

SYNTHESIS OF 9,11-DIAZAPENTACYCLO[6.4.0.0^{1,3}.0^{2,5}.0^{4,8}]DODECANE-2,4-DIONES

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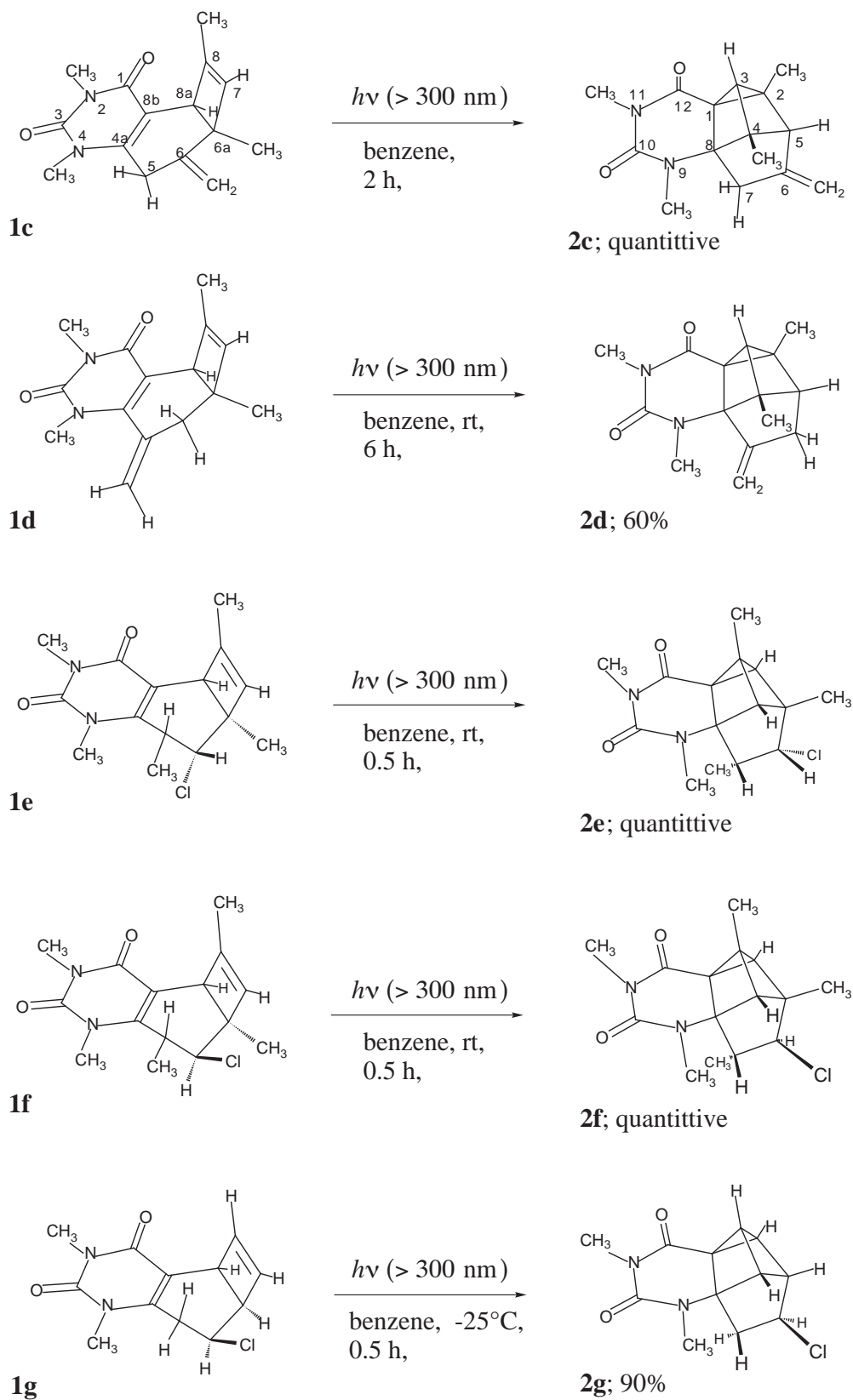
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Abstract — UV-Irradiation of 5,6-dihydrocyclobutaquinazoline-2,4-dione derivatives (**1c-g**) furnished the corresponding 9,11-diazapentacyclo[6.4.0.0^{1,3}.0^{2,5}.0^{4,8}]dodecane-10,12-diones (**2c-g**) in fair yields, whereas photoreaction of cyclobutaquinazoline-2,4-dione (**1h**) produced quinazoline-2,4-dione (**4**) and cyclooctapyrimidine (**5**).

Photocycloaddition of aromatic or heteroaromatic compounds has been recognized to give rise to the formation of a variety of complicated unique ring systems in one step, and hence the photochemistry has been studied intensively from synthetic and mechanistic points of view.¹ In the course of our studies on the acid-catalyzed photoreaction of pyrimidine bases with substituted benzenes, we have reported that photoreaction of 6-chloro-1,3-dimethyluracil (6-CIDMU) with *p*- and *m*-xylenes gave rise to the formation of 9,11-diazapentacyclododecanes consisting of a [6.4.0.0^{1,3}.0^{2,5}.0^{4,8}] system (**2a, b**)² with a methylene group at C6 and a [6.4.0.0^{1,3}.0^{2,6}.0^{4,8}] system (**3a, b**) with a methylene group at C5.³ In an extension of this photoreaction, we have carried out the photoreaction with mesitylene to give the highly strained pentacyclo[6.4.0.0^{1,3}.0^{2,5}.0^{4,8}]dodecane derivative (**2c**),^{4, 5} as well as the pentacyclo[6.4.0.0^{1,3}.0^{2,6}.0^{4,8}]dodecane derivative (**3c**).⁵ In addition, we have demonstrated that the highly strained pentacyclo[6.4.0.0^{1,3}.0^{2,5}.0^{4,8}]dodecane system (**2c**) results from the intramolecular [2+2] cycloaddition of the cyclobutaquinazoline derivative (**1c**),⁴ generated from the initially produced cyclooctapyrimidine derivative by way of the sequential electrocyclic processes, while the compound consisting of a pentacyclo[6.4.0.0^{1,3}.0^{2,6}.0^{4,8}]dodecane system (**3c**) rises from an acid-catalyzed [$\pi 4s + \pi 2a$] type of

electrocyclic rearrangement of the tautomer of cyclooctapyrimidine.⁶



Scheme 1. Photorearrangement of cyclobutaquinazolines (**1**) into 9,11-diaza-pentacyclo[6.4.0.0^{1,3}.0^{2,5}.0^{4,8}]dodecane-10,12-diones (**2**)

Interestingly each pentacyclo[6.4.0.0^{1,3}.0^{2,5}.0^{4,8}]dodecane (**2a-c**) includes a methylene group at C-6 as a component, suggesting that the presence of a methylene group at C-6 in the precursory cyclobutaquinazoline may serve importantly for the construction of the ring system. Meanwhile during our continuing studies, a variety of cyclobutaquinazoline derivatives have gathered in our hands. This encouraged us to make a general view of the synthesis of diazapentacyclo[6.4.0.0^{1,3}.0^{2,5}.0^{4,8}]dodecanes (**2**). In the present paper, we wish to describe our findings that the highly strained pentacyclo[6.4.0.0^{1,3}.0^{2,5}.0^{4,8}]dodecane derivatives (**2**) were produced in satisfactory yields from the cyclobutaquinazolines with their C5=C6 double bonding released.

Photoreaction of the 6-methylene derivative of 5,6,6a,8a-tetrahydro-2,4,5,6a,8-pentamethylcyclobuta[*f*]-quinazoline-1,3-dione (**1c**) has been reported to afford the corresponding pentacyclododecane derivative (**2c**) quantitatively.⁴ We carried out the UV-irradiation of the 5-methylene derivative (**1d**)⁷ (6 h) under the similar conditions. At the initial stage of the UV-irradiation, NMR spectroscopy showed that desired pentacyclododecane (**2d**) and an unidentified product are formed in the ratio of *ca.* 1:1.

However the latter seemed quite unstable and soon disappeared, resulting in the formation of desired pentacyclododecane (**2d**) as the sole product in 60% yield. UV-irradiation of 6-chlorocyclobuta[*f*]quinazoline derivative (**1g**) for 30 min gave **2g** as the sole product. Similarly, irradiation of 5,6-*trans* isomer of 6-chloro-2,4,5,6a,8-pentamethylcyclobutaquinazoline (**1f**)⁵ for 30 min gave **2f** quantitatively. Similar photoreaction of the *cis* isomer (**1e**) (30 min) afforded **2e** quantitatively.

The structure of **2d** was confirmed by the X-Ray crystallographic analysis (Figure 1).

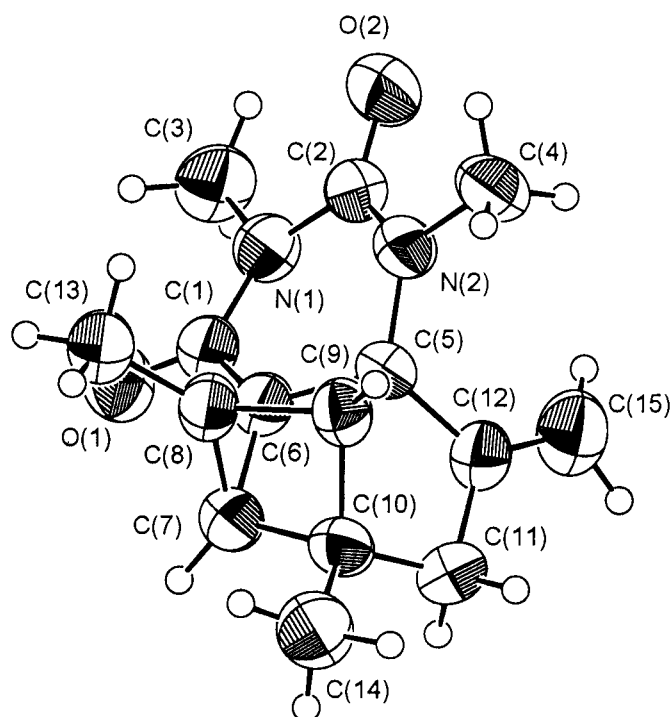


Figure 1. Molecular structure of **2d**

The X-Ray crystallography of **2d** shows that the sp^3 carbons composing the three-membered and the four-membered rings are considerably strained. The three internal angles of the cyclopropane moiety are 57.8° , 60.1° , and 62.1° , respectively (see Table 3), which depart to a great extent from the ideal angle of an sp^3 -hybridized atom (109.5°). Similarly the internal angles of the two cyclobutane rings are strained to around 90° .

The structural assignments for **2e**, **2f**, and **2g** were made essentially on the basis of their $^1\text{H-NMR}$ spectroscopy and NOE experiments. These results are shown in Table 1 and Figure 2, respectively.

Table 1. $^1\text{H-NMR}$ data (CDCl_3) for **2e**, **2f**, and **2g**

Proton No	2e	2f	2g
	Chemical shift δ ($J = \text{Hz}$)		
2	2.78 (d, $J_{2,4} = 5.0$)	2.65 (d, $J_{2,4} = 5.0$)	2.91 (ddd, $J_{2,4} = 4.9$, $J_{2,3} = 3.4$, $J_{2,5} = 2.4$)
3			3.42 (d, $J_{3,2} = 3.4$)
C3- CH_3	1.50 (3H, s)	1.52 (3H, s)	
4	2.45 (d, $J_{4,2} = 5.0$)	2.62 (d, $J_{4,2} = 5.0$)	3.04 (dd, $J_{4,2} = 4.9$, $J_{4,5} = 4.4$)
5			3.54 (dd, $J_{5,2} = 2.4$, $J_{5,4} = 4.4$)
C5- CH_3	1.47 (3H, s)	1.50 (3H, s)	
6	3.91 (d, $J_{6,7} = 10.6$)	3.70 (d, $J_{6,7} = 3.8$)	4.28 (dd, $J_{6,7a} = 2.4$, $J_{6,7b} = 7.8$)
7 (Ha)	2.31 (dq, $J_{7,6} = 10.6$, $J_{7,C7-CH_3} = 7.1$)	2.31 (dq, $J_{7,6} = 3.8$, $J_{7,C7-CH_3} = 7.0$)	1.99 (dd, $J_{7a,7b} = 14.7$, $J_{7a,6} = 2.4$)
7 (Hb)			2.55 (dd, $J_{7b,7a} = 14.7$, $J_{7b,6} = 7.8$)
C7- CH_3	1.03 (3H, d, $J_{C7-CH_3, 7} = 7.1$)	1.12 (3H, d, $J_{C7-CH_3, 7} = 7.0$)	
N9- CH_3	2.93 (3H, s)	3.00 (3H, s)	3.01 (3H, s)
N11- CH_3	3.19 (3H, s)	3.19 (3H, s)	3.20 (3H, s)

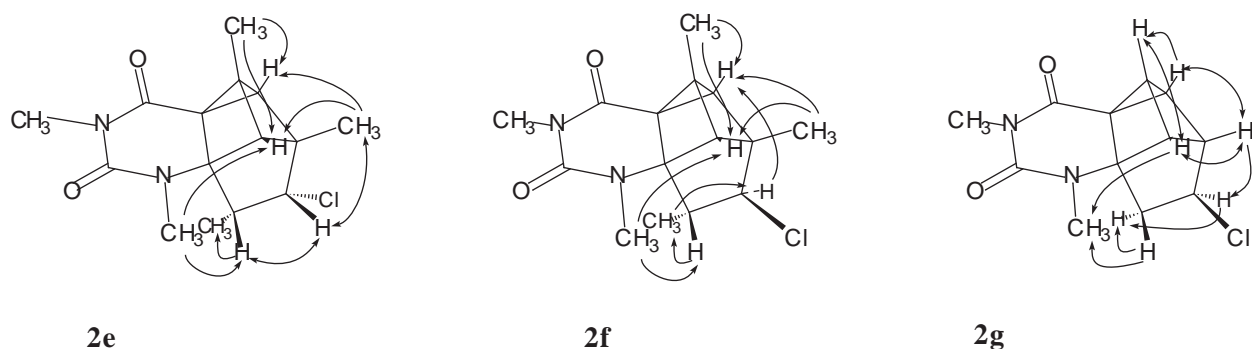
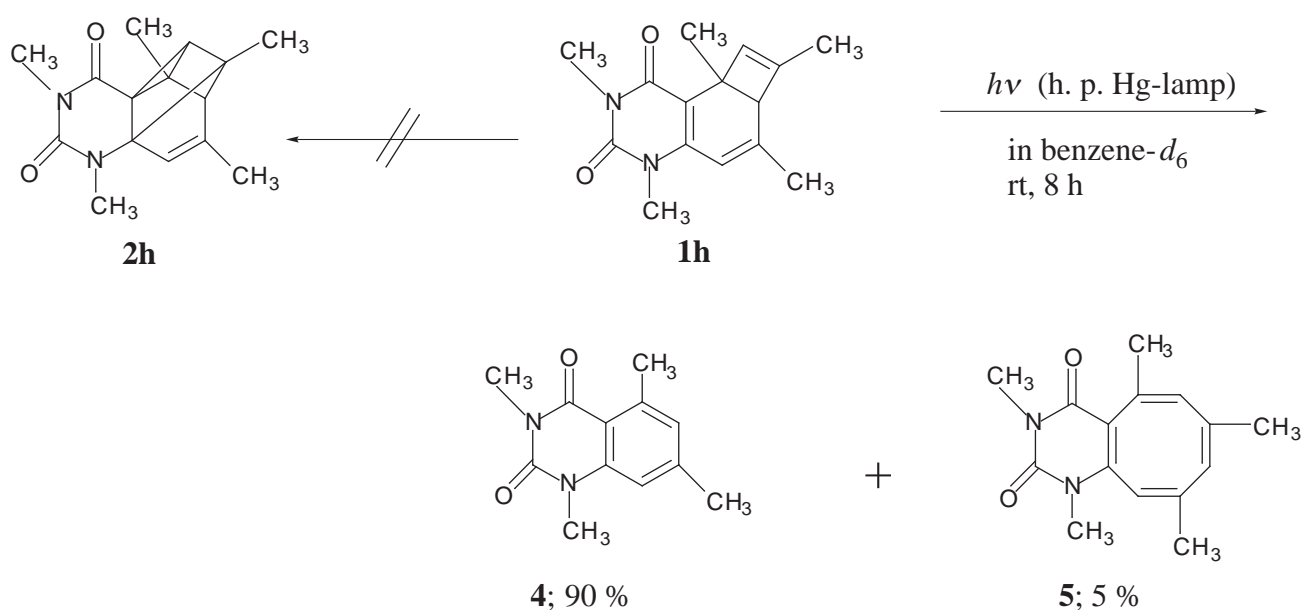


Figure 2. Optimized structures of **2e**, **2f**, and **2g**,⁸ and the NOE correlations.

We then carried out the photolysis of cyclobutaquinazoline (**1h**),⁷ which retains the double bond between C5-C6 unchanged. UV-irradiation of **1h** in benzene-*d*₆ gave quinazoline (**4**) preferentially (90 %)⁹ and a small amount of cyclooctapyrimidine (**5**, 5 %) instead of giving the pentacyclododecane derivative (**2h**).



Yields are based on 74 % **1h** consumed.

Scheme 2.

Thus the present study strongly suggest that the release of the C5-C6 double bonding may be essential for the formation of the pentacyclododecanes (**2**) consisting of a pentacyclo[6.4.0.0^{1,3}.0^{2,5}.0^{4,8}]dodecane system.

EXPERIMENTAL

General methods

NMR spectra were measured with a JEOL JNM-EX400 (400 MHz) spectrometer, and ¹H-NMR chemical shifts are given on the δ (ppm) scale, based on signals due to solvents; CDCl₃ (δ 7.26), C₆D₆ (δ 7.15). ¹³C-NMR chemical shifts were recorded based on those of the signals of solvents; CDCl₃ (δ 77.0), C₆D₆ (δ 128.0). MS and high-resolution MS (HRMS) were measured on a JEOL JMS-DX303 spectrometer with an ionization potential of 70 eV.

Silica gel LC (Si-HPLC) was conducted on a Shim-Pac PREP-Sil (H) (25 cm x 20 mm *i.d.*) (silica gel), using a Shimadzu LC-6A apparatus with monitoring at 254 nm.

Materials

Synthesis and the characterization for **1d**,⁷ **1g**,¹⁰ **1f**,⁵ **1h**,⁷ and **2d**⁷ have been reported in the preceding papers.

Compound (**1e**) was obtained in 4 % yield together with the alternative trans isomer (**1f**) in 2.2 % yield and the other cycloadducts including from the photoreaction of 6-CIDMU and mesitylene as reported in the previous paper by treating the resulting reaction mixture with Si-HPLC (ethyl acetate-hexane, 1: 3), without submitting to RP-HPLC.⁵

rel-(5*R*,6*R*,6*aR*,8*aR*)-6-Chloro-5,6,6*a*,8*a*-tetrahydro-2,4,5,6*a*,8-pentamethylcyclobuta[*f*]quinazoline-1,3-dione (**1e**): Colorless oil. ¹H-NMR (C₆D₆) δ : 0.82 (3H, d, J = 7.1 Hz, C5-CH₃), 1.32 (3H, s, C6*a*-CH₃), 1.95 (3H, t-like, J = 1.3 Hz, C8-CH₃), 2.39 (1H, dq, J = 4.3, 7.1 Hz, H-5), 2.59 (3H, s, N4-CH₃), 3.27 (3H, s, N2-CH₃), 3.52 (1H, br s, H-8*a*), 4.08 (1H, d, J = 4.3 Hz, H-6), 5.91 (1H, t-like, J = 1.3 Hz, H-7). ¹³C-NMR (C₆D₆) δ : 13.96 (C5-CH₃), 17.07 (C8-CH₃), 21.06 (C6*a*-CH₃), 27.78 (N2-CH₃), 30.19 (N4-CH₃), 40.04 (5), 44.66 (6*a*), 50.67 (8*a*), 67.84 (6), 107.45 (8*b*), 137.66 (7), 148.58 (8), 150.52 (4*a*), 151.76 (3), 162.09 (1). HMBC; H-8*a* with C-8*b*, C-8, C-7, C-6*a*, C-4*a*; C8-CH₃ with C-8*a*, C-8, C-7, C-6*a*, C-6; H-7 with C-8*a*, C-6*a*; C6*a*-CH₃ with C-8*a*, C-7, C-6*a*, C-6; H-6 with C-7, C-6*a*, C6*a*-CH₃, C-5, C5-CH₃, C-4*a*; H-5 with C-8*b*, C-7, C-6, C5-CH₃, C-4*a*; C5-CH₃ with C-6, C-5, C-4*a*; N4-CH₃ with C-8, C-10; N11-CH₃ with C-10, C-12. NOE; H-2 with C3-CH₃, C5-CH₃; C3-CH₃ with H-2, H-4; H-4 with C8-CH₃, C6*a*-CH₃, H-6; C6*a*-CH₃ with H-8*a*, H-7, H-6; H-6 with H-7, C6*a*-CH₃, H-5; H-5 with H-6, C5-CH₃, N4-CH₃; C5-CH₃ with H-5, N4-CH₃; N4-CH₃ with C5-CH₃, H-5. MS m/z (%); 296 (M⁺⁺², 4), 294 (M⁺, 12), 259 (71), 219 (51), 202 (14), 162 (100), 134 (19). HRMS; Calcd for C₁₅H₁₉N₂O₂³⁵Cl: 294.1135. Found: 294.1154.

UV-irradiation

UV-irradiation was carried out externally using a 500 W high-pressure mercury lamp (Eiko-sha) in a degassed Pyrex tube (16 mm *i. d.*, 1 mm thickness) (> 300 nm) or in an NMR sample tube (5 mm Φ , 528-pp, Wilmad Glass) on a merry-go-round apparatus at room temperature unless cited therein. Low-temperature photoreaction

was performed in an ethanol bath equipped with a cooling apparatus (CryoCool Immersion cooler CC-80, Neslab). The yields were determined by $^1\text{H-NMR}$, and given on the basis of the starting materials consumed (70-90 %).

Photoreaction of 1d-----Irradiation of a solution of **1d** (6 mM) in benzene- d_6 in an NMR sample tube for 6 h resulted in the 84 % conversion of **1d** and gave 7-methylene-9,11-dimethyl-9,11-diazapentacyclo-[6.4.0.0 1,3 .0 2,5 .0 4,8]dodecane-10,12-diones (**2d**)⁷ in 60 % yield.

X-Ray Crystallographical analysis of 2d-----The diffraction experiment was carried out using a colorless transparent prism with dimension of 0.5 x 0.45 x 0.35 mm. The diffract meter Mac Science MXC18K was used with monochromated $\text{CuK}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) at 25°C. The unit cell dimensions were determined from angular setting of 22 reflections (2θ values in the range of 50-60°), affording the following crystal data: $\text{C}_{15}\text{H}_{18}\text{N}_2\text{O}_2$, Mr = 258.00, a = 12.183(4), b = 8.891(2), c = 24.915(6) Å, V = 2698.6(12)Å³, orthorhombic, Pca2₁, Z = 8, Dx = 1.270 g/cm³. 2630 unique reflections ($2\theta \leq 140^\circ$) were measured, of which 2333 with $|F_0| \geq 3.00\sigma$ (F0) were considered as observed. The structure was solved by maXus. The refinement of atomic parameters was carried out using block diagonal least-squares method with anisotropic temperature factors. Hydrogen atoms were located on the difference-Fourier maps and refined with isotropic temperature factors. The atomic scattering factors were taken from International Tables for X-Ray Crystallography (1974). The final R factor is 0.045 (wR = 0.037).

The intramolecular bond lengths and the intramolecular bond angles are listed in Table 2 and 3, respectively.

Table 2. Bond Lengths (Å) and Standard Deviations in Parenthesis (H omitted)

atom	atom	distance	atom	atom	distance
O (1)	C (1)	1.222 (3)	O (2)	C (2)	1.228 (3)
N (1)	C (1)	1.384 (3)	N (1)	C (2)	1.418 (3)
N (1)	C (3)	1.466 (3)	N (2)	C (2)	1.351 (3)
N (2)	C (4)	1.436 (4)	N (2)	C (5)	1.432 (3)
C (1)	C (6)	1.433(3)	C (5)	C (6)	1.527 (3)
C (5)	C (9)	1.542 (3)	C (5)	C (12)	1.502 (3)
C (6)	C (7)	1.516 (4)	C (6)	C (8)	1.545 (3)
C (7)	C (8)	1.479 (3)	C (7)	C (10)	1.521 (3)
C (8)	C (9)	1.584 (3)	C (8)	C (13)	1.478 (3)
C (9)	C (10)	1.561 (4)	C (10)	C (11)	1.502 (3)
C (10)	C (14)	1.557 (4)	C (11)	C (12)	1.515 (4)
C (12)	C (15)	1.335 (4)			

Table 3. Bond Angles (°) and Standard Deviations in Parenthesis (H omitted)

atom	atom	atom	angle	atom	atom	atom	angle	atom	atom	atom	angle
C (1)	N (1)	C (2)	123.3 (2)	C (1)	N (1)	C (3)	117.5 (2)	C (2)	N (1)	C (3)	117.5 (2)
C (2)	N (2)	C (4)	119.6 (2)	C (2)	N (2)	C (5)	122.5 (2)	C (4)	N (2)	C (5)	117.3 (2)
O (1)	C (1)	N (1)	120.7 (2)	O (1)	C (1)	C (6)	125.8 (2)	N (1)	C (1)	C (6)	113.5 (2)
O (2)	C (2)	N (1)	118.2 (2)	O (2)	C (2)	N (2)	122.5 (2)	N (1)	C (2)	N (2)	119.3 (2)
N (2)	C (5)	C (6)	108.5 (2)	N (2)	C (5)	C (9)	119.6 (2)	N (2)	C (5)	C (12)	118.6 (2)
C (6)	C (5)	C (9)	85.8 (2)	C (6)	C (5)	C (12)	112.8 (2)	C (9)	C (5)	C (12)	106.8 (2)
C (1)	C (6)	C (5)	123.0 (2)	C (1)	C (6)	C (7)	129.7 (2)	C (1)	C (6)	C (8)	123.7 (2)
C (5)	C (6)	C (7)	105.9 (2)	C (5)	C (6)	C (8)	93.8 (2)	C (7)	C (6)	C (8)	57.8 (2)
C (6)	C (7)	C (8)	62.1 (2)	C (6)	C (7)	C (10)	103.5 (2)	C (8)	C (7)	C (10)	93.4 (2)
C (6)	C (8)	C (7)	60.1 (2)	C (6)	C (8)	C (9)	83.7 (2)	C (6)	C (8)	C (13)	128.0 (2)
C (7)	C (8)	C (9)	86.6 (2)	C (7)	C (8)	C (13)	134.5 (2)	C (9)	C (8)	C (13)	135.2 (2)
C (5)	C (9)	C (8)	91.7 (2)	C (5)	C (9)	C (10)	95.2 (2)	C (8)	C (9)	C (10)	87.9 (2)
C (7)	C (10)	C (9)	86.0 (2)	C (7)	C (10)	C (11)	115.7 (2)	C (7)	C (10)	C (14)	112.8 (2)
C (9)	C (10)	C (11)	108.1 (2)	C (9)	C (10)	C (14)	114.0 (2)	C (11)	C (10)	C (14)	116.3 (2)
C (10)	C (11)	C (12)	103.5 (2)	C (5)	C (12)	C (11)	106.5 (2)	C (5)	C (12)	C (15)	126.8 (3)
C (11)	C (12)	C (15)	126.7 (2)	O (3)	C (16)						

Photoreaction of 1e----Irradiation of a 6 mM solution of **1e** (0.003 mmol, 1.0 mg) in benzene-*d*₆ (0.5 mL) in an NMR sample tube for 30 min resulted in the 60 % conversion of **1e** to give **2e** quantitatively, which was isolated by Si-HPLC with 25 % ethyl acetate in hexane.

rel-(1*R*,2*S*,3*R*,4*R*,5*S*,6*S*,7*R*,8*S*)-6-Chloro-3,5,7,9,11-pentamethyl-9,11-diazapentacyclo[6.4.0.0^{1,3}.0^{2,5}.0^{4,8}]dodecane-10,12-diones (**2e**): MS *m/z* (%); 296 (M⁺+2, 1), 294 (M⁺, 3), 279 (4), 259 (95), 218 (21), 202 (40), 174 (34), 162 (100), 145 (42), 91 (60). HRMS; Calcd for C₁₅H₁₉N₂O₂³⁵Cl: 294.1135. Found: 294.1160.

Photoreaction of 1f----- Irradiation of a solution of **1f** (0.003 mmol, 1.0 mg) in benzene-*d*₆ (0.5 mL) in an NMR sample tube for 30 min resulted in the consumption of **1f** in 67 % to give **2f** predominantly.

rel-(1*R*,2*S*,3*R*,4*R*,5*R*,6*R*,7*R*,8*S*)-6-Chloro-3,5,7,9,11-pentamethyl-9,11-diazapentacyclo[6.4.0.0^{1,3}.0^{2,5}.0^{4,8}]dodecane-10,12-diones (**2f**): Colorless oil. ¹H-NMR (C₆D₆) δ: 0.78 (3H, d, *J* = 7.0 Hz, C7-CH₃), 1.10 (3H, s, C3-CH₃), 1.19 (3H, s, C5-CH₃), 1.95 (1H, d, *J* = 5.0 Hz, 4-H), 2.06 (1H, dq, *J* = 3.8, 7.0 Hz, 7-H), 2.23 (1H, d, *J* = 5.10 Hz, 2-H), 2.57 (3H, s, N9-CH₃), 3.20 (1H, d, *J* = 3.8 Hz, 6-H), 3.29 (3H, s, N11-CH₃). ¹³C-NMR (C₆D₆) δ: 10.38 (C3-CH₃),

12.84 (C7-CH₃), 17.41 (C5-CH₃), 27.67 (N11-CH₃), 29.89 (N9-CH₃), 32.26 (1), 36.74 (2), 44.03 (3), 50.30 (7), 52.30 (4), 53.49 (5), 68.76 (6), 68.98 (8), 155.10 (10), 165.78 (12). HMBC; H-2 with C-4, C-12, C3-CH₃; C3-CH₃ with C-1, C-2, C-3, C-4; H-4 with C-1, C-2, C5-CH₃, C-8, C-12; C5-CH₃ with C-2, C-4, C-5, C-6; H-6 with C-2, C-4, C-5, C7-CH₃, C-8; H-7 with C-1, C-6, C7-CH₃, C-8; C7-CH₃ with C-6, C-7, C-8; N9-CH₃ with C-8, C-10; N11-CH₃ with C-10, C-12. MS *m/z* (%); 296 (M⁺+2, 0.3), 294 (M⁺, 1), 279 (2), 259 (33), 218 (64), 202 (28), 174 (11), 168 (100). HRMS; Calcd for C₁₅H₁₉N₂O₂³⁵Cl: 294.1135. Found: 294.1120.

Photoreaction of 1g -----A solution of **1g** (25.5 mg, 0.1 mmol) (2 mM) in benzene (50 mL) was put portion-wise (5 mL each) into ten degassed Pyrex tubes, and irradiated at -25°C for 30 min. Si-HPLC of the reaction mixture with 25% ethyl acetate in hexane afforded **2g** (2.3 mg, 9 %) and unchanged **1g** (23 mg, 90 %), successively.

Similar irradiation (30 min) in the presence of TFA (0.5 mmol, 10 mM) accelerated the photoreaction to consume 81 % of **1g**, and gave **2g** in improved yield (90 %).

6-Chloro-9,11-dimethyl-9,11-diazapentacyclo[6.4.0.0^{1,3}.0^{2,5}.0^{4,8}]dodecane-10,12-diones (**2g**): ¹H-NMR (CDCl₃); see Table 1. MS *m/z* (%); 254 (M⁺+2, 0.5), 252 (M⁺, 0.4), 253 (1), 251 (1.2), 217 (100), 160 (75). HRMS; Calcd for C₁₂H₁₃N₂O₂³⁵Cl: 252.0666. Found: 252.0664, Calcd for C₁₂H₁₃N₂O₂³⁷Cl: 254.0637. Found: 254.0630.

Photoreaction of 6,7,8a-trimethylcyclobutaquinazoline-1,3-dione (1h) ----- Irradiation of a solution of **1h** (0.0205 mmol, 5.3 mg) in benzene-*d*₆ (0.5 mL) in an NMR sample tube for 8 h. After evaporation of the solvent, the resulting mixture was submitted to Si-HPLC with 20 % ethyl acetate in hexane to give **4** (3.1 mg, 70%) and 1,3,5,7,9-pentamethylcyclooctapyrimidine (**5**) (0.2 mg, 4 %), together with unchanged **1h** in 23 % (1.2 mg).

1,3,5,7-Tetramethylquinazoline-2,4-dione (**4**): ¹H-NMR (C₆D₆) δ: 1.98 (3H, s, C7-CH₃), 2.89 (3H, s, C5-CH₃), 2.96 (3H, s, N1-CH₃), 3.36 (3H, s, N3-CH₃), 6.19 (1H, s, H-8), 6.47 (1H, s, H-6). NOE; C7-CH₃ with H-8, H-6; C5-CH₃ with H-6; H-8 with N1-CH₃, C7-CH₃, N9-CH₃; C7-CH₃. MS *m/z* (%); 218 (M⁺, 96), 161 (50), 133 (100), 106 (11). HRMS; Calcd for C₁₂H₁₄N₂O₂: 218.1055. Found: 218.1056.

1,3,5,7,9-Pentamethylcyclooctapyrimidine-2,4-dione (5): Colorless crystals, mp 113-114°C (recrystallized from 2-propanol). ¹H-NMR (C₆D₆) δ: 1.47 (3H, s, C9-CH₃), 1.59 (3H, s, C7-CH₃), 2.19 (3H, s, C5-CH₃), 2.79 (3H, s, N1-CH₃), 3.24 (3H, s, N3-CH₃), 5.19 (1H, br s, H-10), 5.33 (1H, br s, H-8), 5.67 (1H, br s, H-6). ¹³C-NMR (C₆D₆) δ: 22.90 (C5-CH₃), 23.12 (C7-CH₃), 23.46 (C9-CH₃), 27.81 (N1-CH₃), 31.69 (N3-CH₃), 113.15 (4a), 119.75 (10), 126.68 (8), 130.55 (6), 136.45 (5), 140.68 (7), 145.47 (9), 147.33 (10a), 151.75 (2), 160.78 (4). HMBC: H-10 with C9, C9-CH₃, C8, C4a; C9-CH₃ with C10, C9, C8; H-8 with C10, C7-CH₃, C6; C7-CH₃ with C8, C7, C6; H-6 with C8, C5-CH₃, C4a; C5-CH₃ with C6, C5, C4a; N3-CH₃ with C4, C2; N1-CH₃ with C10a, C2. NOE: H-10 with N1-CH₃, C9-CH₃, C9-CH₃ with H-10, H-8; H-8 with C7-CH₃, C9-CH₃, C7-CH₃ with H-8, H-6, H-6 with C7-CH₃, C5-CH₃, C7-CH₃ with C-6; N1-CH₃ with H-10. Ms *m/z* (%): 258 (M⁺, 100), 243 (61), 218 (7), 200 (9), 186 (49), 158 (44), 143 (8), 128 (11), 115 (16), 91 (19). HRMS: Calcd for C₁₅H₁₈N₂O₂: 258.1368. Found: 258.1369.

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