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On Amination and Diazotization of Azulene and Its Derivatives

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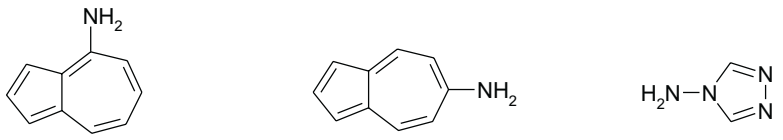
A practical procedure for synthesis of 6-aminoazulene (**3**) *via* Vicarious Nucleophilic Substitution of Hydrogen (VNS) amination of azulene with 4-amino-1,2,4-triazole is reported. Amination with use of *N,N,N*-trimethylhydrazinium iodide (TMHI) of more electrophilic azulene derivatives, substituted at position 1- with CN or COPh group, afforded a mixture of 4-, 6-, and 8-aminoazulenes. Attempts to convert 6-aminoazulene (**3**) into diazonium salt failed, only formation of small quantities of the "auto-coupling" product, 1-(azulen-6-ylazo)-azulen-6-yl-amine, was observed.

Key words: azulene derivatives, amination, Vicarious Nucleophilic Substitution, diazotization

Amination of azulene (**1**) with potassium amide – the Chichibabin type reaction – gives 4-aminoazulene (**2**) in low yield (10%) [1]. Recently we have reported that 6-aminoazulene (**3**) can be synthesized *via* Vicarious Nucleophilic Substitution of Hydrogen (VNS) [2] in azulene with 4-amino-1,2,4-triazole (**4**) [3]. However, the product, due to its instability, was isolated and characterized as acyl derivative in moderate yield (38%). 6-Aminoazulene is an attractive intermediate, because it can be converted, *via* diazotization, into a variety of 6-substituted azulenes. For this reason we have attempted to optimize the amination process and to elaborate a practical method of synthesis of **3** in quantities sufficient for further investigations including diazotization studies.



2 **3** **4**

Figure 1

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RESULTS AND DISCUSSION

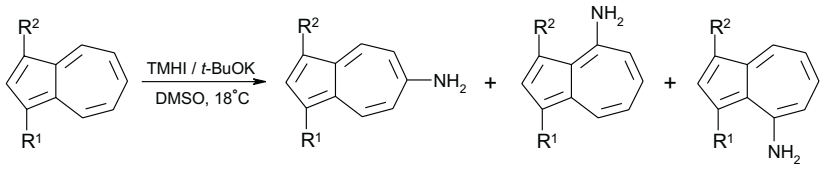
In order to optimize synthesis of 6-aminoazulene, a variety of aminating agents were tested under various conditions: temperature, solvent, the order of addition of reagents, reaction time, the character and concentration of the base and ratio of the substrates. As it was found earlier [3a] sulphenamides, which are efficient agents for amination of nitroarenes [4], do not enter VNS amination of azulene. The use of methoxyamine (CH_3ONH_2) in the presence of CuCl(I) catalyst, reported by Seko to be also an efficient agent for amination of nitroarenes [5], gave a difficult to separate mixture of 4- and 6-aminoazulenes in a moderate yield (20% and 15%, respectively). Recently introduced *N,N,N*-trimethylhydrazinium iodide (TMHI) [6] was even less efficient, giving in the best experiment (1.5-fold excess of TMHI, 5-fold excess of *t*-BuOK, liquid ammonia, 5 h) only 20% of the desired product **3**.

The amination of azulene proceeds the most effectively with 4-amino-1,2,4-triazole [3]. This triazole was reported earlier for preparation, *via* VNS, many amino-nitroarenes and nitro-heteroarenes [7,8]. The reaction carried-out in DMSO at 18°C during 2 h with 3-fold excess of **4** and 6-fold excess of *t*-BuOK over azulene afforded the product **3**, which could be isolated without protection of NH_2 group, in 62% yield (79% when recovered azulene was taken into account). The reaction can be carried-out with *ca* 0.5–1.0 g of **1**. However, for the larger scale the reaction needs a longer time, up to 6 h, for completion. In the above experiments the formation of traces of 4-aminoazulene (**2**) was observed. According to ^{1}H NMR analysis of the crude post-reaction mixtures, the ratio of **2**/**3** was below 1:40.

We have found that 6-aminoazulene is unstable under acidic conditions, thus, when the reaction mixtures were quenched with distilled water instead of aqueous solution of mineral acid or solid NH_4Cl [2], the product was sufficiently stable to be isolated as such and even purified by flash chromatography. Pure crystalline 6-aminoazulene can be stored in refrigerator for months, being valuable starting material for further transformations. On the other hand, the reaction of more electrophilic azulenes substituted in position 1- with CN (**5a**) or COPh (**5b**) group with TMHI proceeds satisfactorily giving beside 6-amino derivatives **6a** and **6b** also 4- and 8-aminoazulenes, **7a,b** and **8a,b**, respectively. Again these minor amination products were isolated in pure form as such (in some cases in the yields up to 14%) and fully characterized. Reported earlier amination of azulenes **5a,5b** with 4-amino-1,2,4-triazole [3] gave only 6-amino-derivatives. Herein, the formation of 6-substituted product exclusively was observed for azulene-1,3-dicarboxylic acid diethyl ester **5c** (62%) (Scheme 1).

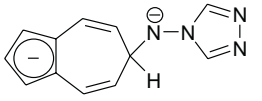
We have also found that azulene can enter oxidative nucleophilic substitution of hydrogen, when treated with 4-amino-1,2,4-triazole in the presence of excess of *t*-BuOK and oxygen in liquid ammonia giving azulen-6-yl-[1,2,4]triazol-4-yl-amine (**10**) in moderate yield of 27%. Since the presence of a great excess of *t*-BuOK was necessary for this reaction, one can assume that actually the deprotonated σ^H-adduct (**9**) is oxidized with oxygen as it was observed in some examples of ONSH in

Scheme 1

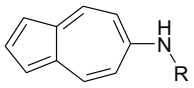


5 (recovery)		**6**	**7**	**8**
(12%)	**a:** R^1 = CN, R^2 = H	44%	14%	7%
-	**b:** R^1 = COPh, R^2 = H	36%	6%	5%
(25%)	**c:** R^1,R^2 = CO_2Et	62%	[0%]	

nitroarenes [9]. Indeed, the oxidative substitution does not proceed, when stoichiometric amount of *t*-BuOK was used. In another experiment, in which strong MnO_4^- oxidant was used instead of O_2, the reaction did not occur, as well – probably due to mutual unfavorable electrostatic interactions of the negatively charged species (**9** and $KMnO_4^-$). In both of these cases most of the starting azulene was recovered



9



10: R = 4-(1,2,4-triazolo)-
11: R = $COCH_3$
12: R = CO_2Me

Figure 2

In the next step we have studied diazotization process of 6-aminoazulene. Till now, not much is known about generation of azulene diazonium salts and their further reactions. Reported examples are limited to conversion of 2-amino-azulene-1,3-dicarboxylic acid dimethyl ester [10–13] and 1-aminoazulene [14], *via* diazotization of the NH_2 group, into the diazonium salts subsequently reduced [13] or coupled with β-naphthol [14,15]. Typical replacement of diazonium group (N_2^+) by the Sandmayer reaction has not been observed [12]. It is also known that aryldiazonium salts react with azulene giving 1-arylazaazulenes [14,16]. Conversion of amino group located in 7-membered ring into diazonium salt has never been reported.

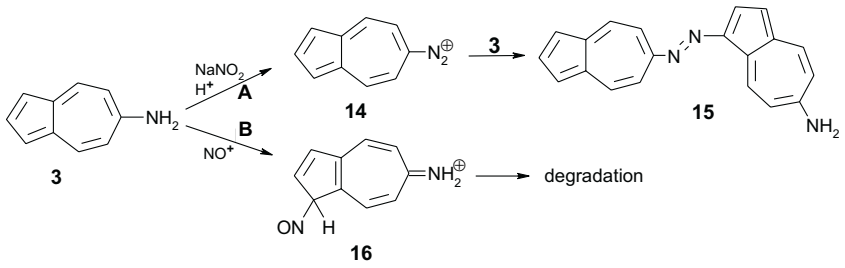
Numerous attempts to convert **3** into the corresponding diazonium salt using various diazotization methods such as: $NaNO_2$ in HCl, $NaNO_2$ in H_2SO_4, or using nitrosyl sulphate ($ONOHSO_3$), were unsuccessful. The diazotization *via N*-substituted aminoazulene (acetylo-, **11**; uretane, **12**) in HCl or in $CH_3CO_2H/C_2H_5CO_2H$ (–20°C) gave negative results, as well. On the other hand, when 6-aminoazulene was treated with *para*-bromophenyl diazonium chloride, the coupling proceeded giving 6-amino-1-(4-bromofenylazo)-azulene (**13**) in good yield (68%). This probably explain the failure of the generation of the desired salt **14**, which once formed could immediately

react with another molecule of **3**, present in the reaction mixture, to begin a cascade of transformations in which the starting material is consumed.

All attempts to capture the expected diazonium salt, *e.g.* with β-naphthol or deaminate it with solvents [17,18], resulted in degradation of **3** and no formation of a defined product was observed. However, treatment of a solution of **3** in a mixture of acetic and propionic acids at –20°C with subequimolar quantity of $NaNO_2$ gave small amounts of the "auto-coupling" product, 1-(azulen-6-ylazo)-azulen-6-yl-amine (**15**) (Scheme 2, pathway A).

The above results could also suggest that the competing reaction of NO^+ with 5-membered ring consumes effectively the substrate. This is in accordance with deamination of 2,6-diamino-azulene-1,3-dicarboxylic acid diethyl ester [11], where two electronwithdrawing CO_2Et substituents "protect" the 5-membered ring towards NO^+ attack, hence the NH_2 group in position 2- could be diazotized and reductively removed.

Scheme 2



In this work the practical synthesis of 6-aminoazulene and its isolation in a free base form was elaborated. It was also shown that amination of some substituted azulenes (**5a,5b**) with TMHI proceeds in positions 6-, 4-, and 8-. For the first time the minor isomers, substituted in positions 4- and 8-, were identified. Attempts to form azulene diazonium salts from 6-amino derivatives gave negative results. However, we observed the formation of 1-(azulen-6-ylazo)-azulen-6-yl-amine (**15**). This is the first example of the reaction of very active azulene diazonium salt, generated from the amino group in 7-membered ring.

EXPERIMENTAL

^{1}H NMR spectra were recorded with a Varian GEMINI-200 spectrometer operating at 200 MHz. Coupling constants *J* are expressed in hertz [Hz]. The assignment of the chemical shifts accompanied by asterisks*) may be exchanged. Mass spectra were measured with an AMD 604 (AMD Intectra GmbH, Germany) spectrometer (electron impact method); *m/z* values are given as a % of relative intensity. Melting points are uncorrected. TLC analysis was performed on aluminum foil plates precoated with silica gel 60F 254 Merck. Silica gel 200–300 mesh (Merck AG) was used for column chromatography. All amination experiments were carried-out under argon.

6-Aminoazulene (3): To a stirred solution of azulene (**1**) (640 mg, 5 mmol) and 4-amino-1,2,4-triazole (1260 mg, 15 mmol) in DMSO (15 mL) under argon at 18°C a solution of *t*-BuOK (3.36 g, 30 mmol) in DMSO (5 mL) was added. The reaction was continued for 6 h, then the mixture was poured into distilled water (100 mL) and extracted with CH_2Cl_2 (5 × 20 mL). The combined organic layers were washed with water (2 × 30 mL) and dried over anhydrous $MgSO_4$. The solvent was evaporated and the crude product was purifed by flash chromatography eluted with n-hexane to give 140 mg of azulene (22%), then with $CHCl_3$ to give 441 mg of 6-aminoazulene (62%) as red crystals; m.p. 109–110°C ($CHCl_3$), lit. [11] m.p. 106–107°C (EtOH). ^{1}H NMR ($CDCl_3$): 8.03 (d, *J* = 10.7, 2 H, H-4 & H-8), 7.39 (t, *J* = 3.7, 1 H, H-2), 7.15 (d, *J* = 3.7, 2 H, H-1 & H-3), 6.41 (d, *J* = 10.7, 2 H, H-5 & H-7), 4.55 (broad s, 2 H, NH_2). MS, *m/z* (% rel. int.): 144 (11), 143 (100, $M^{+\bullet}$), 142 (6), 126 (4), 117 (5), 116 (24), 115 (37). Elemental anal. Calcd. for $C_{10}H_9N$ (143.19): C 83.88; H 6.34; N 9.78. Found: C 83.79; H 6.26; N 9.61.

Amination of azulene with CH_3ONH_2. To a stirred solution of azulene (64 mg, 0.5 mmol), CH_3ONH_2 (42 mg, 0.5 mmol) and CuCl (5 mg, 0.05 mmol) in DMF (3 mL) at 18°C *t*-BuOK (168 mg, 1.5 mmol) was added in one portion and the reaction was continued for 2 h under argon. The mixture was quenched with saturated aqueous NH_4Cl (15 mL) and extracted with CH_2Cl_2 (3 × 10 mL). The combined organic layers were washed with water (20 mL) and dried over anhydrous $MgSO_4$. The solvent was evaporated and the crude mixture was purifed by flash chromatography eluted with n-hexane to give 25 mg (39%) of the starting azulene, then with $CHCl_3$ to give mixture of 4- and 6-aminoazulenes **2** and **3** (25 mg).

Separation of 4- and 6-amino- isomers proved somewhat troublesome. Small sample of compound **2** was isolated by rechromatography for full characterization; the products ratio **2/3** was determined on the basis of ^{1}H NMR of the crude mixture. Yields – **2** (20%), **3** (15%).

4-Aminoazulene (2): oil. ^{1}H NMR ($CDCl_3$): 8.16 (d, *J* = 9.6, 1 H, H-8), 7.47 (t, *J* = 3.9, 1 H, H-2), 7.39 (dd, *J* = 10.5, 9.6, 1 H, H-6), 7.19 (dd, *J* = 3.9, 1.6, 1 H, H-1*), 7.08 (dd, *J* = 3.9, 1.6, 1 H, H-3*), 6.77 (apparent t, *J* = 9.6, 1 H, H-7), 6.67 (d, *J* = 10.5, 1 H, H-5), 5.20 (broad s, 2 H, NH_2). MS, *m/z* (% rel. int.): 144 (12), 143 (100, $M^{+\bullet}$), 142 (6), 126 (4), 117 (9), 116 (46), 115 (51); HR-MS calcd. for $C_{10}H_9N$ – 143.0735, found – 143.0720.

Amination of azulene derivatives with *N,N,N*-trimethylhydrazinium iodide (TMHI). To a stirred solution of azulene derivative (**5a–c**, 0.5 mmol) and TMHI (101 mg, 0.5 mmol) in DMSO (1.5 mL) at room temperature *t*-BuOK (168 mg, 1.5 mmol) was added in one portion and the reaction was continued under argon at 18°C for: 7 h (**5a**), 2.5 h (**5b**), 4 h (**5c**). The mixture was worked-up as in the procedure for preparation of 6-aminoazulene. After chromatography (eluent: n-hexane to $CHCl_3$), the starting azulenes (**5**) and 8-amino-derivatives (**8**) were isolated. The fraction containing 4-amino- and 6-aminoazulene was rechromatographed with $CHCl_3$/MeOH (20:1) solvent system to give pure isomers **6** and **7**. Yields – see Scheme 1.

Amination of azulene, **1** (reaction scale – 1 mmol), according to the above procedure (TMHI – 1.5-fold excess, *t*-BuOK – 5-fold excess, in $NH_{3(liq.)}$/THF (10:1) – 10 mL; reaction time – 5 h) gave 20% of 6-aminoazulene (**3**).

6-Amino-azulene-1-carbonitrile (6a): 37 mg (44%), yellow-brown crystals; m.p. 198–198.5°C ($CHCl_3$/MeOH, 20:1). ^{1}H NMR ($CDCl_3$): 8.25 (d, *J* = 10.8, 1 H, H-8), 8.07 (d, *J* = 11.0, 1 H, H-4), 7.52 (d, *J* = 4.1, 1 H, H-2), 6.99 (d, *J* = 4.1, 1 H, H-3), 6.68 (d, *J* = 10.8, 1 H, H-7), 6.64 (d, *J* = 11.0, 1 H, H-5), *ca* 5.00 (broad s, 2 H, NH_2). MS, *m/z* (% rel. int.): 169 (13), 168 (100, $M^{+\bullet}$), 167 (4), 151 (4), 142 (5), 141 (24), 140 (29), 127 (6), 115 (4), 114 (15), 113 (8); HR-MS calcd. for $C_{11}H_8N_2$ – 168.0687, found – 168.0694.

4-Amino-azulene-1-carbonitrile (7a): 12 mg (14%), brown crystals; m.p. 219–221°C ($CHCl_3$/MeOH, 20:1). ^{1}H NMR ($CDCl_3$): 8.39 (d, *J* = 10.0, 1 H, H-8), 7.63 (d, *J* = 4.3, 1 H, H-2), 7.57 (dd, *J* = 11.1, 9.8, 1 H, H-6), 7.04 (apparent t, *J* = 9.5, 1 H, H-7), 6.95 (d, *J* = 4.3, 1 H, H-3), 6.90 (d, *J* = 11.1, 1 H, H-5), 5.54 (broad s, 2 H, NH_2). MS, *m/z* (% rel. int.): 169 (14), 168 (100, $M^{+\bullet}$), 167 (8), 149 (5), 142 (9), 141 (33), 140 (30), 127 (5), 115 (5), 114 (15), 113 (8); HR-MS calcd. for $C_{11}H_8N_2$ – 168.0687, found – 168.0674.

8-Amino-azulene-1-carbonitrile (8a): 6 mg (7%), brown crystals; m.p. 138–140.5°C ($CHCl_3$). ^{1}H NMR ($CDCl_3$): 8.08 (d, *J* = 10.0, 1 H, H-4), 7.59 (d, *J* = 4.1, 1 H, H-2), 7.45 (ddd, *J* = 11.4, 9.2, 1.3, 1 H, H-6), 6.98 (d, *J* = 4.1, 1 H, H-3), 6.88 (apparent t, *J* = 9.6, 1 H, H-5), 6.76 (d, *J* = 11.4, 1 H, H-7), 6.32 (broad s, 2 H, NH_2). MS, *m/z* (% rel. int.): 169 (13), 168 (100, $M^{+\bullet}$), 167 (3), 151 (2), 142 (8), 141 (36), 140 (27), 127 (3), 115 (5), 114 (18), 113 (8); HR-MS calcd. for $C_{11}H_8N_2$ – 168.0687, found – 168.0705.

*6-Amino-1-benzoiloazulene (**6b**)*: 45 mg (36%), brown crystals; m.p. 135–137°C ($CHCl_3$/MeOH, 20:1). ^{1}H NMR ($CDCl_3$): 9.43 (d, *J* = 11.1, 1 H, H-8), 8.14 (d, *J* = 10.7, 1 H, H-4), 7.86–7.69 (m, 2 H, H-Ph), 7.60–7.46 (m, 4 H, H-Ph & H-2), 6.98 (d, *J* = 4.1, 1 H, H-3), 6.81 (dd, *J* = 11.1, 2.5, 1 H, H-7), 6.71 (dd, *J* = 10.7, 2.5, 1 H, H-5), 4.95 (broad s, 2 H, NH_2). MS, *m/z* (% rel. int.): 248 (19), 247 (100, $M^{+\bullet}$), 246 (7), 219 (5), 218 (3), 171 (11), 170 (90), 142 (6), 116 (2), 115 (10), 114 (2), 77 (4); HR-MS calcd. for $C_{17}H_{13}NO$ – 247.0997, found – 247.1003.

*4-Amino-1-benzoiloazulene (**7b**)*: 7 mg (6%), brown crystals; m.p. 167–170°C ($CHCl_3$/MeOH, 20:1). ^{1}H NMR ($CDCl_3$): 9.46 (d, *J* = 9.8, 1 H, H-8), 7.78–7.71 (m, 2 H, H-Ph), 7.53–7.44 (m, 3 H, H-Ph), 7.42 (d, *J* = 4.2, 1 H, H-2), 7.36–7.26 (m, 1 H, H-6), 7.06 (d, *J* = 4.2, 1 H, H-3), 6.86 (apparent t, *J* = 9.8, 1 H, H-7), 6.65 (d, *J* = 11.2, 1 H, H-5), 5.40 (broad s, 2 H, NH_2). MS, *m/z* (% rel. int.): 248 (16), 247 (84, $M^{+\bullet}$), 246 (27), 219 (3), 218 (6), 171 (13), 170 (100), 142 (10), 116 (5), 115 (16), 114 (4), 77 (6); HR-MS calcd. for $C_{17}H_{13}NO$ – 247.0997, found – 247.0989.

*8-Amino-1-benzoiloazulene (**8b**)*: 6 mg (5%), yellow-red crystals; m.p. 102–104°C ($CHCl_3$). ^{1}H NMR ($CDCl_3$): 7.92 (d, *J* = 9.0, 1 H, H-4), 7.73–7.68 (m, 2 H, H-Ph), 7.51–7.40 (m, 3 H, H-Ph), 7.39 (d, *J* = 4.3, 1 H, H-2), 7.35–7.23 (m, 1 H, H-6), 6.82 (d, *J* = 4.3, 1 H, H-3), 6.76 (apparent t, *J* = 9.0, 1 H, H-5), 6.73 (d, *J* = 11.5, 1 H, H-7), NH_2 – undetected. MS, *m/z* (% rel. int.): 248 (18), 247 (96, $M^{+\bullet}$), 246 (15), 231 (19), 230 (100), 218 (4), 217 (6), 203 (7), 202 (6), 171 (6), 170 (46), 142 (2), 127 (18), 116 (4), 115 (25), 114 (5), 105 (6), 77 (10); HR-MS calcd. for $C_{17}H_{13}NO$ – 247.0997, found – 247.1004.

*6-Amino-azulene-1,3-dicarboxylic acid diethyl ester (**6c**)*: The reaction was carried-out in 0.11 mmol scale; 20 mg (62%), yellow crystals; m.p. 233–235°C ($CHCl_3$), lit. [11] m.p. 236–237°C (EtOH). ^{1}H NMR ($CDCl_3$): 9.40 (apparent d, *J* = 11.4, 2 H, H-4 & H-8), 8.34 (s, 1 H, H-2), 6.88 (apparent d, *J* = 11.4, 2 H, H-5 & H-7), 5.20 (broad s, 2 H, NH_2), 4.38 (q, *J* = 7.1, 4 H, 2 × CH_2), 1.42 (t, *J* = 7.1, 6 H, 2 x CH_3). MS, *m/z* (% rel. int.): 288 (18), 287 (100, $M^{+\bullet}$), 272 (5), 259 (7), 244 (5), 243 (13), 242 (69), 216 (7), 215 (43), 214 (66), 187 (12), 186 (6), 170 (15), 169 (5), 143 (16), 141 (6), 140 (5), 130 (10), 115 (5); HR-MS calcd. for $C_{16}H_{17}O_4N$ – 287.1158, found – 287.1182.

Oxidative amination of azulene (1). In a three-necked flask azulene (128 mg, 1 mmol) and 4-amino-1,2,4-triazole (84 mg, 1 mmol) were dissolved in THF (1 mL). Then ammonia was condensed directly into the reaction flask to produce 10 mL of liquid. After addition of *t*-BuOK (560 mg, 5 mmol) the oxygen was passed throughout the stirred mixture during *ca* 4 h. The mixture was quenched with NH_4Cl (3.0 g, 60 mmol), the solvents were evaporated and to the residue chloroform (30 mL) was added. The solution was dried over anhydrous $MgSO_4$ and chromatographed using n-hexane as eluent to give 16 mg of azulene (13%), then with $CHCl_3$/MeOH (20:1) to give 57 mg of azulen-6-yl-[1,2,4]triazol-4-yl-amine (**10**) (27%) as violet crystals; m.p. *ca* 120° ($CHCl_3$/MeOH – 20:1; with decomposition). ^{1}H NMR (acetone-d_6): 9.75 (broad s, 1 H, NH), 8.67 (s, 2 H, H-triazole), 8.21 (apparent d, *J* = 10.7, 2 H, H-4 & H-8), 7.52 (t, *J* = 3.8, 1 H, H-2), 7.24 (d, *J* = 3.8, 2 H, H-1 & H-3), 6.41 (apparent d, *J* = 10.8, 2 H, H-5 & H-7). MS, *m/z* (% rel. int.): 211 (9), 210 (57, $M^{+\bullet}$), 181 (20), 155 (7), 154 (16), 143 (8), 141 (10), 140 (5), 128 (15), 127 (34), 126 (11), 116 (14), 115 (100); HR-MS calcd. for $C_{12}H_{10}N_4$ – 210.0906, found – 210.0896.

*Azulen-6-yl-carbamic acid methyl ester (**12**)*:

Method A. To a solution of 6-aminoazulene (**3**) (155 mg, 1.10 mmol) in pyridine (15 mL) a solution of methyl chloroformate (105 mg, 1.10 mmol) in acetone (4 mL) was added at 0°C. After 8 h an additional 105 mg (1.10 mmol) of $ClCO_2Me$ was added and the reaction was left at 0°C for 2 days. Then, the mixture was poured to water (50 mL) and it was extracted with CH_2Cl_2 (4 × 15 mL). The combined organic layers were washed with water (2 × 15 mL), dried over anhydrous $MgSO_4$ and after evaporation of the solvent chromatographed using n-hexane/$CHCl_3$ (1:1) to give 11 mg of the substrate **3** (35%) and 10 mg of azulen-6-yl-carbamic acid methyl ester (5%).

Method B. To a solution of 6-aminoazulene (**3**) (62 mg, 0.43 mmol) in Et_2O (2 mL) NEt_3 (726 mg, 1.0 mL, 7.17 mmol) and $ClCO_2Me$ (164 mg, 1.74 mmol) in Et_2O (6 mL) were added. The reaction mixture was left for 1 month at 0°C and worked-up as in Procedure A to give 14 mg (16%) of the desired product **12**; violet oil. ^{1}H NMR ($CDCl_3$): 8.53 (broad s, 1 H, NH), 8.17 (apparent d, *J* = 11.1, 2 H, H-4 & H-8), 7.56 (t, *J* = 4.1, 1 H, H-2), 7.36 (d, *J* = 4.1, 2 H, H-1 & H-3), 7.23 (d, *J* = 11.1, 2 H, H-5 & H-7), 3.85 (s, 3 H, OCH_3). MS, *m/z* (% rel. int.): 201 (27, $M^{+\bullet}$), 169 (28), 143 (38), 142 (100), 141 (46), 130 (10), 129 (76), 128 (78), 127 (23), 116 (12), 115 (53).

*6-Amino-1-(4-bromofenylazo)-azulene (**13**)*: To a stirred solution of *para*-bromophenyl diazonium chloride (0.15 mmol), prepared according to known method [18], 6-aminoazulene (21 mg, 0.15 mmol) was added in CH_3CO_2H (0.5 mL). After 30 min. of stirring the reaction mixture was poured into aqueous 10% NaOH (50 mL) and extracted with CH_2Cl_2 (2 × 20 mL). The combined organic layers were dried over anhydrous $MgSO_4$, evaporated to dryness and chromatographed using $CHCl_3$/MeOH (20:1) solvent system as eluent to give 33 mg of the desired product (68%); red crystals, m.p. 190–192°C ($CHCl_3$/MeOH, 20:1, with decomposition). ^{1}H NMR ($CDCl_3$): 8.97 (d, J = 10.8, 1 H, H-8), 7.99 (d, J = 10.2, 1 H, H-4), 7.80 (apparent d, J = 8.5, 2 H, H-C_6H_4Br), 7.75 (d, J = 4.2, 1 H, H-2), 7.58 (d, J = 8.5, 2 H, H-C_6H_4Br), 7.14 (d, J = 4.2, 1 H, H-3), 6.71 (d, J = 10.2, 1 H, H-5), 6.55 (d, J = 10.8, 1 H, H-7), 4.88 (broad s, 2 H, NH_2). MS, *m/z* (% rel. int.): 328 (5) & 326 (9) [isotopic M+H], 327 (28) & 325 (28) [isotopic $M^{+\bullet}$], 311 (4), 309 (4), 299 (2), 297 (2), 218 (3), 170 (30), 143 (11), 142 (100), 141 (9), 140 (5), 116 (9), 115 (51), 114 (9); HR-MS calcd. for $C_{16}H_{12}N_3Br$ – 325.0215, found – 325.0210.

*1-(Azulen-6-ylazo)-azulen-6-yl-amine (**15**)*: In a stirred mixture of acetic and propionic acids (1:1, 2 mL) at –20°C 6-aminoazulene (66 mg, 0.46 mmol) was dissolved, and to this solution $NaNO_2$ (10 mg, 0.15 mmol) was added. After 5 min the reaction mixture was poured into aqueous 10% NaOH (30 mL) and extracted with CH_2Cl_2 (2 × 20 mL). The combined organic layers were dried over anhydrous $MgSO_4$ and after evaporation of the solvent chromatographed using $CHCl_3$/MeOH (20:1) solvent system as eluent to give 31 mg of the starting 6-aminoazulene (47%) and 4 mg of 1-(azulen-6-ylazo)-azulen-6-yl-amine (6%); deep-violet crystals, decomposition >120°C. ^{1}H NMR (acetone-d_6): 8.98 (apparent d, J = 10.9, 1 H, H-8), 8.48 (apparent d, J = 10.9, 2 H, H-4′ & H-8′), 8.04 (apparent d, J = 10.8, 1 H, H-4), 7.95 (apparent d, J = 10.9, 2 H, H-5′ & H-7′), 7.75 (t, J = 3.8, 1 H, H-2′), 7.57 (d, J = 4.6, 1 H, H-2), 7.33 (d, J = 3.8, 2 H, H-1′ & H-3′), 7.19 (broad s, 2 H, NH_2), 7,08 (d, J = 4.6, 1 H, H-3), 7.04 (dd, J = 10.9, 2.3, 1 H, H-7), 6.85 (dd, J = 10.8, 2.3, 1 H, H-5). MS, *m/z* (% rel. int.): 297 (20, $M^{+\bullet}$), 270 (8), 269 (28), 268 (15), 252 (7), 218 (7), 158 (29), 157 (14), 155 (14), 153 (28), 149 (11), 146 (29), 143 (46), 142 (46), 141 (13), 139 (10), 136 (25), 131 (30), 130 (21), 129 (12), 116 (31), 115 (67), 107 (38), 106 (25), 105 (29), 91 (61), 89 (54), 78 (37), 77 (100), 69 (31), 55 (88), 44 (53), 41 (42), 39 (41); HR-MS calcd. for $C_{20}H_{15}N_3$ – 297.1266, found – 297.1230.

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