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Nucleophilic Substitution of 4*H*-Imidazoles by Thioles: New Starting Materials for Tetraazafulvalenes and Fused Heterocycles

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Summary. Different reactivities towards the 4*H*-imidazoles **1** depending on the nature of the sulfur containing nucleophile were observed. Whereas H_2S and aromatic thioles led to 4,5-diamino-imidazoles in the course of a reduction process, treatment with aliphatic mercaptanes resulted in a substitution-reduction-dimerization cascade which finally gave *bis*-imidazoles. Their oxidative modification in presence of *m*-chloroperbenzoic acid then allowed new 1,3,5,7-tetraazafulvalenes to be easily obtained. Treatment of the *bis*-imidazoles with acetylene dimethyldicarboxylate caused cleavage of the central bond, thus leading to the formation of derivatives which are of interest for the transformation into fused heterocycles such as imidazo[4,5-*b*]azepines.

Keywords. Fused heterocycles; 4*H*-Imidazoles; Nucleophilic substitution; 1,3,5,7-Tetraazafulvalenes.

Introduction

We have recently reported a new synthesis of 4*H*-imidazoles of type **1** [1]. These heterocycles can be regarded as 1,3,6-triazafulvenes and have received particular attention not only from structural and theoretical [2] but also from synthesis points of view [3,4]. Up to now, possibilities for varying the peripheric residues at the positions 4 and 5 of the imidazole ring have been relatively restricted due to the low stabilities of the starting materials employed. These synthesis problems have now been solved by a new nucleophilic exchange reaction in the course of which the cyclic iminium salt **2** possessing the resonance structure of a $(4n)\pi$-bond system **2′** [5] have to be considered in order to explain the reaction pathway. Using this method, arylamino, alkylamino, and hydrazino substructures as well as NH_2-groups can be introduced in the 4- and 5-position of the heterocycle **1** [6]. Continuing our investigations, we now report upon the reactivity of **1** and **2** towards sulfur containing nucleophiles.

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Results and Discussion

Depending on the nature of the SH-nucleophile employed, different reactivities towards the 4*H*-imidazoles **1** were observed. A quantitative reduction of **1** to form the corresponding 4,5-diamino-imidazoles **3** could be achieved by passing a constant stream of H_2S through the reaction mixture containing catalytical amounts of mineral acids. A comparable reaction course was observed by treatment of **1** with thiophenols. In addition to **3**, the oxidatively formed diaryldisulfides could be isolated and spectroscopically characterized. An efficient access to the imidazoles **3**, which are heterocyclic analogues to electron-rich olefines, has been already realized by reduction of **1** with zinc, with ascorbic acid, or by reduction with metallic lithium and subsequent hydrolysis of the preformed trianion [7]. In direct contrast to the SH and SPh nucleophiles, a more complicated reaction was observed when alkylthioles were employed. Substitution of one of the arylamine residues in the first step of the reaction resulted in the mixed substituted derivative **4**. A comparable difference in thiolysis reactions of aromatic and aliphatic thioles has been already reported [8]. However, in the presence of an excess of the thiol, the intermediate **4** underwent an electron transfer reaction yielding the diazacyclopentadienyl radical **5** which could be detected by ESR measurements. Analogous to dithiazolyl radicals [9], **5** dimerized under formation of biimidazole systems of type **6**. Treatment of **1a–c** with ethanethiol or 2-mercaptoethanol thus gave rise to the bluish fluorescent derivatives **6a–d** in good yields. We succeeded in determining the structure of **6a**, which is illustrated in Fig. 1. In the crystal of **6a**, both imidazole rings occupy different planes which are shifted parallel to each other. The thioether subunits are

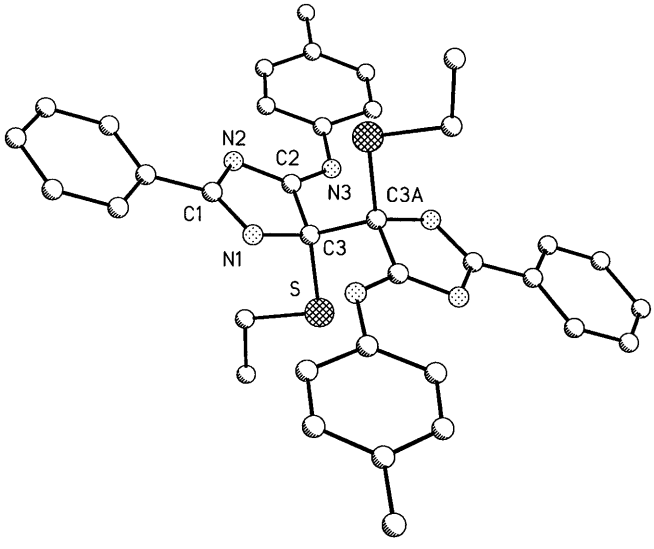
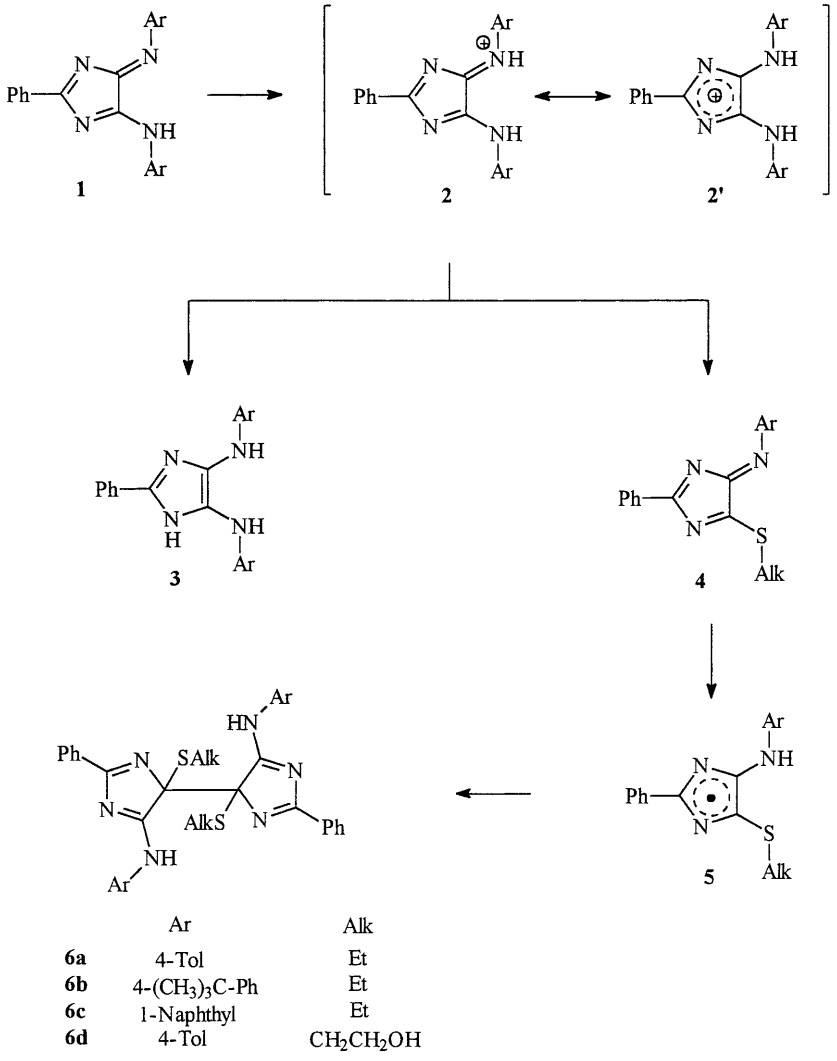


Fig. 1. Crystal structure of **6a**; the numbering corresponds to that used for the X-ray analysis*; symmetry transformation used to generate equivalent atoms: A $-x+2,\ -y, -z+1$

* Selected distances (Å) and angles (°): C1-N1 1.297(5), N1-C3 1.465(5), C3-C2 1.523(6), C2-N2 1.310(5), N2-C1 1.418(5), C2-N3 1.344(5), C3-C3A 1.545(8), C3-S 1.844(5); N1-C1-N2 117.9(4), C1-N2-C2 103.1(3), C1-N1-C3 105.0(3), N1-C3-C2 102.3(3), N1-C3-S1 111.3(3)



	Ar	Alk
6a	4-Tol	Et
6b	4-$(CH_3)_3C$-Ph	Et
6c	1-Naphthyl	Et
6d	4-Tol	CH_2CH_2OH

Scheme 1

located in an *anti*-position orthogonally above and beneath the plane of the ring system. The bond length of the central C-C-bond (1.545(8) Å) corresponds to a typical Csp^3-Csp^3 single bond [10]. In the ^{13}C NMR spectrum of **6a**, the signal of the two quaternary ring carbon atoms appeared at $\delta = 102.8$ ppm which confirms a sp^3 hybridized bonding state in solution. The NH protons were detected as a sharp singlet at $\delta = 12.50$ ppm. In addition, all NMR spectra of compounds **6** indicated a diastereoselective dimerization reaction due to the presence of a doubled set of signals especially evident for the aromatic protons. A ratio of 8:1 prefering the *anti*-isomer was found. Most likely, steric aspects are responsible for this diastereoselective differentiation. This is in accord with the small number of diastereoselective radical reactions known to present date [11]. As shown in Fig. 1, the arylamino groups achieves a maximum separation from the sterically demanding thioether substructure only in the *anti*-form. In addition, the strong intramolecular

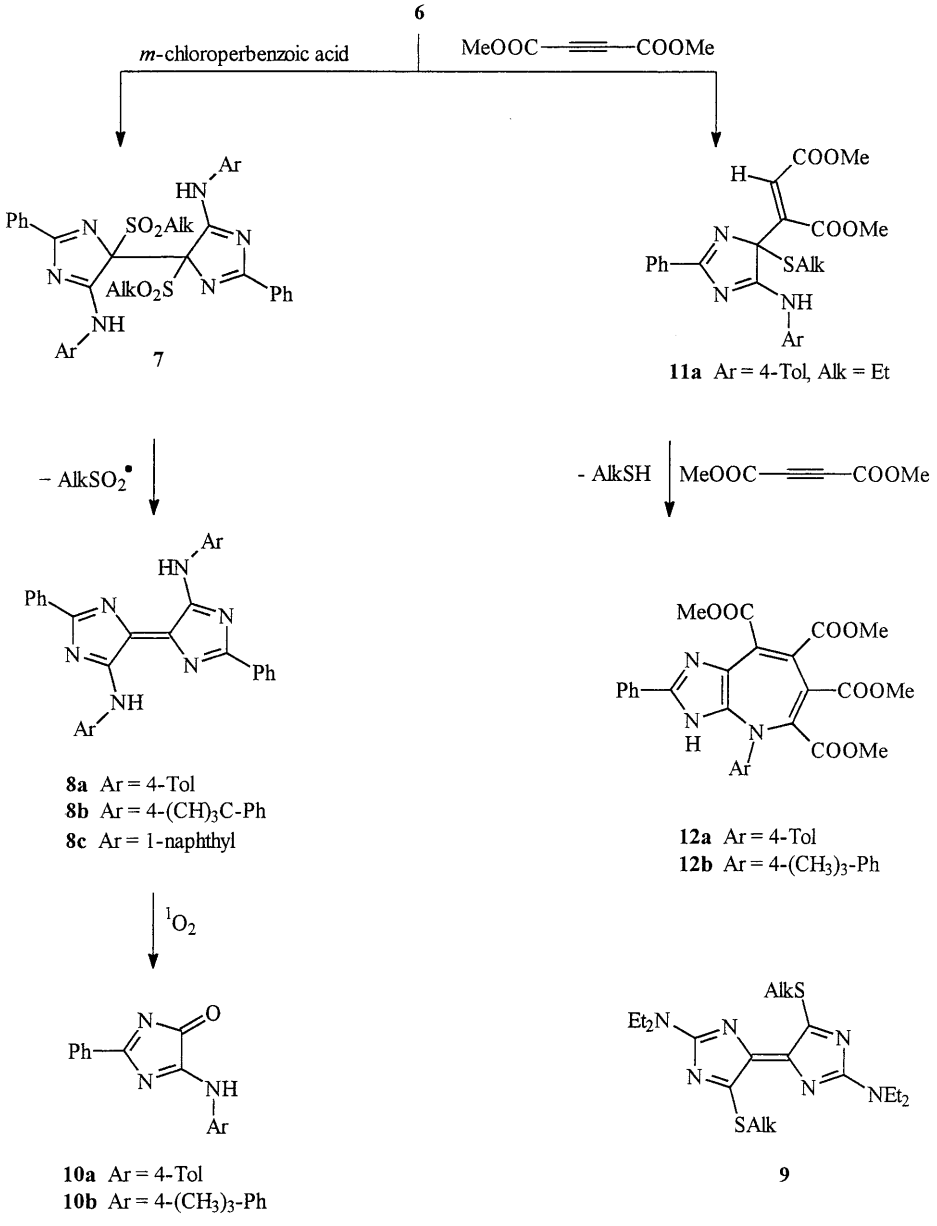
hydrogen bond between the NH proton and the ring nitrogen can be realized only in the *anti*-orientation.

In contrast to reactivities reported for diazathioorthooxalates [12], derivatives of type **6** do not loose diethyldisulfide. In addition, the formation of a central double bond could not be induced either by increasing the temperature or by changing the solvent. The expected elimination reaction took place only after addition of *m*-chloroperbenzoic acid to afford the 1,3,5,7-tetraazafulvalenes **8a–c** as microcrystalline blue solids. In the first step, both thioether groups are apparently oxidized to the sulfones **7** [13] which are then subsequently decomposed thermally to give the corresponding sulfonyl radicals [14]. Such an oxidative activation has already been described for the synthesis of tetrathiafulvalenes starting from orthothiooxalates [15]. The new 1,3,5,7-tetraazafulvalenes **8** are nearly insoluble in common organic solvents. The determination of the configuration of the central double bond was therefore not feasible. However, the (*E*)-configuration in **8** seems to be favoured due to the prefixation in the educts **6**. The purity of the products was confirmed by combustion analysis and mass spectra. The remarkable and strong bathochromic absorptions of the compounds **8** are comparable with those of the heterofulvalenes **9** [12]. Both systems contain a vinylene homologous indigoid chromophore [16, 17] which has been modified by imino substituents. In comparision to **9**, the exchange of the SCH_3 group by an arylamino residue in **8** results in a bathochromic shift of the longest wavelength absorption of about 50 nm.

A closely related reaction occured when singlet oxygen was employed as the oxidizing agent. Under mild conditions, the oxo derivatives **10** were obtained as yellowish compounds in good yields. The mechanism is assumed to proceed through the formation of the initial product **7**, which leads to the fulvalenes **8** and then under cleavage of the central double bond [18] to the product **10**.

Upon treatment of **6** with acetylenedimethyldicarboxylate, an addition reaction was observed in which the colourless product **11** was formed. ^1H, ^{13}C NMR, and MS spectroscopic data confirmed the structural assignments of the 4*H*-imidazole derivative **11a**. The ^1H NMR spectrum of **11a** revealed – in addition to the characteristical signal pattern for the ethyl and tolyl residues – two sharp singlets at $\delta = 9.47$ and 6.38 ppm. A comparison with HMQC experiments showed that the first singlet can be assigned to the NH-proton and the second one at lower field to the CH-group. Whereas in NOESY measurements the NH-proton showed dipolar coupling only with the neighbouring protons of the aryl moity, no cross peaks were observed for the CH group. These findings point to an arrangement as represented in formula **11**, although comparable addition reactions mainly lead to derivatives of fumaric acid [16]. Due to the chiral centre, the CH_2-group of the ethyl residue is diastereotopic as is shown by the presence of a doubled quartett in the ^1H NMR spectrum of **11a**. Furthermore, the signal of a quaternary ring carbon atom in **11a** appeared at high field (83.9 ppm), thus indicating a sp^3 hybridized bonding state.

Upon use of an excess of acetylenedimethyldicarboxylate, a second addition reaction forming imidazo[4,5-*b*]azepines of type **12** was observed. This indicates a high synthetic potential for heterocycles **11**. A mechanistic interpretation of the described ring fusion reaction is not yet available. Despite the large number of well-documented reactions involving acetylenedicarboxylates [19], there exist only a few examples which show any similarity to our experimental findings [20, 21]. The



Scheme 2

derivatives presented here can be considered as being further evidence for unexpected ring transformation reactions. We will present our concept for the mechanism of this reaction as well as the application of **11** as a versatile starting material for the synthesis of heterobicycles in a forthcoming paper.

Experimental

All reagents were of commercial quality (Aldrich, Fluka, Merck) and were used as received. Solvents were dried and purified using standard techniques. Reactions were monitored by TLC on plastic plates

coated with neutral alumina with fluorescence indicator (Polygram ALOX N/UV_{254} from Macherey-Nagel). Separations by flash chromatography were carried out on neutral alumina (Merck, aluminium oxide 90 active neutral, activity V, particle size 0.063–0.2 mm, 70–230 mesh ASTM). Melting points were measured with a Galen III (Boetius system) from Cambridge Instruments and are uncorrected. UV/Vis spectra were obtained using a Perkin Elmer Lambda 19 spectrophotometer. The ^{1}H and ^{13}C NMR spectra were obtained on Bruker DRX 400 and Bruker AC 250 spectrometers (^{1}H NMR shifts: relative to ^{1}H signals of the solvent). Mass spectra were taken from measurements on a Finnigan MAT SAQ 710 mass spectrometer. Elemental analyses were carried out with an automatic analyzer LECO CHNS 932. Their results were in good agreement with the calculated values.

General procedure for the reaction of sulfur containing nuleophiles with 4H-imidazoles

Concentrated HCl was added in catalytical amounts (3 drops) to a solution of 1.0 mmol **1** in 30 cm^3 *THF*. The colour of the solution immediately turned to green because of the formation of the protonated heterocycle **2**. An excess of alkylmercaptane (1 cm^3) was subsequently added before the solution was heated to 50°C. The progress of the reaction was monitored by TLC. Reaction times were usually chosen between 1 and 4 h. After filtration, the solvent was removed *in vacuo*, and the residue was purified either by column chromatography (eluent: ethyl acetate/*n*-heptane, 1:5) or by recrystallization from acetone/*n*-heptane to yield the products **6a**–**d**.

4,4′-Bis-ethylsulfanyl-2,2′-diphenyl-N5,N5′-di-(4-tolyl)-4H,4′H-[4,4′]biimidazolyl-5,5′-diamine (**6a**; $C_{36}H_{36}N_6S_2$)

Yield: 0.24 g (77%); colourless crystals; m.p.: 182°C; ^{1}H NMR (400 MHz, δ, *DMSO*-d_6): 12.49 (s, 2H, NH), 7.94 (d, $J = 7.85$ Hz, 4H), 7.43 (t, $J = 7.67$ Hz, 4H), 7.32 (t, $J = 7.45$ Hz, 2H), 7.27 (d, $J = 8.26$ Hz, 4H), 6.94 (d, $J = 8.23$ Hz, 4H), 2.70 (m, 4H, CH_2), 2.18 (s, 6H, CH_3-Tol), 1.13 (t, $J = 7.28$ Hz, 6H, CH_3) ppm; ^{13}C NMR (100 MHz, δ, *DMSO*-d_6): 147.5, 143.2, 142.5, 130.5, 129.4, 129.1, 128.9, 128.7, 126.2, 124.7, 120.4, 115.0, 102.8, 30.3, 20.2, 14.5 ppm; MS (CI): *m/z* (%) = 619 [M+2H^+] (2), 310 [1/2 M^+] (100), 280 (22), 118 (11).

4,4′-Bis-ethylsulfanyl-2,2′-diphenyl-N5,N5′-bis-(4-tert.-butyl-phenyl)-4H,4′H-[4,4′]biimidazolyl-5,5′-diamine (**6b**; $C_{42}H_{48}N_6S_2$)

Yield: 0.22 g (63%); greenish crystals; m.p.: 156°C; ^{1}H NMR (250 MHz, δ, $CDCl_3$): 7.77 (d, $J = 8.12$ Hz, 4H), 7.34-7.20 (m, 14H), 5.98 (brs, 2H, NH), 2.55 (q, $J = 7.34$ Hz, 4H), 1.24 (s, 18H), 1.16 (t, $J = 7.34$ Hz, 6H) ppm; ^{13}C NMR (62 MHz, δ, $CDCl_3$): 143.9, 142.5, 129.7, 128.8, 128.7, 128.5, 126.0, 125.8, 124.9, 115.6, 34.0, 31.5, 31.2, 15.2 ppm; MS (ESI): *m/z* (%) = 725.2 [M+Na^+] (12), 352.1 [1/2 M^+] (100).

4,4′-Bis-ethylsulfanyl-2,2′-diphenyl-N5,N5′-bis-α-naphthyl-4H,4′H-[4,4′]biimidazolyl-5,5′-diamine (**6c**; $C_{42}H_{36}N_6S_2$)

Yield: 0.20 g (58%); greenish solid; m.p.: 194°C; ^{1}H NMR (250 MHz, δ, $CDCl_3$): 8.02 (d, $J = 7.09$ Hz, 4H), 7.92 (t, $J = 7.02$ Hz, 4H), 7.83 (m, 6H), 7.52–7.32 (m, 14H), 6.69 (s, 2H, NH), 2.61 (q, $J = 7.34$ Hz, 4H), 1.22 (t, $J = 7.32$ Hz, 6H) ppm; ^{13}C NMR (62 MHz, δ, $CDCl_3$): 148.5, 144.5, 138.7, 134.4, 129.6, 128.9, 128.9, 128.7, 126.5, 125.5, 125.1, 125.0, 124.1, 120.1, 110.6, 103.0, 31.4, 15.3 ppm; MS (ESI): *m/z* (%) = 713.1 [M+Na^+] (10), 400.1 (22), 368.1 (34), 346 (100).

4,4′-Bis-(2-hydroxy-ethylsulfanyl)-2,2′-diphenyl-N5,N5′-di-(4-tolyl)-4H,4′H[4,4′]biimidazolyl-5,5′-diamine (**6d**; $C_{36}H_{36}N_6S_2O_2$)

Yield: 0.17 g (54%); greenish crystals; m.p.: 211°C; ^{1}H NMR (250 MHz, δ, *DMSO*-d_6): 12.48 (s, 2H), 7.94 (d, $J = 7.39$ Hz, 4H), 7.55 (s, 2H), 7.43 (t, $J = 7.18$ Hz, 4H), 7.32 (m, 6H), 6.96 (d, $J = 6.37$ Hz, 4H), 2.75 (q, $J = 6.65$ Hz, 4H), 2.18 (s, 6H) ppm; ^{13}C NMR (62 MHz, δ, *DMSO*-d_6): 147.8, 143.1, 142.1, 130.2, 128.9, 128.6, 128.0, 126.3, 124.7, 115.0, 101.9, 59.8, 39.7, 20.2 ppm; MS (CI): *m/z* (%) = 325 [1/2 M+H$^+$] (65), 280 (78), 118 (52), 71 (38), 57 (100).

General procedure for the synthesis of 1,3,5,7-tetraazafulvalenes **8**

m-Chloroperbenzoic acid (0.19 g, 1.2 mmol) was added to a solution of 1.0 mmol **6** in 50 cm^3 toluene. The solution was then stirred under reflux for 1–2 h while a dark coloured precipitate was slowly formed. The bluish-black solid was collected by filtration and repeatedly washed with toluene and acetone to yield the 1,3,5,7-tetraazafulvalenes **8**.

2,6-Bis-phenyl-4,8-bis-(4-tolylamino)-1,3,5,7-tetraazafulvalene (**8a**; $C_{32}H_{26}N_6$)

Yield: 0.21 g (43%); black crystals; m.p.: 357°C; MS (CI): *m/z* (%) = 495 [M+H$^+$] (100), 479 (8), 247 (5), 121 (27), 93 (8); UV/Vis (*DMSO*): λ_{max} (lgε) = 288 (3.81), 424 (3.65), 633 (3.65), 681 (3.54) nm.

2,6-Bis-phenyl-4,8-bis-(4-tert.-butylphenylamino)-1,3,5,7-tetraazafulvalene (**8b**; $C_{38}H_{38}N_6$)

Yield: 0.24 g (41%); black solid; m.p.: >360°C; MS (CI): *m/z* (%) = 579 [M+H$^+$] (100), 521 (10), 121 (18), 93 (13); UV/Vis (*DMSO*): λ_{max} (lgε) = 285 (3.79), 424 (3.63), 448 (3.62), 636 (3.59), 678 (3.56) nm.

2,6-Bis-phenyl-4,8-bis-(α-naphthylamino)-1,3,5,7-tetraazafulvalene (**8c**; $C_{38}H_{26}N_6$)

Yield: 0.18 g (33%) black solid; m.p.: 340°C; MS (CI) = *m/z* (%): 567 [M+H$^+$] (78), 442 (7), 121 (43), 93 (100), 144 (8); UV/Vis (*DMSO*): λ_{max} (lgε) = 415, 646 (3.75), 720 (3.74), 857 (3.79) nm.

General procedure for the synthesis of the imidazolones **10**

A biimidazole derivative **6** (1.0 mmol) was dissolved in 20 cm^3 CH_2Cl_2, and 5 mg tetraphenylporphyrine were added. A constant stream of dry O_2 was passed through the reaction mixture at $-20°$ for 3 h while externally irradiating with a Na vapour lamp. The solution turned greenish, and a yellow precipitate was formed. The microcrystalline solid was collected by filtration and repeatedly washed with CH_2Cl_2 to yield the corresponding imidazolones **10**.

2-Phenyl-5-(4-tolylamino)-imidazol-4-one (**10a**; $C_{16}H_{13}N_3O$)

Yield: 0.15 g (58%); yellow crystals; m.p.: 264°C; ^{1}H NMR (400 MHz, δ, *DMSO*-d_6): 12.47 (s, 1H, NH), 8.16 (d, $J = 7.48$ Hz, 2H), 7.61 (m, 3H), 7.23 (d, $J = 8.08$ Hz, 2H), 7.13 (d, $J = 8.12$ Hz, 2H), 2.27 (s, 3H) ppm; ^{13}C NMR (100 MHz, δ, *DMSO*-d_6): 153.8, 144.6, 137.6, 134.9, 129.6, 129.4, 128.8, 128.6, 127.8, 126.7, 119.1, 21.1 ppm; MS (CI): *m/z* (%) = 264 [M+H$^+$] (100), 154 (3), 122 (5), 108 (10), 89 (7); UV/Vis (*DMSO*): λ_{max} (lgε) = 271 (5.11), 475 (3.14) nm.

5-(4-tert.-Butyl-phenylamino)-2-phenyl-imidazol-4-one (**10b**; $C_{19}H_{19}N_3O$)

Yield: 0.14 g (47%); yellow crystals; m.p.: 215°C; ^{1}H NMR (250 MHz, δ, *DMSO*-d_6): 8.19 (d, $J = 8.65$ Hz, 2H), 7.61 (m, 3H), 7.43 (d, $J = 8.44$ Hz, 2H), 7.37 (d, $J = 8.58$ Hz, 2H), 1.31 (s, 9H) ppm; ^{13}C NMR (62 MHz, δ, *DMSO*-d_6): 145.0, 138.8, 133.9, 128.9, 128.4, 128.2, 128.0, 127.6, 125.7, 125.4, 124.9, 34.3, 31.1 ppm; MS (CI): *m/z* (%) = 307 [M+H$^+$] (96), 292 (100), 276 (27), 159 (96), 149 (36), 134 (95), 117 (32), 104 (66), 91 (17), 77 (50); UV/Vis (*DMSO*): λ_{max} (lgε) = 286 (4.10), 379 (3.64), 426 (3.65) nm.

2-(4-Ethylsulfanyl-2-phenyl-5-phenylamino-4H-imidazol-4-yl)-but-2-en-dicarboxylicacid dimethylester (**11a**; $C_{24}H_{25}N_3O_4S$)

A solution of 0.6 g **6a** (1.0 mmol) and 0.3 g acetylenedimethyldicarboxylate (2.0 mmol) dissolved in 20 cm^3 *THF* was heated for 3 h under reflux. The formation of a colourless product could be monitored by TLC. After completion of the reaction, the solvent was evaporated, and the residue was purified by column chromatography (ethylacetate/*n*-heptane 1:5).

Yield: 0.2 g (45%); colourless solid; m.p.: 101°C; ^{1}H NMR (400 MHz, δ, $CDCl_3$): 9.47 (s, 1H, NH), 8.38 (d, $J = 8.04$ Hz, 2H, *o*-Ph), 7.76 (d, $J = 8.44$ Hz, 2H, Tol), 7.54–7.45 (m, 3H, *m*-, *p*-Ph), 7.20 (d, $J = 8.25$ Hz, 2H, Tol), 3.96 (s, 3H, CH_3OOC), 3.70 (s, 3H, CH_3OOC), 2.60 (m, 2H, CH_2), 2.34 (s, 3H, CH_3-Tol), 1.19 (t, $J = 7.48$ Hz, 3H, CH_3) ppm; ^{13}C NMR (100 MHz, δ, $CDCl_3$): 178.2, 175.5, 169.4, 164.7, 143.1, 136.1, 133.8, 131.8, 131.6, 129.5, 129.2, 128.3, 124.1, 119.5, 83.9, 53.3, 52.1, 24.5, 20.8, 14.0 ppm; MS (CI): *m/z* (%) = 452 [M+H$^+$] (100), 420 (5), 390 (63), 358 (4), 269 (10), 143 (7).

General procedure for the synthesis of imidazo[4,5-b]azepines **12**

A solution of 0.5 mmol **6** and 0.3 g acetylenedimethyldicarboxylate (2.0 mmol) in 20 cm^3 toluene was heated under reflux for two days. The colourless product **11** was first formed which then slowly added a second molecule acetylenedimethyldicarboxylate to give the final product **12** which was purple. After completion of the reaction the solvent was evaporated and the residue was purified by column chromatography (ethylacetate/*n*-heptane 1:5) to yield the imidazo[4,5-*b*]azepines **12**.

2-Phenyl-9-(4-tolyl)-1H-imidazo[4,5-b]azepin-5,6,7,8-tetracarboxylic acid tetramethylester (**12a**; $C_{28}H_{25}N_3O_8$)

Yield: 0.08 g (31%) purple crystals; m.p.: 166–167°C; ^{1}H NMR (250 MHz, δ, $CDCl_3$): 7.54 (d, $J = 7.84$ Hz, 2H), 7.46–7.35 (m, 3H), 7.25 (d, $J = 8.71$ Hz, 2H), 7.05 (d, $J = 8.30$ Hz, 2H), 6.66 (s, 1H, NH), 3.90 (s, 3H), 3.86 (s, 3H), 3.81 (s, 3H), 3.13 (s, 3H), 2.26 (s, 3H) ppm; ^{13}C NMR (62 MHz, δ, $CDCl_3$): 166.6, 165.6, 163.8, 160.9, 141.0, 140.5, 139.4, 131.4, 130,8, 130.5, 129.9, 129.8, 129.6, 128.9, 128.7, 127.3, 125.7, 125.1, 116.7, 53.6, 53.1, 52.9, 52.3, 20.6 ppm; MS (EI): *m/z* (%) = 531 [M$^+$] (100), 498 (10), 413 (17), 381 (44), 357 (15), 310 (17), 252 (22), 194 (17), 91 (37); UV/Vis ($CHCl_3$): λ_{max} (lgε) = 259 (4.24), 350 (3.81), 521 (3.33) nm.

2-Phenyl-9-(4-tert.-butyl-phenyl)-1H-imidazo[4,5-b]azepin-5,6,7,8-tetracarboxylicacid tetramethylester (**12b**; $C_{31}H_{31}N_3O_8$)

Yield: 0.06 g (12%); purple solid; m.p.: 158–162°C; ^{1}H NMR (400 MHz, δ, $CDCl_3$): 7.55 (d, $J = 7.96$ Hz, 2H), 7.43 (m, 3H), 7.32 (m, 4H), 3.90 (s, 3H), 3.86 (s, 3H), 3.81 (s, 3H), 3.13 (s, 3H), 1.27 (s, 9H) ppm; ^{13}C NMR (100 MHz, δ, $CDCl_3$): 143.9, 129.7, 128.9, 128.7, 127.2, 126.2, 125.8, 116.3, 53.5, 53.1, 52.8, 52.2, 31.4 ppm; MS (CI): *m/z* (%) = 574 [M+H$^+$] (100).

Crystal structure determination

The intensity data were collected on a Nonius KappaCCD diffractometer using graphite-monochromated Mo-K_α radiation. Data were corrected for *Lorentz* and polarization effects but not for absorption [22, 23]. The structures were solved by direct methods (SHELXS [24]) and refined by full-matrix least squares techniques against F_o^2 (SHELXL-97 [25]). The hydrogen atom of the amino group was located by difference *Fourier* synthesis and refined isotropically. The other hydrogen atoms were included at calculated positions with fixed thermal parameters. All nonhydrogen atoms were refined anisotropically [25]. XP (SIEMENS Analytical X-ray Instruments, Inc.) was used for the structure representations.

Crystal data for **6a**: $C_{36}H_{36}N_6S_2 \cdot \frac{1}{2}C_3H_6O$; $M = 645.87\,g \cdot mol^{-1}$, colourless prisms, size $0.30 \times 0.28 \times 0.20\,mm^3$, triclinic, space group P-1; $a = 9.7593(6)$, $b = 10.5440(7)$, $c = 11.4990(9)$ Å, $\alpha = 107.827(3)$, $\beta = 101.124(3)$, $\gamma = 110.100(3)°$, $V = 997.29(12)$ Å^3, $T = 20°C$, $Z = 1$, $\rho_{calcd} = 1.075\,g \cdot cm^{-3}$, $\mu(\text{Mo-}K_\alpha) = 1.66\,cm^{-1}$, F(000) = 342, 8223 reflections in $h(-12/0)$, $k(-12/13)$, $l(-13/14)$ measured in the range $3.90° \leq \Theta \leq 26.37°$; completeness: $\Theta_{max} = 98.3\%$, 4003 independent reflections; $R_{int} = 0.097$, 2463 reflections with $F_o > 4\sigma(F_o)$, 220 parameters, 0 restraints, $R1_{obs} = 0.1053$, $wR^2_{obs} = 0.2643$, $R1_{all} = 0.1608$, $wR^2_{all} = 0.2931$, $GOOF = 1.339$; largest difference peak and hole: $1.004/-0.417\,e \cdot Å^{-3}$. Further details are available upon request from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ on quoting the depository number CCSD-144291, the names of the authors, and the citation of the paper.

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