Elsayed M. Afsah*, Ahmed A. Fadda, Samir Bondock and Mohamed M. Hammouda

Synthesis and some reactions of functionalized 11,12-dihydro-5*H*-dibenzo[*b*,*g*]azonines

Abstract: Dihydro-5*H*-dibenzo[*b*,*g*]azonine-6,13-dione (**2**) has been used as a precursor in the synthesis of the indolo[2,3-*e*]dibenzo[*b*,*g*]azonine and tribenzo[*b*,*g*,*j*][1,6] diazacyclododecine ring systems **6** and **7** respectively *via* a Fischer indolization/periodate oxidation sequence. Fischer indolization of the (1,4-phenylenedihydrazono) derivative **8** gave the polycyclic system **9**. The Schmidt reaction of **2** led to the formation of the benzimidazo[1,2-*b*] [2]benzazepine ring system **11**. The Mannich reaction of **2** led to the spirocyclic system **15**. The reactions of **2** with aldimines and aromatic aldehydes were also investigated.

Keywords: dibenzo[*b*,*g*]azonines; indolo-dibenzo[*b*,*g*] azonines; Mannich bases; periodate oxidation.

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1 Introduction

The azonine ring system has been the object of considerable synthetic efforts [1–8], because this system is present as a part in various alkaloids. A number of azonines and benzoazonines have been studied with interest centered on their potential pharmaceutical activity as antimalarials [9], analgesics [10], antihypertensive [11] and CNS activity [12].

The dibenzo[*d*,*f*]azonine ring system is the main part in the laurifonine, laurifine and laurifinine alkaloids [13]. The azonine core is present in the vinblastine and vincristine alkaloids [14, 15] which possess significant antitumor activity and have been widely used clinically. However, the literature on benzoazonines, dibenzoazonines, azoninoindoles and related compounds is relatively limited [16–21].

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In view of this, and in connection with our studies in this area [8], we report here on the synthesis and some reactions of the title compounds which possess considerable synthetic and pharmaceutical interest.

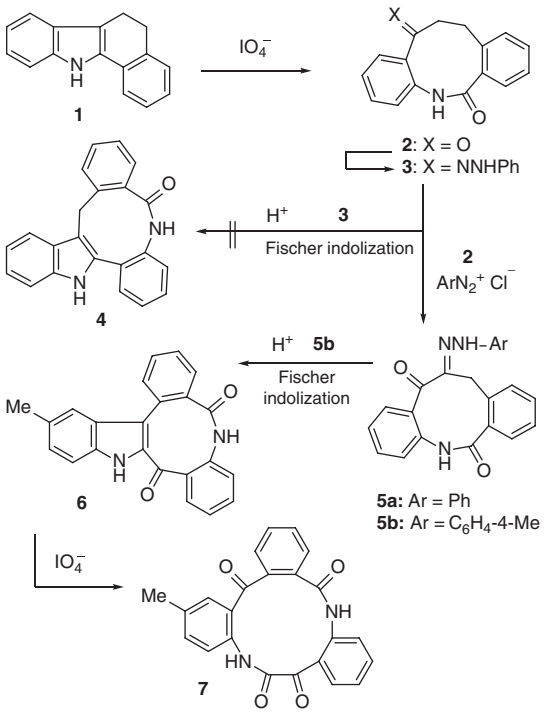
2 Results and discussion

According to an earlier report [22], the periodate oxidation of 5,6-dihydro-11*H*-benzo[*a*]carbazole (**1**) afforded 11,12-dihydro-5*H*-dibenzo[*b*,*g*]azonine-6,13-dione (**2**). The present work is concerned with attempts to extend the scope of the periodate oxidation of indoles to include the indolo-dibenzo[*b*,*g*]azonines, as a route to higher heterocyclic systems (Scheme 1). Attempted synthesis of the indolo-dibenzo[*b*,*g*]azonine system **4** *via* acid-catalyzed Fischer indolization of the phenylhydrazone **3** yielded a dark-red gummy product, which was difficult to purify.

In an alternative route to the indolo-dibenzo[*b*,*g*] azonine ring system, compound **2** was treated with diazotized aniline or *p*-toluidine to give 12-(arylhydrazono)-11,12-dihydro-5*H*-dibenzo[*b*,*g*]azonine-6,13-diones (**5a**, **b**). Fischer indolization of **5b** afforded a single product which was identified as 5,6-dihydro-15-methyl-indolo[2,3-*e*]dibenzo[*b*,*g*]azonine-5,11-dione (**6**). The periodate oxidation of **6** took place quite smoothly and provided a convenient access to the generation of the functionalized 12-membered macrocyclic system **7**. The mass spectrum of **7** showed the molecular ion at $m/z = 384$ (19 %).

In the course of our investigation, the coupling reaction of **2** with bis(diazotized) *p*-phenylenediamine afforded 12,12′-(1,4-phenylenedihydrazono)-bis(11,12-dihydro-5*H*-dibenzo-[*b*,*g*]azonine-6,13-dione) (**8**), which was subjected to Fischer indolization to afford **9** (Scheme 2). However, the periodate oxidation of **9** was not feasible due to its insolubility in commonly used solvents.

On the other hand, an attempt to prepare the dibenzo[1,4]diazecine ring system **10** by treating **2** with hydrazoic acid under Schmidt reaction conditions led to the formation of 1,2-dihydro-9*H*-benzimidazo[1,2-*b*][2] benzazepin-9-one (**11**), *via* in situ cyclodehydration of **10**, as confirmed by analytical and spectral data (Scheme 3).



Scheme 1: Synthesis of indolo[2,3-*e*]dibenzo[*b*,*g*]azonine-5, 11-dione (**6**) and its oxidation to **7**.

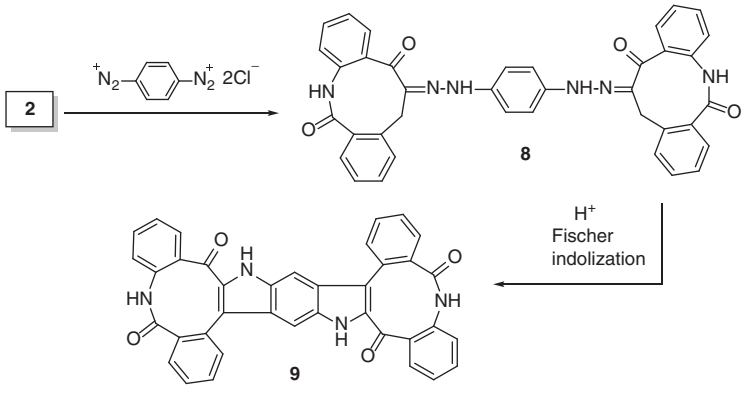
The mass spectrum of **11** indicated the molecular ion peak at *m/z* = 248 (25 %) and the ^{1}H NMR spectrum revealed two triplets at δ = 3.25 (1-H$_2$) and 3.28 (2-H$_2$). In addition, the ^{13}C NMR spectrum displays signals at δ = 25.62 (C-2), 28.61 (C-1), 142.55 (C-2a) and 172.34 (CO). The assignment of the NH group between the CO group and the aryl moiety of **10** is based on previous studies on the Schmidt rearrangement [23, 24], and also by analogy with the formation of tetrahydro-1*H*-benzo[*b*]azocin-2-one [25] and hexahydro-benzo[*b*][1,4]diazecin-2,7-dione [8] from 1-benzosuberone and tetrahydro-1*H*-benzo[*b*]azonine-2,7-dione, respectively. In addition, there is much evidence that bulky substituents at the α-position exert stereocontrol on the reaction [25–28].

In connection with our studies in the area of Mannich bases [8, 29–33] and in view of the widespread and increasing interest in the biological activities of Mannich bases and related compounds, we investigated the Mannich reaction of **2** with piperidine and formaldehyde anticipating the formation of the Mannich base **12**. Unexpectedly, however, it gave a product which was identified as the spirocyclic system **14** (Scheme 4).

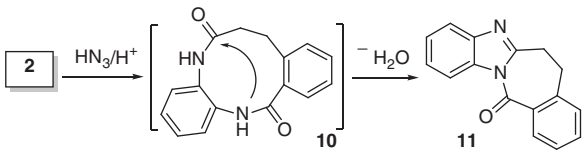
The formation of **14** may be attributed to the spontaneous deamination of **12** to give **13**, which undergoes Diels–Alder dimerization to afford **14**. This result is in line with the reported formation of spirocyclic systems by the Mannich reaction with tetrahydro-1*H*-benzo[*b*]azonine-2,7-dione [8], thiochromanone [34] and [1]benzazepin-2,5-(3*H*,4*H*)-dione [35].

On the other hand, the reaction of aldimines with cycloalkanones has opened routes to the corresponding Mannich bases [30, 36–38]. However, the attempted reaction of benzalaniline with **2** failed to give the expected base **15**, leading instead to the formation of 10-phenylamino-11*H*-indeno[1,2-*b*]quinoline (**17**) (Scheme 5). The IR spectrum of **17** revealed the absence of carbonyl groups and showed a strong band at 3456 cm^{-1} (NH). Its mass spectrum exhibited a molecular ion peak at *m/z* = 308 (31 %), and the ^{1}H NMR spectrum revealed two singlets at δ = 2.40 (10-H$_2$) and 2.92 (NH). The formation of **17** rather than **15** may be attributed to the tendency of **2** to cyclize readily under mild basic conditions to give 5*H*-indeno[1,2-*b*]quinolin-10(11*H*)-one (**16**), which reacted with aniline, resulting from decomposition of benzalaniline, to afford **17** (Scheme 5).

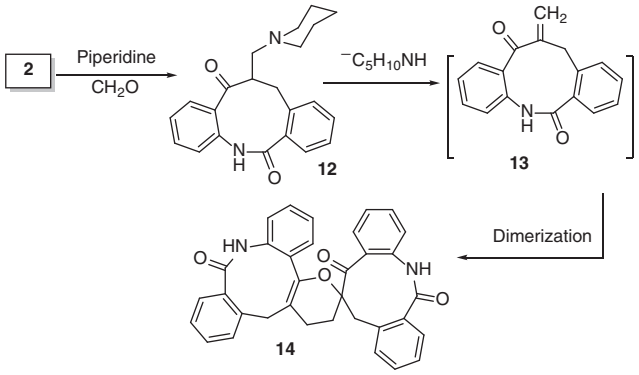
These results are analogous to the formation of 9-phenylamino-1*H*-cyclopenta[*b*]quinoline from



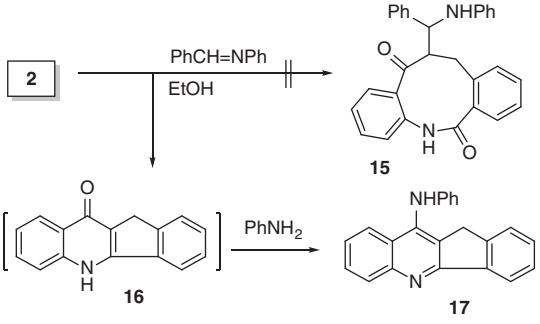
Scheme 2: Fischer indolization of the 1,4-phenylenedihydrazono derivative **8**.



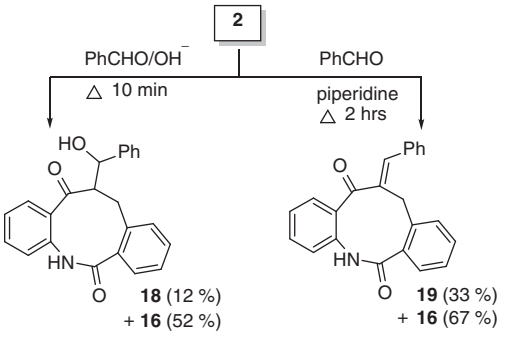
Scheme 3: Schmidt reaction of **2**.



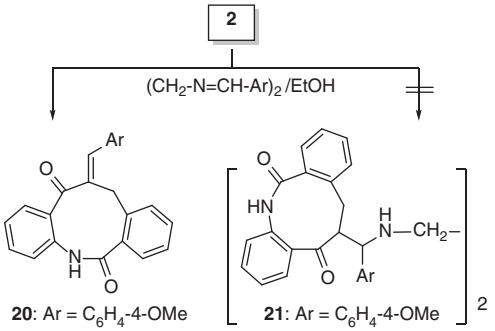
Scheme 4: Attempted Mannich reaction of 2.



Scheme 5: Reaction of **2** with benzalaniline.



Scheme 6: Aldol condensation of **2** with benzaldehyde.



Scheme 7: Reaction of *N*,*N*′-bis(*p*-anisylidene)ethylenediamine with **2**.

tetrahydro-1*H*-benzo[*b*]azonine-2,7-dione and benzalaniline [8]. In this connection, the synthesis of compound **16** has been achieved in a 45 % yield upon treatment of **2** with aqueous sodium hydroxide at room temperature, and it was identical (m.p. and IR spectrum) to an authentic sample previously prepared by heating of **2** at 180 °C [22].

In line with this, the base-catalyzed condensation of **2** with benzaldehyde led to the formation of indenoquinolinone **16** as the main product besides the aldol product **18** or the benzylidene derivative **19**, depending on the reaction conditions (Scheme 6).

In addition, the reaction of compound **2** with *N*,*N*′-bis(*p*-methoxybenzylidene)ethylenediamine afforded 12-(4-methoxybenzylidene)-11,12-dihydro-5*H*-dibenzo[*b*,*g*]azonine-6,13-dione (**20**), as the sole product, rather than the expected bis-(Mannich base) **21** (Scheme 7). This may be rationalized on the basis of a mechanism which involves the spontaneous deamination of the bis-(Mannich base) **21** to give **20** as the end product. This reaction is of particular interest, because it offers access with good yields to the arylidene derivatives of compound **2**.

3 Experimental section

All melting points (uncorrected) were determined on a Gallenkamp electric melting point apparatus (Sanyo Gallenkamp, Southborough, UK). Elemental microanalyses were carried out on a Carlo Erba 1108 Elemental Analyzer (Heraeus, Hanau, Germany), at Microanalytical Unit, Faculty of Science, Cairo University. Infrared spectra were measured on a Mattson 5000 FTIR spectrometer (Mattson Instruments, Inc., Madison, WI, USA). ^{1}H and ^{13}C NMR data were obtained in $CDCl_3$ or $[D_6]$DMSO solution on a Varian XL 300 MHz instrument (Varian, Inc., California, USA) using TMS as internal standard. Chemical shifts are reported in ppm (δ) downfield from internal TMS. Mass spectra were recorded on a GC-MS QP-1000 EX Shimadzu instrument (Shimadzu, Tokyo, Japan). The course of the reaction and the purity of the synthesized compounds

were monitored by TLC using EM science silica gel coated plates, 0.25 nm, 60 GF 254 (Merck, Germany) with visualization by irradiation with an ultraviolet lamp. Compounds **7**, **8**, **9** and **18** are of limited solubility in the common ^{1}H NMR solvents. Compounds **1** and **2** [22] were prepared as previously described. All chemicals used were of pure grade and were purchased from Aldrich (WI, USA).

3.1 13-(Phenylhydrazono)-11,12-dihydro-5*H*-dibenzo[*b*,*g*]azonine-6-one (3)

To a solution of **2** [22] (1 g, 4 mmol) in ethanol (10 mL), phenylhydrazine (0.43 g, 4 mmol) and acetic acid (0.2 mL) were added. The reaction mixture was heated on a water bath for 5 min, and stirred for 90 min at room temperature. The product obtained on cooling was filtered and crystallized from ethanol to give **3**. M.p. 234 °C. Yield 15 % (yellow leaflets). – IR (KBr): ν = 3440 (NH lactam), 3379 (NH hydrazone), 1710 (CO), 1430, 1325, 1121 cm^{-1}. – $C_{22}H_{19}N_3O$ (341.41): calcd. C 77.40, H 5.61, N 12.31; found C 77.32, H 5.51, N 12.16.

3.2 12-(Arylhydrazono)-11,12-dihydro-5*H*-dibenzo[*b*,*g*]azonine-6,13-diones (5a, b)

Diazotized aniline or *p*-toluidine (4 mmol) was added with stirring to a cold solution of **2** (1 g, 4 mmol) in pyridine (15 mL). The reaction mixture was stirred for 30 min at 5–10 °C and for 2 h at room temperature. The product obtained on dilution with water was filtered off, dried and purified by preparative chromatography on Al_2O_3 using methanol–diethyl ether (2:1) as eluent to give compounds **5a**, **b**.

3.3 12-(Phenylhydrazono)-11,12-dihydro-5*H*-dibenzo[*b*,*g*]azonine-6,13-dione (5a)

M.p. 293 °C (chloroform). Yield 36 % (greenish needles). – IR (KBr): ν = 3409 (NH lactam), 3225 (NH hydrazone), 1710 (CO), 1692 (CO), 1333, 1210 cm^{-1}. – ^{1}H NMR ([D$_6$]DMSO): δ = 1.54 (s, 2H, 11-H_2), 7.12–7.53 (m, 13H, aromatic), 9.21 (s, 1H, CON*H*), 10.53 ppm (s, 1H, N*H* hydrazone). – ^{13}C NMR ([D$_6$]DMSO): δ = 32.15 (C-11), 117.11, 119.30, 125.13, 129.07, 131.24, 136.44, 141.18 (all Ar-*C*), 154.51 (*C*=N), 174.22 (*C*O), 182.34 ppm (*C*O). – MS (EI, 70 eV): *m/z* (%) = 355 (21) [M]$^+$, 336 (4), 200 (16), 184 (45), 138 (15), 122 (100), 76 (48). – $C_{22}H_{17}N_3O_2$ (355.39): calcd. C 74.35, H 4.82, N 11.82; found C 74.20, H 4.74, N 11.69.

3.4 12-(*p*-Tolylhydrazono)-11,12-dihydro-5*H*-dibenzo[*b*,*g*]azonine-6,13-dione (5b)

M.p. 312 °C (dichloromethane). Yield 23 % (dark brown powder). – IR (KBr): ν = 3420 (NH lactam), 3288 (NH hydrazone), 1719 (CO), 1705 (CO), 1210 cm^{-1}. – ^{1}H NMR ([D$_6$]DMSO): δ = 1.45 (s, 2H, 11-H_2), 2.20 (s, 3H, Ar-CH_3), 7.12–7.53 (m, 12H, aromatic), 9.11 (s, 1H, CON*H*), 10.12 ppm (s, 1H, N*H* hydrazone). – MS (EI, 70 eV): *m/z* (%) = 369 (9) [M]$^+$, 278 (2) [M–(C$_6$H$_4$-Me)]$^+$, 229 (4), 200 (16), 150 (55), 122 (100). – $C_{23}H_{19}N_3O_2$ (369.42) calcd. C 74.78, H 5.18, N 11.37; found C74.63, H 5.11, N 11.21.

3.5 5,6-Dihydro-15-methyl-indolo[2,3-*e*]dibenzo[*b*,*g*]azonine-5,11-dione (6)

This compound was obtained by treating **5b** (0.6 g, 1.6 mmol) with hot 20 % sulfuric acid (6 mL) on a water bath for 30 min, poured onto water (30 mL) and basified with NH_4OH. The product was purified by crystallization from DMSO to give **6**. M.p. 278 °C. Yield 18 % (dark-green crystals). – IR (KBr): ν = 3412 (NH indolic), 3356 (NH lactam), 1710 (CO), 1685 (CO), 1523, 1335, 1223 cm^{-1}. – ^{1}H NMR ([D$_6$]DMSO): δ = 2.20 (s, 3H, Ar-CH_3), 7.12–7.67 (m, 11H, aromatic), 8.15 (s, 1H, N*H* indolic), 10.36 ppm (s, 1H, N*H* amide). – ^{13}C NMR ([D$_6$]DMSO): δ = 28.13 (*C*H$_3$-Ar), 113.10, 119.21, 121.14, 125.33, 129.76, 132.14, 135.07, 139.66, 141.24, 143.16 (all Ar-*C*), 174 (*C*O), 182 ppm (*C*O). – MS (EI, 70 eV): *m/z* (%) = 352 (11) [M]$^+$, 353 (6) [M + 1]$^+$, 291 (14), 264 (15), 240 (16), 215 (22), 201 (20), 144 (100), 77 (26). – $C_{23}H_{16}N_2O_2$ (352.39): calcd. C 78.39, H 4.57, N 7.95; found C 78.28, H 4.48, N 7.87.

3.6 2-Methyltribenzo[*b*,*g*,*j*][1,6]diazacyclododecine-6,7,13,18(5*H*,12*H*)-tetraone (7)

A solution of **6** (0.20 g, 0.57 mmol) in pyridine (10 mL) was added to a solution of sodium periodate (0.25 g, 1.14 mmol) in water (5 mL). After standing at room temperature for 20 h, the solvent was removed at reduced pressure, and the product obtained was washed successively with water (3 × 10 mL) and boiling pyridine (3 × 5 mL) to give **7**. M.p. > 300 °C. Yield 32 % (colorless powder). – IR (KBr): ν = 3445 (NH lactam), 1730 (CO), 1710 (CO), 1690 (CO), 1620 (CO), 1210 cm^{-1}. – MS (EI, 70 eV): *m/z* (%) = 385 (5) [M + 1]$^+$, 384 (13) [M]$^+$, 369 (40), 310 (100), 309 (80), 249 (17), 203 (14), 182 (44), 76 (62). – $C_{23}H_{16}N_2O_4$ (384.38): calcd. C 71.87, H 4.20, N 7.29; found C 71.77, H 4.12, N 7.11.

3.7 12,12′-(1,4-Phenylenedihydrazono)-*bis*(11,12-dihydro-5*H*-dibenzo-[*b*,*g*]azonine-6,13-dione) (8)

This compound was obtained from **2** (1 g, 4 mmol) and bis(diazotized)-*p*-phenylenediamine (2 mmol) in pyridine (15 mL), following the same procedure as described above for compounds **5a** and **b**. The product was washed with boiling chloroform–methanol (4:1). M.p. > 300 °C. Yield 54 % (dark-green powder). – IR (KBr): ν = 3404 (NH lactam), 3330 (NH hydrazone), 1709 (CO), 1680 (CO), 1585, 1315, 1210 cm^{-1}. – MS (EI, 70 eV): *m/z* (%) = 632 (5) $[M]^+$, 629 (4) $[M]^+$, 232 (100), 214 (7), 210 (10), 184 (11), 136 (18). – $C_{38}H_{28}N_6O_4$ (632.67): calcd. C 72.14, H 4.46, N 13.28; found C 72.07, H 4.34, N 13.12.

3.8 Fischer indolization of 8: synthesis of 9

A mixture of **8** (0.30 g, 0.47 mmol) and 20 % sulfuric acid (5 mL) was heated on a water bath for 30 min, poured onto water (20 mL) and basified with NH_4OH. The product was filtered and washed with boiling pyridine to give **9**. M.p. > 300 °C. Yield 33 % (dark-brown powder). – IR (KBr): ν = 3405 (NH indolic), 3420 (NH lactam), 1712 (CO), 1683 (CO), 1322, 1212 cm^{-1}. – MS (EI, 70 eV): *m/z* (%) = 598 (5) $[M]^+$, 473 (27), 324 (18), 260 (26), 216 (20), 232 (100), 166 (35), 154 (21), 92 (17). – $C_{38}H_{22}N_4O_4$ (598.61): calcd. C 76.24, H 3.70, N 9.36; found C 76.12, H 3.64, N 9.24.

3.9 1,2-Dihydro-9*H*-benzimidazo[1,2-*b*][2]benzazepin-9-one (11)

To a solution of **2** (0.5 g, 2 mmol) in chloroform (30 mL) containing 90 % sulfuric acid (4 mL) at 0 °C was added sodium azide (0.13 g, 2 mmol). After stirring for 1 h at 0 °C and 4 h at 25 °C, the reaction mixture was diluted with ice water (50 mL) and basified with NH_4OH. The product was filtered and crystallized from ethyl acetate–diethyl ether (2:1) to give **11**. M.p. 116 °C. Yield 54 % (colorless powder). – IR (KBr): ν = 1683 (CO), 1597, 1550, 1315, 1212 cm^{-1}. – ^{1}H NMR ([D$_6$]DMSO): δ = 3.25 (t, J = 7.5 Hz, 2H, 1-H_2), 3.28 (t, J = 7.5 Hz, 2H, 2-H_2), 7.35–8.41 ppm (m, 8H, aromatic). – ^{13}C NMR ([D$_6$]DMSO): δ = 25.62 (C-2), 28.61 (C-1), 116.12, 124.33, 127.14, 128.53, 129.73, 131.24, 136.27, 139.44, 140.88 (all Ar-*C*), 142.55 (C-2a), 172.34 ppm (*C*O). – MS (EI, 70 eV): *m/z* (%) = 248 (25) $[M]^+$, 247 (75), 218 (25), 145 (12), 134 (9), 118 (35), 108 (12),105 (2.5), 93 (9), 89 (100). – $C_{16}H_{12}N_2O$ (248.28): calcd. C 77.40, H 4.87, N 11.28; found C 77.32, H 4.74, N 11.13.

3.10 1′H-Spiro[dibenzo[*b*,*g*]azonine-12,3′-dibenzo[*b*,*g*]pyrano[2,3-*d*]azonine]-6,10′,13 (2′*H*, 5*H*, 9′*H*,11*H*,15′*H*)-trione (14)

A solution of **2** (0.50 g, 2 mmol), piperidine (0.22 g, 2.5 mmol) and formaldehyde (0.08 g, 2.6 mmol) in acetic acid (15 mL) was heated on a water bath at 90 °C for 30 min. A pale-yellow powder separated was filtered and crystallized from ethyl acetate to give **14**. M.p. > 300 °C. Yield 26 % (pale-yellow powder). – IR (KBr): ν = 3456 (NH lactam), 3423 (NH lactam), 1730 (CO), 1722 (CO), 1693 (CO), 1344, 1282, 1115 cm^{-1}. – ^{1}H NMR ([D$_6$]DMSO): δ = 2.31(m, 4H, CH_2CH_2), 2.71 (m, 2H, CH_2) 2.82 (m, 2H, CH_2), 7.45–8.15 (m, 16H, aromatic), 9.10 (s, 1H, CON*H*), 9.61 ppm (s, 1H, CON*H*). – ^{13}C NMR ([D$_6$]DMSO): δ = 24.54, 27.23, 29.14, 32.14 (4 × CH_2), 84.51 (spiro *C*), 94.45 (olefinic *C*), 118.72, 120.18, 122.48, 123.14, 125.68, 126.24, 127.08, 127.54, 128.12, 128.77, 129.37, 129.79, 130.54, 131.11, 132.38, 132.71, 134.07, 135.52, 136.70, 137.64, 139.15, 140.51, 141.11, 142.83 (all Ar-*C*), 146.21 (olefinic *C*), 172.12 (*C*ONH),175.08 (*C*ONH),186.41 ppm (*C*O). – MS (EI, 70 eV): *m/z* (%) = 526 (4) $[M]^+$, 508 (21) $[M–18]^+$, 232 (14), 214 (28), 186 (70), 146 (40), 120 (56), 105 (7), 92 (50), 77 (25), 50 (100). – $C_{34}H_{26}N_2O_4$ (526.58): calcd. C 77.55, H 4.98, N 5.32; found C 77.49, H 4.86, N 5.28.

3.11 5*H*-Indeno[1,2-*b*]quinolin-10(11*H*)-one (16)

Compound **2** (1 g, 4 mmol) was dissolved in cold sodium hydroxide solution (8 %, 15 mL); a yellow solution was obtained which after a few seconds warmed up slightly and became colorless. On neutralization with dilute HCl, a colorless powder was obtained, which was filtered and crystallized from ethyl acetate to give **16**. M.p. > 300 °C (> 300 °C [22]). Yield 35 % (colorless powder). – IR (KBr): ν = 3456 (NH), 1625 (CO), 1344, 1282, 1115 cm^{-1}. – ^{1}H NMR ([D$_6$]DMSO): δ = 2.42 (s, 2H, CH_2), 3.5 (bs, 1H, N*H*), 7.45–7.92 ppm (m, 8H, aromatic). – ^{13}C NMR ([D$_6$]DMSO): δ = 35.27 (CH_2), 101.15 (olefinic *C*), 117.21, 119.42, 120.71, 125.15, 127.14, 128.64, 129.07, 130.35, 131.54, 134.04, 142.24, 145.92 (all Ar-*C*), 152.85 (olefinic *C*), 182.16 ppm (*C*O). – MS (EI, 70 eV): *m/z* (%) = 232 (100) $[M]^+$, 204 (69) 128(14), 214 (28), 101 (19), 92 (7), 77 (79).

3.12 10-Phenylamino-11*H*-indeno[1,2-*b*]quinoline (17)

A solution of **2** (1 g, 4 mmol) and benzalaniline (0.73 g, 4 mmol) in ethanol (15 mL) and one drop of concentrated hydrochloric acid was heated on a water bath for 5 min.

After standing at room temperature for 8 h and neutralization with NH_4OH, the solvent was removed at reduced pressure, and the product was crystallized from ethyl acetate to give **17**. M.p. > 300 °C. Yield 45 % (pale-yellow powder). – IR (KBr): ν = 3456 (NH), 1344, 1282, 1115 cm^{-1}. – ^1H NMR ([D_6]DMSO): δ = 2.39 (s, 2H, CH_2), 2.92 (bs, 1H, NH), 7.50–7.59 ppm (m, 13H, aromatic). – ^{13}C NMR ([D_6]DMSO): δ = 32.44 (*C*H_2), 116.76, 117.54, 120.46, 121.42, 124.08, 126.27, 128.51, 129.70, 132.11, 134.48, 136.22, 137.10, 138.57, 139.34, 140.04, 140.52, 142.36, 143.61, 144.70, 145.17 (all Ar-*C*), 162.48 ppm (*C*=N). – MS (EI, 70 eV): *m/z* (%) = 308 (31) $[M]^+$, 290 (7) $[M–18]^+$, 258 (26), 232 (100), 186 (70), 146 (40), 120 (56), 105 (7), 92 (50), 77 (25), 50 (100). – $C_{22}H_{16}N_2$ (308.38): calcd. C 85.69, H 5.23, N 9.08; found C 85.58, H 5.16, N 8.87.

3.13 12-[Hydroxyl(phenyl)methyl]-11, 12-dihydro-5*H*-dibenzo[*b*,*g*]azonine-6, 13-dione (18)

A solution of **2** (1.00 g, 4 mmol) and benzaldehyde (0.42 g, 4 mmol) in ethanol (15 mL) and two drops of 15 % sodium hydroxide solution was warmed on a water bath for 10 min. The product which was separated upon heating was filtered and crystallized from ethyl acetate to give **18**. M.p. > 300 °C. Yield 12 % (pale-yellow powder). – IR (KBr): ν = 3550 (OH), 3416 (NH lactam), 1715 (CO), 1693 (CO), 1344, 1282, 1115 cm^{-1}. – MS (EI, 70 eV): *m/z* (%) = 357 (4) $[M]^+$, 339 (21) $[M–18]^+$, 232 (14), 214 (28), 186 (70), 146 (40), 120 (56), 105 (7), 92 (50), 77 (25), 50 (100). – $C_{23}H_{19}NO_3$ (357.39): calcd. C 77.29, H 5.36, N 3.92; found C77.16, H 5.20, N 3.81.

Neutralization of the filtrate after separation of **18** with dilute HCl gave compound **16**. M.p. > 300 °C. Yield 52 %. It was identical (m.p. IR and ^1H NMR spectra) to an authentic sample previously prepared [22].

3.14 12-Benzylidene-11,12-dihydro-5*H*-dibenzo[*b*,*g*]azonine-6,13-dione (19)

A solution of **2** (1.00 g, 4 mmol) and benzaldehyde (0.42 g, 4 mmol) in ethanol (15 mL) and two drops of piperidine was refluxed on a water bath for 2 h. After cooling to room temperature, the reaction yielded a mixture of two products which were separated by preparative chromatography on Al_2O_3 using diethyl ether–petroleum ether 60–80 °C (4:1) as eluent. Compound **19**, m.p. > 300 °C (ethanol). Yield 33 % (yellow crystals). – IR (KBr): ν = 3523 (NH lactam), 1722 (CO), 1678 (CO), 1315, 1220, 1110 cm^{-1}. – ^1H NMR ([D_6]DMSO): δ = 2.32 (s, 2H, 11-H_2), 4.82 (s, 1H, Ph-C*H*=), 6.90–7.40 (m, 13H, aromatic), 9.20 ppm (s,1H, CON*H*). – ^{13}C NMR ([D_6]DMSO): δ = 33.54 (*C*H_2), 119.14, 120.18, 121.64, 123.73, 124.48, 125.53, 127.41, 128.50, 130.75, 131.09, 131.89, 133.35, 135.47, 136.94, 137.37, 138.67, 139.44, 140.17, 140.69, 141.15 (all Ar and olefinic *C*), 171.79 (*C*ONH), 189.04 ppm (*C*O). – MS (EI, 70 eV): *m/z* (%) = 339 (16) $[M]^+$, 200 (94), 170 (12), 91 (53), 77 (12), 55 (100). – $C_{23}H_{17}NO_2$ (339.38): calcd. C 81.39, H 5.05, N 4.13; found C 81.27, H 4.88, N 4.05.

The second product was identified as compound **16**. M.p. > 300 °C (ethyl acetate). Yield 67 %. It was identical (m.p. IR and ^1H NMR spectra) to an authentic sample previously prepared [22].

3.15 12-(4-Methoxybenzylidene)-11, 12-dihydro-5*H*-dibenzo[*b*,*g*]azonine-6, 13-dione (20)

A solution of **2** (1.00 g, 4 mmol) and *N*,*N*′-bis (4-methoxybenzylidene)ethane-1,2-diamine (0.59 g, 2 mmol) in ethanol (15 mL) and two drops of concentrated HCl was heated on a water bath for 20 min. After cooling to room temperature the product was crystallized from ethyl acetate to give **20**. M.p. 293 °C. Yield 45 % (yellow powder). – IR (KBr): ν = 3456 (NH), 1715 (CO), 1690 (CO), 1344, 1282, 1115 cm^{-1}. – ^1H NMR ([D_6]DMSO): δ = 2.40 (s, 2H, 11-H_2), 2.92 (bs, 1H, NH), 3.63 (s, 3H, OCH_3), 5.42 (s,1H, Ar-C*H*=), 7.50–7.59 ppm (m, 12H, aromatic). – ^{13}C NMR ([D_6]DMSO): δ = 32.42 (*C*H_2), 52.70 (*C*H_3), 115.07, 115.32, 125.41, 125.62, 126.28, 126.75, 129.57, 130.44, 131.11, 131.45, 132.04, 132.89, 133.38, 134.27, 135.69, 136.33, 138.49, 140.33, 158.89 (all Ar and olefinic *C*), 171.46 (*C*ONH), 188.74 ppm (*C*O). – MS (EI, 70 eV): *m/z* (%) = 369 (31) $[M]^+$, 290 (7), 258 (26), 232 (100), 186 (70), 146 (40), 120 (56), 105 (7), 92 (50), 77 (25), 50 (100). – $C_{24}H_{19}NO_3$ (369.41): calcd. C 78.03, H 5.18, N 3.79; found C 77.86, H 5.05, N 3.66.

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Graphical synopsis

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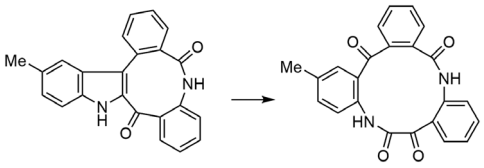
Synthesis and some reactions of functionalized 11,12-dihydro-5*H*-dibenzo[*b*,*g*]azonines



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