Ketene-*N*,*N*-acetals as Key Intermediates in the Formation of Tetraazapentafulvadienes

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Dedicated to Prof. E. Anders, FSU Jena on the occasion of his 60th birthday

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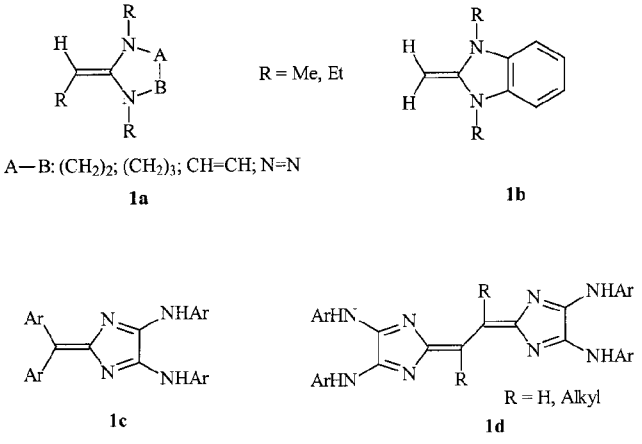
The easily accessible bis-amidines **2** react with adamantane-1-carbonyl chloride **3** to yield the 4*H*-imidazole **4**. If the carbonic acid chloride contains an α-hydrogen, the reaction takes a completely different path. In this case, tetraazapentafulvadienes **11** are formed via a cascade reaction that contains two single electron transfer (SET) steps. Cyclic ketene-*N*,*N*-acetals **7** are postulated to be the initial intermediates, which then readily form radical cations, the presence of which could be confirmed by ESR measurements even though intramolecular trapping proved impossible due to their extreme reactivity. DFT calculations at the B3LYP/6-311+G(d,p) level support these experimental findings. The crucial ketene-*N*,*N*-acetals **7** can be stabilized through steric interactions and/or the introduction of conjugated substructures, thus leading to the formation of fulvenoid structures such as **14a** and **14b**.

Introduction

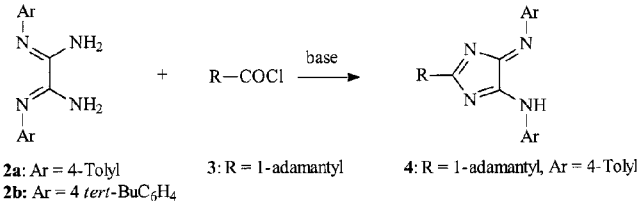
Cyclic 1,1-diaminoethenes of type **1a** and **1b** (Scheme 1) are quite rare, and only a few examples have been reported in the literature.[1−9] These compounds are suspected to possess a large charge density at the β-carbon, as observed experimentally by their photoelectron spectra[9] and the well-documented ^{13}C NMR upfield shift of the β-carbon.[6−8] These derivatives possess dipolarophilic qualities,[10] are strong neutral bases[6,7] and reactive nucleophiles,[6−9] and have been employed as dienophiles in inverse electron demand Diels−Alder reactions.[6,7] In spite of these interesting electronic properties, synthetically useful oxidation reactions[11−13] involving ketene-*N*,*N*-acetals are practically unknown. In this article, we describe a simple route to the heterofulvenes **1c** as well as the tetraazapentafulvadienes **1d**, both of which can be obtained from the ketene-*N*,*N*-acetals which are formed in the course of a reaction cascade.



Scheme 1

Results and Discussion

Recently we described a simple synthetic approach to the fulvenoid 4*H*-imidazoles **4** (R = aryl) by the cyclisation of the bis-amidines **2** with aromatic carbonic acid chlorides **3** (Scheme 2).[14]



Scheme 2

We extended the scope of this synthesis to include aliphatic carbonic acids. To begin with, we employed carbonic acid chlorides that did *not* contain an α-hydrogen. As an example, adamantane-1-carbonyl chloride **3** reacts smoothly to give the expected product **4**. The structural data for **4** are similar to those reported for other 4*H*-imid-

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azoles.[15,16] In addition, the solid state structure of **4** (Figure 1) could be determined by X-ray analysis; the characteristic bond length alternation observed for 4*H*-imidazoles is clearly visible.

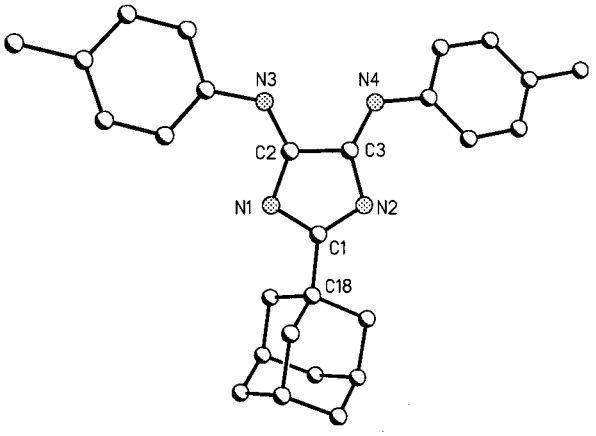
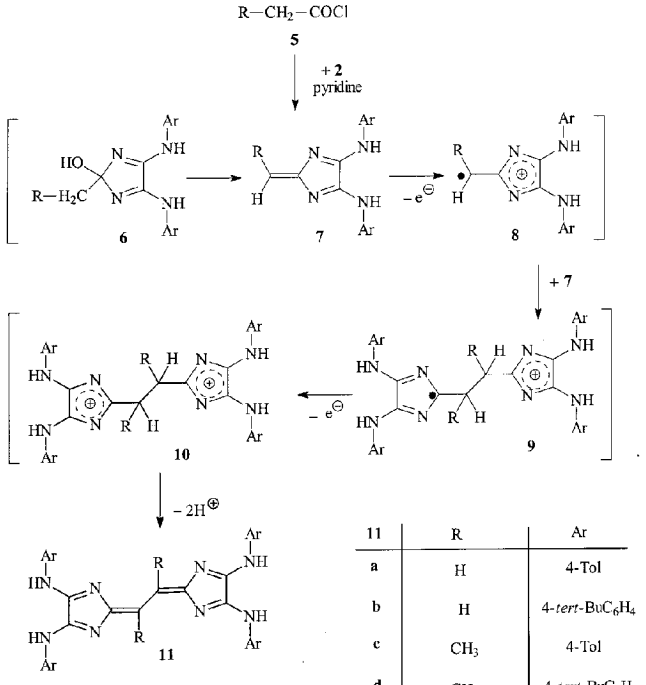


Figure 1. X-ray crystal structure of derivative **4**; selected distances [Å]: N1−C2 1.323(5), N2−C1 1.329(5), N3−C2 1.315(5), N4-N3 1.295(5), C1−C18 1.502(5), N1−C1 1.411(5), N2−C3 1.376(5), N3−N4 1.412(5), C2−C3 1.506(5)

If acid chlorides that contain α-hydrogens are employed, a completely different reaction cascade is observed (Scheme 3). Acetyl chloride **5a**, for example, reacts almost instantly with an amidine **2** in the presence of pyridine to give a violet solution. The major product, compound **11a**, could be isolated from the mixture and fully characterized (MS, NMR). Compound **11a** has previously been prepared by an independent synthetic route.[17] We postulate that compound **7** is a key intermediate for this oxidative dimerization.

The five-membered ring **7** is in equilibrium with several tautomers (Scheme 4), all of which are energetically stable, as confirmed by B3YLP/6-311+G(d,p) calculations. These tautomers can be described as being both ketene-*N*,*N*-acetals and diazapentafulvenes,[18] and are unusual examples of 1,1-disubstituted olefins. In the gas phase, tautomer **7a** is the most stable one and is 1.1 kcal/mol and 4.8 kcal/mol more stable than tautomers **7b** and **7c**, respectively. Exploration of solvation effects on the tautomeric equilibrium by means of the B3LYP-COSMO model (solvents: tetrahydrofuran, acetonitrile and water) demonstrated that although solvation affects the absolute energy of the tautomers (solvation stabilizes the molecules considerably relative to their gas phase energy), it has no significant influence on their relative stabilities. Tautomer **7a** is therefore expected to be overwhelmingly present in solution.

Unfortunately, the tautomers **7** are far too reactive to isolate or characterize in any form. We assume that they undergo a fast SET reaction to form the radical cations **8** in which either an *N*-acylpyridinium salt (present in excess) or oxygen (presence of air) functions as an electron accepting reagent. B3LYP calculations support this assumption: the radical cation **8a** (formed directly from **7a** by removal of an electron) is a stable species at the unrestricted B3LYP/6-311+G(d,p) level of theory.

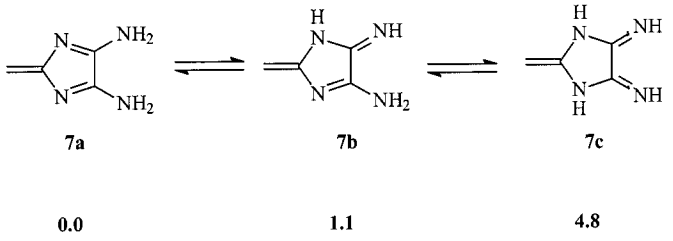


5	R
a	H
b	CH_3
c	C_2H_5
d	n-C_4H_9
e	n-C_5H_{11}
f	n-$C_{12}H_{25}$
g	$(CH_2)_3CH{=}CH_2$

11	R	Ar
a	H	4-Tol
b	H	4-*tert*-BuC_6H_4
c	CH_3	4-Tol
d	CH_3	4-*tert*-BuC_6H_4
e	C_2H_5	4-Tol
f	C_2H_5	4-*tert*-BuC_6H_4
g	n-C_4H_9	4-Tol
h	n-C_5H_{11}	4-Tol
i	n-$C_{12}H_{25}$	4-Tol
j	$(CH_2)_3CH{=}CH_2$	4-Tol

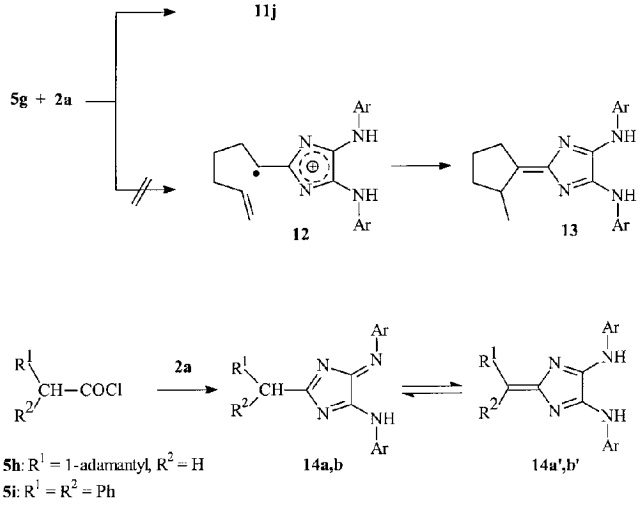
Scheme 3

Due to the excess of neutral ketene-*N*,*N*-acetal **7** in solution, **8** can very easily react with it to form a distonic radical cation **9**, which is then oxidized further to yield the dication **10** (also a stable species according to our computations). A double deprotonation finally gives the conjugated system **11**. ESR spectroscopic tracking of the reaction between the amidine **2b** and compound **5c** yielded broad signals that did not exhibit a hyperfine structure (g = 2.0135) — a characteristic of delocalized radical cations. An attempt was made to trap the intermediate radical cation **8j** with 6-heptenoic acid chloride **5g** to form the 5-exo-product **13** by intramolecular addition.[19] The major product of this reaction, however, was found to be compound **11j** (Scheme 5), which was isolated as shiny bronze crystals that were structurally characterized by NMR spectroscopy. A trapping product corresponding to compound **13** could not be isolated. The C−C connection forming the dimer **11** can be compared to the oxidative dimerization of ketene acetals and enamines.[20] Oxidation of the distonic radical cation **9** to form the dication **10** is very probably due to the low oxidation potential of α-aminomethyl radicals.[21] The few available literature citations support the oxidation of ketene-*N*,*N*-acetals to radical cations and their subsequent dimerization.[11−13] The electrochemical oxidation of styr-



Scheme 4. Tautomeric forms of compound **7** according to B3LYP/6-3II+G(d,p) model calculations (R = H; Ar replaced with H for computational simplicity)

enes,[22] as well as the oxidative dimerization of dithiapentafulvenes,[23] seem to follow an analogous reaction pathway.



Scheme 5

The homologous acid chlorides **5b**−**f** undergo similar reactions yielding the violet tetraazapentafulvadienes **11a**−**11i** as the major products. All of these show a characteristic strong UV/Vis absorption band between 520 and 590 nm with molar extinction coefficients of about 4.30. In addition, they can all be easily protonated with mineral acids to form insoluble salts which allow a better isolation.

1-Adamantaneacetic acid chloride **5h** reacts with the amidine **2a** to form a yellow cyclization product **14a**, which, according to NMR spectroscopy, is in equilibrium with a tautomeric form **14a′**. Due to steric hindrance, this compound does not dimerize. If a second substituent is introduced at the α-C atom, the reaction stops after cyclization to yield the conjugated, energetically preferred tautomer as demonstrated in the case of diphenylacetyl chloride **5i**, which reacts to form the 1,4-diazapentafulvene **14b′**.

Experimental Section

All reagents were of commercial quality (Aldrich, Lancaster, Fluka, Merk). Solvents were dried and purified using standard techniques. Reactions were monitored by thin layer chromatography (TLC) on plastic plates coated with neutral alumina containing a fluorescence indicator (Polygram ALOX/ UV_{254} from Machery Nagel). Column chromatography was carried out on neutral alumina (Merck, aluminium oxide 90 active neutral, activity I, particle size 0.063−0.2 mm, 70−230 ASTM) which was tuned to activity V with 15% water. Melting points were measured with a Galen III (Boetius system) from Cambridge Instruments, and left uncorrected. UV/Vis spectra were obtained using a Perkin−Elmer Lambda 19 spectrophotometer. The ^1H and ^{13}C NMR spectra were obtained with a Bruker DRX 400 (400 MHz) or a Bruker AC 250 (250 MHz) spectrometer. Mass spectra were measured with a Finnigan MAT SAQ 710 mass spectrometer. The ESR spectra were recorded with a Bruker ESP 300 E spectrometer. Elemental analyses were carried out in-house with an automatic analyzer LECO CHNS 932.

2-(1-Adamantyl)-5-(4-tolylamino)-4-(4-tolylimino)-4*H*-imidazole (4): The oxalamidine **2a** (267 mg, 1 mmol) was dissolved in a mixture of dry pyridine (1 mL) and anhydrous THF (20 mL). Adamantane-1-carbonyl chloride **3** (397 mg, 2 mmol) was then added in one portion and the mixture was heated under reflux for 1 h. The solvent was then removed in vacuo and the residue was purified by column chromatography (alumina; toluene/acetone 20:1). Yield: 169 mg (41%); mp: 178−179 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.80 (s, 6 H, CH_2), 2.09 (s, 9 H, CH/CH_2), 2.35 (s, 6 H, CH_3), 7.20 (m, 4 H, CH), 7.78 (m, 4 H, CH). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.2 (CH_3), 28.1 (CH_2), 36.8 (CH_2), 38.6 (C_q), 39.5 (CH), 123.5 (br., CH), 129.7 (CH), 136.3 (C_q), 163.5 (C_q) 203.3 (C2). UV/Vis ($CHCl_3$): λ (lgε) = 337 (4.1), 558 (3.5). HRMS (CI/MeOH): calcd. for $C_{27}H_{30}N_4$ 410.2470; found $C_{27}H_{31}N_4$ [M + H^+] 411.2548.

Tetraazapentafulvadienes of Type 11. General Procedure: The corresponding oxalamidine **2** (1 mmol) was dissolved in a mixture of dry pyridine (1 mL) and anhydrous THF (20 mL). The acyl chloride **5** (2 mmol) was added in one portion and the mixture was then heated under reflux for 1 h. The solvent was removed in vacuo and the residue was dissolved in acetone (20 mL). Hydrochloric acid (37%, 2 mL) and water (3 mL) were added and the dark precipitate was filtered off, washed with water and dried. The residue was purified by reprecipitation (addition of water to a solution of **11** in a mixture of methanol (15 mL) and hydrochloric acid (37%, 1 mL)].

***N*,*N′*-Di-*p*-tolyl-2-[2-(4,5-di-*p*-tolylaminoimidazol-2-ylidene)-ethylidene]-2*H*-imidazole-4,5-diamine (11a):** Yield: 191 mg (66%). Analytical data were in agreement with those reported previously.[17]

***N*,*N′*-Di-*p*-*tert*-butylphenyl-2-[2-(4,5-di-*p*-*tert*-butylphenylamino-imidazol-2-ylidene)ethylidene]-2*H*-imidazole-4,5-diamine (11b):** Yield: 260 mg (70%); mp: 198−200 °C. ^1H NMR (400 MHz, [D_6]DMSO): δ = 1.24 (s, 36 H, CH_3), 6.94 (s, 2 H), 7.23 (m, 8 H, CH), 7.43 (m, 8 H, CH), 7.67 (m, 4 H, CH), 7.78 (m, 4 H, CH), 8.61 (s, 2 H, NH), 8.67 (s, 2 H, NH). ^{13}C NMR (100 MHz, [D_6]DMSO): δ = 31.7, 34.6, 115.1, 119.1, 119.2, 123.5, 123.8, 125.8, 126.0, 136.9, 137.2, 152.2, 152.3, 155.3. UV/Vis (THF):

λ(lgε) = 525 (4.8), 562 (4.9). MS (CI): *m/z* (%) = 747 (67) [M$^+$], 374 (10), 160 (22), 148 (100). $C_{48}H_{58}N_8$ (747.04): calcd. C 77.17, H 7.83, N 15.00; found C 77.31, H 7.90, N 14.88.

2-[1-Methyl-2-(4,5-di-*p*-tolylaminoimidazol-2-ylidene)propylidene]-*N,N′*-di-*p*-tolyl-2*H*-imidazole-4,5-diamine (11c): Yield: 152 mg (50%); mp: 89−91 °C. ^{1}H NMR (250 MHz, [D$_6$]DMSO): δ = 2.11 (s, 6 H, CH_3), 2.20 (s, 12 H, CH_3), 7.23 (m, 8 H, CH), 7.79 (m, 8 H, CH). ^{13}C NMR (62 MHz, [D$_6$]DMSO): δ = 18.4 (CH_3), 19.7 (CH_3), 116.0/ 116.1 (CH), 127.0/127.5 (CH), 129.0/129.1 (C_q), 135.8/135.9 (C_q), 149.0 (C_q), 149.7 (C_q), 157.5 (C_q). UV/Vis (THF): λ (lgε) = 346 (4.4), 514 (4.1). MS (CI): *m/z* (%) = 607 (10) [M + 1], 391 (100), 363 (65), 327 (30), 305 (100), 271 (55), 164 (100), 108 (95). HRMS (ESI/MeOH): calcd. for $C_{38}H_{38}N_8$ 606.3219; found $C_{38}H_{39}N_8$ [M + H$^+$] 607.3307.

2-[1-Methyl-2-(4,5-di-*p*-*tert*-butylphenylaminoimidazol-2-ylidene)-propylidene]-*N,N′*-di-*p*-*tert*-butylphenyl-2*H*-imidazole-4,5-diamine (11d): Yield: 186 mg (48%); mp: 160−163 °C. ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 1.21 (s, 36 H, CH_3), 2.16 (s, 6 H, CH_3), 7.38 (m, 8 H, CH), 7.78 (m, 8 H, CH). ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 18.0 (CH_3), 31.7 (CH_3), 34.4 (C_q), 118.0 (CH), 126.1 (CH), 128.1, 138.4, 144.6, 152.5, 152.6, 157.1(C_q). UV/Vis (THF): λ (lgε) = 347 (4.5), 504 (3.8). MS (CI): *m/z* (%) = 776 (10) [M + 1], 447 (30), 346 (15), 206 (100), 190 (10), 134 (10). $C_{50}H_{62}N_8$ (775.09): calcd. C 77.48, H 8.06, N 14.46; found C 77.39, H 7.98, N 14.33.

2-[1-Ethyl-2-(4,5-di-*p*-tolylaminoimidazol-2-ylidene)butylidene]-*N,N′*-di-*p*-tolyl-2*H*-imidazole-4,5-diamine (11e): Yield: 99 mg (31%); mp: 142−145 °C. ^{1}H NMR (250 MHz, [D$_8$]THF): δ = 1.20 (br. m, 6 H, CH_3), 2.04/2.32 (2s, 12 H, CH_3), 2.62 (m, 4 H, CH_2), 7.15 (m, 8 H, CH), 7.32 (m, 4 H, CH), 7.98 (m, 4 H, CH) 10.03/ 12.57 (2s, 4 H, NH). ^{13}C NMR (62 MHz, [D$_8$]THF): δ = 12.8, 13.8 (CH_3), 19.6, 19.7 (CH_3), 24.0 (CH_2), 119.4 (CH), 128.6, 128.9 (CH), 123.2, 125.4, 133.0, 134.6, 148.0, 148.8, 148.9, 157.2 (C_q). UV/Vis (THF): λ (lgε) = 351 (4.3), 556 (4.2), 594 (4.2). MS (CI): *m/z* (%) = 635 (1) [M$^+$], 377 (10), 319 (5), 269 (15), 178 (20), 108 (100). $C_{40}H_{42}N_8$ (634.82): calcd. C 75.68 H 6.67 N 17.65; found C 75.58 H 6.78 N 17.56.

2-[1-Ethyl-2-(4,5-di-*p*-*tert*-butylphenylaminoimidazol-2-ylidene)-butylidene]-*N,N′*-di-*p*-*tert*-butylphenyl-2*H*-imidazole-4,5-diamine (11f): Yield: 209 mg (52%); mp > 180 °C (dec.). ^{1}H NMR (250 MHz, [D$_8$]THF): δ = 0.80−1.23 (br. m, 46 H, CH_2/CH_3), 7.28 (m, 8 H, CH), 7.63 (m, 4 H, CH), 7.98 (br. m, 4 H, CH), 9.98 (s, 4 H, NH). UV/Vis (THF): λ (lgε) = 350 (4.3), 561 (4.3), 596 (4.3). MS (CI): *m/z* (%) = 804 (5) [M + 1], 502 (30), 353 (100), 337 (55), 297 (30), 220 (20), 150 (45), 134 (35). HRMS (ESI/MeOH): calcd. for $C_{52}H_{66}N_8$ 802.5410; found $C_{52}H_{67}N_8$ [M + H$^+$] 803.5486.

2-[1-Butyl-2-(4,5-di-*p*-tolylaminoimidazol-2-ylidene)hexylidene]-*N,N′*-di-*p*-tolyl-2*H*-imidazole-4,5-diamine (11g): Yield: 169 mg (49%); mp: 160−164 °C. ^{1}H NMR (400 MHz, [D$_8$]THF): δ = 0.88−0.99 (br. m, 6 H, CH_3), 1.31 (m, 4 H, CH_2), 1.48 (m, 4 H, CH_2), 1.61 (m, 4 H,CH_2), 2.07 (s, 6 H, CH_3), 2.29 (s, 6 H, CH_3), 6.95 (m, 4 H, CH), 7.16 (m, 4 H, CH), 7.36 (br. m, 4 H, CH), 7.91 (br. m, 4 H, CH) 10.21 (s, 4 H, NH). ^{13}C NMR (100 MHz, [D$_8$]THF): δ = 13.3/13.4 (CH_3), 20.0/20.1 (CH_3), 22.3/22.7/24.4/ 31.1/31.9 (CH_2), 120.3 (CH), 129.4/129.6 (CH), 149.6 (C_q). UV/Vis (THF): λ (lgε) = 356 (4.4), 558 (4.1). MS (CI): *m/z* (%) = 691 (15) [M + 1], 347 (20), 187 (10), 108 (100). $C_{44}H_{50}N_8$ (690.93): calcd. C 76.49, H 7.29, N 16.22; found C 76.57, H 7.34, N 16.14.

2-[1-Pentyl-2-(4,5-di-*p*-tolylaminoimidazol-2-ylidene)heptylidene]-*N,N′*-di-*p*-tolyl-2*H*-imidazole-4,5-diamine (11h): Yield: 176 mg (49%); mp: 144−147 °C. ^{1}H NMR (250 MHz, [D$_8$]THF): δ = 0.92 (m, 6 H, CH_3), 1.30−1.50 (m, 8 H, CH_2), 2.05 (s, 6 H, CH_3), 2.38 (s, 6 H, CH_3), 2.50 (br. m, 8 H, CH_2), 6.70 (m, 4 H, CH), 7.12 (m, 8 H, CH), 8.09 (m, 4 H, CH) 10.19/10.75/11.64 (3 s, 4 H, NH). ^{13}C NMR (62 MHz, [D$_8$]THF): δ = 13.0, 13.2 (2CH_3), 19.6, 19.7 (2 × CH_3-Tol.), 22.0, 23.7, 26.2, 31.0, 31.2 (5 × CH_2), 118.6, 118.8 (2 × CH), 128.7, 129.0 (2 × CH), 131.5, 134.1, 146.5, 146.8, 169.2 (C_q). UV/Vis (THF): λ (lgε) = 558 (4.2), 595 (4.2). MS (CI): *m/z* (%) = 719 (10) [M$^+$], 509 (10), 459 (10), 443 (10), 313 (30), 201 (60), 130 (20), 108 (100). HRMS (ESI/MeOH): calcd. for $C_{46}H_{54}N_8$ 718.447; found $C_{46}H_{55}N_8$ [M + H$^+$] 719.4557.

2-[1-Dodecyl-2-(4,5-di-*p*-tolylaminoimidazol-2-ylidene)-tetradecylidene]-*N,N′*-di-*p*-tolyl-2*H*-imidazole-4,5-diamine (11i): Yield: 210 mg (46%); mp: 139−141 °C. ^{1}H NMR (250 MHz, [D$_8$]THF): δ = 0.87 (m, 6 H, CH_3), 1.28 (br. m, 40 H, CH_2), 2.10 (s, 6 H, CH_3), 2.36 (s, 6 H, CH_3), 2.66 (br. m, 4 H, CH_2), 6.74 (m, 4 H, CH), 7.08 (m, 4 H, CH), 7.18 (m, 4 H, CH), 8.13 (m, 4 H, CH), 10.18, 11.05, 11.99 (3 s, 4 H, NH). ^{13}C NMR (62 MHz, [D$_8$]THF): δ = 13.4 (CH_3), 19.9, 20.1 (2 × CH_3), 23.6, 29.0−33.3, 36.7 (br., CH_2), 119.0 (br., CH), 129.0 (br., CH), 134.4, 135.0, 137.5, 149.9, 150.2, 172.7, 173.4 (C_q). UV/Vis (THF): λ (lgε) = 559 (3.9). MS (CI): *m/z* (%) = 915 (10) [M$^+$], 459 (10), 425 (30), 318 (10), 107 (100). $C_{60}H_{82}N_8$ (915.36): calcd. C 78.73, H 9.03, N 12.24; found C 78.84, H 9.11, N 12.09.

2-[1-Pent-4-enyl-2-(4,5-di-*p*-tolylaminoimidazol-2-ylidene)hept-6-enylidene]-*N,N′*-di-*p*-tolyl-2*H*-imidazole-4,5-diamine (11j): Yield: 197 mg (55%); mp: 170−175 °C (dec.). ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 1.71 (s, 4 H, CH_2), 2.10 (s, 6 H, CH_3), 2.19 (s, 4 H, CH_2), 2.32 (s, 6 H, CH_3), 2.85 (s, 4 H, CH_2), 4.96 (d, *J* = 10.1 Hz, 2 H, *trans*-CH=C*H*$_2$), 5.05 (d, *J* = 16.6 Hz, 2 H, *cis*-CH=C*H*$_2$), 5.84 (m, 2 H, -CH=), 6.89 (m, 4 H, CH), 7.22 (m, 8 H, CH), 7.74 (m, 4 H, CH), 12.58 (br., 4 H, NH). ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 20.7, 20.8 (2CH_3), 29.2 (CH_2), 30.5 (CH_2), 33.3 (CH_2), 115.4 (=CH_2), 120.0 120.7 (br., CH), 123.9 (C_q), 130.0 (CH), 133.6 (C_q), 136.4 (C_q), 138.1 (CH), 144.7 (C_q), 148.3 (C_q). UV/Vis ($CHCl_3$): λ (lgε) = 587 (4.3). MS (CI): *m/z* (%) = 715 (20) [M], 439 (10), 359 (25), 283 (15), 257 (100), 229 (30), 21 (10), 108 (100). HRMS (ESI/MeOH): calcd. for $C_{46}H_{50}N_8$ 714.4158; found $C_{46}H_{51}N_8$ [M + H$^+$] 715.4245.

1,4-Diazapentafulvenes of Type 14. General Procedure: The corresponding oxalamidine **2** (1 mmol) was dissolved in a mixture of dry pyridine (1 mL) and anhydrous THF (20 mL). The acyl chloride (2 mmol) was added in one portion and the mixture was heated under reflux for 1 h. The solvent was then removed in vacuo and the residue was purified by column chromatography (alumina; toluene/acetone 10:1).

6-Adamantyl-2,3-bis(4-tolylamino)-1,4-diazapentafulvene (14a): Yield: 144 mg (34%); mp: 106−108 °C. ^{1}H NMR (400 MHz, [D$_8$]THF, 323 K): δ = 1.71 (br. m, 14 H, CH_2/CH), 1.97 (br., 6 H, CH_3), 2.31 (m, 3 H, CH), 6.75−7.92 (br. m, 8 H, CH). ^{13}C NMR (100 MHz, [D$_8$]THF, 323 K): δ = 19.8 (CH_3), 28.9 (br., CH), 33.6 (C_q), 35.8 (br., CH_2), 42.5 (br., CH_2), 48.9 (br., CH_2), 119.1 (br., CH), 128.9 (br., CH), 139.4, 166.6, 168.1, 171.4 (C_q). UV/Vis ($CHCl_3$): λ (lgε) = 346 (3.9), 462 (3.2). MS (CI), *m/z* (%) = 425 (5) [M + 1], 284 (25), 195 (10), 177 (100), 135 (43), 107 (17). HRMS (ESI/MeOH): calcd. for $C_{28}H_{32}N_4$ 424.2627; found $C_{28}H_{33}N_4$ [M + H$^+$] 425.2699.

6,6-Diphenyl-2,3-bis(4-tolylamino)-1,4-diazapentafulvene (14b): Yield: 199 mg (45%); mp: 140−145 °C. ^{1}H NMR (400 MHz, [D$_8$]THF): δ = 2.30 (br. m, 6 H, CH_3), 6.80−7.90 (br. m, 18 H, CH). ^{13}C NMR (100 MHz, [D$_8$]THF): δ = 19.8 (CH_3), 120−130 (br. m, CH/C_q), 135.7, 138.1, 141.5, 148.6 (C_q). UV/Vis ($CHCl_3$):

λ)lgε) = 406 (3.9). MS (CI), *m*/*z* (%) = 443 (45) [M + 1], 355 (30), 338 (60), 318 (35), 302 (100), 268 (60), 248 (20), 183 (90), 167 (45), 150 (80). $C_{30}H_{26}N_4$ (442.56): calcd. C 81.42, H 5.92, N 12.66; found C 81.51, H 6.01, N 12.51.

Computational Details: Full geometry optimizations (i.e. without symmetry constraints) were carried out with the Gaussian 98[24] suite of programs at the hybrid B3LYP/6-311+G(d,p) level. All stationary points found were rigorously characterized as energy minima by verifying that no imaginary modes exist for the conformer/tautomers considered (vibrational analysis). The relative stabilities and energies of formation reported in this article contain a correction (unscaled) for the zero-point vibrational energy. The COSMO solvation model[25] was used to compute the effect of the free energy of solvation (ε = 7.58, tetrahydrofuran; ε = 36.64, acetonitrile; ε = 78.39, water) on the tautomeric equilibrium of compound **7**.

Crystal Structure Determination: The intensity data for the compounds 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.[26,27] The structure was solved by direct methods (SHELXS[28]) and refined by full-matrix least-squares techniques against F_o^2 (SHELXL-97 [29]). For the N3 of **4**, the hydrogen atom was located by difference Fourier synthesis and refined isotropically. The other hydrogen atoms were included at calculated positions with fixed thermal parameters. All non-hydrogen atoms were refined anisotropically.[29] XP (SIEMENS Analytical X-ray Instruments, Inc.) was used for structure representations.

Crystal Data for 4:[30] $C_{27}H_{30}N_4$, M_r = 410.55 g·mol^{-1}, orange prism, size 0.18 × 0.12 × 0.10 mm^3, orthorhombic, space group $P2_12_12_1$, a = 6.5601 (3), b = 11.3116 (4), c = 29.668 (1) Å, V = 2201.5 (2) Å^3, T = −90 °C, Z = 4, $\rho_{calcd.}$ = 1.239 gcm^{-3}, μ (Mo-K_α) = 0.74 cm^{-1}, F(000) = 880, 3735 reflections in h(−8/8), k(−14/14), l(−36/36), measured in the range 3.40° ≤ Θ ≤ 27.47°, completeness Θ_{max} = 86.6%, 3735 independent reflections, 3100 reflections with $F_o > 4\sigma(F_o)$, 284 parameters, 0 restraints, $R1_{obs}$ = 0.089, $wR2_{obs}$ = 0.159, $R1_{all}$ = 0.108, $wR2_{all}$ = 0.167, GOOF = 1.119, Flack parameter −6 (5) (racemic twin), largest difference peak and hole: 0.284/−0.315 e Å^{-3}.

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[30] Crystallographic data (excluding structure factors) for the structure(s) included in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-164150 (**4**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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