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Extended mesoionic systems: synthesis and characterization of monocyclic, polycyclic and macrocyclic pyrimidinium-olate derivatives and their photochemical behavior

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Abstract—Mesoionic pyrimidinium-olate derivatives have been known to undergo photoreactions upon irradiation with UV light to form bis(beta-lactame) structures for about two decades. Here, new mono-, poly- and macrocyclic mesoions were prepared and their photochemical rearrangement behavior was investigated. The synthesized compounds were characterized by NMR, IR, UV/Vis spectroscopy, elemental analysis and mass spectrometry. The extension of the aromatic core leads to a significant red-shift of the absorption maximum from ~380 to ~430 nm, indicating a strong electronic coupling of the mesoionic base chromophore with the annellated aromatic subunit. The rigidity of the extended aromatic system prevents polycyclic mesoions from shifting to their bis(beta-lactame) isomers, while the alkyl bridge of the 16-membered macrocycle in an ansa-mesoion does not inhibit photochemical rearrangement.

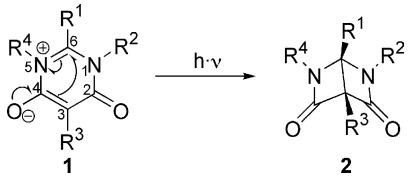
1. Introduction

Since the discovery of the five-membered Sydnone system[1] there has been growing interest in mesoions as heterocyclic compounds and in their reactions. Six-membered mesoionic ring systems are known that undergo various 1,4-dipolar cycloaddition reactions, for example, with alkenes, ketones and singulet oxygen.[2–6] Mesoionic 6-oxo-1,6-dihydropyrimidin-3-ium-4-olates (**1**) are cross-conjugated mesomeric betaines whose positive and negative charges are exclusively restricted to separate parts of the molecules' π-electron system. Their irradiation with UV light irreversibly results in the formation of the much less polar bis(beta-lactames) (**2**), as shown in Scheme 1. The bis(beta-lactame) structure of the photo products was first reported by Gotthardt et al.[3] in 1986 and is consistent with the ^{13}C NMR spectroscopic data (particularly for the C–C bridge across the 3.6-positions).

Since such mesoions are photoactive compounds with interesting physical properties, such as photoinduced change of polarity, refractive index, and density, new polymeric materials have been synthesized that contain mesoions either in the side chains or in the backbone.[7,8] Unfortunately, reversible photoswitching has not yet been reported with this class of compounds, and little is known about the photoreactivity of polycyclic and macrocyclic mesoionic compounds. In this paper, we present the synthesis and photochemical behavior of mesoionic structures with an extended conjugated π-system and carbon framework.

2. Results and discussion

Monocyclic mesoions **5a** and **5b** were synthesized starting from 1,3-diphenylthiourea (**3**) and pentyl bromide, using a modified literature procedure.[9] The resulting *N*,*N*′-disubstituted amidine *S*-pentyl-1,3-diphenylisothiourea **4** was reacted with substituted malonic acid (R = methyl, butyl) and dicyclohexylcarbodiimide (DCC) as a condensing agent at room temperature (Scheme 2) to yield the mesoionic structures **5**. As **5b** resembles the cleaved macrocyclic



Scheme 1. Photochemical conversion of mesoionic 6-oxo-1,6-dihydropyrimidin-3-ium-4-olates **1** to bis(beta-lactames) **2**.

Keywords: Polycyclic mesoions; Pyrimidinium-olates; Photocyclization reaction.

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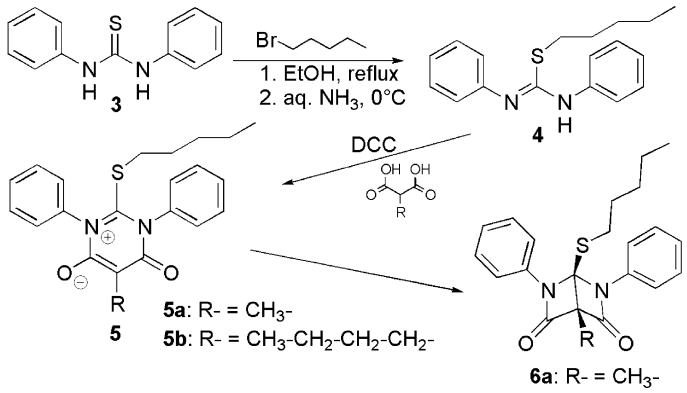
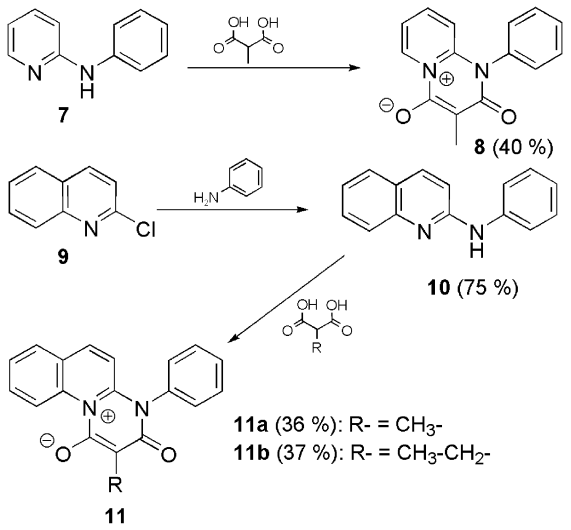


Scheme 2. Synthesis of monocyclic mesoions **5**.

structure **21** with a symmetrically broken ansa ring, it can be regarded as a model structure for the synthetic incorporation of the photoactive substance into a macrocyclic system at the 3- and 6-position, which is discussed further below. Irradiation of **5a** in dichloromethane at 365 nm gave the colorless photoproduct **6a** as an oil, although the substituent lengths at the 3- and 6-position should give rise to crystalline bis(beta-lactame) derivatives after the photoreaction.[3]

The routes to polycyclic mesoions are based on the same strategy via *N*,*N*′-disubstituted amidines **7** and **10** (Scheme 3). The latter was synthesized from 2-chloroquinone and aniline by nucleophilic aromatic substitution according to a literature procedure.[11]

Less polar solvents are better suited for the photocyclization reaction of mesoions **5** (solubility provided), due to their ability to stabilize the transition states to the much less polar bis(beta-lactames).[10] In fact, the absorption maxima in acetonitrile solution are shifted to shorter wavelengths as compared to those in dichloromethane. This indicates negative solvatochromism because the energy difference between ground state and excited state (HOMO–LUMO), which is correlated to the activation energy, is inversely proportional to the absorption wavelength. The larger



Scheme 3. Synthesis of polycyclic mesoions **8** and **11**.

activation energy barrier in acetonitrile compared to dichloromethane also accounts for the longer photoreaction times required in acetonitrile.

Alcohols are not appropriate as solvents for the photocyclization reaction, since product decomposition is observed by thin layer chromatography.[10] With different substitution patterns of the mesoionic systems, it can be shown that the long wavelength absorption maximum strongly depends on the number of rings in the aromatic core and weakly on the alkyl chain length at positions 3 and 6. The corresponding UV/Vis spectra from 10^{-4} mol l^{-1} dichloromethane solutions and compound colors are shown in Figure 1.

Due to the fact that the desired photochemical back reaction from the bis(beta-lactame) **2** to the pyrimidinium-olate **1** is not observed in conventional monocyclic mesoions, polycyclic compounds with extended aromatic systems were synthesized and their switching behavior was investigated. These investigations should address the question whether the extension of the aromatic system can lead to a reversible photoreaction. The long wavelength UV/Vis absorption maximum of the mesoions shows a significant red-shift with increasing ring number of the aromatic core, which indicates an enlarged delocalization of the mesoionic aromatic system. The reason for the bathochromic shift from ~380 to ~430 nm of **11** compared to the simple mesoions **5** can be found in the electronic coupling of the mesoionic base chromophore with the formal styrene subunit leading to a new extended orbital structure. The coupling of the aromatic cores is substantially higher than in the mesoion **5** with a principally isoelectronic pi-electron system including the phenyl substituent and free sulfur electron pair. Additionally, alkyl chain extension at the 3- and 6-position of the mesoionic core also leads to a weak bathochromic shift due to changes of the polarity in the vicinity of the mesoionic core similar to a solvent effect (compare in Fig. 1 compounds **5a**: 3-methyl, **5b**: 3-butyl, and **21**: 3,6-undecamethylene bridge; or **11a**: 3-methyl, and **11b**: 3-ethyl).

The UV spectra of the polycyclic mesoions show specific new features that can be attributed to the *N*,*N*′-disubstituted amidine substructure: a strong absorption band at 290–300 nm, and a double band at 320–330 nm for the two-ring

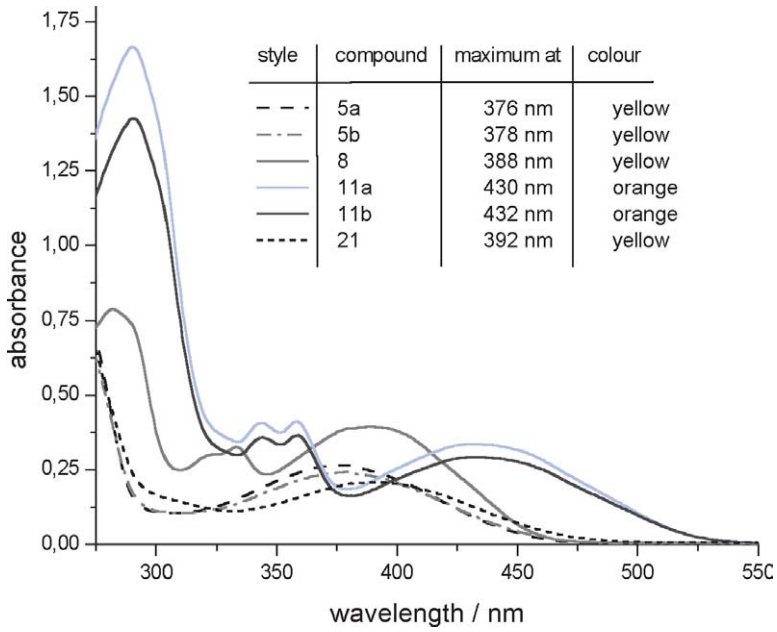
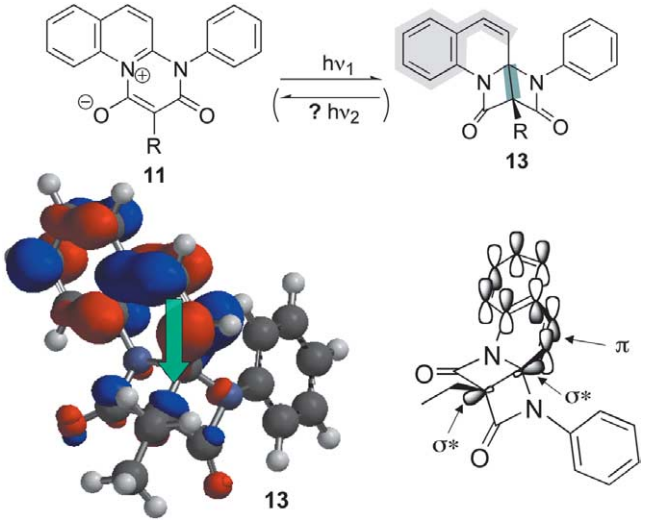


Figure 1. UV/Vis-spectra with the long wavelength absorption maxima of all synthesized mesoionic systems (10^{-4} mol l^{-1} in dichloromethane solution).

system **8** and even more distinct at 340–360 nm for the three-ring system **11**, respectively.

It was speculated that a photochemical ring opening of the hypothetical bis(beta-lactame) **13** might take place based on the fact, that the *ortho*-amino styrene fragment in **13** can be in hyperconjugation with the highly strained transannular σ-bond of the bis(beta-lactame) substructure. This hypothesis is supported by the structure of the LUMO of **11** (calculated by semiempirical PM3) which shows high orbital coefficients in the styrene subunit and a lobe at the carbon in position 3 (Scheme 4). This LUMO orbital should primarily control the course of the reaction upon photoexcitation. Thus, the styrene fragment, which is the largest chromophore in **13**, should be selectively excited by irradiation at



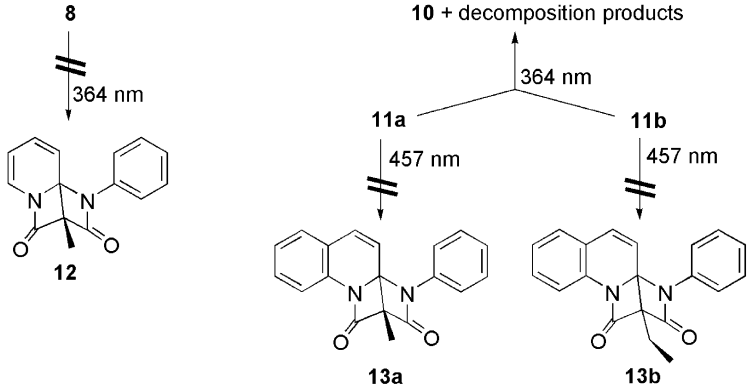
Scheme 4. Top: hypothetical photoreaction of **11** to **13** (with styrene subunit in light grey and transannular σ-bond in dark green). Bottom: left: LUMO of bis(beta-lactame) **13b** with the transannular σ-bond marked with an arrow; right: LUMO of **13b** with skeched π-orbitals of aromatic subunit and σ^*-orbitals of transannular σ-bond.

the longest energy absorption in **13**. The excited π-system could then directly interact with the almost parallely oriented antibonding orbital of the transannular σ-bond to break this bond and again form the polycyclic mesoion.

Surprisingly, none of the three annulated compounds formed the bis(beta-lactame) isomer upon irradiation in degassed dichloromethane solution (Scheme 5). Laser irradiation of **8** at 364 nm and of **11** at 457 nm led to very slow decomposition, whereas the starting compound **10** could be re-isolated after irradiation and fragmentation of **11** at the shorter wavelength absorption of 364 nm (double band feature in Fig. 1).

The major structural differences of polycyclic mesoions compared to simple mesoions are provided by the forced planarity of the molecular framework in contrast to the possible phenyl ring rotation in **5**. In addition, the conjugation pathways between the phenyl ring and the 6-position of the mesoion core (for numbering refer to Scheme 1) are different. As discussed before, the conjugation pathway in the annulated derivatives leads to a new orbital structure with longer wavelength absorption, but photoexcitation of the mesoionic core is still possible. What is to be held responsible for the lacking photorearrangement of the annulated systems **8** and **11** is the rigidity of the aromatic scaffold, which sterically hinders the photocyclization reaction in contrast to monocyclic systems, thus preventing the excited planar mesoionic core to convert to the roof-shaped photoproduct.

Ansa-bridged macrocyclic mesoions are not known from literature, so there is no data available addressing a possible hindrance of photocyclization due to the attachment of an alkyl bridge between the 3- and 6-position (designated R^1 and R^3 in Scheme 1). Synthesis of the macrocycle **21** was performed in 7 steps, as shown in Scheme 6.[12] ω-Bromoundecanol **14**, whose alcohol functionality was protected by 3,4-dihydro-2*H*-pyran (**15**),[13] was coupled with malonic acid di-*tert*-butyl ester using basic conditions.



Scheme 5. Results of the laser irradiation experiments with **8** and **11** in solution.

After acidic deprotection of the alcohol group[13] the resulting alcohol **17** was tosylated using 4-methyl-benzenesulfonyl chloride and pyridine in dichloromethane. Alkylation of 1,3-diphenylthiourea by the tosylate **18** leads to the formation of the corresponding isothiourea **19**. The soft nucleophilic sulphur makes 1,3-diphenylthiourea a good candidate for the reaction with soft electrophiles such as alkyl halogenides and sulphonates. The rather polar solvent *tert*-butyl alcohol stabilizes the intermediate *S*-alkyl-thiouronium salt. Basic workup yielded the desired diester **19**.

Basic saponification reactions for transforming **19** to **20** are not applicable here since the isothiourea functionality would decompose to 1,3-diphenylurea and the corresponding thiol.[14] Acidic deprotection of **19** with trifluoroacetic acid in dichloromethane was successful and led to complete conversion of the *tert*-butyl diester to the free carboxylic diacid after a few hours. Cyclization of **20** to the mesoionic macrocycle **21** was achieved using pseudo-dilution conditions with DCC in dichloromethane.

Irradiation of **21** in degassed dichloromethane gave the bis(beta-lactame) macrocycle **22**. The uniformity of the photocyclization process is proven by the isosbestic points in the UV/Vis spectra of Figure 2 and the detection of only one new spot by TLC.

3. Conclusion

Mesoions with an extended aromatic core show a shifted absorption maximum to longer wavelength compared to the 6-membered parent derivatives, but the stiffness of the molecular framework in such annulated systems prevents photochemical rearrangement to the roof-shaped bis(beta-lactames). This leaves the question if bis(beta-lactames) with extended aromatic systems in principle show a photochemical back reaction to their corresponding mesoions. This has to be investigated further, for example, by modifying the aromatic backbone.

In contrast, the long alkyl bridge of a macrocyclic ansa-

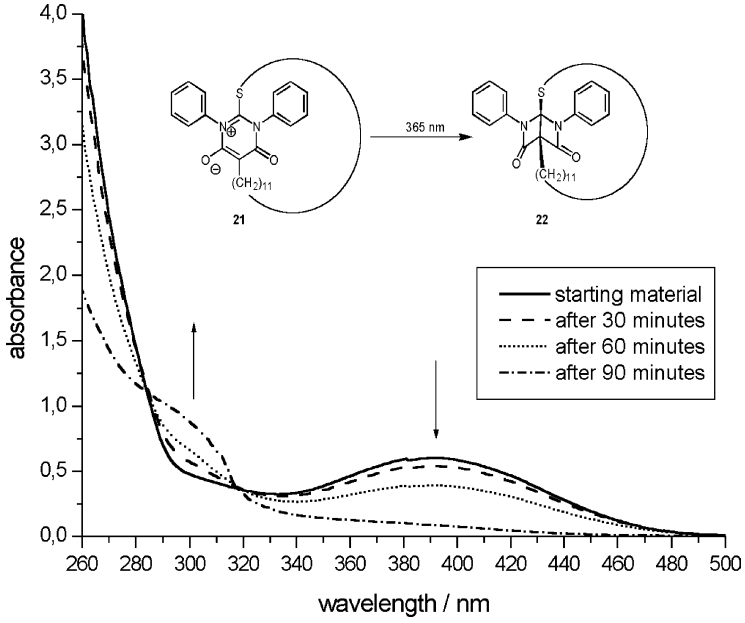
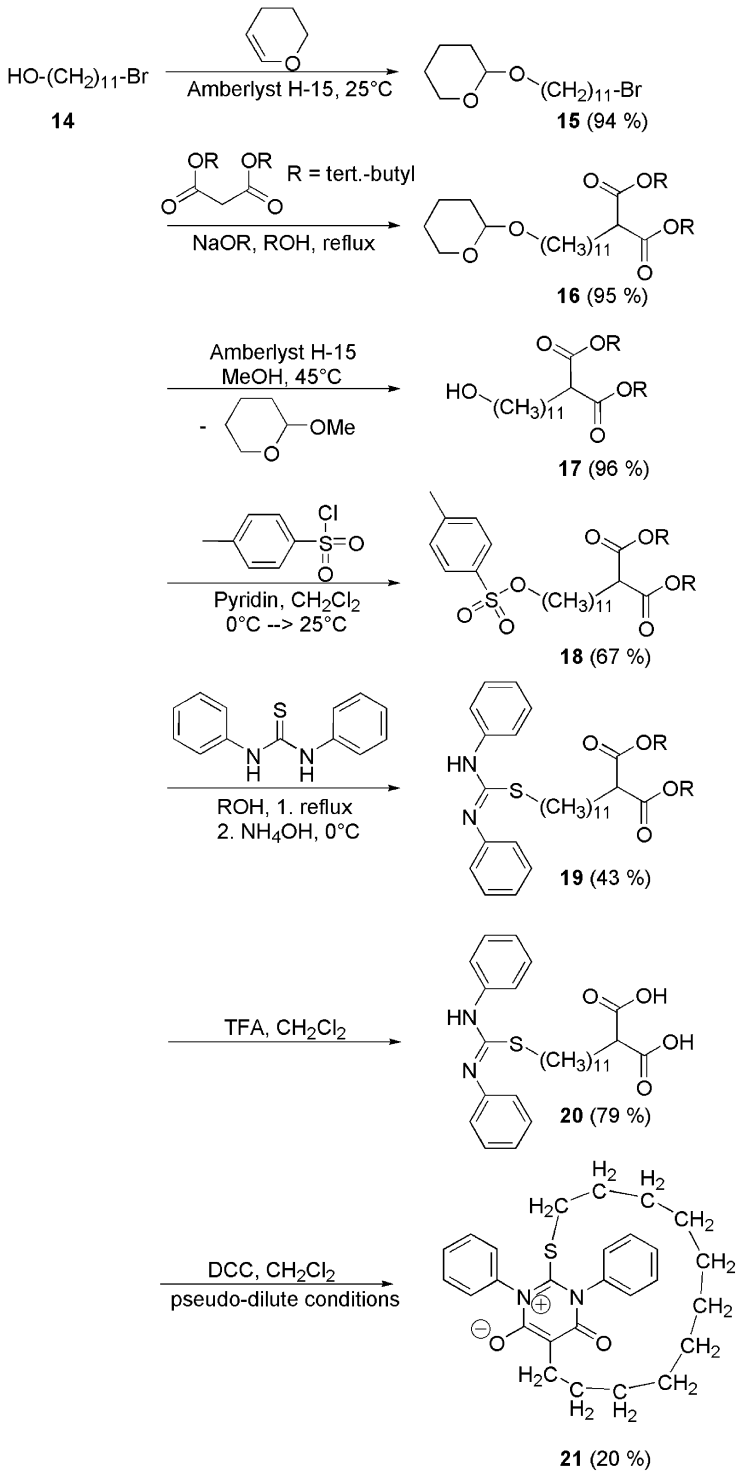


Figure 2. UV/Vis-spectra for the irradiation experiment of **21** (irradion with a UVP UV crosslinker consisting of 5 Sylvania lamps F8W/BL350 8 W each at 350 nm maximum, 10^{-4} mol l^{-1} in dichloromethane solution, Argon atmosphere).



Scheme 6. Synthetic route to the macrocyclic mesoion **21**.

mesoion does not markedly change intramolecular strain nor the electronic system, hence the photochemical rearrangement process is unhindered. This provides the possibility to incorporate the mesoionic function into flexible macrocyclic systems as a photosensitive unit, which may lead to interesting new material properties for macrocyclic systems, such as catenanes and cyclic ligands for biomolecular binding studies.

4. Experimental

4.1. General

All NMR spectra were acquired on Bruker Spectrospin 250 and AMX 500 spectrometers with the corresponding deuterated solvents as internal standard, IR spectra were measured on a Perkin Elmer Paragon 1000, EI- and FD-MS

spectra on a TRIO-2000 and ZAB 2-SE-FPD by VG-Instruments, UV/Vis spectra on a Perkin–Elmer Lambda 2 using 1×10^{-4} mol dichloromethane solutions of the respective substances. Melting points were measured on a Büchi B-545 apparatus and are uncorrected. **5a** was irradiated with a 600 W medium pressure mercury lamp with pyrex glass filter. **8**, **11a** and **11b** were irradiated using an Ar-Laser at 364 nm (0.25 W) and 457 nm (1.00 W), **21** using a UV crosslinker by UVP with 5 lamps (Sylvania F8W/BL350, 8 W each). Irradiation experiments were performed at 10^{-3} mol/l in degassed and argon-flushed dichloromethane.

Chemicals were purchased from ABCR, Merck and Sigma-Aldrich and were used without further purification. Solvents were dried with standard methods and stored over molecular sieve (4 Å).

S-Pentyl-1,3-diphenyl-isothiourea **4**. Pentyl bromide (15.10 g, 100 mmol, 1.4 equiv) was slowly added to a stirred suspension of **3** (16.34 g, 71.6 mmol) in ethanol (60 ml). The mixture was heated to reflux while the thiourea dissolved completely. After 25 h the reaction mixture was cooled and poured into aqueous ammonium hydroxide solution (220 ml, 2%) at 0 °C with rigorous stirring. The aqueous phase was decanted from the oil and extracted with diethyl ether, the combined organic phases were dried and concentrated. The crude product was purified by MPLC over silica (petrol ether/acetone 5:1) yielding a pale yellow waxy solid (12.76 g, 60%). TLC R_F 0.64 (petrol ether/acetone 5:1). IR (neat) 3383, 3057, 3028, 2956, 2929, 2858, 1624, 1586 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$) δ 0.93 (t, $J=7$ Hz, 3H), 1.31–1.36 (m, 4H), 1.63 (quint., $J=7.2$ Hz, 2H), 2.73 (t, $J=6.9$ Hz, 2H), 6.41 (s, br, 1H), 7.12 (t, $J=7.2$ Hz, 2H), 7.28 (d, $J=7.2$ Hz, 4H), 7.36 (t, $J=7.2$ Hz, 4H). ^{13}C NMR (63 MHz, $CDCl_3$) δ 13.9, 22.1, 29.2, 30.8, 31.7, 121.5, 123.6, 129.0, 143.8. MS (FD) *m/z* 298 $[M]^+$.

Preparation of mesoions **5**, **8**, and **11**. A typical procedure is exemplified for 5-methyl-6-oxo-1,3-diphenyl-2-pentylthio-pyrimidinium-4-olate **5a** as follows. To a stirred suspension of **4** (770 mg, 2.6 mmol) and methylmalonic acid (305 mg, 2.6 mmol) in dichloromethane (3 ml), DCC (1065 mg, 5.2 mmol) in dichloromethane (3 ml) was added with a syringe while the temperature was maintained at about 20 °C by water cooling. The mixture turned yellow and 1,3-dicyclohexylurea precipitated, showing the reaction progress. After stirring for another 3.5 h at ambient temperature the urea was filtered off and washed with dichloromethane. The filtrate was evaporated to dryness, dissolved in the minimum amount of toluene to which a 20-fold excess of hexane was slowly added. The product precipitated, was filtered and washed with hexane to yield yellow plates (770 mg, 78%), mp 174–175 °C. TLC R_F 0.63 (dichloromethane/methanol 20:1). IR (KBr) 3059, 3036, 2961, 2922, 2857, 1648, 1590 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$) δ 0.75 (t, $J=7$ Hz, 3H), 0.87–1.00 (m, 2H), 1.01–1.12 (m, 2H), 1.14–1.26 (m, 2H),1.95 (t, $J=7.9$ Hz, 2H), 1.96 (s, 3H), 7.30–7.34 (m, 4H), 7.46–7.49 (m, 6H). ^{13}C NMR (63 MHz, $CDCl_3$) δ 9.6, 13.6, 21.7, 28.9, 30.1, 36.0, 92.5, 128.3, 129.3, 129.6, 137.3, 159.5, 159.6. UV (CH_2Cl_2) 226 (3.22), 376 (0.22) nm (log *e*). MS (EI) *m/z* 380 $[M]^+$, 294, 119, 91, 83, 77, 71, 69, 59, 56, 55. $C_{22}H_{24}N_2O_2S$ (380.50): calcd C 69.44 H 6.36 N 7.36; found C 69.31 H 6.51 N 7.46.

The other compounds were prepared in a similar manner. If necessary, purification was performed with chromatographic standard methods, using the TLC solvents.

4.1.1. 5-Butyl-6-oxo-1,3-diphenyl-2-pentylthio-pyrimidinium-4-olate 5b. Yellow solid, mp 108–109 °C. TLC R_F 0.89 (dichloromethane/methanol 20:1). IR (KBr) 3063, 3050, 2955, 2928, 2857, 1648, 1594 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$) $\delta=0.74$ (t, $J=7.1$ Hz, 3H), 0.85 (t, $J=7.3$ Hz, 3H), 0.87–1.00 (m, 2H), 1.01–1.12 (m, 2H), 1.14–1.26 (m, 2H), 1.26–1.40 (m, 2H), 1.41–1.58 (m, 2H), 1.95 (t, $J=7.4$ Hz, 2H), 2.44 (t, $J=7.7$ Hz, 2H), 7.31–7.34 (m, 4H), 7.44–7.49 (m, 6H). ^{13}C NMR (63 MHz, $CDCl_3$) δ 13.6, 13.9, 21.6, 22.9, 24.5, 28.8, 30.0, 30.1, 36.0, 97.2, 128.3, 129.2, 129.5, 137.3, 159.5, 159.7. UV (CH_2Cl_2) 234 (1.38), 383 (0.15) nm (log *e*). MS (FD) *m/z* 422 $[M]^+$. $C_{25}H_{30}N_2O_2S$ (422.58): calcd C 71.06 H 7.16 N 6.63; found C 70.70 H 7.02 N 7.03.

4.1.2. 3-Methyl-2-oxo-1-phenyl-1,2-dihydropyrido[1,2-*a*]pyrimidin-5-ium-4-olate 8. Yellow solid, mp ca. 290 °C (dec.). TLC R_F 0.12 (petrol ether/acetone 5:1). IR (KBr) 3110, 3070, 2926, 2854, 1638, 1627, 1586 cm^{-1}. ^1H NMR (250 MHz, d_6-DMSO) δ 1.92 (s, 3H), 6.73 (d, $J=8.85$ Hz, 1H), 7.39–7.49 (m, 3H), 7.53–7.66 (m, 3H), 8.04 (ddd, $J=1.58$, 1.90, 8.85 Hz, 1H), 9.22 (dd, $J=1.26$, 6.95 Hz, 1H). ^{13}C NMR (63 MHz, d_6-DMSO) δ 10.3, 87.8, 114.6, 116.2, 129.2, 129.3, 130.0, 130.1, 136.3, 142.2, 146.5, 153.8, 159.7. UV (CH_2Cl_2) 234 (1.74), 282 (0.40), 332 (0.17), 388 (0.20) nm (log *e*). MS (FD) *m/z* 253 $[M+H]^+$. $C_{15}H_{12}N_2O_2$ (252.27): calcd C 71.42 H 4.79 N 11.10; found C 71.16 H 5.25 N 11.00.

4.1.3. 2-Methyl-3-oxo-4-phenyl-3,4-dihydropyrimido[1,2-*a*]chinolin-11-ium-1-olate 11a. Orange solid, mp 232 °C (dec.). TLC R_F 0.27 (ethyl acetate). IR (KBr) 3323, 3150, 3047, 2921, 2854, 1685, 1636, 1610, 1561, 1518 cm^{-1}. ^1H NMR (250 MHz, d_6-DMSO) δ 1.94 (s, 3H), 6.70 (d, $J=9.5$ Hz, 1H), 7.44–7.48 (m, 2H), 7.58–7.70 (m, 4H), 7.82 (ddd, $J=1.58$, 1.90, 8.85 Hz, 1H,), 8.00 (dd, $J=1.58$, 7.9 Hz, 1H); 8.30 (d, $J=9.48$ Hz, 1H), 9.64 (d, $J=8.85$ Hz, 1H). ^{13}C NMR (63 MHz, d_6-DMSO) δ 10.6, 90.1, 114.0, 122.3, 124.1, 126.8, 129.0, 129.4, 130.0, 130.9, 134.4, 136.8, 141.5, 148.2, 158.5, 159.4. UV (CH_2Cl_2) 240 (2.45), 288 (1.12), 342 (0.25), 358 (0.25), 430 (0.20) nm (log *e*). MS (EI) *m/z* 302 $[M]^+$, 274, 273, 245, 219, 218, 128, 83, 77. $C_{19}H_{14}N_2O_2$ (302.33): calcd C 75.48 H 4.67 N 9.27; found C 75.22 H 4.77 N 9.15.

4.1.4. 2-Ethyl-3-oxo-4-phenyl-3,4-dihydropyrimido[1,2-*a*]chinolin-11-ium-1-olate 11b. Orange solid, mp 217–218 °C (dec.). TLC R_F 0.49 (ethyl acetate). IR (KBr) 3321, 3144, 3020, 2950, 2923, 2859, 1682, 1633, 1617, 1560, 1518 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$) δ 1.21 (t, $J=7.27$, 7.58 Hz, 3H), 2.68 (q, $J=7.27$, 7.58 Hz, 2H), 6.75 (d, $J=9.5$ Hz, 1H), 7.29–7.33 (m, 2H), 7.55–7.65 (m, 4H), 7.74–7.82 (m, 2H), 7.93 (d, $J=9.5$ Hz, 1H), 9.77 (d, $J=8.9$ Hz, 1H). ^{13}C NMR (63 MHz, $CDCl_3$) δ 12.8, 18.8, 99.5, 113.1, 123.5, 124.3, 127.3, 128.67, 128.73, 129.9, 130.6, 131.7, 135.2, 136.5, 141.2, 147.9, 158.9, 159.9. UV (CH_2Cl_2) 240

(2.85), 290 (1.12), 344 (0.28), 358 (0.28), 432 (0.23) nm (log *e*). MS (FD) *m/z* 317 $[M+H]^+$. $C_{20}H_{16}N_2O_2$ (316.35): calcd C 75.93 H 5.10 N 8.86; found C 75.77 H 5.12 N 8.90.

4.1.5. 4-Methyl-1-pentylsulfanyl-2,6-diphenyl-2,6-diaza-bicyclo[2.2.0]hexane-3,5-dione 6a. 76 mg (0.2 mmol) **5a** were dissolved in degassed dichloromethane (200 ml) and irradiated for 3.5 h with a medium pressure mercury lamp (600 W) through a pyrex glass filter. The solvent was removed in vacuo and the crude product purified by preparative TLC (petrol ether/acetone 5:1) to yield a colorless oil. TLC R_F 0.38 (petrol ether/acetone 5:1). IR (neat): 3065, 2958, 2930, 2859, 1782, 1750, 1599, 753, 691 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$) δ 0.85 (t, $J=7$ Hz, 3 H), 1.20–1.36 (m, 4H), 1.53–1.65 (m, 2H), 1.73 (s, 3H), 2.68 (t, $J=7.2$ Hz, 2H), 7.12–7.18 (m, 2H), 7.26–7.33 (m, 4H), 7.56 (d, $J=7.9$ Hz, 4H). ^{13}C NMR (63 MHz, $CDCl_3$) δ 7.0, 13.8, 22.0, 28.4, 30.4, 30.8, 79.5, 85.5, 119.7, 125.9, 129.2, 136.2, 162.7. UV (CH_2Cl_2) 232 (2.06) nm (log *e*). MS (FD) *m/z* 398 $[M+H_2O]^+$, 133.

4.1.6. 2-(11-Bromo-undecyloxy)-tetrahydro-pyran 15. To a stirred suspension of 11-bromo-1-undecanol (15.07 g, 60 mmol) and 3,4-dihydro-2*H*-pyrane (6.06 g, 72 mmol) in cyclohexane (30 ml) amberlyst H-15 (1.50 g, 10 mequiv) was added. After stirring for 4.5 h at ambient temperature the residue was filtered off and the solvent removed in vacuo. The crude product was purified by distillation (a small piece of potassium hydroxide was added to the flask), yielding **15** as a colorless oil (18.92 g, 94%), bp 145–150 °C, 0.15 mbar. TLC R_F 0.66 (petrol ether/acetone 50:1). IR (neat) 2930, 2854 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$) δ 1.25–1.87 (series of m, 24H), 3.37 (t, $J=6.9$ Hz, 2H), 3.30–3.88 (series of m, 4H), 4.54 (m, 1H). ^{13}C NMR (63 MHz, $CDCl_3$) δ 19.7, 25.5, 26.2, 28.1, 28.7, 29.4, 29.5, 29.7, 30.8, 32.8, 33.9, 62.3, 67.6, 98.8. MS (EI) *m/z* 337/335 $[M]^+$, 85 $[THP]^+$.

4.1.7. 2-[11-(Tetrahydro-pyran-2-yloxy)-undecyl]-malonic acid di-*tert*-butyl ester 16. 0.57 g sodium metal was dissolved in 20 ml *tert*-butanol at elevated temperature. Malonic acid di-*tert*-butyl ester (5.36 g, 24.8 mmol) and **15** (7.51 g, 23.6 mmol) were added successively with a syringe. The reaction mixture was refluxed overnight, until **15** was no longer detected by TLC. After removing most of the solvent in vacuo water was added to the cold reaction mixture to dissolve the sodium bromide precipitate. The aqueous phase was decanted and extracted twice with diethyl ether, dried and concentrated to yield 10.56 g (95%) of the product as a colorless viscous oil. TLC R_F 0.72 (petrol ether/acetone 5:1). IR (neat) 2977, 2928, 2855, 1748, 1729 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$) δ 1.16–1.32 (m, 16H), 1.41 (s, 18H), 1.42–1.53 (m, 6H), 1.65–1.82 (m, 4H), 3.05 (t, 1H), 3.28–3.37 (m, 1H), 3.42–3.46 (m, 1H), 3.63–3.72 (m, 1H), 3.78–3.85 (m, 1H), 4.54 (s, 1H). ^{13}C NMR (63 MHz, $CDCl_3$) δ 19.6, 25.4, 26.2, 27.1, 27.9, 28.5, 29.2, 29.3, 29.4, 29.5, 29.5, 29.7, 30.7, 53.9, 62.2, 67.6, 81.0, 98.7, 169.0. MS (EI) *m/z* 472 $[M+1]^+$.

4.1.8. 2-(11-Hydroxy-undecyl)-malonic acid di-*tert*-butyl ester 17. Amberlyst H-15 (674 mg, 10 mequiv) was added to a solution of **16** (10.56 g, 22.4 mmol) in methanol (40 ml) and the mixture was stirred at 45 °C for 10 h until **16** could no longer be traced by TLC. The residue was filtered off and the solvent removed in vacuo to yield 8.34 g (96%) of the crude product as colorless oil. TLC R_F 0.18 (petrol ether/acetone 5:1). IR (neat) 3414, 2978, 2921, 2855, 1742, 1725 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$) δ 1.13–1.35 (m, 16H), 1.39 (s, 18H), 1.45–1.57 (m, 2H), 1.65–1.78 (m, 2H), 2.49 (s, 1H), 3.04 (t, $J=7.6$ Hz, 1H), 3.56 (t, $J=6.6$ Hz, 2H). ^{13}C NMR (63 MHz, $CDCl_3$) δ 25.6, 27.1, 27.8, 28.5, 29.1, 29.2, 29.3, 29.4, 29.4, 29.5, 32.6, 53.9, 62.8, 81.1, 169.0. MS (FD) *m/z* 387 $[M]^+$.

4.1.9. 2-[11-(Toluene-4-sulfonyloxy)-undecyl]-malonic acid di-*tert*-butyl ester 18. 17 (8.16 g, 21.1 mmol) and pyridine (3.34 g, 42.2 mmol) were dissolved in dichloromethane (90 ml) and cooled to 0 °C in an ice-bath. *p*-Toluenesulfonic acid chloride (4.02 g, 21.1 mmol) was slowly added and the mixture stirred for 3 days at ambient temperature. After washing with water the organic phase was concentrated and the crude product purified by column chromatography on silica (petrol ether/acetone 5:1), yielding a colorless oil (7.59 g, 67%). TLC R_F 0.32 (petrol ether/acetone 5:1). IR (neat) 3072, 2977, 2928, 2855, 1742, 1727, 1598, 1367, 1177, 816 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$) δ 1.16–1.24 (m, 16H), 1.41 (s, 18H), 1.53–1.64 (m, 2H), 1.67–1.80 (m, 2H), 2.41 (s, 3H), 3.06 (t, $J=7.6$ Hz, 1H), 3.97 (t, $J=6.5$ Hz, 2H), 7.30 (d, $J=8.2$ Hz, 2H), 7.75 (d, $J=8.2$ Hz, 2H). ^{13}C NMR (63 MHz, $CDCl_3$) δ 21.6, 25.2, 27.1, 27.9, 28.5, 28.7, 28.8, 29.2, 29.2, 29.3, 29.3, 29.4, 53.9, 70.6, 81.1, 127.8, 129.7, 133.2, 144.5, 169.0. MS (FD) *m/z* 541 $[M]^+$, 206, 172 $[tosyl\text{-}OH]^+$.

4.1.10. 2-[11-(*N*,*N*′-Diphenyl-carbamimidoylsulfanyl)-undecyl]-malonic acid di-*tert*-butyl ester 19. A solution of **18** (7.30 g, 13.5 mmol) and **3** (3.08 g, 13.5 mmol) in *tert*-butanol (20 ml) was refluxed while the thiourea completely dissolved. After 16 h most of the solvent was removed in vacuo and ethanol (20 ml) was added to the brownish reaction mixture. Then the mixture was poured into an aqueous ammonium hydroxide solution (41 ml, 2%) at 0 °C with rigorous stirring. The aqueous phase was decanted from the oil and the remaining water was distilled off as an azeotrope with chloroform. The crude product was purified by MPLC over silica (petrol ether/acetone 5:1) yielding a waxy solid that was recrystallized from hexane to give a pale yellow solid (3.49 g, 43%), mp 80–81 °C. TLC R_F 0.40 (petrol ether/acetone 5:1). IR (KBr) 3362, 3057, 3030, 2977, 2927, 2854, 1737, 1727, 1626, 1588, 1368, 755, 694 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$) δ 1.13–1.32 (m, 16H), 1.40 (s, 18H), 1.47–1.52 (m, 2H), 1.62–1.76 (m, 2H), 2.61 (t, br, $J=$ 7.1 Hz, 2H), 3.06 (t, $J=7.6$ Hz, 1H), 5.90 (s, br, 1H), 7.02 (t, $J=7.2$ Hz, 2H), 7.18 (d, $J=7.2$ Hz, 4H), 7.25 (t, $J=7.2$ Hz, 4H). ^{13}C NMR (63 MHz, $CDCl_3$) δ 27.1, 27.9, 28.5, 28.6, 29.0, 29.2, 29.2, 29.3, 29.4, 29.5, 31.7, 53.9, 81.1, 121.6, 123.7, 129.0, 169.0. MS (FD) *m/z* 596 $[M]^+$.

4.1.11. 2-[11-(*N*,*N*′-Diphenyl-carbamimidoylsulfanyl)-undecyl]-malonic acid 20. 19 (500 mg, 0.84 mmol) and trifluoroacetic acid (1.91 g, 16.8 mmol, 20 equiv) were dissolved in dichloromethane (10 ml) and stirred for 10 h at ambient temperature. After the volatile part was removed in vacuo, the product was used without further purification. Colorless oil (320 mg, 79%). TLC R_F 0.30 (dichloromethane/methanol/25%NH_3 in water 13:6:1). IR (neat)

3207, 2980, 2929, 2857, 1722, 1605, 1573, 1172, 759, 693 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$) δ 1.10–1.40 (m, 16H), 1.46–1.60 (m, 2H), 1.85–1.95 (m, 2H), 3.02 (t, br, 2H), 3.40 (t, $J=7.2$ Hz, 1H), 5.90 (s, br, 1H),7.29–7.44 (m, 10H), 9.74 (s, br, 2H). ^{13}C NMR (63 MHz, $CDCl_3$) δ 26.9, 27.7, 28.3, 28.6, 28.9, 29.0, 30.9, 32.1, 51.2, 126.0, 129.7, 130.2, 133.7, 174.9. MS (FD) *m/z* 485 $[M]^+$, 441 $[M-CO_2]^+$.

4.1.12. 16-Aza-17-azonia-16,17-diphenyl-18-oxido-15-oxo-2-thia-bicyclo-[11.2.2]octadeca-1(17),14(18)-diene 21. DCC (87 mg, 0.42 mmol) in dichloromethane (50 ml) was added to a stirred solution of **20** (100 mg, 0.21 mmol) in dichloromethane (150 ml) with a syringe while the temperature was maintained at about 20 °C by water cooling. The mixture turned yellow and 1,3-dicyclohexylurea precipitated, showing the progress of the reaction. After stirring overnight at ambient temperature the urea was filtered off and washed with dichloromethane. The filtrate was concentrated and the crude product purified by preparative TLC (petrol ether/acetone 5:1) yielding a yellow solid (19 mg, 20%), mp 171 °C. IR (KBr) 2926, 2854, 1649, 1358, 1244 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$) δ 1.25–1.65 (m, 18H), 2.20 (t, $J=6$ Hz, 2H), 2.58 (t, $J=6$ Hz, 2H), 7.27–7.58 (m, 10H). ^{13}C NMR (63 MHz, $CDCl_3$) δ 24.1, 25.9, 26.8, 26.9, 27.1, 27.8, 28.6, 30.6, 36.1, 97.8, 128.4, 128.9, 129.2, 129.8, 137.5, 159.6. UV (CH_2Cl_2) 392 (0.60) nm (log *e*). MS (FD) *m/z* 531, 448 $[M]^+$. HRMS found M^+ 448.2190. $C_{27}H_{32}N_2O_2S$ requires 448.2185.

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