Photochemical Ring Enlargement of Macrocyclic *N*-Phenyl Imides into Cyclophanes

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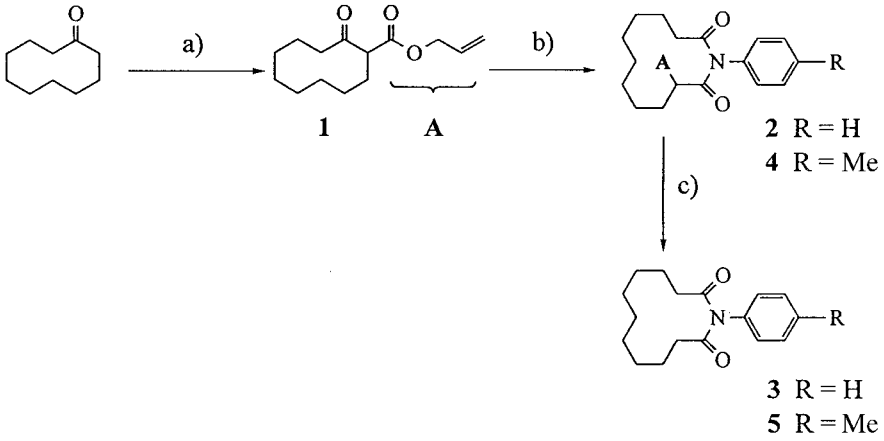
Dedicated to Professor *Albert Eschenmoser* on the occasion of his 75th birthday

Allylic *N*-phenyl imides containing 12- and 14-membered rings, such as compounds **3** and **12**, are easily synthesized by ring enlargement from cycloalkanones and phenyl isocyanates. Irradiation of **3** and **12** in EtOH and MeCN, with high- and low-pressure Hg lamps, led, *via* the photo-*Fries* rearrangement, to the same primary products: the orthocyclophane **8** and the paracyclophane **9** from **3** (*Scheme 2*), and the corresponding compounds **13** and **14** from **12** (*Scheme 3*). Besides the primary photorearrangement products, secondary products, the aminocyclophanes **10** and **11**, or **15** and **16**, respectively, were also formed. The total yields of the four products were very high when the *N*-phenyl imides were irradiated in MeCN with a low-pressure Hg lamp: 97 and 93%, respectively. If the *para*-position in **3** or **12** is blocked by a Me group, the *para*-photo-*Fries* rearrangement is prevented. In this case, only one primary photoproduct is formed: the corresponding orthocyclophane (**17** or **23**, resp.). The most remarkable result was observed on irradiation of the 12-membered *N*-(4-tolyl) imide **5** in MeCN (low-pressure lamp). It reacted nearly quantitatively to give only two products: 15-methyl-1-aza[12]orthocyclophane-2,12-dione (=16-methyl-2-azabicyclo[12.4.0]octadeca-1(14),15,17-triene-3,13-dione; **17**) in 80% yield and 17-amino-14-methyl[11]metacyclophane-1,11-dione (=17-amino-15-methyl-bicyclo[11.3.1]heptadeca-1(17),13,15-triene-2,12-dione; **19**) in 16% yield (*Scheme 5*).

Introduction. – Over recent years, it has become easy to prepare macrocyclic *N*-phenyl imides of different ring sizes in good yield by ring enlargement from cycloalkanones with two fewer ring members [1][2]. Treatment of 2-oxocycloalkane-1-carboxylic acids (*e.g.*, the cyclodecanone derivative **1**) with an aryl isocyanate (such as phenyl isocyanate) leads to the formation of a ring-enlarged imide (like **2**), two ring members larger. The (allyloxy)carbonyl moiety may be removed by using $Pd(PPh_3)_4$, HCO_2H, and Et_3N [3][4] (*Scheme 1*).

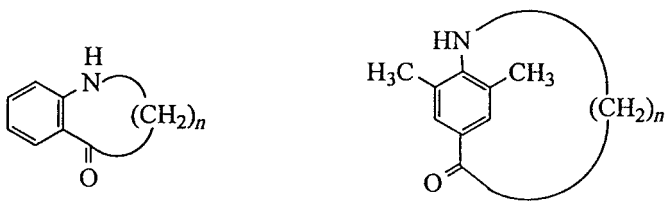
Results and Discussion. – We were interested in whether these *N*-phenyl imides would be suitable as starting materials for the preparation of cyclophanes; a transformation for which the photo-*Fries* rearrangement was expected to be well-suited (for reviews, see [5]). This photochemical rearrangement had been studied in detail for acetanilide [6]; in that case, the production of aniline, as well as of the desired 2-amino- and 4-aminoacetophenones had been observed. In terms of the mechanism, it had been concluded that the cleavage of the N–C(O) bond proceeds homolytically, from the singlet state S_1 [7][8], and that intramolecular recombination of the two radicals produced takes place in a solvent 'cage' [9]. Cyclic analogs of acetanilide – *N*-phenyl lactams with 7-, 8-, and 13-membered rings – exclusively form orthocyclophanes of the general formula **6**, with 9-, 10-, or 15-membered rings. Paracyclophanes of type **7**

Scheme 1



a) NaH, diallyl carbonate, THF, 6 h reflux; 91%. b) R = H: NaH, THF, PhNCO; 67%; R = Me: NaH, THF, 4-tolyl isocyanate; 89%. c) Et_3N, HCOOH, THF, $Pd(PPh_3)_4$; 85%.

may be obtained from *N*-phenyl lactams if the *ortho*-positions of the lactams are blocked by Me groups, and the ring contains at least seven CH_2 groups [10].



6 $n = 5, 6, 11$ **7** $n \geq 7$

Irradiation of *N*,*N*-diacetylaniline in MeCN gives rise to the *ortho*- and *para*-rearrangement products 2- and 4-acetamidoacetophenone in 30 and 25% yields, respectively, as well as the fragmentation product acetanilide (45%) [11]. Secondary photorearrangement products were not detected. Similar results were obtained on irradiation of *N*,*N*-diacetylnaphthalenamine, in which case a *meta*-substitution product was also observed in small amounts (1%) [11]. The *N*-phenyl imides mentioned above are cyclic analogs of *N*,*N*-diacetylaniline, and consequently should also be expected to give *ortho*- and *para*-rearrangement products on irradiation. Whether products of double rearrangement – secondary photorearrangement products, in other words – would be detectable remained to be seen. Moreover, it would serve to clarify whether this method might possibly be suitable for the synthesis of certain cyclophanes.

If the *N*-phenyl imide **3** was irradiated in MeCN solution at 0° with a 100-W low-pressure Hg lamp, the starting material was converted completely after 24 h. Four isomerization products resulted, in an overall yield of 97%. The results are shown in

Scheme 2. The two main products are the *ortho*- and the *para*-rearrangement products **8** and **9**, respectively; the latter, with a yield of 44%, predominating significantly over the former (33%). The other two isomers, **10** and **11**, are the products of secondary photo-*Fries* rearrangements of the primary compounds **8** and **9**, respectively. The symmetrical 17-amino[11]metacyclophane-1,11-dione (=17-aminobicyclo[11.3.1]heptadeca-1(17),13,15-triene-2,12-dione; **10**) can be formed by irradiation of the orthocyclophane **8**, while 13-amino[11]metacyclophane-1,11-dione (=14-aminobicyclo[11.3.1]heptadeca-1(16),13(17),14-triene-2,12-dione; **11**) could arise from irradiation of either or both of the primary products **8** and **9**. The photochemistry of **3** was also examined under different experimental conditions; the results are summarized in *Table 1*. In EtOH solution, with both high- and low-pressure Hg lamps, the products are the same as those arising from irradiation in MeCN. The yields are altered, however.

Scheme 2

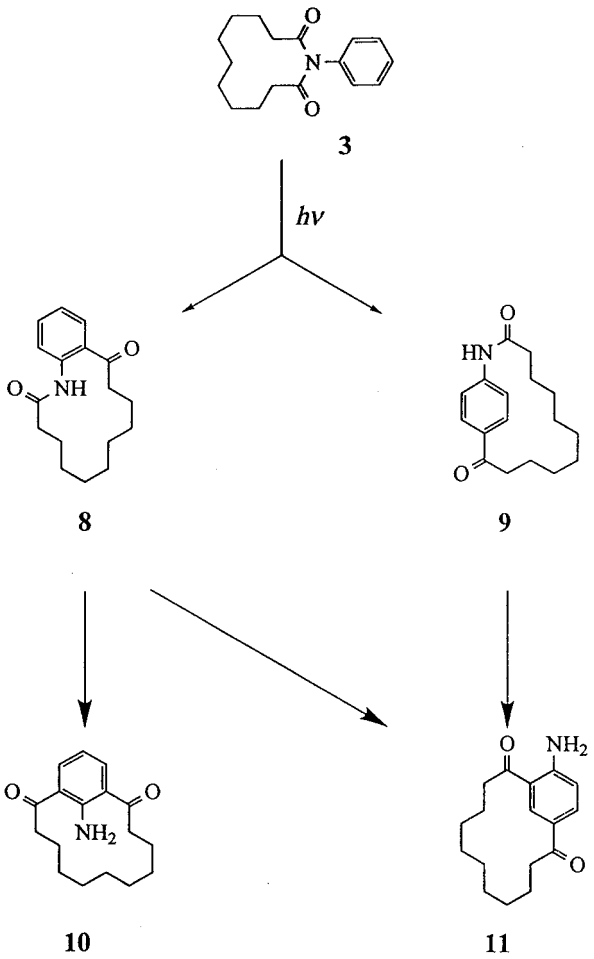
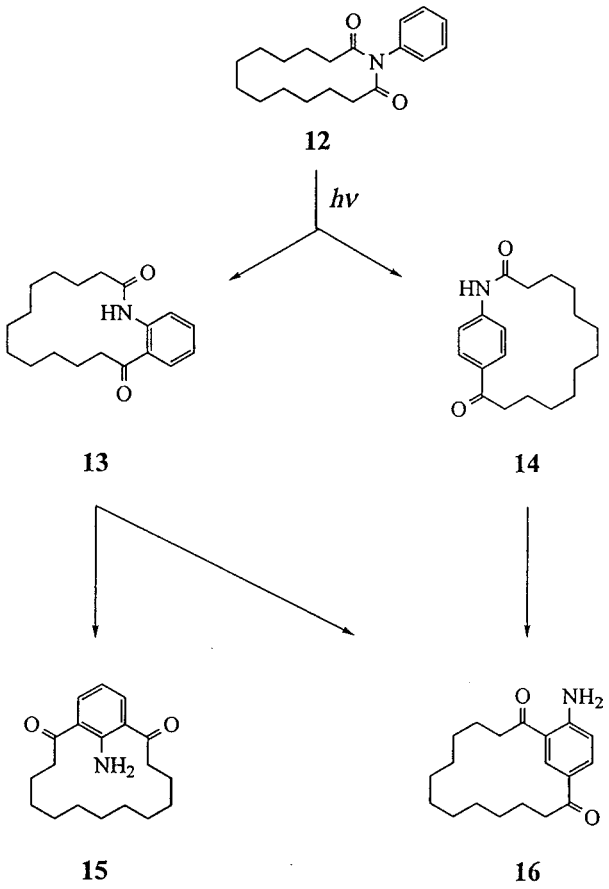


Table 1. *Irradiation of* N-*Phenyl Imide* **3**. Yields in % (*cf. Scheme 2*).

Products	High-pressure lamp EtOH ($c = 10.99 \times 10^{-3}$ mol/l), 1.5 h	Low-pressure lamp EtOH ($c = 8.79 \times 10^{-3}$ mol/l), 1.5 h	Low-pressure lamp MeCN ($c = 8.79 \times 10^{-3}$ mol/l), 24 h
8	37	10	33
9	23	4	44
10	2	–	2
11	4	–	18
Total yield	66	14	97

The homologue of the starting material **3**, 1-phenyl-1-azacyclotetradecane-2,14-dione (**12**) [4], also undergoes *Fries* rearrangement on photochemical treatment. The corresponding homologous products are formed (*cf. Scheme 3* and *Table 2*). Since the reaction times were different, the yields do not bear direct comparison. The highest total yield here, 93%, was also found in the case of irradiation in MeCN with a low-pressure

Scheme 3



Hg lamp. The main product is once more the paracyclophane **14**, with a yield of 50%. Its structure and configuration were verified by X-ray crystal-structure analysis (*Fig. 1*).

Table 2. *Irradiation of* N-*Phenyl Imide* **12**. Yields in % (*cf. Scheme 3*).

Products	High-pressure lamp EtOH ($c = 13.29 \times 10^{-3}$ mmol/l), 45 min	Low-pressure lamp EtOH ($c = 13.29 \times 10^{-3}$ mmol/l), 16 h	Low-pressure lamp MeCN ($c = 5.32 \times 10^{-3}$ mmol/l), 3 h
13	29[a])	34[a])	12
14	25[a])	41[a])	50
15	–	–	12
16	–	–	19
Total yield	54	75	93

[a]) Values relative to consumed **12**.

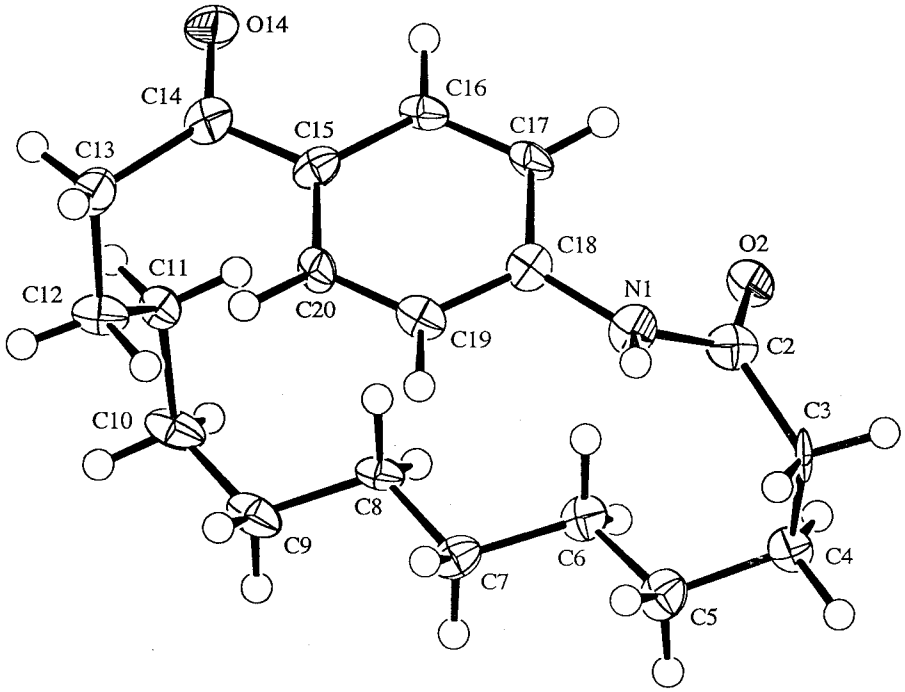


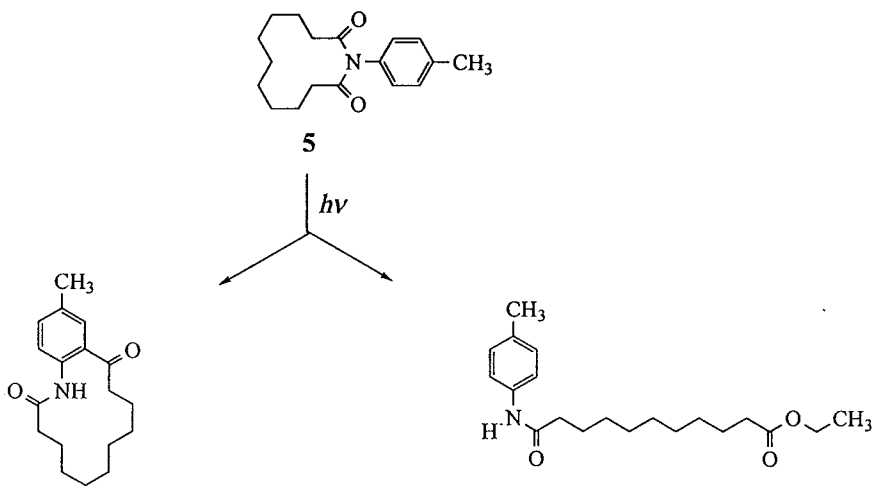
Fig. 1. *X-Ray crystal structure of 1-aza[14]paracyclophane-2,14-dione* (**14**) *in ORTEP representation* (ellipsoids with 50% probability)

It now also seemed of interest to us to examine how the photo-*Fries* rearrangement would be affected by blocking the *para*-position with a Me group. The synthesis of the relevant cyclic *N*-(4-tolyl) imide by ring-enlargement with 4-tolyl isocyanate was performed with cyclodecanone, analogously to that of **3** (*cf. Scheme 1*).

1-(4-Tolyl)-1-azacyclododecane-2,12-dione (**5**) was irradiated in absolute EtOH for 3.5 h, with a low-pressure Hg lamp. The orthocyclophane **17** was produced in 31%

yield, together with 35% of starting material **5**. As well as this, the open-chain EtOH addition product **18** could be isolated in 21% yield (*Scheme 4*).

Scheme 4



[a]) In parentheses, the chemical yields with respect to the starting material converted.

Reactions of this kind proceed especially well in polar, protic solvents. However, as shown in *Scheme 4*, the risk of side reactions with the solvent is high, and so irradiation was once more performed in MeCN with a low-pressure Hg lamp. The results of this experiment are shown in *Scheme 5*; the reaction was terminated after 15 h.

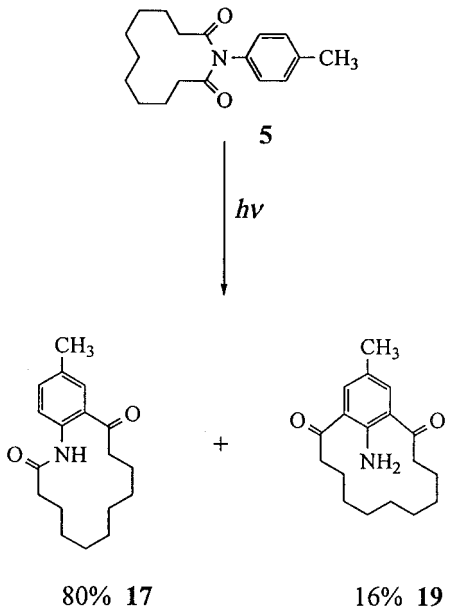
No starting material could be detected by TLC, and fragmentation products and side products were also evident in only trace amounts. The total product yield of 96% comprised of only two compounds: the orthocyclophane **17** (80%) and the symmetrical amino-metacyclophane **19** (16%), as primary and secondary photorearrangement products, respectively.

It was now only a question of clarifying whether reaction behavior is dependent on ring size. It was hence considered appropriate to prepare the 14-membered *N*-(4-tolyl) imide **22** and to subject it to the same conditions as those under which a 96% conversion had been achieved for the 12-membered *N*-(4-tolyl) imide **5**.

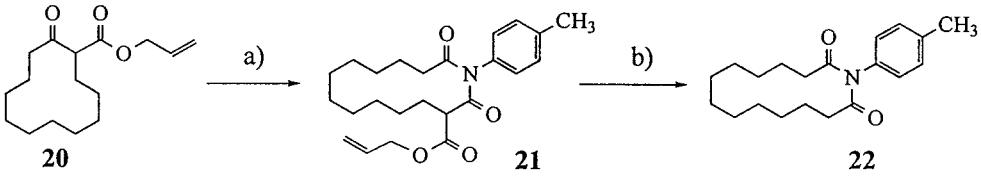
The preparation of the desired compound **22**, starting from the activated cyclododecanone **20**, proceeded analogously to the reactions described above (*Scheme 6*). Irradiation was carried out in MeCN, as for the 12-membered **5**, for 16.5 h, with a low-pressure Hg lamp.

In contrast with the experiment with the 12-membered imide, starting material was still present after 16.5-h irradiation of **22**. As shown in *Scheme 7*, orthocyclophane **23** had been produced in 63% chemical yield (74% relative to converted starting material); no secondary photorearrangement product could be detected. Evidently, the 14-membered *N*-(4-tolyl) imide **22** is photochemically less reactive than the 12-membered representative **5**.

Scheme 5



Scheme 6

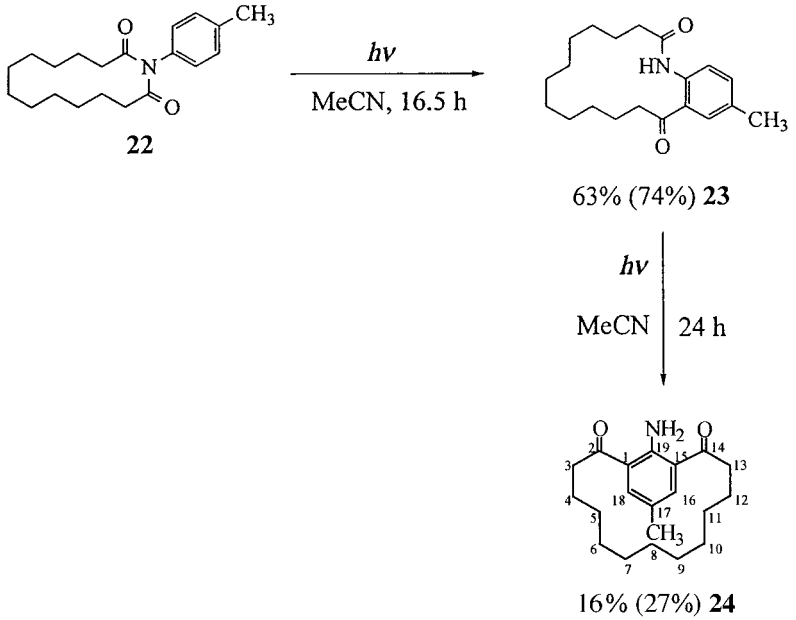


a) NaH, THF, 4-Tolyl isocyanate; 70%. b) Et_3N, HCOOH, THF, $Pd(PPh_3)_4$; 80%.

It now also seemed important to us to settle whether further irradiation of the ortho-cyclophane **23** would produce the symmetrical amino-metacyclophane **24**, in analogy with that of the non-methylated imides **3** and **12**. Even after 24-h irradiation of **23**, 40% of the starting material could still be isolated. All the same, the desired and expected symmetrical amino-metacyclophane **24** had indeed been produced in 16% yield (or 27% relative to converted starting material **23**), with the remainder consisting of decomposition products. Continuing the irradiation raised the yield only trivially, but also led to further decomposition products. The N–H bond here proves to be highly capable of dissipating excitation energy without radiation [12]. This confirms observations according to which amides are generally more likely than not to be photostable [13].

It proved possible to grow crystals of amino-metacyclophane **24** suitable for X-ray crystal-structure analysis and thus corroborate its structure (see *Fig. 2*). As had already been noticed for paracyclophane **14**, interpretable NMR spectra could be obtained only under special measuring conditions, by cooling to 250 K in this instance. This is presumably due to the multiplicity of conformations existing in solution.

Scheme 7



In the crystal, each amine H-atom forms an intramolecular H-bond with the adjacent C=O O-atom, hence forming a six-membered ring. It should be emphasized that the plane defined by the benzene system and the NH_2 and the two C=O groups is almost perpendicular to that of the aliphatic macrocycle. Intermolecular H-bonds are not formed, as can be seen from the view of the unit cell of **24** in *Fig. 3*.

Conclusion. – In this work, it was shown that 12- and 14-membered *N*-phenyl imides undergo easy photochemical rearrangement to give ortho-, meta-, and paracyclophanes. The reaction proceeds especially well in MeCN with irradiation from a low-pressure Hg lamp. The overall yields are higher than 90% in these cases, notably high for photochemical processes. Since macrocyclic *N*-phenyl imides are also easily accessible in good yields by ring-enlargement reactions from cycloalkanones, these preparations of those cyclophanes described appear to us to be worth recommending as synthetic methods.

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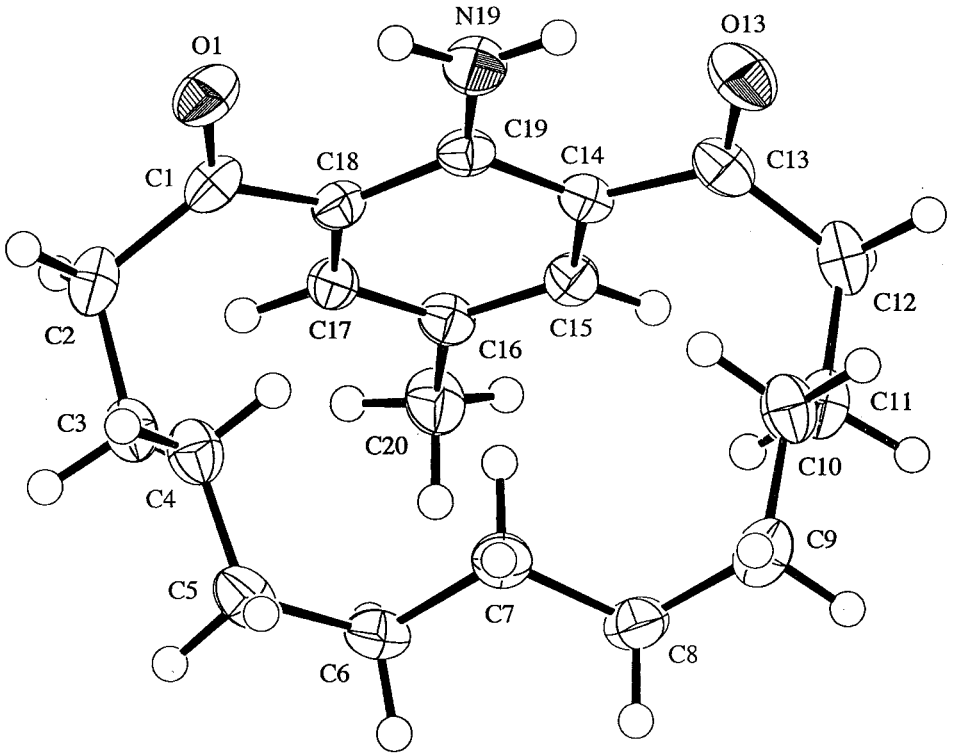

Fig. 2. *X-Ray crystal structure of 19-amino-16-methyl[13]metacyclophane* (**24**) *in ORTEP representation* (ellipsoids with 50% probability)

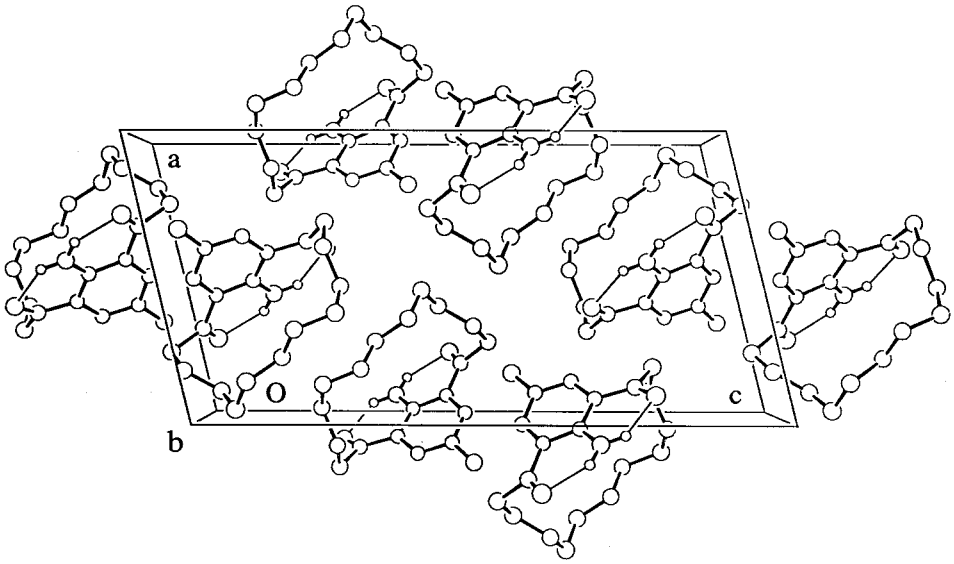

Fig. 3. *View of the unit cell of 19-amino-16-methyl[13]metacyclophane* (**24**)

Experimental Part

General. All organic solvents were distilled and dried (THF over Na, and MeCN and EtOH over molecular sieves (3 Å)) and then degassed. All reactions were performed under Ar or N_2. Chromatography: Kieselgel *Merck 60* (40–63 μm). FC = flash chromatography. M.p.: *Mettler FP-5/FP-52*. UV (EtOH): *Perkin-Elmer 555*; values in nm (log ε). IR ($CHCl_3$): *Perkin-Elmer 297*; values in [cm^{-1}]. ^{1}H-NMR: at 300 or 600 MHz in $CDCl_3$ or (D_6)DMSO; *Bruker AC 300*, *Bruker ARX 300*, or *Bruker AMX 600*; δ in ppm relative to TMS (= 0 ppm) as internal standard, J in Hz. ^{13}C-NMR: at 75.6 MHz (*Bruker ARX 300*) or 131.2 MHz (*Bruker AMX 600*) in $CDCl_3$ or (D_6)DMSO: δ in ppm relative to TMS (= 0 ppm) as internal standard; multiplicities from DEPT experiments. EI (70 eV) and CI-MS: with NH_3 as ionizing gas; *Finnigan SSQ 700* oder *Varian MAT 90*; ESI-MS: *Finnigan TSQ 700*; values in *m*/*z*.

1. *Prop-2-enyl 2-Oxocyclodecane-1-carboxylate* (**1**). Cyclooctanone (3.0 g, 19.5 mmol) and NaH (0.96 g, 24.0 mmol, 60% NaH in paraffin oil) were added to THF (75 ml) and diallyl carbonate (2.85 ml, 19.9 mmol) was slowly added, according to [2][3]. The mixture was heated under reflux for 4 h. It was then cooled to 0°, neutralized with 2.5N aq. HCl, and extracted with CH_2Cl_2. The extracts were dried (Mg_2SO_4), solvent was removed under vacuum, and the residue was purified by FC (hexane/AcOEt 10:1) to give **1** (3.7 g, 15.6 mmol, 85%). Light yellow oil. IR: 3090*w*, 2940*s*, 2860*m*, 1740*s*, 1705*s*, 1605*s*, 1475*m*, 1445*m*, 1380*m*, 1360*w*, 1325*m*, 1225 (br.), 1160*m*, 1100*m*, 1030*w*, 1015*w*, 990*m*, 940*m*. ^{1}H-NMR: 12.89 (*s*, 0.5 H, enol-OH); 6.02–5.81 (*m*, C*H*=CH_2); 5.37–5.21 (*m*, CH=CH_2); 4.69–4.56 (*m*, CH_2O); 3.91–3.86 (*m*, 0.5 H, H–C(1)); 2.73–2.45 (*m*, CH_2(3)); 2.43–2.15 (*m*, CH_2(10)); 2.00–1.29 (*m*, 12 H). ^{13}C-NMR (two tautomeric forms or conformers): 208.61 (*s*, CO); 175.51; 173.15 (2*s*, COOR); 132.18, 131.53 (*d*, *C*H=CH_2); 118.59, 117.60 (*t*, CH=*C*H_2); 99.53 (*s*, C(1), enol); 65.78, 64.72 (*t*, CH_2O); 57.62 (*d*, keto C(1)); 42.18 (*t*, C(3)); 30.15, 27.43, 27.23, 25.88, 25.63, 25.26, 25.13, 25.09, 25.05, 24.27, 23.46, 23.20, 20.93, 20.42 (14*t*, 7 CH_2). EI-MS: 238 (13, $M^{+\bullet}$), 152 (14), 124 (33), 109 (12), 98 (32), 97 (12), 95 (17), 84 (16), 83 (14), 82 (16), 81 (20), 70 (11), 69 (21), 68 (12), 67 (28), 57 (21), 56 (11), 55 (100), 54 (13), 53 (13).

2. *Prop-2-enyl 1-Phenyl-2,12-dioxo-1-azacyclododecane-3-carboxylate* (**2**). To a mixture of **1** (1.0 g, 4.2 mmol) in abs. THF (20 ml) was added NaH (202 mg, 5.1 mmol, 60% NaH in paraffin oil). The mixture was stirred for 30 min at r.t. Phenyl isocyanate (0.46 ml, 0.50 g, 4.2 mmol) in abs. THF (2 ml) was added dropwise to the now orange-yellow colored soln., and stirring was continued for 1 h at r.t. After cooling to 0°, the soln. was neutralized with 1N aq. HCl and solvent was evaporated. The residue was extracted with CH_2Cl_2, dried, and purified by FC (hexane/AcOEt 5:1) to give **2** (1.01 g, 2.8 mmol, 67%). Colorless oil. IR: 2925*s*, 2860*s*, 1740*s*, 1700*s*, 1650*w*, 1595*m*, 1490*m*, 1465*w*, 1445*m*, 1355*m*, 1270*m*, 1175*m*, 1120*m*, 1090*w*, 990*m*, 935*m*. ^{1}H-NMR: 7.48–7.37 (*m*, H–C(3′), H–C(4′), H–C(5′)); 7.18 (*d*, J = 1.7, H–C(2′), H–C(5′)); 5.93–5.80 (*m*, C*H*=CH_2); 5.34–5.18 (*m*, CH=CH_2); 4.61–4.58 (*m*, CH_2O); 4.30–4.25 (*dd*, J = 4.2, 6.3, H–C(3)); 2.75–2.67 (*m*, 1 H); 2.28–2.16 (*m*, 2 H); 2.03–1.85 (*m*, 2 H); 1.56–1.24 (*m*, 1 H). ^{13}C-NMR: 177.01 (*s*, C(2)); 172.78 (*s*, C(12)); 169.34 (*s*, COOR); 137.80 (*d*, *C*H=CH_2); 131.58 (*s*, C(1′)); 129.69 (*d*, C(2′), C(6′)); 128.82 (*d*, C(4′)); 128.23 (*d*, C(3′), C(5′)); 118.00 (*t*, CH=CH_2); 65.57 (*t*, CH_2O); 50.61 (*d*, C(3)); 35.16 (*t*, C(11)); 29.33 (*t*, C(4)); 25.19, 24.07, 23.78, 23.66, 23.28 (5*t*, 6 CH_2). CI-MS: 375 (20, $[M+NH_4]^+$), 359 (20), 358 (100, $[M+H]^+$), 195 (10), 136 (12).

3. *1-Phenyl-1-azacyclododecane-2,12-dione* (**3**). To a soln. of **2** (1.01 g, 2.8 mmol) in abs. THF (20 ml) was added, with stirring, a mixture of HCO_2H (210 μl, 6 mmol) and Et_3N (990 μl, 7.5 mmol), followed by $Ph(PPh_3)_4$ (163 mg) in abs. THF (2 ml). It was stirred for 1 h at r.t., solvent was removed under vacuum, and the residue was purified by FC (hexane/AcOEt 20:1) to give **3** (660 mg, 2.4 mmol, 85%). Colorless crystals. M.p. 73.6–74.9°. UV: λ_{max} 210 (4.13), 238 (3.96); λ_{min} 219 (3.79). IR: 2930*s*, 2860*m*, 1700*s*, 1600*m*, 1490*w*, 1465*w*, 1440*w*, 1350*w*, 1295*w*, 1270*w*, 1160*m*, 1120*m*, 1080*w*. ^{1}H-NMR: 7.48–7.36 (*m*, H–C(3′), H–C(4′), H–C(5′)); 7.15 (*d*, J = 6.8, H–C(2′), H–C(6′)); 2.62–2.57 (*t*, J = 6.4, CH_2(3), CH_2(11)); 1.81–1.73 (*m*, 4 H); 1.49–1.41 (*m*, 10 H). ^{13}C-NMR: 177.66 (*s*, 2 CO); 138.65 (*s*, C(1′)); 129.72 (*d*, C(2′), C(6′)); 128.00 (*d*, C(4′)); 128.19 (*d*, C(3′), C(5′)); 37.71 (*t*, C(3), C(11)); 25.53, 25.01, 23.94, 23.39 (4*t*, 7 CH_2). CI-MS: 291 (13, $[M+NH_4]^+$), 275 (19), 274 (100, $[M+H]^+$). EI-MS: 273 (12, $M^{+\bullet}$), 176 (19), 148 (15), 135 (55), 134 (18), 94 (12), 93 (100), 92 (12), 55 (11).

4. *1-Aza[12]orthocyclophane-2,12-dione* (= *2-Azabicyclo[12.4.0]octadeca-1(14),15,17-triene-3,13-dione*; **8**), *1-Aza[12]paracyclophane-2,12-dione* (= *2-Azabicyclo[12.2.2]octadeca-1(16),14(15),17-triene-3,13-dione*; **9**), *17-Amino[11]metacyclophane-1,11-dione* (= *17-Aminobicyclo[11.3.1]heptadeca-1(17),13,15-triene-2,12-dione*; **10**), *and 13-amino[11]metacyclophane-1,11-dione* (= *14-Aminobicyclo[11.3.1]heptadeca-1(16),13(17),14-triene-2,12-dione*; **11**). 4.1. *Irradiation of* **3** *in EtOH*. All irradiation experiments were carried out without filters.

a) *Low Pressure*. A soln. of **3** (120 mg, 0.4 mmol) in anh. degassed EtOH ($c = 8.79 \times 10^{-3}$ mol/l) was irradiated for 5 h in a *Schlenk* vessel at 0° under Ar, with a 100-W low-pressure Hg lamp (*Engelhard Hanovia*

Inc., Newark, N.Y., USA). Solvent was removed and the residue separated by prep. TLC (hexane/AcOEt 9:1). Starting material could no longer be detected: **8** (12 mg, 10%, faster-running) and **9** (4.8 mg, 4%).

b) *High Pressure.* A soln. of **3** (300 mg, 1.1 mmol) in anh., degassed EtOH ($c = 10.99 \times 10^{-3}$ mol/l) was irradiated for 1.5 h at 18° under N_2, with a 450-W high-pressure Hg lamp (*Engelhard Hanovia Inc.*). Solvent was removed, and the residue was separated by prep. TLC, by which starting material could no longer be detected: **10** (6 mg, 2%, fastest-running), **8** (110 mg, 37%), **11** (11 mg, 4%), and **9** (68 mg, 23%).

4.2. *Irradiation of* **3** *in MeCN.* A soln. of **3** (120 mg, 0.4 mmol) in anh. degassed MeCN ($c = 8.79 \times 10^{-3}$ mol/l) was irradiated for 24 h in a *Schlenk* vessel at 0° under Ar, with a 100-W low-pressure Hg lamp. Solvent was removed, and the residue was separated by prep. TLC (hexane/AcOEt 9:1). Starting material could no longer be detected: **10** (2.4 mg, 2%), **8** (39.6 mg, 33%), **11** (21.6 mg, 18%), and **9** (52.8 mg, 44%).

Data of **8**: Colorless crystals. M.p. 110.2–112.3°. UV: λ_{max} 234 (4.10), 264 (3.60), 326 (3.31); λ_{sh} 272 (3.60); λ_{min} 214 (3.55), 250 (3.56), 284 (2.85). IR: 3300 (br.), 2920*s*, 2860*m*, 1680*s*, 1660*s*, 1600*w*, 1580*s*, 1510*s*, 1440*s*, 1295*m*, 1160*m*. ^{1}H-NMR: 10.67 (*s*, NH); 8.39 (*d*, $J = 8.3$, H–C(14)); 7.71 (*d*, $J = 8.2$, H–C(17)); 7.55–7.52 (*m*, H–C(15)); 7.17–7.12 (*m*, H–C(16)); 2.96–2.93 (*m*, 1 CH_2); 2.48–2.44 (*m*, 1 CH_2); 1.86–1.71 (*m*, 2 CH_2); 1.39–1.22 (*m*, 4 CH_2); 1.08–1.03 (*m*, 1 CH_2). ^{13}C-NMR: 207.13 (*s*, CO); 172.58 (*s*, NHCO); 137.91 (*s*, C(18)); 133.49 (*d*, C(14)); 129.18 (*d*, C(17)); 126.59 (*s*, C(13)); 122.99, 122.87 (2*d*, C(15), C(16)); 40.51 (*t*, C(11)); 37.95 (*t*, C(3)); 28.09, 26.82, 25.90, 25.56, 24.95, 22.88 (6*t*, 7 CH_2). EI-MS: 273 (16, $M^{+\bullet}$), 174 (43), 161 (15), 148 (13), 146 (16), 136 (10), 135 (72), 120 (100), 119 (14), 93 (15), 92 (26), 55 (25).

Data of **9**: Colorless crystals. Melting range 166–172.0°. UV: λ_{max} 204 (4.13), 268 (4.02); λ_{min} 234 (3.60). IR: 3380*s*, 2995*w*, 2850*m*, 1670*s*, 1600*s*, 1580*w*, 1510*w*, 1440*m*, 1350 (br.), 1200*s*, 1085*w*, 1040*w*, 1015*w*, 995*w*, 925*w*. ^{1}H-NMR (300 MHz, (D_6)DMSO): 9.53 (*s*, NH); 7.88 (*d*, $J = 8.5$, H–C(15), H–C(17)); 7.37 (*d*, $J = 8.4$, H–C(14), H–C(18)); 2.91–2.86 (*t*, $J = 6.4$, CH_2(11)); 2.30–2.24 (*t*, $J = 8.4$, CH_2(3)); 1.64–0.59 (*m*, 14 H). ^{13}C-NMR (300 MHz, (D_6)DMSO): 203.61 (*s*, CO); 174.47 (*s*, NHCO); 142.64 (*s*, C(16)); 135.73 (*s*, C(13)); 129.32 (*d*, C(15), C(17)); 126.00 (C(14), C(18)); 38.10 (*t*, C(11)); 32.83 (*t*, C(3)); 27.56, 27.28, 27.03, 26.43, 26.07, 25.70, 23.50 (7*t*, 7 CH_2). EI-MS: 273 (11, $M^{+\bullet}$), 174 (14), 149 (21), 148 (16), 136 (14), 135 (100), 120 (78), 119 (26), 93 (32), 92 (17), 91 (22), 85 (10), 84 (27), 77 (11), 72 (23), 69 (19), 66 (30), 59 (44), 57 (23), 55 (43).

Data of **10**: Oil with a green cast. IR: 3440*s*, 3320*m*, 2920*s*, 2850*m*, 2730*w*, 1665*s*, 1600*m*, 1555*s*, 1440*m*, 1310*w*, 1295*w*, 1220 (br.), 1160*w*, 1100*w*, 990*w*, 955*w*, 920*w*. ^{1}H-NMR: 8.01–7.88 (br. *s*, NH_2); 7.74 (*d*, $J = 7.7$, H–C(15), H–C(13)); 6.68–6.63 (*t*, $J = 7.7$, H–C(14)); 3.27–3.19 (*m*, 2 H); 2.42–2.34 (*m*, 2 H); 1.74–0.70 (*m*, 14 H). ^{13}C-NMR: 206.70 (*s*, 2 CO); 148.82 (*s*, C(17)); 135.77 (*d*, C(13), C(15)); 120.38 (*s*, C(12), C(16)); 112.96 (*d*, C(14)); 42.50, 28.03, 27.23, 27.18, 26.27 (5*t*, 9 CH_2). EI-MS: 274 (13, $[M+H]^+$), 273 (69, $M^{+\bullet}$), 177 (37), 174 (49), 163 (11), 162 (32), 161 (18), 160 (16), 159 (100), 148 (16), 146 (14), 145 (18), 144 (17), 135 (48), 133 (15), 120 (25), 119 (28), 93 (40), 91 (21), 85 (21), 83 (24).

Data of **11**: Oil with a green cast. IR: 3500*m*, 3330*m*, 2930*s*, 2850*m*, 1640*s*, 1610*s*, 1580*m*, 1460*w*, 1440*w*, 1410*w*, 1330*w*, 1305*w*, 1290*w*, 1260*w*, 1220 (br.), 1160*m*, 1130*m*, 1095*w*, 905*w*, 830*w*. ^{1}H-NMR (300 MHz, (D_6)DMSO): 8.38 (*d*, $J = 2.0$, H–C(17)); 8.22–7.86 (br., NH_2); 7.78 (*d*, $J = 8.9$, H–C(15)); 6.86 (*d*, $J = 8.8$, H–C(14)); 2.83–2.74 (2*m*, 4 H); 1.62–1.30 (*m*, 13 H). ^{13}C-NMR (300 MHz,(D_6)DMSO): 203.71 (*s*, C(1)); 198.43 (*s*, C(11)); 155.49 (*s*, C(16)); 135.77 (*d*, C(17)); 133.09 (*d*, C(15)); 122.48 (*s*, C(12)); 118.00 (*d*, C(14)); 113.31 (*s*, C(13)); 38.84, 36.76, 26.62, 24.90, 24.71, 24.56, 24.50, 23.47 (8*t*, 9 CH_2). EI-MS: 274 (18, $[M+H]^+$), 273 (100, $M^{+\bullet}$), 177 (11), 174 (46), 162 (15), 161 (13), 148 (12), 135 (13), 133 (14), 120 (14), 119 (32), 91 (19), 55 (27).

5. *Prop-2-enyl 1-Phenyl-2,14-dioxo-1-azacyclotetradecane-3-carboxylate.* Treatment of **20** [2] (1.01 g, 3.8 mmol), NaH (205 mg, 5.1 mmol, 60% NaH in paraffin oil), and PhNCO (0.45 ml, 0.49 g, 4.1 mmol) in abs. THF (20 ml) as in *Exper. 2* gave the desired compound (0.85 g, 2.2 mmol, 59%) after FC (hexane/AcOEt 5:1) as a colorless oil. IR: 2930*s*, 2860*s*, 1740*s*, 1705*s*, 1595*w*, 1485*m*, 1440*w*, 1350*m*, 1270*w*, 1120*w*, 990*w*, 935*w*. ^{1}H-NMR: 7.49–7.41 (*m*, 3 arom. H); 7.14 (*d*, $J = 6.5$, H–C(2′), H–C(6′)); 5.96–5.83 (*m*, C*H*=CH_2); 5.34–5.20 (*m*, CH=CH_2); 4.63–4.60 (*m*, CH_2O); 4.17–4.13 (*m*, H–C(3)); 2.78–2.74 (*m*, 1 H); 2.36–2.28 (*m*, 1 H); 2.11–2.03 (*m*, 1 H); 1.94–1.80 (*m*, 2 H); 1.57–1.28 (*m*, 16 H). ^{13}C-NMR: 176.38 (*s*, C(2)); 172.47 (*s*, C(14)); 169.32 (*s*, COO); 138.54 (*s*, C(1′)); 131.79 (*d*, C*H*=CH_2); 129.78 (2*d*, C(2′), C(6′)); 128.90 (*d*, C(3′), C(5′)); 118.32 (*t*, CH=CH_2); 65.76 (*t*, CH_2O); 52.69 (*d*, C(3)); 37.04 (*t*, C(13)); 29.25, 26.26, 26.01, 25.95, 25.88, 25.65, 25.21, 24.85, 24.14 (9*t*, 9 CH_2). CI-MS (NH_3): 403 (11, $[M+NH_4]^+$), 387 (24), 386 (100, $[M+H]^+$), 284 (13), 267 (17), 195 (18), 178 (18).

6. *1-Phenyl-1-azacyclotetradecane-2,14-dione* (**12**). Prop-2-enyl 1-phenyl-2,14-dioxo-1-aza-cyclotetradecane-3-carboxylate (820 mg, 2.1 mmol) in abs. THF (10 ml), HCO_2H (160 µl), Et_3N (740 µl), and $Pd(PPh_3)_4$ (123 mg) in abs. THF (2 ml) were converted into **12** (609 mg, 2.0 mmol, 85%) as per *Exper. 3*. (FC: hexane/

AcOEt 4:1). Colorless oil. UV: λ_{max} 212 (4.17); λ_{sh} 230 (4.06). UV (MeOH): λ_{max} 225.6. IR: 2930*s*, 2860*s*, 1705*s*, 1595*w*, 1490*w*, 1455*w*, 1435*w*, 1355*w*, 1365*w*, 1120*w*, 1060*m*, 900*w*. ^{1}H-NMR: 7.48–7.37 (*m*, 3 H); 7.13–7.10 (*m*, 2 H); 2.63–2.59 (*m*, 4 H); 1.73–1.64 (*m*, 4 H); 1.46–1.29 (*m*, 14 H). ^{13}C-NMR: 176.94 (*s*, 2 CO); 139.19 (*s*, C(1′)); 129.76 (*d*, C(2′), C(6′)); 128.79 (*d*, C(3′), C(5′)); 128.59 (*d*, C(4′)); 36.84, 26.18, 26.05, 25.91, 24.93, 24.77 (6*t*, 11 CH_2). CI-MS: 319 (4, $[M+NH_4]^+$), 303 (21), 302 (100, $[M+H]^+$), 236 (7). EI-MS: 301 (18, $M^{+\cdot}$), 204 (16), 148 (10), 135 (69), 94 (12), 93 (100), 92 (13), 55 (13), 41 (17).

7. *1-Aza[14]orthocyclophane-2,14-dione* (=*2-Azabicyclo[14.4.0]icosa-1(16),17,19-triene-3,15-dione*; **13**), *1-Aza[14]paracyclophane-2,14-dione* (=*2-Azabicyclo[14.2.2]icosa-1(18),16,19-triene-3,15-dione*; **14**), *19-Amino[13]metacyclophane-1,13-dione* (=*19-Aminobicyclo[13.3.1]nonadeca-1(19),15,17-triene-2,14-dione*; **15**), *and 15-Amino[13]metacyclophane-1,13-dione* (=*16-Aminobicyclo[13.3.1]nonadeca-1(18),15(19),16-triene-2,14-dione*; **16**).

7.1. *Irradiation of* **12** *in EtOH*. All irradiation experiments were carried out without filters.

a) *Low Pressure:* A soln. of **12** (400 mg, 1.3 mmol) in anh. and degassed EtOH (100 ml; $c = 13.29 \times 10^{-3}$ mol/l) was irradiated for 16 h in a *Schlenk* vessel at 0° under Ar, with a 100-W low-pressure Hg lamp. Solvent was removed and the residue separated. The fastest-running fraction, containing starting material **12** and compound **13**, was separable only by repeated application of this eluent system; if reclamation of starting material is not considered important, then it is possible to work with $CHCl_3$/hexane (saturated with NH_3) as the eluent system. (Under these conditions, **12** reacts with NH_3 by ring-opening to give *N*-monophenyltridecanediamide.) The repeated running of prep. TLCs was sometimes abstained from, as reclamation of starting material was deemed too laborious; running the prep. TLC with hexane/$CHCl_3$ (saturated with NH_3) 2:1 could accelerate and improve the separation of the components: **13** (74 mg, 18 or 34%, resp.) and **14** (91 mg, 23 or 41%, resp.).

b) *High Pressure.* A soln. of **12** (400 mg, 1.3 mmol) in anh. and degassed EtOH (100 ml; $c = 13.29 \times 10^{-3}$ mol/l) was irradiated for 45 min at 18° under N_2, with a 450-W high-pressure Hg lamp. After removal of solvent, the residue was separated by prep. TLC (hexane/AcOEt 4:1). Only by repeated application of prep. TLC was it possible to separate starting material from **13** (91 mg, 23 or 29%, resp., fastest-running) and **14** (80 mg, 20 or 25%, resp.).

7.2. *Irradiation of* **12** *in MeCN*. All irradiation experiments were carried out without filters. A soln. of **12** (80 mg, 0.26 mmol) was irradiated in MeCN (50 ml; $c = 5.32 \times 10^{-3}$ mol/l) for 3 days as described for *Exper. 4.2*. Solvent was removed and the residue chromatographed on silica gel (60 mg) with hexane/$CHCl_3$ (saturated with 25% aq. NH_4OH): **15** (9.6 mg, 12%), **13** (9.6 mg, 12%), **16** (15.2 mg, 19%), and **14** (40 mg, 50%).

Data of **13**: Colorless crystals. Melting range 91.3–95.1°. UV (EtOH): λ_{max} 204, 233, 262, 326; λ_{min} 212, 250, 284. IR: 3300 (br.), 2925*s*, 2860*m*, 1680*s*, 1655*s*, 1605*w*, 1580*s*, 1510*s*, 1450*s*, 1350*w*, 1300*m*, 1265 (br.), 1160*w*, 1120*w*, 1100*w*, 970*w*. ^{1}H-NMR (300 MHz, (D_6)DMSO): 11.72 (*s*, NH); 8.16 (*d*, *J* = 8.3, H–C(16)); 7.93 (*d*, *J* = 7.9, H–C(19)); 7.55 (*t*, *J* = 8.6, H–C(17)); 7.23–7.17 (*m*, H–C(18)); 3.04–3.00 (*m*, CH_2); 2.38–2.34 (*m*, 1 CH_2)); 1.69–1.61 (*m*, 2 CH_2); 1.28–1.11 (*m*, 7 CH_2). ^{13}C-NMR (300 MHz, (D_6)DMSO): 205.24 (*s*, CO); 171.67 (*s*, NHCO); 138.16 (*s*, C(20)); 133.56 (*d*, C(16)); 130.39 (*d*, C(19)); 126.24 (*s*, C(15)); 123.36, 121.83 (2*d*, C(17), C(18)); 39.15 (*t*, C(13)); 37.56 (*t*, C(3)); 27.24, 26.92, 26.61, 26.38, 26.10, 25.44, 25.13, 22.57 (9*t*, 9 CH_2). CI-MS: 303 (16), 302 (100, $[M+H]^+$). EI-MS: 301 (34, $M^{+\cdot}$), 299 (17), 177 (12), 174 (20), 136 (15), 135 (100), 120 (49), 93 (23), 57 (16), 45 (11), 41 (11).

Data of **14**: Colorless crystals. M.p. 157.8–158.4°. UV (EtOH): λ_{max} 218, 232, 289; λ_{min} 224, 246. IR: 3420*m*, 3380*s*, 2990*w*, 2920*s*, 2850*m*, 1670*s*, 1600*s*, 1510*m*, 1445*m*, 1400*w*, 1365 (br.), 1340*w*, 1320*w*, 1305*w*, 1270*m*, 1110*w*, 1000*m*. ^{1}H-NMR (600 MHz, (D_6)DMSO, 360 K; assignment based on 2D-NMR experiments): 9.60 (*s*, NH); 7.77 (*d*, *J* = 8.9, H–C(17), H–C(19)); 7.64 (*d*, *J* = 8.7, H–C(16), H–C(20)); 2.84–2.80 (*t*, *J* = 6.5, CH_2(13)); 2.32 (*t*, *J* = 6.5, CH_2(3)); 1.68–1.53 (*m*, 4H); 1.29–1.20 (*m*, 2 H); 1.06–0.81 (*m*, 8 H); 0.78–0.67 (*m*, 4 H). ^{13}C-NMR (600 MHz, (D_6)DMSO, 360 K; assignment based on 2D-NMR experiments): 201.81 (*s*, CO); 173.01 (*s*,NHCO); 142.86 (*s*, C(18)); 133.11 (*s*, C(15)); 128.58 (*d*, C(17), C(19)); 118.95 (C(16), C(20)); 38.60 (*t*, C(13)); 35.97 (*t*, C(3)); 28.75, 27.89, 27.80, 27.57, 27.28, 26.06, 25.39, 24.87 (8*t*, 9 CH_2). EI-MS: 301 (41, $M^{+\cdot}$), 148 (14), 135 (100), 120 (54). CI-MS: 603 (100, $[2M+H]^{+\cdot}$), 319 (7, $[M+NH_4]^+$), 303 (13), 302 (72, $[M+H]^+$), 301 (12, $M^{+\cdot}$), 135 (15). Anal. calc. for $C_{19}H_{27}NO_2$ (301.42): C 75.71, H 9.03, N 4.65; found: C 75.59, H 8.93, N 4.61.

Single crystals suitable for X-ray crystal-structure determination were obtained from Et_2O/hexane (*cf. Fig. 1*).

Data of **15**: Oil with a light green cast. IR: 3420*s*, 3305*m*, 3000*w*, 2925*s*, 2850*m*, 1655*s*, 1605*m*, 1555*s*, 1450*m*, 1360*w*, 1310*w*, 1300*w*, 1220 (br.), 1160*w*, 1110*w*, 1000*w*, 960*w*, 910*w*, ^{1}H-NMR: 8.63–8.57 (br. *s*, NH_2); 7.83

(*d*, *J* = 7.8, H–C(15), H–C(17), 2 arom. H); 6.61 (*t*, *J* = 7.8, H–C(16)); 3.51–3.32 (br. *s*, 2 H); 2.52–2.24 (*m*, 2 H); 1.86–0.63 (*m*, 18 H). ^{13}C-NMR: 205.89 (*s*, 2 CO); 151.33 (*s*, C(19)); 137.04 (*d*, C(15), C(17)); 119.44 (*s*, C(14), C(18)); 112.62 (*d*, C(16)); 41.33, 27.83, 27.70, 27.16, 26.13, 25.99 (6*t*, 11 CH_2). EI-MS: 302 (19, $[M+H]^+$), 301 (100, $M^{+\cdot}$), 177 (37), 174 (14), 162 (23), 149 (45), 136 (12), 135 (68), 134 (11), 133 (13), 120 (31), 55 (13), 41 (20).

Data of **16**: Oil with a pale green cast. IR: 3500*m*, 3330*m*, 3000*w*, 2930*s*, 2860*m*, 1640*s*, 1615*s*, 1580*m*, 1460*w*, 1440*w*, 1415*w*, 1370*w*, 1330*w*, 1300*w*, 1160*m*, 1120*w*, 830*w*. ^{1}H-NMR: 8.37 (*d*, *J* = 2.0, H–C(19)); 7.96 (*d*, *J* = 8.8, H–C(17)); 6.94–6.71 (br., NH_2); 6.69 (*d*, *J* = 8.8, H–C(16)); 2.95–2.82 (2*m*, 4 H); 1.77–1.67 (*m*, 4 H); 1.51–1.25 (*m*, 14 H). ^{13}C-NMR: 203.66, 199.07 (2*s*, CO); 154.29 (*s*, C(18)); 134.29 (*d*, C(19)); 133.89 (*d*, C(17)); 125.09 (*s*, C(14)); 117.77 (*d*, C(16)); 115.49 (*s*, C(18)); 39.87, 38.29, 27.18, 26.76, 26.66, 26.38, 26.34, 26.07, 26.01, 25.48 (10*t*, 11 CH_2). EI-MS: 302 (20, $[M+H]^+$), 301 (100, $M^{+\cdot}$), 299 (12), 202 (15), 190 (21), 189 (12), 188 (11), 177 (47), 174 (50), 163 (14), 162 (71), 161 (19), 160 (10), 148 (28), 146 (14), 135 (24), 133 (17), 120 (25), 119 (40), 91 (19), 69 (14), 55 (43), 43 (40), 42 (17), 41 (60).

8. *Prop-2-enyl 1-(4-Tolyl)-2,12-dioxo-1-azacyclododecane-3-carboxylate* (**4**). Treatment of **1** (508 mg, 2.1 mmol), NaH (101 mg, 2.5 mmol, 60% NaH in paraffin oil), and 4-tolyl isocyanate (0.30 ml, 0.31 g, 2.4 mmol) in abs. THF (10 ml) as described in *Exper. 2* gave, after FC (hexane/AcOEt 5:1), compound **4** (566 mg, 1.5 mmol, 74%). Colorless oil. IR: 2925*s*, 2860*m*, 1740*s*, 1700*s*, 1650*w*, 1585*w*, 1505*m*, 1465*m*, 1440*m*, 1355*m*, 1270*m*, 1175*m*, 1155*m*, 1120*m*, 1085*w*, 1020*w*, 990*w*, 935*w*. ^{1}H-NMR: 7.24 (2*d*, *J* = 8.0, H–C(2′), H–C(6′)); 7.05 (2*d*, *J* = 8.3, H–C(3′), H–C(5′)); 5.94–5.81 (*m*, C*H*=CH_2); 5.34–5.19 (*m*, CH=CH_2); 4.61–4.59 (*m*, CH_2O); 4.27–4.22 (*m*, H–C(3)); 2.79–2.71 (*m*, 1 H); 2.38 (*s*, Me); 2.30–2.15 (*m*, 2 H); 2.00–1.89 (*m*, 2 H); 1.58–1.41 (*m*, 11 H). ^{13}C-NMR: 176.27 (*s*, C(2)); 172.93 (*s*, C(12)); 169.51 (*s*, COO); 139.00 (*s*, C(1′)); 135.26 (*s*, C(4′)); 131.73 (*d*, *C*H=CH_2); 130.46 (2*d*, C(6′)); 128.07 (2*d*, C(3′), C(5′)); 118.09 (*t*, CH=*C*H_2); 65.64 (*t*, CH_2O); 50.77 (*d*, C(3)); 25.31, 24.27, 23.96, 23.80, 23.43 (5*t*, 6 CH_2); 21.11 (*q*, Me). CI-MS: 389 (18, $[M+NH_4]^+$), 373 (22), 372 (100, $[M+H]^+$).

9. *1-(4-Tolyl)-1-azacyclododecane-2,12-dione* (**5**). As described in *Exper. 3*, compound **4** (518 mg, 1.4 mmol) in abs. THF (5 ml), HCO_2H (105 µl), Et_3N (490 µl), and $Pd(PPh_3)_4$ (80 mg) in abs. THF (1.0 ml) were treated to give **5** (347 mg, 1.2 mmol, 86%) (FC: hexane/AcOEt 4:1). Colorless crystals. M.p. 114.0–115.4°. UV: λ_{max} 206 (4.10), 227 (3.97); λ_{min} 217 (3.93). IR: 2930*s*, 2860*m*, 1700*s*, 1520*m*, 1465*w*, 1445*w*, 1359*m*, 1295*w*, 1275*w*, 1220*m*, 1175*w*, 1160*m*, 1120*m*, 1085*w*. ^{1}H-NMR: 7.24 (*d*, *J* = 8.5, H–C(2′), H–C(6′)); 7.02 (*d*, *J* = 8.3, H–C(3′), H–C(5′)); 2.60 (*t*, *J* = 6.3, 4 H); 2.38 (*s*, Me); 1.80–1.72 (*m*, 4 H); 1.51–1.40 (*m*, 10 H). ^{13}C-NMR: 177.85 (*s*, 2 CO); 138.68 (*s*, C(1′)); 136.08 (*s*, C(4′)); 130.49 (*d*, C(2′), C(6′)); 127.99 (*d*, C(3′), C(5′)); 34.78 (*t*, C(3), C(11)); 25.65, 26.11, 24.05, 23.50 (4*t*, 7 CH_2); 21.21 (*q*, Me). EI-MS: 287 (9, $M^{+\cdot}$), 190 (7), 162 (7), 148 (5), 108 (10), 107 (100), 106 (14), 105 (6), 91 (7), 55 (12), 41 (10).

10. *15-Methyl-1-aza[12]orthocyclophane-2,12-dione* (=*16-Methyl-2-aza[12.4.0]octadeca-1(14),15,17-triene-3,13-dione*; **17**). *Ethyl 11-[(4-Methylphenyl)amino]-11-oxoundecanoate* (**18**), *and 17-Amino-14-methyl[11]metacyclophane-1,11-dione* (=*17-Amino-15-methylbicyclo[11.3.1]heptadeca-1(17),13,15-triene-2,12-dione*; **19**). 10.1. *Irradiation of* **5** *in EtOH*. A soln. of **5** (290 mg, 1.0 mmol) was irradiated in EtOH (50 ml; $c = 20.21 \times 10^{-3}$ mol/l) for 3.5 h, with the low-pressure Hg lamp, as described in *Exper. 4.1*. The solvent was removed, and the residue was chromatographed on silica gel, with hexane/AcOEt 4:1: **5** (100 mg, fastest-running), **17** (90 mg, 47%), and **18** (61 mg, 32%).

10.2. *Irradiation of* **5** *in MeCN*. Compound **5** (50 mg, 0.17 mmol) was irradiated in MeCN (50 ml; $c = 3.48 \times 10^{-3}$ mol/l) for 15 h, with the low-pressure Hg lamp, as described in *Exper. 4.2*. The solvent was removed and the residue chromatographed on silica gel (30 g), with hexane/AcOEt 5:1: **17** (40 mg, 80%) and **19** (8 mg, 16%).

Data of **17**: Colorless crystals. M.p. 106.0–109.0°. UV: λ_{max} 236 (4.27), 263 (3.84), 326 (3.35); λ_{min} 216 (3.83), 252 (3.80), 284 (2.95). IR: 3350 (br.), 2925*s*, 2855*m*, 1675*s*, 1660*s*, 1585*m*, 1500*s*, 1450*m*, 1300*m*. ^{1}H-NMR: 10.53 (*s*, NH); 8.25 (*d*, *J* = 8.4, H–C(17)); 7.50 (*s*, H–C(14)); 7.33 (*d*, *J* = 8.4, H–C(16)); 2.95–2.92 (*m*, CH_2(11)); 2.46–2.42 (*m*, CH_2(3)); 1.37–1.21 (*m*, 8 H); 1.09–1.02 (*m*, 2 H). ^{13}C-NMR: 207.13 (*s*, CO); 172.27 (*s*, NHCO); 135.38 (*s*, C(18)); 134.09 (*d*, C(14)); 132.46 (*s*, C(13)); 129.37 (*d*, C(17)); 126.63 (*s*, C(15)); 122.74 (*d*, C(16)); 40.43 (*t*, C(11)); 37.86 (*t*, C(3)); 28.05, 26.73, 25.81, 25.46, 24.91, 22.81 (6*t*, 7 CH_2); 20.81 (*q*, Me). EI-MS: 288 (17), 287 (100, $M^{+\cdot}$), 244 (12), 188 (36), 176 (10), 175 (11), 162 (13), 160 (11), 149 (55), 135 (16), 134 (65), 107 (11), 106 (16), 55 (12), 41 (18).

Data of **18**: Colorless crystals. M.p. 99.8°. IR: 3430*m*, 2920*s*, 2850*m*, 1725*s*, 1680*s*, 1595*w*, 1510*s*, 1400*w*, 1370*w*, 1310*w*, 1175*m*, 1090*m*. ^{1}H-NMR: 10.71 (*s*, NH); 7.46 (*d*, *J* = 8.4, H–C(2′), H–C(6′)); 7.07 (*d*, *J* = 8.3, H–C(3′), H–C(5′)); 4.03 (*q*, *J* = 7.1, $COOCH_2$Me); 2.29–2.25 (*m*, 4 H); 2.23 (*s*, Me); 1.59–1.48 (*m*, 4 H); 1.25 (*s*, 10 H); 1.17 (*t*, *J* = 7.1, $COOCH_2$*Me*). ^{13}C-NMR: 173.01 (*s*, NHCO); 171.13 (*s*, COO); 137.03 (*s*, C(1′)); 131.86

(*s*, C(4′)); 129.12 (*d*, C(2′), C(6′)); 119.21 (*d*, C(3′), C(5′)); 59.75 (*t*, $COOCH_2Me$); 36.53, 33.67, 28.88, 28.81, 28.57, 25.30, 24.61 (7*t*, 9 CH_2); 20.55 (*q*, Me); 14.27 (*q*, $COOCH_2Me$). CI-MS: 335 (18), 334 (100, $[M+H]^+$), 290 (33).

Data of **19**: Oil with a light green cast. IR: 3440*m*, 3330*m*, 2990*w*, 2920*w*, 2850*s*, 1665*s*, 1550*s*, 1445*m*, 1295*w*, 1230 (br.), 990*w*, 960*w*, 915*w*, 870*w*. ^{1}H-NMR: 7.55 (*s*, NH_2); 7.27 (*s*, H–C(13), H–C(15)); 3.28–3.20 (*m*, 2 H); 2.41–2.34 (*m*, 2 H); 2.33 (*s*, Me); 1.79–0.67 (*m*, 14 H). ^{13}C-NMR: 206.73 (*s*, 2 CO); 146.86 (*s*, C(17)); 136.16 (*d*, C(13), C(15)); 121.80 (*s*, C(12), C(16)); 120.35 (*s*, C(14)); 42.49, 28.04, 27.35, 27.27, 26.31 (5*t*, 9 CH_2); 20.30 (*q*, Me). EI-MS: 288 (32, $[M+H]^+$), 287 (100, $M^{+\bullet}$), 191 (19), 188 (12), 160 (11), 149 (13).

11. *Prop-2-enyl 1-(4-Tolyl)-2,14-dioxo-1-azacyclotetradecane-3-carboxylate* (**21**). Treatment of **20** (610 mg, 2.3 mmol), NaH (110 mg, 2.7 mmol, 60% NaH in paraffin oil), and 4-tolyl isocyanate (0.39 ml, 365 mg, 2.8 mmol) in abs. THF (15 ml), as described in *Exper. 2*, gave, after chromatography (hexane/AcOEt 10:1), **21** (639 mg, 1.6 mmol, 70%). Colorless oil. IR: 2925*s*, 2860*m*, 1735*s*, 1700*s*, 1650*w*, 1510*w*, 1450*m*, 1355*m*, 1270*m*, 1170*m*, 1120*w*, 1040*w*, 990*w*, 940*w*. ^{1}H-NMR: 7.25 (*d*, $J=7.9$, H–C(2′), H–C(5′)); 7.02 (*d*, $J=8.3$, H–C(3′), H–C(5′)); 5.96–5.83 (*m*, $CH{=}CH_2$); 5.34–5.20 (*m*, $CH{=}CH_2$); 4.63–4.60 (*m*, CH_2O); 4.16–4.11 (*m*, H–C(3)); 2.85–2.80 (*m*, 1 H); 2.39 (*s*, Me); 1.94–1.78 (*m*, 2 H); 1.59–1.37 (*m*, 17 H). ^{13}C-NMR: 176.55 (*s*, C(2)); 172.55 (*s*, C(14)); 169.37 (*s*, COOR); 138.95 (*s*, C(1′)); 135.86 (*s*, C(4′)); 131.81 (*d*, $CH{=}CH_2$); 130.45 (*d*, C(2′), C(6′)); 128.59 (*d*, C(3′), C(5′)); 118.28 (*t*, $CH{=}CH_2$); 65.74 (*t*, CH_2O); 52.66 (*d*, C(3)); 37.06 (*t*, C(13)); 29.27 (*t*, C(4)); 26.25, 26.00, 25.88, 25.62, 25.20, 24.84, 24.17, 21.13 (8*t*, 9 CH_2); 14.16 (*q*, Me). CI-MS: 417 (20, $[M+NH_4]^+$), 401 (23), 400 (100, $[M+H]^+$).

12. *1-(4-Tolyl)-1-azacyclotetradecane-2,14-dione* (**22**). Compound **21** (574 mg, 1.4 mmol) in abs. THF (10 ml), HCO_2H (110 µl), Et_3N (500 µl), and $Pd(PPh_3)_4$ (100 mg) in abs. THF (0.5 ml) were converted into **22** (360 mg, 1.1 mmol, 80%) as described in *Exper. 3* (FC: hexane/AcOEt 4:1). Colorless crystals. M.p. 79.3–80.4°. UV: λ_{max} 208 (4.15); λ_{sh} 222 (4.07). IR: 2925*s*, 2860*m*, 1700*s*, 1510*m*, 1460*m*, 1440*w*, 1355*m*, 1275*m*, 1240*w*, 1175*w*, 1125*w*, 1085*w*, 1020*w*. ^{1}H-NMR: 7.24 (*d*, $J=7.6$, H–C(2′), H–C(6′)); 6.99 (*d*, $J=8.2$, H–C(3′), H–C(5′)); 2.61 (*t*, $J=6.6$, 4 H); 2.39 (*s*, Me); 1.72–1.63 (*m*, 4 H); 1.45–1.36 (*m*, 14 H). ^{13}C-NMR: 177.06 (*s*, 2 CO); 138.58 (*s*, C(1′)); 136.49 (*s*, C(4′)); 130.41 (*d*, C(2′), C(6′)); 128.45 (*d*, C(3′), C(5′)); 36.79 (*t*, C(3), C(14)); 26.17, 26.04, 25.89, 24.91, 24.76 (5*t*, 9 CH_2); 21.15 (*q*, Me). CI-MS: 317 (20), 316 (100, $[M+H]^+$). EI-MS: 315 (31, $M^{+\bullet}$), 178 (12), 149 (469), 108 (12), 107 (100), 106 (20), 105 (11), 91 (10), 55 (17), 43 (15), 41 (12).

13. *1-Aza-17-methyl[14]orthocyclophane-2,14-dione* (=*18-Methyl-2-azabicyclo[14.4.0]icosa-1(16),17,19-triene-3,15-dione*; **23**). A soln. of **22** (100 mg, 0.3 mmol) was irradiated in MeCN (50 ml; $c=6.35\times10^{-3}$ mol/l) for 16.5 h, with the low-pressure Hg lamp, as described in *Exper. 4.2*. Solvent was removed, and the residue chromatographed on silica gel (40 g), with hexane/AcOEt 4:1, to give **23** (63 mg, 74%), and **22** (15 mg).

Data of **23**: M.p. 122.0–124.0°. IR: 3300*s*, 3000*w*, 2935*s*, 2860*m*, 1680*s*, 1650*s*, 1590*s*, 1510*s*, 1460*m*, 1415*w*, 1355*w*, 1300*m*, 1250 (br.), 1165*w*, 1125*w*, 980*w*, 910*w*, 885*w*, 830*m*. ^{1}H-NMR: 11.41 (*s*, NH); 8.51 (*d*, $J=8.5$, H–C(19)); 7.64 (*s*, H–C(16)); 7.34 (*d*, $J=8.55$, H–C(18)); 3.00 (*t*, $J=5.8$, CH_2(14)); 2.45 (*t*, $J=6.4$, H–C(2)); 2.36 (*s*, Me); 1.84–1.70 (*m*, 4 H); 1.37–1.23 (*m*, 14 H). ^{13}C-NMR: 205.70 (*s*, CO); 172.53 (*s*, NHCO); 137.60 (*s*, C(20)); 135.03 (*d*, C(16)); 131.87 (*s*, C(15)); 130.48 (*d*, C(19)); 123.41 (*s*, C(17)); 121.55 (*d*, C(18)); 39.23, 39.01, 27.88, 27.67, 27.45, 27.17, 26.74, 26.01, 25.86, 23.22 (10*t*, 11 CH_2); 20.79 (*q*, Me). EI-MS: 316 (12, $[M+H]^+$), 315 (62, $M^{+\bullet}$), 287 (11), 188 (38), 175 (15), 162 (17), 160 (14), 150 (11), 149 (77), 134 (100), 107 (21), 106 (29), 55 (15), 41 (22).

14. *19-Amino-16-methyl[13]metacyclophane-1,13-dione* (=*19-Amino-17-methylbicyclo[13.3.1]nonadeca-1(19),15,17-triene-2,14-dione*; **24**). A soln. of **23** (50 mg, 0.2 mmol) in MeCN (50 ml; $c=3.17\times10^{-3}$ mol/l) was irradiated for 24 h, with the low-pressure Hg lamp, as described in *Exper. 4.2*. Solvent was removed and the residue was chromatographed on silica gel (40 g), with hexane/Et_2O 4:1. It was possible to isolate **24** (8.5 mg, 27%) as an oil with a light green cast. The oil crystallized later. IR: 3440*s*, 3320*m*, 3000*w*, 2915*s*, 2869*m*, 1660*s*, 1630*w*, 1550*s*, 1469*w*, 1445*m*, 1350*w*, 1330*w*, 1315*w*, 1290*w*, 1260*w*, 1235 (br.), 1180*w*, 1165*w*, 1100*m*, 1000*m*, 980*w*, 935*w*, 880*w*, 860*w*, 750 (br.), 660*m*, 630*m*. ^{1}H-NMR (600 MHz, 250 K): 8.46 (*s*, NH_2); 7.68 (*s*, H–C(15), H–C(17)); 3.48–3.44 (*m*, 2 H); 2.37–2.32 (*m*+*s*, CH_2, Me); 1.72–1.58 (*m*, 4 H); 1.27–1.21 (*m*, 2 H); 1.17–0.93 (*m*, 8 H); 0.80–0.72 (*m*, 2 H); 0.69–0.56 (*m*, 2 H). ^{13}C-NMR (600 MHz, 250 K): 205.83 (*s*, 2 CO); 149.38 (*s*, C(19)); 137.39 (*d*, C(17), C(15)); 121.31, 119.58 (2*s*, C(14), C(16), C(18)); 41.30 (*t*, C(2), C(11)); 27.84, 27.76, 27.14, 26.18, 26.07 (5*t*, 9 CH_2); 20.40 (*q*, Me). EI-MS: 316 (20, $[M+H]^+$), 315 (100, $M^{+\bullet}$), 202 (10), 191 (19), 188 (20), 176 (31), 162 (14), 160 (13), 149 (41), 148 (13), 147 (10), 146 (14), 134 (25), 133 (21), 120 (12), 107 (57), 106 (16), 105 (25), 91 (21), 84 (12), 79 (11), 77 (11), 69 (17), 57 (17), 55 (37), 43 (30), 42 (10), 41 (40).

Single crystals suitable for X-ray crystal-structure determination were obtained from cyclohexane (*Figs. 1* and *2*).

15. *X-Ray Crystal-Structure Determination of* **14** *and* **24** (see *Table 3* and *Figs. 1–3*)[1]). Intensities were measured on a *Rigaku AFC5R* diffractometer with MoK_α radiation (graphite monochromator, $\lambda = 0.71069$ Å) and a 12-kW rotating-anode generator. Reflection intensities were corrected for *Lorentz* and polarization factors, but not absorptions. Structure interpretation using direct methods was with the SHELXS86 program system [14]. All heavy atoms were refined using anisotropic temp. factors. For **14**, all H-atoms were placed in geometrically calculated positions with an (X–H) distance of 0.95 Å and assigned fixed isotropic factors with a value of $1.2U_{eq}$ of the C- or the N-atom. For **24**, it was possible to locate all H-atoms by difference electron-density calculations; their positions were refined with individual isotropic temp. factors. For refinement, full-matrix, least-squares procedures were applied against *F*. In the case of **24**, a correction for secondary extinctions was inserted. The crystals of **14** were very thin needles and only weakly diffracting. They crystallized in a polar space group; the absolute structure was not determined, however, but selected arbitrarily. Crystallographic data are given in *Table 3*, and molecular structures in *Figs. 1–3*. These figures were produced with the ORTEP-II

Table 3. *Crystallographic Data for Compounds* **14** *and* **24**

	14	**24**
Crystallized from	Et_2O/hexane	cyclohexane
Empirical formula	$C_{19}H_{27}NO_2$	$C_{20}H_{29}NO_2$
Molecular weight [g mol^{-1}]	301.43	315.45
Crystal color	colorless	pale yellow
Crystal form	needles	prisms
Crystal size [mm]	$0.07 \times 0.15 \times 0.55$	$0.22 \times 0.33 \times 0.48$
Temp. [K]	183(1)	173(1)
Crystal system	monoclinic	monoclinic
Space group	$P2_1$	$P2_1/n$
Z	2	4
Lattice parameters		
Number of centered reflections	17	25
2θ Region [°]	11–20	33–40
a [Å]	5.110(5)	10.496(3)
b [Å]	19.458(3)	8.523(2)
c [Å]	8.496(4)	20.899(2)
β [°]	103.49(6)	103.48(1)
V [Å^3]	821(1)	1818.2(6)
D_x [g cm^{-3}]	1.219	1.152
μ(MoK_α) [mm^{-1}]	0.0779	0.0731
Scan type	$\omega/2\theta$	$\omega/2\theta$
$2\theta_{(max)}$ [°]	50	55
Number of measured reflections	1666	4689
Number of symmetry-independent reflections	1485	4168
Number of reflections used [$I > 2\sigma I$]	862	2870
Number of variables	198	325
R	0.0545	0.0455
wR[a])	0.0416	0.0402
Goodness of fit	1.431	1.737
Secondary extinction coefficient	–	$7.6(8) \times 10^{-7}$
Last Δ_{max}/σ	0.0001	0.0002
$\Delta\rho$ (max; min) [e Å^{-3}]	0.20; −0.22	0.23; −0.21

[a]) Minimized function $\Sigma w\,(|F_o| - |F_c|)^2$; $w = [\sigma^2(F_o) + (0.005F_o)^2]^{-1}$

[1]) The crystallographic data (excluding structural factors) for **14** and **24** have been deposited at the *Cambridge Crystallographic Data Centre* as deposition No. CCDC-138246 and 138247. Copies of the data can be obtained, free of charge on application to the *CCDC*, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44(1223)336033; e-mail: deposit@ccdc.cam.ac.uk).

program [15]. Neutral diffraction coefficients for heavy atoms were taken from [16a]; those for H-atoms from [17]. Anomalous dispersion effects were taken account of in F_c [18]; the values for f' and f'' come from [16b]. All calculations were performed using the TEXSAN software packet [19].

REFERENCES

[1] T. Koch, V. I. Ognyanov, M. Hesse, *Helv. Chim. Acta* **1992**, *75*, 62.
[2] T. Koch, M. Hesse, *Helv. Chim. Acta* **1994**, *77*, 819.
[3] J. Tsuji, M. Nisar, I. Shimizu, *J. Org. Chem*. **1985**, *50*, 3416.
[4] T. Koch, M. Hesse, *Synthesis* **1992**, 931.
[5] D. Wöhrle, M. W. Tausch, W.-D. Stohrer, 'Photochemie', Wiley-VCH, Weinheim, 1998.
[6] H. Shizuka, I. Tanaka, *Bull. Chem. Soc. Jpn*. **1968**, *41*, 2343.
[7] H. Shizuka, *Bull. Chem. Soc. Jpn*. **1969**, *42*, 52.
[8] H. Shizuka, *Bull. Chem. Soc. Jpn*. **1969**, *42*, 57.
[9] J. Franck, E. Rabinowitch, *Trans. Faraday Soc*. **1934**, *30*, 120.
[10] M. Fischer, *Tetrahedron Lett*. **1969**, 2281.
[11] Y. Katsuhara, H. Maruyama, Y. Shigemitsu, Y. Odaira, *Tetrahedron Lett*. **1973**, 1323.
[12] J. Stumpe, A. Mehlkorn, K. Schwetlich, *J. Photochem.* **1978**, *8*, 1.
[13] J. D. Coyle, *Pure Appl. Chem*. **1988**, *60*, 941.
[14] G. M. Sheldrick, 'SHELXS86', *Acta Crystallogr., Sect. A* **1990**, *46*, 467.
[15] C. K. Johnson, 'ORTEP-II, Report ORNL-5138', Oak Ridge National Laboratory, Oak Ridge, Tennessee, 1976.
[16] a) E. N. Maslen, A. G. Fox, M. A. O'Keefe, in 'International Tables for Crystallography', Ed. A. J. C. Wilson, Kluwer Academic Publishers, Dordrecht, 1992, Vol. C, Table 6.1.1.1, S. 477; b) D. C. Creagh, W. J. McAuley, *ibid*. Table 4.2.6.8, S. 219.
[17] R. F. Stewart, E. R. Davidson, W. T. Simpson, *J. Chem. Phys.* **1965**, *42*, 3175.
[18] J. A. Ibers, W. C. Hamilton, *Acta Crystallogr*. **1964**, *17*, 781.
[19] 'TEXSAN Single Crystal Structure Analysis Software, Version 5.0', Molecular Structure Corporation, The Woodlands, Texas, 1989.

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