[3 + 2] Cycloadditions with Azirines under the Conditions of Photoinduced Electron Transfer: A New Method for the Synthesis of Imidazoles and Heterophanes[1]

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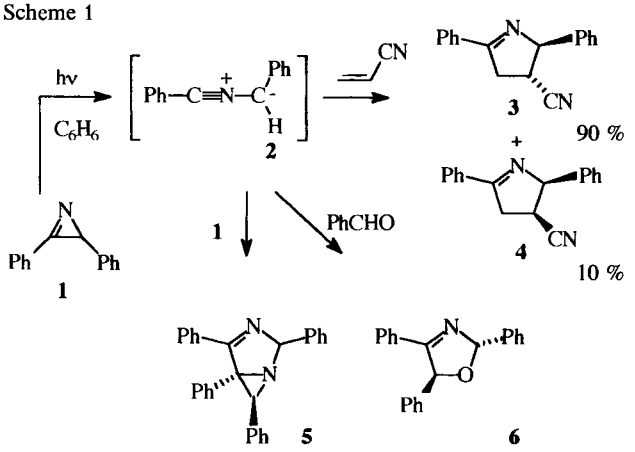
With the opening of azirine rings under the conditions of photoinduced electron transfer a new synthon for the synthesis of heterocycles is available. The formed 2-azaallenyl radical cation readily reacts with imines to form *N*-substituted imidazoles in reasonable yields. The synthesis of pyrrolophanes and imidazolophanes from bicyclic azirines is possible as well. With oligocyclic azirines complex heteroaromatic systems and even a porphyrin system can be built up.

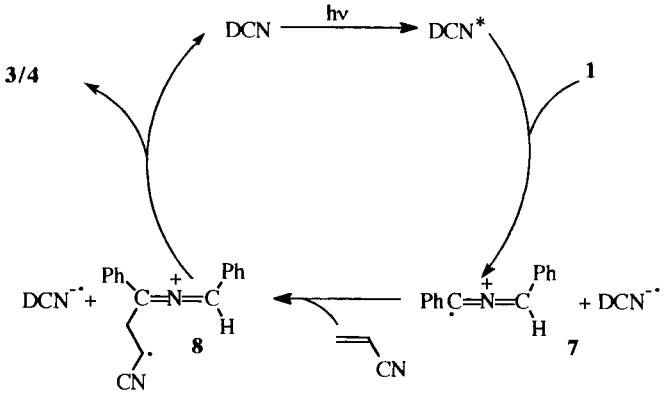
The photochemical 1,3-dipolar cycloaddition of azirines has proved to be a very useful approach to N-heterocycles[2]. The direct irradiation into the n-π^* bond of an aryl-substituted azirine **1** with light of 280 nm wavelength leads to the opening of the three-membered ring and to the formation of a nitrile ylide **2**[3].

Scheme 1



Compound **2** readily reacts with acceptor-substituted olefins such as acrylonitrile to yield 90% of the *trans*-pyrrolidine **3** besides **4** in 10% yield. The reaction of **2** with appropriate aldehydes affords oxazolines **6**[4]. If there is no sufficiently reactive dipolarophile available for the nitrile ylide it reacts with further azirine to form the diazabicyclus **5**[5]. The reactivity of the ylide intermediate is limited as well as the scope of azirines involved in this reaction. Alkyl-substituted azirines absorb at about 230 nm and irradiation has therefore to be performed with UV light which destroys the products formed[6]. In order to overcome these limitations we have studied the reaction of azirines under the conditions of photoinduced electron transfer (PET)[7]. Like other three-membered rings azirines can be opened when allowed to react with an electron acceptor in a polar solvent. The irradiation into the absorption band of the acceptor, in this case 1,4-naphthalenedicarbonitrile (DCN), with appropriate light of 350 nm wavelength leads to an electron transfer from the azirine to the excited sensitizer. The formed azirine radical cation opens spontaneously to the linear 2-azaallenyl radical cation **7**[8]. This species does not react in a concerted manner as the ylide **2** but adds quantitatively via **8** in a multistep process to a reagent like acrylonitrile without the formation of any diastereomeric excess.

Scheme 2



The intermediacy of the 2-azaallenyl radical cation has been proved by electron pulse radiolysis techniques[9]. Figure 1 shows the absorption spectrum of **1** obtained by using time-resolving methods. A large long-lived absorption peak is observed at 370 nm which can be attributed to the generated ylide by a comparison with literature data[9]. The absorbance at 485 nm is assigned to the radical cation on the basis of selective quenching experiments with imines. The lifetime of **7** is τ = 1.43 μs.

Due to the fact that the opening of the azirine ring is independent of the substituent in the 3-position of the azirine, the scope of possible starting materials used for the

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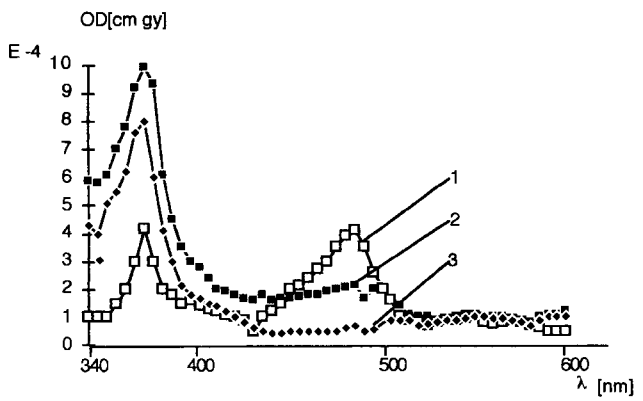
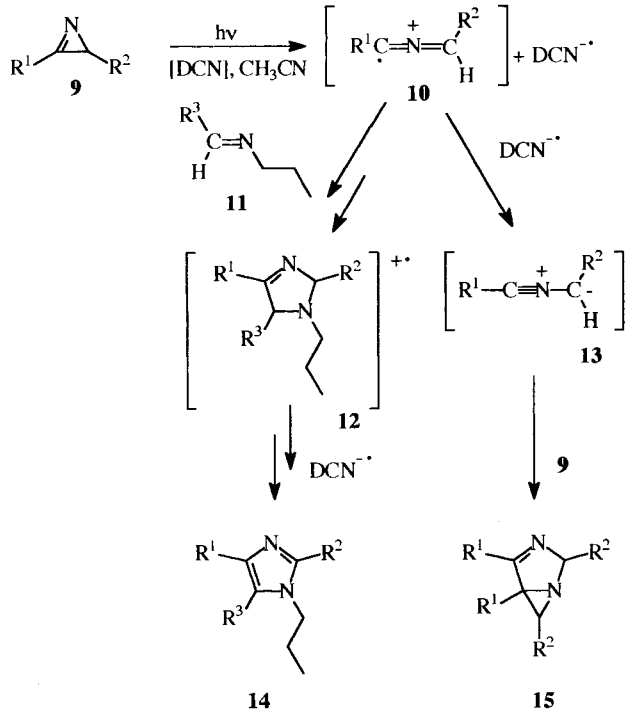


Figure 1. Absorption spectra obtained upon electron pulse radiolysis (van-de-Graaf generator, 3 MeV) of 4 mM 2,3-diphenylazirine **1** in *n*-butyl chloride, deoxygenated with argon. Points were recorded at times after the end of the pulse of 2.5–2.8 μs (1), 3.5–4.0 μs (2), and 9.0–10.0 μs (3)

Scheme 3



9a: R^1 = Ph, R^2 = Ph
9b: R^1 = Ph, R^2 = H
9c: R^1 = *n*-Bu, R^2 = H
9d: R^1 = Ph, R^2 = CH_2OH

11a: R^3 = Ph
11b: R^3 = *p*-MeOPh
11c: R^3 = *n*-Pr

[3 + 2] cycloaddition of azirine compounds under PET conditions is considerably enlarged. The range of application of dipolarophiles in the classic 1,3-dipolar cycloaddition of azirines was rather limited, as there were available only acceptor-substituted olefins and alkynes which were added to some carbonyl compounds. This limitation could be overcome in part. In so far as olefins and alkynes are considered, only marginal enhancements in reactivity could be observed, but addition reactions of imines to the radical cation have been achieved in many cases, a feature not common to the nitrile ylides[4b].

PET-Controlled Reactions of Azirines with Imines leading to the Formation of Imidazoles

The reaction of 2,3-diphenylazirine (**9a**) with the benzaldimine **11a** results in the formation of the *N*-alkyl-substituted imidazole **14a** in 87% yield besides the azirine dimer **15** in 12% yield. The mechanism for this process can be formulated as in Scheme 3.

The 2-azaallenyl radical cation **10** formed by electron transfer from the azirine to the excited sensitizer DCN reacts in a [3 + 2] cycloaddition with the imine in several steps, possibly via an intermediate species **12**, which is converted into the imidazole **14** by back electron transfer and oxidation. Back electron transfer may also be involved in the conversion of **10** to the nitrile ylide **13** which, in contrast to the radical cation, does not react with the imine and therefore only dimerization to **15** takes place. Compared to other methods for preparing *N*-alkyl-substituted imidazoles, the yield of the reaction is very competitive, e.g. compound **14a** is formed by standard carbonyl reactions only in yields of 20–40%[10].

As there is a current interest in the synthesis of imidazoles for pharmaceutic purposes[11] we have tried to check the scope of this new type of synthesis. In Table 1 several synthesized imidazoles with their yields are listed.

Table 1. Yields of imidazoles prepared by [3 + 2] cycloaddition of azirines and imines

	R^1	R^2	R^3	Yield
14a	Phenyl	Phenyl	Phenyl	87%
14b	Phenyl	Phenyl	*p*-Anisyl	82%
14c	Phenyl	Phenyl	*n*-Propyl	25%
14d	Phenyl	CH_2OH	*n*-Propyl	32%
14e	Phenyl	H	Phenyl	12%
14f	Phenyl	H	*p*-Anisyl	9%
14g	Phenyl	H	*n*-Propyl	35%
14h	*n*-Butyl	H	*n*-Propyl	40%

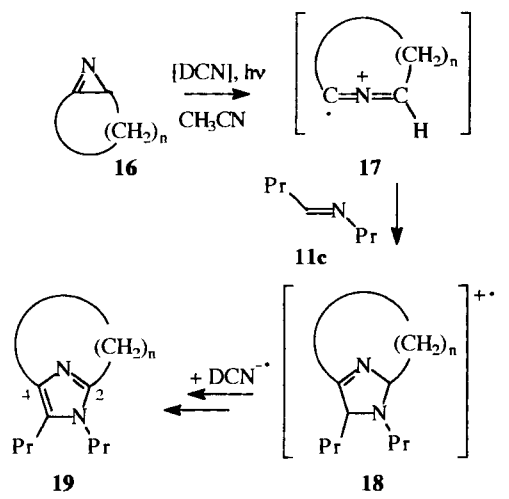
Table 1 shows that several substitution patterns are available in reasonable yields. The reaction of azirines bearing two or one phenyl group in the 3-position with imines furnishes imidazoles in more or less satisfactory yield. A satisfactory yield of the imidazoles is only obtained by the reaction of the alkyl-substituted azirine **9c** with the alkylimine **11c** while with the other imines only minute quantities are obtained. The same applies to the azirine **9d** where a hydroxymethyl group is introduced in the 2-position. Only **14d** has been isolated in considerable amounts. In all cases the side product **15** is formed preferentially, its yield being increased to nearly 100 per cent. Therefore, the ratio of the products formed in this reaction is governed by the competition between imine addition and back electron transfer. The reactions with other azirines have been unsuccessful: A carbonyl substituent in the 2-position of the azirine leads to

a quantitative intramolecular cycloaddition similar to the photoreaction upon direct irradiation[12]. An electron-rich aryl substituent in the 3-position (anisyl, tolyl) prevents the formation of imidazoles in sufficient yields as well. Neither the use of other electron-transfer sensitizers as DCA[13] nor the utilization of the "special salt effect" ($LiClO_4$)[14] has resulted in an optimization of the yields or allowed other substitution patterns to be realized.

Synthesis of [n]Imidazolophanes and [n]Pyrrolophanes

While syntheses of pyrrolophanes are widely applied[15] those of imidazolophanes are quite rate[16]. With the PET-promoted [3 + 2] cycloaddition of azirines it should be possible to synthesize bridged heterophane compounds by using bicyclic azirines **16** as starting material. The reaction with imines is shown in Scheme 4.

Scheme 4



Pr = *n*-Propyl

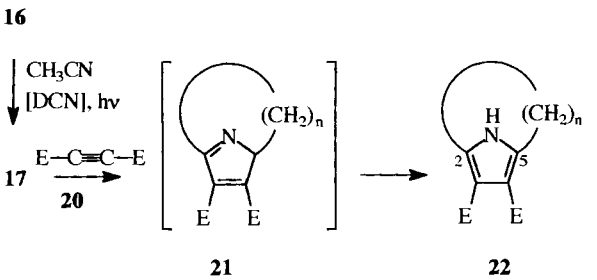
16a : n = 4 **16c/19c** : n = 6
16b/19b : n = 5 **16d/19d** : n = 10

The production of an imidazolophane **19** is only successful for $n = 6$, as the [6](2,4)imidazolophane **19c** can be obtained in 27% yield[17]. Azirines with $n = 5$ or $n = 10$ are converted into imidazolophanes in only minute amounts and in the case of $n = 4$ no reaction at all is observed. With other imines the yield cannot be increased[18].

The synthesis of pyrrolophanes involving addition of an electron-poor alkyne **20** to the cyclic 2-azaallenyl radical cation **17** is much more successful (Scheme 5).

The [6](2,5)pyrrolophane dimethyl ester **22c** has been isolated in 56%. A smaller ring size leads to a decrease of the yield [5](2,5)pyrrolophane **22b** has been obtained only in 9% yield, and [4](2,5)pyrrolophane has not been detected at all. With the azabicyclotridecene **16d** the [10](2,5)-pyrrolophane **22d** is formed in 20% yield[19]. Compound **22d** has already the ring size dimension of several supramolecular compounds.

Scheme 5



E = CO_2Me

22b: n = 5; **22c**: n = 6; **22d**: n = 10

Several years ago, Nozaki has measured the ^{1}H-NMR spectra of several pyrrolophanes and observed a reduced planarity of the pyrrole ring up to the length of the methylene bridges of $n = 8$[20]. The effect of nonplanarity is revealed even more pronounced in ^{13}C-NMR spectra as shown for our pyrrolophanes (Table 2).

Table 2. ^{13}C-NMR spectroscopic data (δ values) of the pyrrole carbon atoms

Compound	C-2	C-3
Pyrrole	118.0	107.7
22b	114.5	110.1
22c	116.5	111.5
22d	124.6	110.0
Dimethyl 2,5-Dimethyl-3,4-pyrrole-carboxylate[a]	127.3	109.7

[a] Increment calculation, see M. Hesse, H. Meier, B. Zeeh, *Spektroskopische Methoden in der organischen Chemie*, Thieme, Stuttgart, **1984**.

The chemical shift of C-3 is not changed significantly by the methylene bridge. On the other hand, the chemical shift of C-2 is important. Table 2 shows that compared with non-bridged pyrrole the C-2 resonance is shifted to higher field, depending on bridge length. This indicates that even in the large system with a ten-membered methylene bridge the pyrrole ring is not planar and has a reduced aromatic ring current leading to reduced chemical shift values.

The [3 + 2] cycloaddition leading to pyrrolophanes is successful only if bisacceptor-substituted alkynes like dimethyl butynedioate are used as dipolarophiles. Other alkynes such as 3-octyne, 1-hexyne and bis(trimethylsilyl)-acetylene do not undergo this cycloaddition. Even the reaction with an alkyne bearing only one electron-accepting group, e.g. methyl-2-butynoate, does not afford an isolable product.

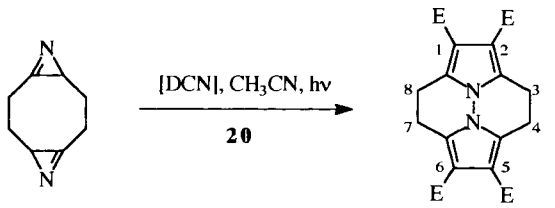
[3 + 2] Cycloadditions with Oligocyclic Azirines

The successful synthesis of [*n*]pyrrolophanes has prompted us to investigate the reactions of oligocyclic azirines in order to develop a synthesis of [2,2]pyrrolophanes[21] and higher heterophanes under PET conditions as well. The

synthesis of the tricyclic bisazirine **23** starting from 1,5-cyclooctadiene is fairly simple. Compound **23** is formed as a mixture of two different isomers with respect to the position of the azirine double bond. These isomers cannot be separated as they do not form two peaks even on capillary GC. For our synthetic purposes, this does not matter, as both isomers lead to the same product.

Nevertheless under PET conditions, the reaction of **23** with dimethyl butynedioate does not furnish a [2,2]pyrrolophane but only the compound **24** in 15% yield (Scheme 6). The ring system of **24** has first been prepared by Paudler and described as 3,4,7,8-tetrahydro-8b,8c-diazabicyclo-[*f,g*]acenapthene[22].

Scheme 6



23 **24** (15 %)

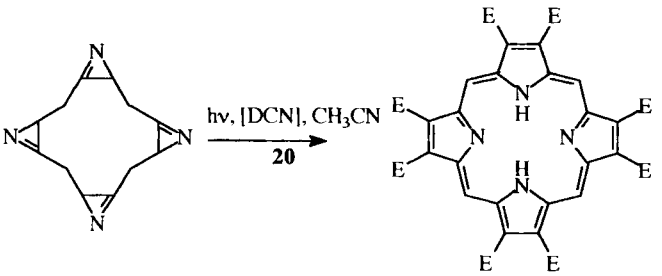
The formation of **24** and the complete lack of a trace of a [2,2]pyrrolophane or a monoannulated product suggests that **24** is formed by a transannular effect after the PET-sensitized opening of the first azirine ring.

The reactions of **23** with the other above-mentioned alkynes and with imines have proved unsuccessful, as no isolable products have been found.

To overcome the restrictions imposed by the mentioned transannular effect we have prepared a tetracyclic azirine starting from the readily available 1,5,9-cyclododecatriene. This compound is again formed as a mixture of two stereoisomers. To our disappointment its reaction with dimethyl butynedioate has furnished only traces of monoanellated products[18].

Porphyrins may be formally regarded as [1,1,1,1]pyrrolophanes. A tetrakisazirine derived from cyclododecane should be employed as useful alternative for the preparation of this important natural system[23]. Thus, the reaction of **25**, the preparation of which is described in ref.[24], with dimethyl butynedioate affords a porphyrin **26** with eight ester groups in 6% yield (Scheme 7).

Scheme 7



25 **26** (6 %)

Several side products with different states of anellation have also been detected by mass spectroscopic techniques. Although the yields of anellated products are very low the number of compounds which can be prepared by the new [3 + 2] cycloaddition of azirines under PET conditions is very large. A new synthesis of different heterocyclic systems has thus become available therefore and further applications are in progress.

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Experimental

Materials: Azirines **1**, **9a**, **9b**, and **9c** were prepared according to literature procedures[25]. Oligocyclic azirines **16b–d**, **23a** and **23b** were prepared in accordance with the procedure developed by Hassner for the synthesis **16c**[26]. Imines **11a**, **11b**, **11c** were prepared as described in ref.[27]. The synthesis of DCN is reported in ref.[28]. For data on **16a**, **19a** and **19d** see ref.[18]. — Solvents were purified according to standard procedures. All syntheses and irradiation were performed in an argon atmosphere.

Instrumental Analysis: NMR spectra: Bruker WM 300. — IR spectra: Perkin-Elmer 298; Shimadzu IR 408. — GC-MS: Varian GC 1400 and Varian MAT CH 7A. — UV spectra: Shimadzu UV-2100. — Elemental analyses: Perkin-Elmer 240 elemental analyzer. — Melting points are uncorrected.

8-Azabicyclo[5.1.0]oct-1(8)-ene (**16b**): Yield 3.7 g, (0.034 mol), 34%, starting from cycloheptene; yellow oil (0.1 mol). — IR (NaCl): $\tilde{\nu}$ = 2950 cm^{-1}, 2800, 1750 (C=N), 1420, 1040. — ^1H NMR (300 MHz, $CDCl_3$): δ = 1.32–1.89 (m, 6H, 3-H–5-H), 2.12 (m, 2H, 6-H), 2.46 (m, 2H, 2-H), 2.75 (m, 1H, 7-H). — ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 20.38, 21.23, 21.38, 22.74, 24.45 (t, C-2–C6), 28.78 (d, C-7), 150.45 (s, C-1). — MS (70 eV), *m/z* (%): 109 (1) [M^+], 108 (8), 95 (72), 80 (44), 67 (60), 54 (64), 41 (100).

$C_7H_{11}N$ (109.2) Calcd. C 76.94 H 10.17 N 12.89
Found C 77.48 H 10.25 N 12.40

13-Azabicyclo[10.1.0]tridec-1(13)-ene (**16d**): Yield 11.6 g, (0.065 mol), 65%, starting from cyclododecene (0.1 mol); yellow oil containing traces of the starting material. — IR (NaCl): $\tilde{\nu}$ = 2920 cm^{-1}, 2850, 1745, 1465, 1440. — UV (acetonitrile): λ_{max} (lg ε) = 192.7 nm (3.602), 280 (2.894). — ^1H NMR (300 MHz, $CDCl_3$): δ = 1.2–1.8 (m, 16H, 3-H–10-H), 1.80 (m, 2H, 11-H), 2.05 (m, 2H, 2-H), 2.79 (m, 1H, 12-H). — ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 21.94, 22.13, 22.65, 23.13, 24.27, 24.66, 25.26, 26.62, 27.88, 28.60 (t, C-2–C-11), 31.01 (d, C-12), 151.90 (s, C-1). — MS (70 eV), *m/z* (%): 179 (22) [M^+], 178 (100), 151 (76), 124 (20), 100 (12), 89 (24), 75 (21), 62 (20), 50 (21).

5,10-Diazatricyclo[7.1.0$^{[4,6]}$.0]deca-(1)10-(4)5-diene (**23a**) *and 5,10-Diazatricyclo[7.1.0$^{[4,6]}$.0]deca-(1)10-(6)5-diene* (**23b**): Yield 1.0 g, 15%, starting from 1,5-cyclooctadiene; yellow oil, mixture of isomers (1:1), GC separation failed. — ^1H NMR (300 MHz, $CDCl_3$): δ = 1.86, 2.05 (m, 8H, CH_2CHN), 2.48, 2.52 (m, 8H, $CH_2C=N$),

3.92, 4.01 (m, 4H, CHN). – ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 20.45, 21.72, 23.55, 25.10 (t, CH_2), 28.76, 29.34 (d, CH), 151.45, 152.82 (s, C=N). – MS (70 eV), *m/z* (%): 134 (6) [M^+], 120 (18), 104 (6), 56 (100).

$C_8H_{10}N_2$ (134.2) Calcd. C 71.60 H 7.52 N 20.87
Found C 72.01 H 7.78 N 19.90

General Procedure for the Synthesis of Imidazoles and Heterophanes: **Note:** Data are given for a single radiation tube. For preparative purposes it is obviously convenient to use more tubes. – A solution of 0.3 mmol of azirine and 1.0 mmol of imine in 10 ml of acetonitrile was filled into a Pyrex tube. Then 0.1 mmol of 1,4-naphthalenedicarbonitrile (18 mg) was added, the tube deoxygenated by bubbling argon through the solution and subsequently sealed.

Irradiation was carried out by means of a Rayonet Photochemical Reactor and 350 nm radiation tubes. Irradiation was maintained fort 6–10 h, for the preparation of heterophanes the period of irradiation was prolonged to 16 h. In the case of **23**, 0.15 mmol of azirine was used. – The solvent was evaporated and the residue separated by flash chromatography on aluminium oxide (Merck Neutral Akt. I) using diethyl ether as eluent.

2,4,5-Triphenyl-1-propylimidazole[28] (**14a**): Prepared from **9a** (58 mg) and **11a** (147 mg), yield 88 mg (87%), colourless crystals, m.p. 92°C. – IR (KBr): $\tilde{\nu}$ = 3000 cm^{-1}, 1590, 1550, 1480, 1435, 1385, 740, 680. – UV (acetonitrile): λ_{max} (lg ε) = 232 nm (4.519), 255 (3.146), 280 (3.230). – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.05 (tt, ^3J = 7.3, ^4J = 2.1 Hz, 3H, CH_3), 1.45 (tq, ^3J = 7.3, 7.7 Hz, 2H, CH_2), 3.95 (tq, ^3J = 7.7, ^4J = 2.1 Hz, 2H, NCH_2), 7.0–7.9 (m, 15H, arom. H). – ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 10.62 (q, CH_3), 23.64 (t, CH_2CH_3), 46.15 (t, NCH_2), 134.42 (s, C-5), 137.50 (s, C-4), 147.49 (s, C-2), 126.04–137.01 (s/d, arom. C). – MS (70 eV), *m/z* (%): 338 (100) [M^+], 295 (28), 193 (8), 165 (34), 89 (38).

$C_{24}H_{22}N_2$ (338.5) Calcd. C 85.17 H 6.55 N 8.28
Found C 84.88 H 6.35 N 8.50

5-(p-Methoxyphenyl)-2,4-diphenyl-1-propylimidazole (**14b**): Prepared from **9a** (58 mg) and **11b** (167 mg), yield 91 mg (82%), colourless crystals, m.p. 125–126°C. – IR (KBr): $\tilde{\nu}$ = 3100 cm^{-1}, 3000, 2920, 1590, 1500, 1440, 1240, 1170, 1005, 860, 745, 680. – UV (acetonitrile): λ_{max} (lg ε) = 218 nm (4.929), 258 (4.803), 300 (4.081). – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.10 (tt, ^3J = 7.3, ^4J = 1.4 Hz, 3H, CH_3), 1.86 (tq, ^3J = 7.3, 9.8 Hz, 2H, CH_2), 3.70 (tq, ^3J = 9.8, ^4J = 1.4 Hz, 2H, NCH_2), 4.18 (s, 3H, OCH_3), 7.0–7.9 (m, 14H, arom. H). – ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 11.73 (q, CH_3), 24.02 (t, CH_2CH_3), 44.15 (t, NCH_2), 63.35 (q, OCH_3), 120.78–135.38 (s/d, arom. C), 138.45 (s, C-4), 140.83 (s, C-5), 145.25 (s, C-2), 162.15 (s, C-OCH_3). – MS (70 eV), *m/z* (%): 368 (100) [M^+], 367 (20), 295 (19), 206 (10), 193 (15), 165 (22), 149 (14), 117 (12), 104 (20), 89 (37), 85 (51), 77 (23), 71 (63), 57 (100).

$C_{25}H_{24}N_2O$ (368.5) Calcd. C 81.49 H 6.57 N 7.60
Found C 81.08 H 6.61 N 7.29

2,4-Diphenyl-1,5-dipropylimidazole (**14c**): Prepared from **9a** (58 mg) and **11c** (113 mg), yield 23 mg (25%), yellow oil. – IR (NaCl): $\tilde{\nu}$ = 3030 cm^{-1}, 2920, 1640, 1590, 1575, 1485, 1440, 1385, 750, 675. – UV (acetonitrile): λ_{max} (lg ε) = 212 nm (3.993), 230 (3.760). – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.95 (m, 6H, 2 CH_3), 1.50 (m, *4H, 2 CH_2), 2.44* (t, ^3J = 7.0 Hz, 2H, 5-CH_2), 3.38 (t, ^3J = 6.8 Hz, 2H, NCH_2), 7.0–7.9 (m, 10H, arom. H). – ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 11.39, 15.23 (q, 2 CH_3), 22.15, 22.89 (t, 2 CH_2CH_3), 29.98 (t, 5-C), 46.15 (t, NCH_2), 123.56–133.31 (s/d, arom. C), 127.89 (s, C-5), 131.82 (s, C-4), 149.89 (s, C-2). – MS (70 eV), *m/z* (%): 304 (97) [M^+], 275 (56), 261 (32), 247 (17), 235 (20), 234 (100), 233 (6), 194 (5), 193 (8), 165 (19), 104 (26), 103 (37), 77 (9), 41 (11).

$C_{21}H_{24}N_2$ (304.4) Calcd. C 82.85 H 7.95 N 9.20
Found C 82.90 H 8.05 N 9.51

4-Phenyl-1,5-dipropyl-2-imidazolemethanol (**14d**): Prepared from **9d** (44 mg) and **11c** (113 mg), yield 25 mg (32%), yellow oil. – IR (NaCl): $\tilde{\nu}$ = 3500 cm^{-1}, 3100, 3000, 2950, 1590, 1560, 1400, 1380, 785, 680. – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.9 (m, 6H, 2 CH_3), 1.60 (m, 4H, 2 CH_2), 2.80 (t, ^3J = 3.1 Hz, 2H, 5-CH_2), 3.35 (t, ^3J = 6.5 Hz, 2H, NCH_2), 4.28 (s, 2H, CH_2OH) 7.5–7.8 (m, 5H, arom. H). – ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 11.69, 13.95 (q, 2 CH_3), 22.05, 23.91 (t, 2 CH_2), 30.88 (t, C-5-*C*), 44.72 (t, N-CH_2), 66.61 (t, CH_2OH), 125.86, 126.42, 127.10 (s/d, arom. C), 127.18 (s, C-5), 128.85 (d, arom. C), 130.51 (s, C-4), 149.75 (s, C-2). – MS (70 eV), *m/z* (%): 258 (4) [M^+], 240 (12), 215 (14), 172 (45), 148 (7), 147 (56), 78 (7), 77 (100), 76 (32), 51 (35).

$C_{16}H_{22}N_2O$ (258.4) Calcd. C 74.96 H 8.65 N 10.93
Found C 75.40 H 7.95 N 10.89

4,5-Diphenyl-1-propylimidazole (**14e**): Prepared from **9b** (35 mg) and **11a** (47 mg), yield 9 mg (12%), yellow oil. – IR (NaCl): $\tilde{\nu}$ = 2950 cm^{-1}, 1600, 1550, 1490, 1440, 750, 690. – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.01 (tt, ^3J = 6.9, ^4J = 2.0 Hz, 3H, CH_3), 1.50 (tq, ^3J = 6.9, 7.5 Hz, 2H, CH_2), 3.85 (tq, ^3J = 7.5, ^4J = 2.0 Hz, 2H, NCH_2), 7.0–7.7 (m, 10H, arom. H), 7.85 (s, 1H, 2-H). – ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 11.90 (q, CH_3), 24.09 (t, CH_2CH_3), 40.98 (t, NCH_2), 124.08–130.51 (s/d, arom. C), 133.52 (s, C-5), 135.50 (s, C-4), 140.08 (d, C-2). – MS (70 eV), *m/z* (%): 262 (0.3) [M^+], 219 (10), 193 (100), 165 (28), 128 (32), 105 (14), 94 (15), 77 (30), 76 (79, 51 (15).

$C_{16}H_{18}N_2$ (262.4) Calcd. C 82.41 H 6.92 N 10.67
Found C 83.08 H 6.45 N 10.03

5-(p-Methoxyphenyl)-4-phenyl-1-propylimidazole (**14f**): Prepared from **9b** (35 mg) and **11b** (167 mg), yield 8 mg (9%), yellow oil. – IR (NaCl): $\tilde{\nu}$ = 3100 cm^{-1}, 3000, 2910, 1595, 1500, 1000, 860, 755, 680. – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.08 (tt, ^3J = 7.1, ^4J = 1.5 Hz, 3H, CH_3), 1.92 (tq, ^3J = 7.1, 9.5 Hz, 2H, CH_2), 3.68 (tq, ^3J = 9.5, ^4J = 1.5 Hz, 2H, NCH_2), 4.20 (s, 3H, OCH_3), 7.1–7.9 (m, 10H, 2-H and arom. H). – ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 12.48 (q, CH_3), 25.11 (t, CH_2CH_3), 44.30 (t, NCH_2), 63.28 (q, OCH_3), 110.85–133.20 (s/d, arom. C), 136.49 (s, C-4), 138.27 (d, C-2), 138.92 (s, C-5), 160.02 (s, C-OCH_3). – MS (70 eV), *m/z* (%): 292 (3) [M^+], 288 (4), 242 (10), 228 (25), 162 (100), 71 (63).

$C_{19}H_{20}N_2O$ (292.4) Calcd. C 78.04 H 6.91 N 9.58
Found C 77.11 H 6.38 N 9.32

4-Phenyl-1,5-dipropylimidazole (**14g**): Prepared from **9b** (35 mg) and **11c** (113 mg), yield 24 mg (35%), yellow oil. – IR (NaCl): $\tilde{\nu}$ = 3010 cm^{-1}, 2950, 1650, 1600, 1450, 1060, 760, 695. – UV (acetonitrile): λ_{max} (lg ε) = 210 nm (3.851), 225 (3.690). – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.05 (m, 6H, 2 CH_3), 1.50 (m, 4H, 2 CH_2), 2.40 (t, ^3J = 5.4 Hz, 2H, 5-CH_2), 3.45 (t, ^3J = 6.2 Hz, 2H, NCH_2), 7.5–7.7 (m, 5H, arom. H), 7.78 (s, 1H, 2-H). – ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 11.53, 13.66 (q, 2 CH_3), 22.74, 23.94 (q, 2 CH_2), 39.91 (t, 5-*C*), 41.90 (t, NCH_2), 124.22, 125.61, 126.78 (s/d, arom. C), 125.77 (s, C-5), 130.72 (d, arom. C), 132.85 (s, C-4), 140.67 (d, C-2). – MS (70 eV), *m/z* (%): 228 (61) [M^+], 195 (3), 176 (4), 146 (8), 118 (20), 94 (13), 93 (100), 91 (16), 89 (8), 77 (30), 76 (10), 51 (13).

$C_{15}H_{20}N_2$ (228.3) Calcd. C 78.91 H 8.83 N 12.26
Found C 78.22 H 9.55 N 11.71

4-Butyl-1,5-dipropylimidazole (**14h**): Prepared from **9c** (29 mg) and **11c** (113 mg), yield 25 mg (40%), yellow oil. – IR (NaCl): $\tilde{\nu}$ =

3010 cm^{-1}, 1590, 1550, 1410, 1380. – ^1H NMR (300 MHz, $CDCl_3$): δ = 1.0 (m, 9H, 3 CH_3), 1.50 (m, 8H, 4 CH_2), 2.50 (m, 4H, 4-CH_2, 5-CH_2), 3.45 (t, ^3J = 7.0 Hz, 2H, NCH_2), 7.65 (s, 1H, 2-H). – ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 11.35, 13.69, 13.70 (q, 3 CH_3), 19.28, 21.05, 22.55, 24.19 (t, 4 CH_2), 29.71, 30.19 (t, 4-C, 5-C), 42.08 (t, NCH_2), 128.72 (s, C-5), 130.97 (s, C-4), 141.73 (d, C-2). – MS (70 eV), *m/z* (%): 208 (1) [M^+], 207 (10), 164 (14), 150 (42), 136 (35), 108 (60), 94 (56), 68 (100).

$C_{13}H_{24}N_2$ (208.3) Calcd. C 74.94 H 11.61 N 13.45
Found C 75.01 H 11.10 N 13.92

1,5-Dipropyl[6](2,4)imidazolophane (**19c**): Prepared from **16c** (37 mg) and **11c** (113 mg), yield 17 mg (27%), yellow oil. – IR (cap.): $\tilde{\nu}$ = 2920 cm^{-1}, 1650, 1510, 1450, 1280. – UV (acetonitrile): λ_{max} (lg ε) = 284.2 nm (3.213), 221.0 (4.655), 196.5 (4.762). – ^1H NMR (300 MHz, $CDCl_3$): δ = 0.9 (m, 6H, 2 CH_3), 1.5 (m, 12H, 6 CH_2), 1.9 (m, 6H, 3 CH_2), 2.9 (t, ^3J = 6.6 Hz, 2H, NCH_2). – ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 11.78, 13.79 (q, 2 C, 2 CH_3), 21.63, 22.42, 23.92, 24.34, 25.38, 25.66 (t, 6 CH_2), 31.17 (t, 5-CH_2), 33.51 (t, 4-CH_2), 35.07 (t, 2-CH_2), 126.45, 128.50 (s, C-4, C-5), 145.16 (s, C-2). – MS (70 eV), *m/z* (%): 234 (18) [M^+], 233 (16), 219 (46), 205 (70), 191 (100), 178 (40), 164 (59), 152 (32), 138 (22), 108 (19), 95 (10), 80 (23), 55 (20), 43 (40).

$C_{15}H_{26}N_2$ (234.4) Calcd. C 76.85 H 11.20 N 11.95
Found C 77.02 H 10.88 N 11.91

Dimethyl [5](2,5)Pyrrolophane-3,4-dicarboxylate (**22b**): Prepared from **16b** (37 mg) and **20** (142 mg), yield 7 mg (9%), brown oil. – IR (cap.): $\tilde{\nu}$ = 3010 cm^{-1}, 1850, 1745. – ^1H NMR (300 MHz, $CDCl_3$): δ = 1.3–1.5 (m, 6H, 3 CH_2), 2.85 (m, 4H, CH_2-C-2), 3.50 (s, 6H, OCH_3). – ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 18.69 (t, CH_2), 25.27 (t, CH_2), 34.71 (t, CH_2), 51.64 (q, 2 OCH_3), 110.12 (s, C-3), 114.48 (s, C-2), 170.21 (s, C=O). – MS (70 eV): *m/z* (%) = 251 (0.1) [M^+], 220 (18), 189 (49), 175 (18), 161 (12), 147 (28), 146 (12), 122 (19), 108 (100), 59 (67).

Dimethyl [6](2,5)Pyrrolophane-3,4-dicarboxylate (**22c**): Prepared from **16c** (37 mg) and **20** (142 mg), yield 44 mg (56%), brown oil. – IR (cap.): $\tilde{\nu}$ = 3440 cm^{-1}, 3100, 3000, 1845, 1740, 1535. – UV (acetonitrile): λ_{max} (lg ε) = 260 nm (3.305), 196 (4.812). – ^1H NMR (300 MHz, $CDCl_3$): δ = 1.3–1.5 (m, 8H, 4 CH_2), 2.8 (m, 4H, CH_2-C-2), 3.50 (s, 6H, OCH_3). – ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 19.48, 24.38, 32.65 (t, 6 CH_2), 52.05 (q, 2 OCH_3), 111.52 (s, C-3), 116.51 (s, C-2), 167.25 (s, C=O). – MS (70 eV), *m/z* (%): 265 (6) [M^+], 234 (39), 216 (40), 206 (47), 174 (18), 166 (24), 159 (20), 148 (16), 147 (18), 122 (8), 94 (10), 91 (21), 79 (23), 59 (100).

$C_{14}H_{19}NO_4$ (265.3) Calcd. C 63.37 H 7.23 N 5.28
Found C 63.62 H 6.88 N 4.91

Dimethyl [10](2,5)Pyrrolophane-3,4-dicarboxylate (**22d**): Prepared from **16d** and **20**, yield 19 mg (20%), brown oil. – IR (cap.): $\tilde{\nu}$ = 3250 cm^{-1}, 2900, 2830, 1715, 1680, 1525, 1320, 1200. – ^1H NMR (300 MHz, $CDCl_3$): δ = 1.0–1.7 (m, 12H, 6 CH_2), 2.77 (m, 4H, CH_2-C-2), 3.79 (s, 6H, OCH_3), 8.80 (s, 1H, NH). – ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 26.23, 26.75, 27.34, 27.76, 29.19 (t, 10 CH_2), 51.16 (q, 2 OCH_3), 109.98 (s, C-3), 124.57 (s, C-2), 165.79 (s, C=O). – MS (70 eV), *m/z* (%): 321 (22) [M^+], 289 (100), 257 (22), 201 (24), 160 (8), 133 (8), 105 (9), 93 (22), 79 (8), 65 (9), 41 (13).

$C_{18}H_{27}NO_4$ (321.4) Calcd. C 67.25 H 8.48 N 4.36
Found C 69.45 H 8.98 N 3.75

Tetramethyl 3,4,7,8-Tetrahydro-8b,8c-diazacyclopent[f,g]acenaphthene-1,2,5,6-tetracarboxylate (**24**): Prepared from **23** (20 mg) and **20** (142 mg), yield 9 mg (15%), brown oil. – IR (cap.): $\tilde{\nu}$ = 3050 cm^{-1}, 3020, 1810, 1745, 1480. – UV (acetonitrile): λ_{max} (lg ε) = 281 nm (4.389), 209 (4.901). – ^1H NMR (300 MHz, $CDCl_3$): δ = 3.52 (s, 12H, OCH_3), 4.70 (s, 8H, CH_2). – ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 35.89 (t, CH_2), 53.06 (q, OCH_3), 112.15 (s, C-1), 118.42 (s, C-8a), 169.24 (s, C=O). – MS (70 eV), *m/z* (%): 416 (0.1) [M^+], 355 (0.4), 293 (0.2), 264 (1.4), 208 (2), 206 (78), 174 (16), 148 (10), 146 (12), 109 (34), 81 (21), 79 (26), 67 (100), 55 (42).

$C_{20}H_{20}N_2O_8$ (416.4) Calcd. C 57.53 H 4.82 N 6.71
Found C 57.61 H 4.98 N 6.40

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