SYNTHESES AND TAUTOMERISATIONS OF AMINO-SUBSTITUTED AND PYRIMIDINE-ANNULATED PYRROLOBENZODIAZEPINES

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Abstract – Different tautomers of 11-amino-substituted pyrrolo[2,1-*c*][1,4]benzodiazepines and 2-substituted 4,7a,12b-triazadibenzo[*e,g*]azulene-1,8-diones were formed depending on the substitution pattern. Syntheses, spectroscopic investigations and an X-Ray analysis are presented.

INTRODUCTION

Pyrrolo[2,1-*c*][1,4]benzodiazepines continue to be of interest from different points of view. Thus, some representatives such as anthramycin (**1**) bind to specific sequences of DNA and have therefore potential as regulators of gene expression with possible application as therapeutic agents.[1] This ring system is also found in some antitumor antibiotics produced by various *Streptomyces* species.[2] In 1999, some new fused pyrrolobenzodiazepines, circumdatins A (**2**), B (**3**), D (**4**) and E (**5**), were isolated from the fungus *Aspergillus ochraceus*.[3]

1

2: R = OMe
3: R = H

4: R = OMe
5: R = H
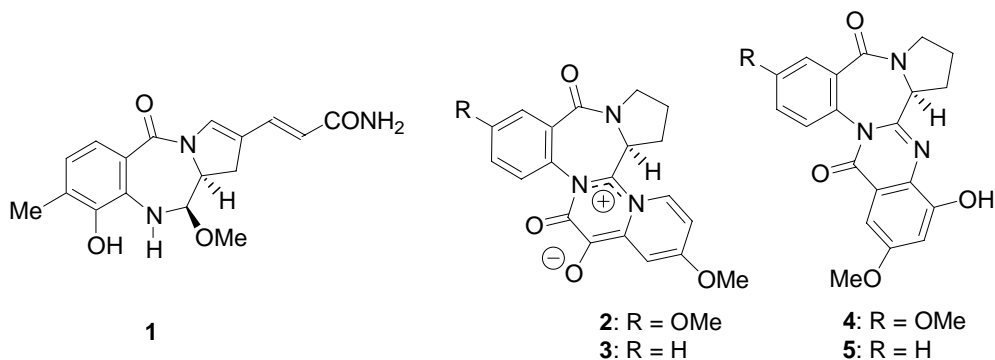
Scheme 1

The (S)-configuration of the α-C-atom of the pyrrolidine ring causes an isohelicity with the minor groove of DNA, so that tautomerism involving this position plays a crucial role for the biological activities of this class of compounds. In continuation of our work on benzodiazepines,[4] pyrrolobenzodiazepines[5,6] and mesomeric betaines[7] we became interested in studying possible tautomerisations of 11-amino-substituted and pyrimidine-annulated pyrrolobenzodiazepines.

RESULTS AND DISCUSSION

We started the syntheses of our target molecules from the readily available monothiolactam (**7**)[8] which was reacted with ammonia, methylamine, and aniline in THF in the presence of mercury(II) chloride to give **8**, **9**, and **10**, respectively. The *N*-unsubstituted amidine (**8**) reacts quantitatively to the starting material (**6**) on heating in water or dilute aqueous sodium hydroxide. In contrast to **9** and **10**, which exist as a mixture of the tautomeric forms (**A**) and (**B**), respectively,[6] only one tautomer of the amidine (**8**) in DMSO-d_6 and MeOD is observable. One broad H/D-exchangeable signal of two protons with a center of gravity at δ = 7.49 ppm in DMSO-d_6 provides strong evidence for the formation of the tautomer (**8A**) under these conditions. Neat reaction of the amidines (**8** – **10**) with 2-ethyl- and 2-benzyl-substituted bis(2,4,6-trichlorophenyl) malonates in a *Zincke* apparatus resulted in the formation of the pyrimidine-annulated pyrrolobenzodiazepines (**11** – **16**) and the leaving group 2,4,6-trichlorophenol which can be distilled off during the reaction. Dependent on the substitution pattern **11** – **16** form different tautomers in solution as well as in the solid state. Thus, only the 4,7a,12b-triazadibenzo[*e,g*]azulenes (**11**) and (**12**) resulting from the N^{11}-unsubstituted pyrrolobenzodiazepine (**8**) were isolated as optically active compounds. These two new compounds form only one tautomer in DMSO-d_6, MeOD, and CDCl$_3$ at room temperature, respectively, as evidenced by ^{1}H NMR spectroscopy. A combination of HMBC and HSQC NMR unambiguously proved the existence of enolic partial structures in **11** and **12** under these conditions, as couplings between 4b-*H* and C-5, C-6, and C-4a were detected. The latest mentioned carbon atom C-4a appears at δ = 157.4 ppm (**11**) and 158.0 ppm (**12**). The carbon atom C-2 is sp^2 hybridized and appears at δ = 103.5 ppm (**11**) and 101.6 ppm (**12**). The hydroxy group causes one broad, H/D-exchangeable signal at δ = 11.45 ppm in DMSO-d_6 and at δ = 6.34 ppm in CDCl$_3$ in the ^{1}H NMR spectra. NOESY experiments of **11**, which possesses the *N*-(3-oxopropenyl)formamidine chromophor, provide evidence for close proximities between the hydroxy group at C-3 and the ethyl group as well as C-5 of the pyrrolidine ring.

In contrast to this, the pyrrolobenzodiazepines derived from the N^{11}-substituted pyrrolobenzodiazepines (**9**) and (**10**) form the tautomers **13** to **16** in DMSO-d_6 at room temperature. No traces of cross-conjugated mesomeric betaines, which would resemble the proposed structures of circumdatins A and B, or enols were detectable. In **13** – **16**, the carbon atom C-2, which appears between δ = 53.6 ppm and 55.8 ppm, unambiguously is sp^3 hybridized. HMBC and HSQC NMR measurements displayed couplings of C-2

with the ethyl group and the benzyl group, respectively.
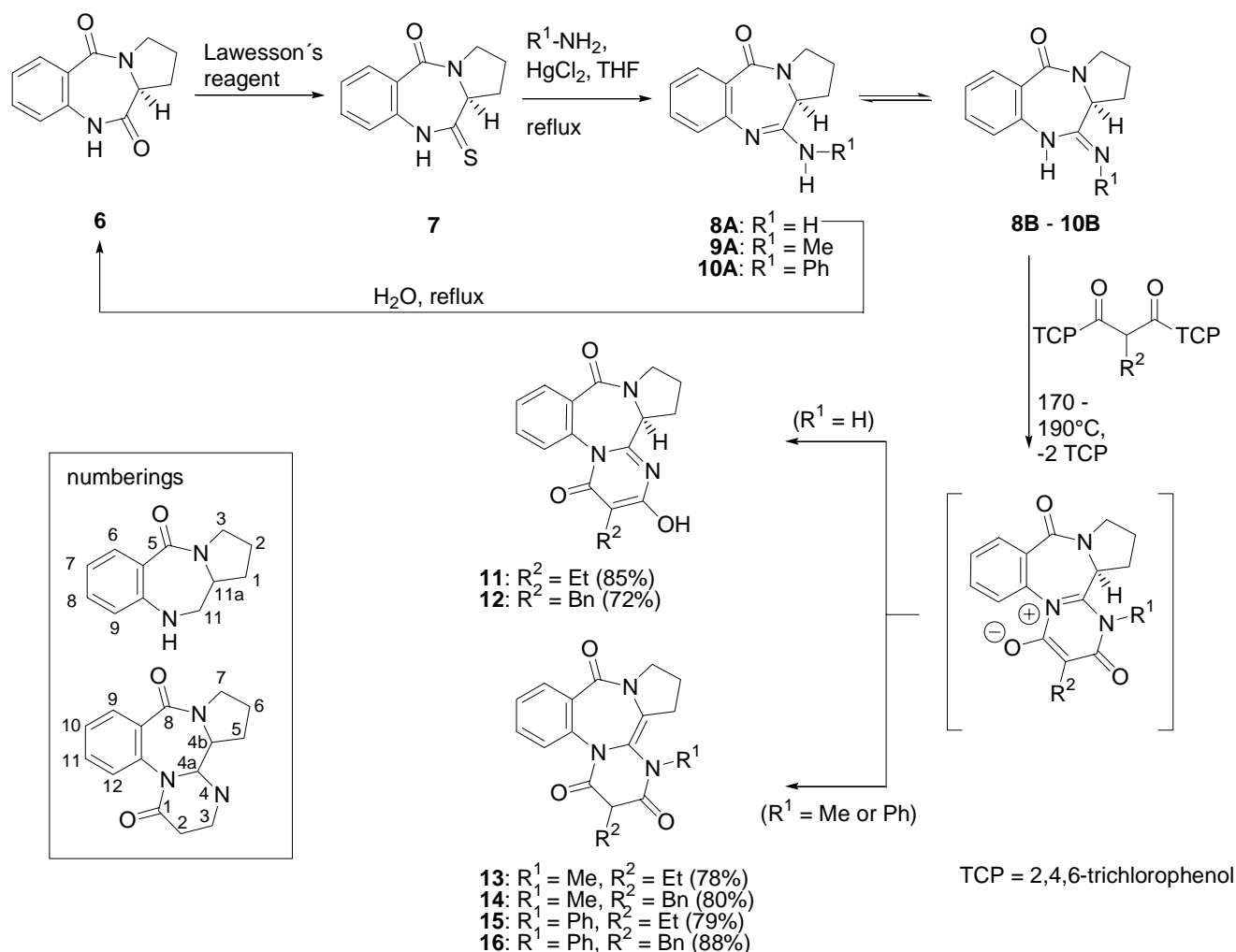
Scheme 2

In order to elucidate a structure in the solid state, we performed an X-Ray single crystal structure analysis of the benzyl derivative (**16**).[9] Single crystals were obtained by slow evaporation of a concentrated solution in 2-butanol. The molecular structure and the crystallographic numbering are shown in Figure 1 and relevant bond distances and angles are given in the Tables 1 and 2. The molecule crystallized with one molecule of 2-butanol in the elemental cell which forms a hydrogen bond to the C12=O12 carbonyl group [crystallographic numbering]. The carbon atom [C3] of the 1,3-diketo moiety is sp^3 hybridized, as its bond angles are 107.89(8)° [C2-C3-C4], 113.80(9)° [C31-C3-C4], and 112.05(9)° [C31-C3-C2], respectively. The bond length C6-C7 was determined to be 132.93(15) pm and corresponds to a $C_{sp}^2=C_{sp}^2$ double bond. The bond angles N1-C6-N5, C6-C7-N11, and C7-C6-N5 are 114.82(9)°, 124.74(10)°, and 123.30(10)°, respectively. The dioxopyrimidine moiety N1-C2-C3-C4-N5-C6 adopts a boat conformation with the benzyl substituent in equatorial position.
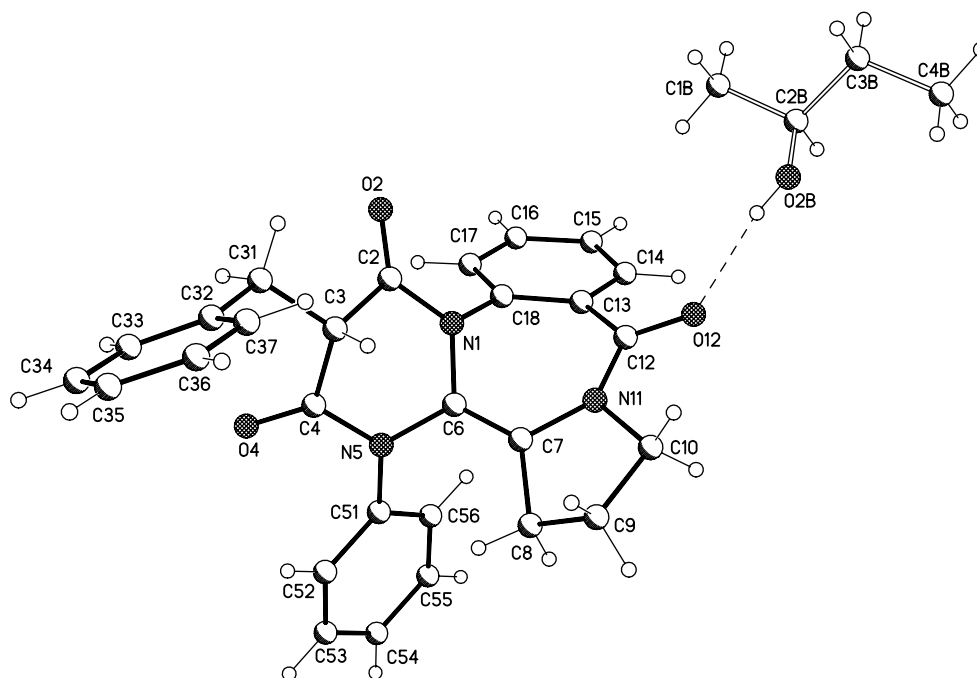
Figure 1: Molecular drawing of 4,7a,12b-triazadibenzo[*e,g*]azulene-1,3,8-trione (**16**).

Table 1. Selected atomic distances (pm) and angles (°) for (**16**).

Bond lengths					
N1-C2	137.63(14)	C4-N5	138.52(13)	C12-C13	149.42(16)
C2-C3	153.22(14)	N5-C6	142.36(13)	C13-C18	139.72(15)
C3-C31	152.40(15)	C6-N1	142.24(13)	C18-N1	143.16(13)
C2-O2	121.34(13)	C7-N11	141.05(14)	C18-C17	139.27(15)
C3-C4	153.41(15)	N11-C12	136.80(15)	C13-C14	140.35(16)
C4-O4	121.51(13)	C12-O12	123.16(14)	N5-C51	143.18(14)
Bond angles					
N1-C2-C3	110.87(9)	C4-N5-C6	115.51(9)	C6-C7-N11	124.74(10)
C2-C3-C4	107.89(8)	C4-N5-C51	123.74(9)	C7-N11-C12	131.28(9)
C3-C4-N5	111.44(9)	N5-C6-N1	114.82(9)	N11-C12-C13	120.84(10)
O2-C2-C3	125.38(10)	C6-N1-C2	116.95(9)	C12-C13-C18	125.44(10)
C3-C4-O4	124.23(10)	N1-C2-O2	123.71(10)	C13-C18-N1	119.64(9)
C2-C3-C31	112.05(9)	N1-C6-C7	121.85(10)	N11-C12-O12	118.71(10)

Table 2. Selected torsion angles for compound (**16**) (°).

N1-C2-C3-C4	-52.26(11)	C2-N1-C6-N5	46.76(12)	N11-C12-C13-C18	32.90(17)
N1-C2-C3-C31	-178.28(9)	C6-N1-C2-C3	3.03(12)	N11-C12-C13-C14	-148.09(11)
C2-C3-C4-O4	-123.15(11)	N1-C6-C7-N11	-0.74(17)	C12-C13-C18-C17	-178.68(11)
C2-C3-C4-N5	56.00(11)	N1-C6-C7-C8	173.45(10)	O12-C12-C13-C14	27.45(16)
C3-C4-N5-C6	-9.41(12)	C6-C7-N11-C12	-30.00(19)	O12-C12-C13-C18	-151.56(12)
C3-C4-N5-C51	-176.84(9)	C6-C7-N11-C10	159.49(11)	C12-C13-C18-N1	1.29(17)
C4-N5-C51-C52	-42.59(15)	C7-N11-C12-O12	-178.65(11)	C6-N1-C18-C13	- 60.62(13)
C4-N5-C6-N1	-42.62(12)	C7-N11-C12-C13	-3.04(18)	C18-N1-C6-N5	-122.19(10)

ACKNOWLEDGEMENTS

EXPERIMENTAL

General methods: The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker ARX-400 and DPX-200 in DMSO-d$_6$ (400 and 200 MHz for ^{1}H NMR) unless otherwise noted. The chemical shifts are reported in ppm relative to internal tetramethylsilane (δ = 0.00 ppm). FT-IR spectra were obtained on a Bruker Vektor 22 in the range of 400 to 4000 cm^{-1} (2.5 % pellets in KBr). The GC-MS spectra were recorded on a GC Hewlett-Packard 5980, Serie II in combination with a MS Hewlett-Packard 5989 B, and on a Varian GC3900 with SAT2100T mass spectrometer.

11-Amino-1,2,3,11a-tetrahydrobenzo[*e*]pyrrolo[1,2-*a*][1,4]diazepin-5-one (8).

To a solution of thiolactam (**7**) (1.16 g, 5.0 mmol) in anhyd THF (50 mL) was added HgCl$_2$ (1.63 g, 6.0 mmol) and pure anhydrous ammonia was bubbled through the mixture for 1 h at 60 °C. After cooling, the resulting suspension was filtered off through a pad of Celite and eluted with methanol. The organic solution was evaporated under reduced pressure at rt. Addition of an acetone/ether mixture afforded a white solid which was washed with ether and recrystallized from anisole/methanol (0.925 g, 86%), mp >240 °C (decomp) [α]$_D^{20}$ = +510.5° (*c* 1.0, DMSO); ^{1}H NMR: δ = 7.79 (dd, *J* = 7.8, 1.5 Hz, 1H, 6-H), 7.49 − 7.54 (m, 1H, 7-H), 7.28 − 7.70 (br m, 2H, NH$_2$), 7.22 (t, *J* = 7.5 Hz, 1H, 8-H), 7.15 (d, *J* = 7.5 Hz, 1H, 9-H), 4.22 (d, *J* = 7.8 Hz, 1H, 11a-H), 3.63 − 3.69 (m, 1H, 3-H), 3.35 − 3.42 (m, 1H, 3-H), 2.43 − 2.59 (m, 1H, 1-H), 2.08 − 2.18 (m, 1H, 1-H), 1.91 − 2.00 (m, 2H, 2-H); ^{13}C NMR: δ = 24.0 (C-2), 26.7 (C-1), 47.4 (C-3), 55.1 (C-11a), 124.6, 125.1, 127.7, 131.0, 132.8, 141.3, 164.3, 165.4 (CO); IR (KBr) 1679, 1614, 1456 cm^{-1}; MS *m/z* (rel. Int.) 215 (M$^+$, 39), 70 (100). Anal. Calcd for C$_{12}$H$_{13}$N$_3$O: C, 66.96; H, 6.09; N, 19.52. Found: C, 66.71; H, 6.27; N, 19.65.

General procedure for the reaction of the cycloamidines (8 – 10) with malonic esters. All of these reactions were carried out *in vacuo* at 3×10^{-2} mbar. An equimolar mixture of the cycloamidine and the corresponding 2-substituted bis(2,4,6-trichlorophenyl)malonate was heated in a *Zincke* apparatus for 10 min at 180-190 °C, whereupon 2,4,6-trichlorophenol was distilled off. The residue was treated with ether (20 mL), the resulting precipitate was collected by filtration and washed with diethylether. The crude solid was recrystallized from the solvents indicated below.

2-Ethyl-3-hydroxy-4b,5,6,7-tetrahydro-4,7a,12b-triazadibenzo[*e,g*]azulene-1,8-dione (11).

Cycloamidine (**8**) (0.430 g, 2.0 mmol) and 2-ethyl bis(2,4,6-trichlorophenyl)malonate (0.982 g, 2.0 mmol) were used, yield 0.529 g (85%), mp >250 °C (nitromethane); $[\alpha]_D^{20}$ = -6.1 ° (*c* 0.5, DMSO); ^{1}H NMR: δ = 11.46 (s, 1H, OH), 7.79 (dd, *J* = 7.6, 1.7 Hz, 1H, 9-H), 7.61 (td, *J* = 7.6, 1.7 Hz, 1H, 10-H), 7.51 − 7.55 (m, 1H, 11-H), 7.49 − 7.51 (m, 1H, 12-H), 4.48 − 4.50 (m, 1H, 4b-H), 3.61 − 3.66 (m, 1H, 7-H), 3.38 − 3.45 (m, 1H, 7-H), 2.74 − 2.81 (m, 1H, 5-H), 2.35 (q, *J* = 7.4 Hz, 2H, CH$_2$), 2.01 − 2.12 (m, 2H, 5,6-H), 1.92 − 1.98 (m, 1H, 6-H), 1.00 (t, *J* = 7.4 Hz, 3H, CH$_3$); ^{13}C NMR: δ = 13.3 (CH$_3$), 17.3 (CH$_2$), 24.2 (C-6), 27.0 (C-5), 47.0 (C-7), 58.9 (C-4b), 103.5 (C-2), 129.2, 129.7, 129.8, 131.1, 132.7, 133.8, 157.4 (C-4a), 163.6, 163.9, 164.3; IR (KBr) 1650, 1554, 1458 cm^{-1}; MS *m/z* (rel. Int.) 311 (M$^+$, 100). Anal. Calcd for C$_{17}$H$_{17}$N$_3$O$_3$ · 0.5 H$_2$O: C, 63.74; H, 5.66; N, 13.12. Found: C, 63.47; H, 5.44; N, 13.34.

2-Benzyl-3-hydroxy-4b,5,6,7-tetrahydro-4,7a,12b-triazadibenzo[*e,g*]azulene-1,8-dione (12).

Cycloamidine (**8**) (0.430 g, 2.0 mmol) and 2-benzyl bis(2,4,6-trichlorophenyl)malonate (1.106 g, 2.0 mmol) were used, yield 0.537 g (72%), mp >250 °C (methanol); $[\alpha]_D^{20}$ = -29.6 ° (*c* 0.5, DMSO); ^{1}H NMR: δ = 11.71 (s, 1H, OH), 7.80 (dd, *J* = 7. 5, 1.1 Hz, 1H, 9-H), 7.59 − 7.64 (m, 1H, 10-H), 7.52 − 7.55 (m, 1H, 11-H), 7.48 (d, *J* = 8.0 Hz, 1H, 12-H), 7.21 − 7.27 (m, 4H, Ph), 7.12 − 7.15 (m, 1H, Ph), 4.50 (d, *J* = 6.3 Hz, 1H, 4b-H), 3.58 − 3.69 (m, 1H, 7-H), 3.37 − 3.44 (m, 1H, 7-H), 3.17 (s, 2H, CH$_2$), 2.75 − 2.77 (m, 1H, 5-H), 2.01 − 2.14 (m, 2H, 5,6-H), 1.92 − 1.97 (m, 1H, 6-H); ^{13}C NMR: δ = 24.1 (C-6), 27.0 (C-5), 29.6 (CH$_2$), 47.0 (C-7), 58.9 (C-4b), 101.6 (C-2), 126.6, 129.0, 129.2, 129.3, 129.7, 129.8, 131.1, 132.6, 133.8, 141.4, 158.0 (C-4a), 163.8, 164.2, 164.5; IR (KBr) 1667, 1626, 1604, 1558, 1458 cm^{-1}; MS *m/z* (rel. Int.) 373 (M$^+$, 100). Anal. Calcd for C$_{22}$H$_{19}$N$_3$O$_3$ · 0.5 H$_2$O: C, 69.10; H, 5.27; N, 10.99. Found: C, 68.89; H, 5.33; N, 10.76.

2-Ethyl-4-methyl-4,5,6,7-tetrahydro-4,7a,12b-triazadibenzo[*e,g*]azulene-1,3,8-trione (13).

Cycloamidine (**9**) (0.458 g, 2.0 mmol) and 2-benzyl bis(2,4,6-trichlorophenyl)malonate (0.982 g, 2.0 mmol) were used, yield 0.507 g (78%), mp 185–187 °C (xylene); $[\alpha]_D^{20}$ = 0 ° (*c* 1.0, CHCl$_3$); ^{1}H NMR (CDCl$_3$): δ = 8.05 (dd, *J* = 8.1, 1.6 Hz, 1H, 9-H), 7.59 (ddd, *J* = 8.1, 7.4, 1.6 Hz, 1H, 10-H), 7.38 − 7.42 (m, 1H, 11-H), 7.35 (dd, *J* = 8.2, 0.8 Hz, 1H, 12-H), 4.00 − 4.06 (m, 2H, 7-H), 3.25 − 3.28 (m, 1H, 2-H), 3.22 (s, 3H, NCH$_3$), 2.72 − 2.77 (m, 2H, 5-H), 2.20 − 2.28 (m, 1H, 6-H), 2.09 (dd, *J* = 7.4/6.3 Hz, 2H, C*H*$_2$CH$_3$), 2.04 − 2.16 (m, 1H, 6-H), 1.16 (t, *J* = 7.4 Hz, 3H, CH$_2$C*H*$_3$); ^{13}C NMR (CDCl$_3$): δ = 12.9 (CH$_3$), 17.2 (CH$_2$), 20.9 (C-6), 29.7 (C-5), 29.7 (NCH$_3$), 49.7 (C-7), 53.6 (C-2), 120.6, 125.8, 127.7, 129.0, 129.7, 132.6, 133.6, 140.5, 165.6 (CO), 167.1 (CO), 168.4 (CO); IR (KBr) 1681, 1632, 1574, 1489, 1452 cm^{-1}; MS *m/z* (rel. Int.) 325 (M$^+$, 100). Anal. Calcd for C$_{18}$H$_{19}$N$_3$O$_3$: C, 66.45; H, 5.89; N, 12.91. Found: C,

66.37; H, 5.92; N, 12.91.

2-Benzyl-4-methyl-4,5,6,7-tetrahydro-4,7a,12b-triazadibenzo[*e,g*]azulene-1,3,8-trione (14).

Cycloamidine (**9**) (0.458 g, 2.0 mmol) and 2-benzyl bis(2,4,6-trichlorophenyl)malonate (0.982 g, 2.0 mmol) were used, yield 0.619 g (80%), mp 185–187 °C (xylene); $[\alpha]_D^{20} = 0$ ° (*c* 1.0, CHCl$_3$); ^{1}H NMR (CDCl$_3$): δ = 8.01 (dd, *J* = 7.7, 1.1 Hz, 1H, 9-H), 7.55 – 7.59 (m, 1H, 10-H), 7.21 – 7.42 (m, 7H, Ph), 3.91 – 4.01 (m, 2H, 7-H), 3.57 – 3.60 (m, 1H, 2-H), 3.42 (d, *J* = 5.7 Hz, 2H, C*H$_2$*Ph), 3.19 (s, 3H, NCH$_3$), 2.62 – 2.72 (m, 2H, 5-H), 2.14 – 2.19 (m, 1H, 6-H), 1.95 – 2.06 (m, 1H, 6-H); ^{13}C NMR (CDCl$_3$): δ = 20.7 (C-6), 29.3 (C-5), 29.7 (*C*H$_2$Ph), 35.7 (NCH$_3$), 49.7 (C-7), 54.9 (C-2), 120.2, 125.7, 126.8, 127.8, 128.8, 129.0, 129.2, 130.1, 132.7, 133.7, 140.4, 140.6, 165.5 (CO), 166.7 (CO), 168.0 (CO); IR (KBr) 1721, 1682, 1644, 1597, 1487, 1450 cm^{-1}; MS *m/z* (rel. Int.) 387 (M$^+$, 100). Anal. Calcd for C$_{23}$H$_{21}$N$_3$O$_3$: C, 71.30; H, 5.46; N, 10.85. Found: C, 71.46; H, 5.48; N, 10.61.

2-Ethyl-4-phenyl-4,5,6,7-tetrahydro-4,7a,12b-triazadibenzo[*e,g*]azulene-1,3,8-trione (15).

Cycloamidine (**10**) (0.582 g, 2.0 mmol) and 2-benzyl bis(2,4,6-trichlorophenyl)malonate (0.982 g, 2.0 mmol) were used, yield 0.612 g (79%), mp 201–202 °C (n-butanol); $[\alpha]_D^{20} = 0$ ° (*c* 1.0, CHCl$_3$); ^{1}H NMR (CDCl$_3$): δ = 8.07 – 8.09 (m, 1H, 9-H), 7.61 – 7.66 (m, 1H, 10-H), 7.41 – 7.46 (m, 2H, Ph), 7.27 – 7.34 (m, 2H, Ph), 7.08 – 7.20 (m, 3H, Ph), 3.94 – 3.98 (m, 2H, 7-H), 3.47 (td, *J* = 6.2, 0.8 Hz, 1H, 2-H), 2.44 – 2.50 (m, 1H, 6-H), 2.08 – 2.15 (m, 2H, C*H$_2$*CH$_3$), 1.82 – 2.02 (m, 3H, 5,6-H), 1.19 (td, *J* = 7.5, 0.8 Hz, 3H, CH$_2$C*H$_3$*); ^{13}C NMR (CDCl$_3$): δ = 12.9 (CH$_3$), 17.3 (CH$_2$), 20.4 (C-6), 29.8 (C-5), 50.0 (C-7), 54.5 (C-2), 119.1, 124.5, 124.8, 126.7, 128.0, 129.2, 129.6, 131.7, 132.9, 133.9, 139.1, 139.9, 165.6 (CO), 166.9 (CO), 167.0 (CO); IR (KBr) 1724, 1684, 1635, 1600, 1490, 1453 cm^{-1}; MS *m/z* (rel. Int.) 387 (M$^+$, 100). Anal. Calcd for C$_{23}$H$_{21}$N$_3$O$_3$: C, 71.30; H, 5.46; N, 10.85. Found: C, 70.93; H, 5.58; N, 10.72.

2-Benzyl-4-phenyl-4,5,6,7-tetrahydro-4,7a,12b-triazadibenzo[*e,g*]azulene-1,3,8-trione (16).

Cycloamidine (**10**) (0.582 g, 2.0 mmol) and 2-benzyl bis(2,4,6-trichlorophenyl)malonate (0.982 g, 2.0 mmol) were used, yield 0.790 g (88%), mp 187–188 °C (2-propanol); $[\alpha]_D^{20} = 0$ ° (*c* 1.0, CHCl$_3$); ^{1}H NMR (CDCl$_3$): δ = 8.06 – 8.08 (m, 1H, 9-H), 7.63 – 7.67 (m, 1H, 10-H), 7.42 – 7.48 (m, 4H, Ph), 7.22 – 7.35 (m, 5H, Ph), 7.15 – 7.19 (m, 1H, Ph), 7.06 – 7.09 (m, 2H, Ph), 3.87 – 3.98 (m, 2H, 7-H), 3.81 (t, *J* = 6.0 Hz, 1H, 2-H), 3.47 (d, *J* = 6.0 Hz, 2H, C*H$_2$*Ph), 2.39 – 2.45 (m, 1H, 5-H), 1.82 – 1.97 (m, 3H, 5, 6-H); ^{13}C NMR (CDCl$_3$): δ = 20.2 (C-6), 29.3 (C-5), 29.8 (*C*H$_2$Ph), 50.0 (C-7), 55.8 (C-2), 118.7, 124.5, 125.8, 126.8, 128.1, 128.9, 129.2, 129.4, 129.7, 130.2, 132.1, 132.9, 134.0, 139.1, 139.8, 140.6, 165.5 (CO), 166.4 (CO), 166.6 (CO); IR (KBr) 1735, 1695, 1633, 1619, 1574, 1496, 1454 cm^{-1}; MS *m/z* (rel. Int.) 449 (M$^+$, 100). Anal. Calcd for C$_{28}$H$_{23}$N$_3$O$_3$ · 0.5 2-propanol): C, 73.89; H, 5.68; N, 8.76. Found: C, 73.70; H, 5.67; N, 8.66.

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9. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-258313. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk). Some crystal data of 16: $C_{28}H_{23}N_3O_3 - 0.5$ 2-butanol; M = 486.55; space group P-1 (no. 2); dimensions 0.50 x 0.30 x 0.20 mm, a = 10.9276(1), b = 11.6818(1), c = 11.6878(1) Å; α = 106.467(1)°, β = 115.771(1)°, γ = 99.841(1)°; V = 1211.44(2) $Å^3$, D_c = 1.334 Mg m^{-3}, Z = 2, μ(MoKα) = 0.088 mm^{-1}; T = 123(2) K; F(000) = 514, 23952 reflections were collected in a Nonius KappaCD diffractometer ($2\Theta_{max.}$ = 55°, -14 $\leq$ h $\leq$ 14, -15 $\leq$ k $\leq$ 15, -15 $\leq$ l $\leq$ 15), 5427 symmetry independent reflections (R_{int} = 0.0292) were used for the structure solution (direct methods)[10] and refinement (full-matrix least-squares on F^2,[11] 330 parameters, 16 restraints), non-hydrogen atoms were refined anisotropically, H atoms localized by difference electron density, and were defined using a riding model; wR2 (all data) = 0.1008 [R1 = 0.0387 for 4856 I>2σ(I)].

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