl Methyl Ketone* (**22**). A mixture of **1** (93.3 mg, 0.71 mmol), methyl vinyl ketone (395 mg, 0.46 ml, 5.64 mmol), two drops of propylene oxide, and anh. benzene (2.5 ml) was degassed under vacuum and heated to 100° for 2.5 h in a *Pyrex* tube sealed under vacuum. After cooling to 20°, the mixture was evaporated. The residue was purified by column chromatography on *Florisil* (4 g, AcOEt/petroleum ether 3:97, 200 ml), yielding 122 mg (85%) of a 71:29 mixture **21**/**22** (b.p. 110°, 0.12 Torr) as a colourless oil. IR ($CHCl_3$): 2990, 2970, 1710, 1660, 880. ^{1}H-NMR (360 MHz, $CDCl_3$): 4.90, 4.64 (2*m*, CH_2=C); 2.92 (*m*, H–C(5)); 2.70 (*m*, H–C(8)); 2.43–1.68 (*m*, 9 H); 2.15 (*s*, CH_3); 1.59, 1.40 (2 *dm*, ^2J = 8, 2 H). ^{13}C-NMR: see the *Table*. MS (70 eV): 202 (24, $M^{+\cdot}$), 183 (15), 159 (100), 143 (23), 117 (65), 91 (61).

Methyl 5,6,7,8-Tetrahydro-6-methylidene-5,8-methanonaphthalene-2-carboxylate (**23**) *and Methyl 5,6,7,8-Tetrahydro-7-methylidene-5,8-methanonaphthalene-2-carboxylate* (**24**). A mixture **17**/**18** (71:29; 93.5 mg, 0.43 mmol), DDQ (220 mg, 0.97 mmol), and anh. C_6H_6 (5 ml) was stirred at 20° for 23 h. After the addition of 5% aq. $Na_2S_2O_5$ soln. (15 ml), the mixture was stirred at 20° for 30 min. The precipitate was eliminated by filtration (*Büchner*) and the org. layer washed successively with 5% aq. $Na_2S_2O_5$ soln. (15 ml, 4 times) and with a sat. aq. $NaHCO_3$ soln. (15 ml, 4 times). After drying ($MgSO_4$), the solvent was evaporated, yielding a 73:27 mixture **23**/**24** (92 mg, 99%) as a colourless oil. UV (isooctane): 245 (12900), 276 (1600), 286 (1400). IR ($CHCl_3$): 3000, 2960, 1715, 1440, 1305, 1270. ^{1}H-NMR (360 MHz, C_6D_6) of **23**: 8.23 (*d*, *J* = 1.3, H–C(1)); 8.22 (*dd*, *J* = 7.8, 1.3, H–C(3)); 7.18 (*d*, *J* = 1.8, H–C(4)); 5.21, 4.81 (2*m*, CH_2=C(6)); 3.67 (*s*, CH_3); 3.56 (*m*, H–C(5)); 3.14 (*m*, H–C(8)); 2.32 (*dm*, ^2J = 16, 1 H); 1.77 (*m*, 2 H); 1.55 (*dm*, ^2J = 9, 1 H). ^{1}H-NMR (360 MHz, C_6D_6) of **24**: 8.27 (*d*, *J* = 1.3, H–C(1)); 8.24 (*dd*, *J* = 07.8, 1.3, H–C(3)); 7.13 (*d*, *J* = 7.8, H–C(4)); 5.21, 4.81 (2*m*, CH_2=C(7)); 3.65 (*s*, CH_3); 3.57 (*m*, H–C(8)); 3.12 (*m*, H–C(5)); 2.32, 1.75, 1.55 (3*m*, 4 H). ^{13}C-NMR of **23** and **24**: see the *Table*. MS (70 eV): 214 (85, $M^{+\cdot}$), 199 (44), 185 (54), 183 (51), 155 (100), 149 (59), 115 (64), 97 (67). Anal. calc. for $C_{14}H_{14}O_2$ (214.26): C 78.48, H 6.59; found: C 78.39, H 6.72.

5,6,7,8-Tetrahydro-6-methylidene-5,8-methanonaphth-2-yl Methyl Ketone (**25**) *and 5,6,7,8-Tetrahydro-7-methylidene-5,8-methanonaphth-2-yl Methyl Ketone* (**26**). A) A mixture **19**/**20** (56:44; 176 mg, 0.88 mmol), DDQ (480 mg, 2.11 mmol), and anh. C_6H_6 (9 ml) was stirred at 20° for 20 h. After the addition of a 5% aq. $Na_2S_2O_5$ soln. (15 ml), the mixture was stirred vigourously for 30 min. The precipitate was filtered off and the org. layer washed successively with 5% aq. $Na_2S_2O_5$ soln. (15 ml, 4 times). After drying ($MgSO_4$), the solvent was evaporated, yielding 149 mg (86%) of a 57:43 mixture **25**/**26** as a colourless oil, b.p. 160°/0.15 Torr. UV (isooctane): 254 (14300), 284 (1800), 294 (1300). IR (CH_2Cl_2): 2980, 1685, 1615, 1360, 1295, 885. ^{1}H-NMR (360 MHz, C_6D_6) of **25**: 8.01 (*d*, *J* = 1.2, H–C(1)); 7.80 (*dd*, *J* = 8, 1.2, H–C(3)); 7.18 (*d*, *J* = 8, H–C(4)); 5.25, 4.86 (2*m*, CH_2=C(6)); 3.60 (*m*, H–C(5)); 3.16 (*m*, H–C(8)); 2.35, 1.81 (2*m*, CH_2(7)); 2.29 (*s*, CH_3); 1.80, 1.60 (2*dm*, ^2J = 9.2, C(5)–CH_2–C(8)). ^{1}H-NMR of **26**: 8.03 (*d*, *J* = 1.2, H–C(1)); 7.85 (*dd*, *J* = 8, 1.2, H–C(3)); 7.13 (*d*, *J* = 8, H–C(4)); 5.25, 4.83 (2*m*, CH_2=C(7)); 3.60 (*m*, H–C(8)); 3.16 (*m*, H–C(5)); 2.25 (*s*, CH_3); 2.35, 1.81, 1.60 (3*m*, 4 H). ^{13}C-NMR: see the *Table*. MS (70 eV): 198 (94, $M^{+\cdot}$), 183 (99), 155 (100), 143 (32), 128 (22), 115 (59). Anal. calc. for $C_{14}H_{14}O$ (198.26): C 84.81, H 7.12; found: C 84.66, H 7.14.

B) A mixture **21**/**22** (71:29; 184 mg, 0.91 mmol), DDQ (930 mg, 4.1 mmol), and anh. C_6H_6 (7 ml) was heated to 80° for 28 h. After cooling to 20°, the mixture was filtered (rinsing with benzene) and washed with a sat. aq. $NaHCO_3$ soln. (50 ml, 8 times). After drying ($MgSO_4$) and concentration to *ca.* 10 ml, the mixture was filtered through a short column of silica gel (3 g, AcOEt/petroleum ether 3:7). After solvent evaporation, the residue was purified by medium-pressure chromatography (*Lobar, Lichroprep Si-60 (Merck)*; AcOEt/petroleum ether 3:97): 33 mg (18%) of a 70:30 mixture **25**/**26**, colourless oil.

9,10,12-Trimethylidenetricyclo[6.2.2.0^{2,7}]dodec-2(7),4-diene-4-yl Methyl Ketone (**29**) *and 9,10,11-Trimethylidenetricyclo[6.2.2.0^{2,7}]dodec-2(7),4-diene-4-yl Methyl Ketone* (**30**). A) A mixture of **2** (127 mg, 0.75 mmol), but-3-yn-2-one (68 mg, 78 µl, 1 mmol), hydroquinone (3 mg), and anh. C_6H_6 (10 ml) was degassed under vacuum and heated to 50° for 19 h. After solvent evaporation and column chromatography on silica gel (6 g, CH_2Cl_2), 78 mg (43%) of a 1:1 mixture **29**/**30** was obtained as a colourless oil.

B) A mixture of but-3-yn-2-one (17.2 µl, 0.22 mmol) and $BF_3 \cdot Et_2O$ (24.8 µl, 0.2 mmol) in anh. CH_2Cl_2 (1 ml) was prepared at −90°. After stirring at −90° for 10 min, **2** (29 mg, 0.17 mmol) in anh. CH_2Cl_2 (1 ml) was added dropwise. After stirring at −90° for 1 h, the mixture was poured onto a vigourously stirred mixture of CH_2Cl_2/H_2O 1:1 (15 ml). The org. layer was collected and washed with H_2O until pH 7. After drying ($MgSO_4$), the solvent was evaporated and the residue purified by column chromatography on silica gel (1.3 g, CH_2Cl_2), yielding 16 mg (38%) of a 62:28 mixture **29**/**30** as a colourless oil. IR (CH_2Cl_2): 3070, 2950, 2910, 2870, 2850, 2820, 1670, 1640, 1620, 1420, 1390, 1370, 1350, 1230, 1140. ^{1}H-NMR ($CDCl_3$): 6.89 (*m*, 1 H); 5.20, 5.18 (2*s*); 4.9 (br. *s*, 1 H); 4.86 (*t*, *J* = 3, 2 H); 4.65 (*m*, 1 H); 3.49, 3.46 (*s*, H–C(1)); 3.05 (*m*, 5 H); 2.42, 2.27 (2*dm*, ^2J = 16, 2 H); 2.31 (*s*, CH_3). ^{13}C-NMR: see the *Table*. MS (70 eV): 239 (11), 238 (57, $M^{+\cdot}$), 236 (53), 223 (51), 221 (42), 195 (98), 193 (67), 181 (65), 180 (58), 179 (59), 178 (77), 165 (100).

Methyl 9,10,12-Trimethylidenetricyclo[6.2.2.0^{2,7}]dodec-2(7),4-diene-4-carboxylate (**31**) *and Methyl 9,10,11-Trimethylidenetricyclo[6.2.2.0^{2,7}]dodec-2(7),4-diene-4-carboxylate* (**32**). A mixture of **2** (146 mg, 0.859 mmol), methyl propynoate (95 µl, 1.12 mmol), hydroquinone (3 mg), and anh. C_6H_6 (6 ml) was degassed under vacuum and heated to 50° for 21 h. After solvent evaporation, the residue was purified by column chromatography on silica gel (7 g, CH_2Cl_2), yielding 76 mg (35%) of a 65:35 mixture **31**/**32** as a colourless oil. IR (CH_2Cl_2): 3080, 2960, 2910, 2880, 1720, 1690, 1650. ^{1}H-NMR ($CDCl_3$): 7.00 (*m*, 1 H); 5.18, 5.15 (2*s*, 2 H); 4.88 (br. *s*, 1 H); 4.83 (*m*, 2 H); 4.63 (*m*, 1 H); 3.75 (*s*, CH_3); 3.44, 3.40 (2*s*, 1 H); 3.06 (br. *s*, 4 H); 2.40, 2.27 (2*dm*, *J* = 16, 2 H). MS (70 eV): 255 (19), 254 (100, $M^{+\cdot}$), 239 (20), 223 (16), 195 (64).

Methyl 9,10,12-Trimethylidenetricyclo[6.2.2.0^{2,7}]dodec-2,4,6-triene-4-carboxylate (**35**) *and Methyl 9,10,11-Trimethylidenetricyclo[6.2.2.0^{2,7}]dodec-2,4,6-triene-4-carboxylate* (**36**). A mixture **31**/**32** (65:35; 92 mg, 0.36 mmol), DDQ (123 mg, 0.54 mmol), and anh. benzene (5 ml) was stirred for 6 h at 20°. Then, 10 ml of 5% aq. $Na_2S_2O_5$ soln. were added. The precipitate was filtered off and washed with benzene. The org. layer was collected and washed with 5% aq. $Na_2S_2O_5$ soln. (10 ml), sat. aq. $NaHCO_3$ soln. (10 ml, 3 times), dried ($MgSO_4$), and evaporated. The residue was purified by chromatography on silica gel (8 g, CH_2Cl_2) and by medium-pressure chromatography (*Lobar, Lichroprep Si-60 (Merck)*, AcOEt/petroleum ether 3:97): 16 mg (17%) of a 65:35 mixture **35**/**36**, colourless oil. ^{1}H-NMR (360 MHz, $CDCl_3$) of **35**: 8.05 (*dd*, *J* = 7.5, 2, H–C(5)); 7.97 (*d*, *J* = 2, H–C(3)); 6.85 (*d*, *J* = 8, H–C(6)); 4.85, 4.79, 4.54 (3*m*, 6 H); 3.55 (*s*, H–C(8), CH_3); 2.88 (*m*, H–C(1)); 1.83 (*m*, CH_2(11)). ^{1}H-NMR (360 MHz, $CDCl_3$) of **36**: 8.00 (*dd*, *J* = 7.5, 2, H–C(5)); 7.93 (*d*, *J* = 2, H–C(3)); 6.89 (*d*, *J* = 8, H–C(6)); 4.90, 4.86, 4.63 (*m*, 6 H); 3.56 (*s*, H–C(1), CH_3); 2.94 (*m*, H–C(8)); 1.83 (*m*, CH_2(12)).

Methyl 1,4,5,6,7,8-Hexahydro-6-dicyanomethylidene-5,8-methanonaphthalene-2-carboxylate (**38**) *and Methyl 1,4,5,6,7,8-Hexahydro-7-dicyanomethylidene-5,8-methanonaphthalene-2-carboxylate* (**39**). A mixture of **37** (230 mg, 1.26 mmol), methyl propynoate (744 mg, 0.74 ml, 8.8 mmol), and anh. benzene (4 ml, degassed under vacuum) was heated in a *Pyrex* tube (sealed under vacuum) to 100° for 2 h. After cooling to 20°, the mixture was evaporated, yielding 330 mg (98%) of a 47:53 mixture **38**/**39** as a colourless oil. IR ($CHCl_3$): 2960, 2240, 1720, 1615. ^{1}H-NMR ($CDCl_3$): 6.96 (*m*, H–C(3)); 3.85 (*m*, H–C(5)); 3.76 (*s*, CH_3); 3.38–2.75 (*m*, 5 H); 2.75–2.35 (*m*, CH_2(7)); 2.30–2.00, 1.83–1.67 (2*m*, C(5)–CH_2–C(8)). ^{13}C-NMR: see the *Table*. MS (70 eV): 266 (21, $M^{+\cdot}$), 234 (100), 207 (30), 205 (32).

Methyl 5,6,7,8-Tetrahydro-6-dicyanomethylidene-5,8-methanonaphthalene-2-carboxylate (**40**) *and Methyl 5,6,7,8-Tetrahydro-7-dicyanomethylidene-5,8-methanonaphthalene-2-carboxylate* (**41**). A mixture **38**/**39** (47:53; 35 mg, 0.13 mmol), DDQ (33 mg, 0.14 mmol), and anh. benzene (5 ml) was heated to 80° for 4.5 h. After cooling to 20°, the precipitate was filtered off and washed with benzene. The soln. was washed with 4% aq. $NaHCO_3$ soln. (25 ml, 4 times), dried ($MgSO_4$), and evaporated: 32 mg (92%) of a 44:56 mixture **40**/**41** colourless oil. UV (isooctane): 231 (15200), 244 (14500), 264 (13800), 282 (sh, 5800), 296 (sh, 400). UV (CH_3CN): 236 (15100), 246 (15400), 264 (13500), 294 (sh, 3800). IR ($CHCl_3$): 2960, 2240, 1720, 1625, 1440, 1300, 1290, 1270. ^{1}H-NMR (CD_3COCD_3, 360 MHz) of **40**: 8.21 (*d*, *J* = 1.8, H–C(1)); 8.03 (*dd*, *J* = 7.7, 1.8, H–C(3)); 7.65 (*d*, *J* = 7.7, H–C(4)); 4.70, 4.00 (2*m*, H–C(5), H–C(8)); 3.99 (*s*, CH_3); 3.29 (*dd*, *J* = 18, 3.6, H_{exo}–C(7)); 2.65 (*dd*, *J* = 18, 4.5, H_{endo}–C(7)); 2.44, 2.38 (2*dm*, ^2J = 10, C(5)–CH_2–C(8)). ^{1}H-NMR (360 MHz, CD_3COCD_3) of **41**: 8.09 (*d*, *J* = 2.3, H–C(1)); 8.04 (*dd*, *J* = 8.1, 2.3, H–C(3)); 7.63 (*d*, *J* = 8.1, H–C(4)); 4.69, 4.00 (2*m*, H–C(5), H–C(8)); 3.99 (*s*, CH_3); 3.29 (*dd*, *J* = 18.5, 3.2, H_{exo}–C(6)); 2.61 (*dd*, *J* = 18.5, 4.1, H_{endo}–C(6)); 2.43, 2.36 (2*dm*, ^2J = 9.9, C(5)–CH_2–C(8)); signal attributions and structures of **40** and **41** were confirmed by NOE measurements between pairs of adjacent protons. ^{13}C-NMR of **40** and **41**: see the *Table*. MS (70 eV): 264 (95 $M^{+\cdot}$), 233 (46), 232 (43), 205 (100). Anal. calc. for $C_{16}H_{12}N_2O_2$ (264.28): C 72.72, H 4.58, N 10.59; found: C 72.45, H 4.72, N 10.50.

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