The Chemical and Structural Properties of 2-Aminobenzylamine Derivatives

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We report a conventional and simple method to synthesize quinazoline and benzodiazepine derivatives by treatment of 2-aminobenzylamine (1) with several π -electron-deficient compounds. Quinazoline derivatives were obtained by treatment of 1 with either tetracyanoethylene or 7,7,8,8-tetracyanoquinodimethane. Benzodiazepine derivatives were formed when 1 was reacted with either 2,3dichloro-1,4-naphthoquinone or 2,3-dichloro-5,6-dicyano-1,4-benzoquinone. Fused quinazoline and benzoazepine derivatives were formed by dry heating of 1 with either naphthalic anhydride, *cis*-1,2,3,6-tetrahydrophthalic anhydride, tetrachlorophthalic anhydride and/or diphenic anhydride, respectively. The NMR spectra and the mass spectrometric data as well as elemental analyses of all new products are consistent with the proposed structures. The structures of the quinazoline derivatives 26 and 28 were further confirmed by single-crystal X-ray structure determination. Plausible mechanisms for the formation of several products are discussed.

Key words: 2-Aminobenzylamine, π Acceptors, Anhydrides, Quinazolines, Diazepines

Introduction

Nitrogen-containing heterocycles are an important class of compounds in medicinal chemistry [1]. There has been considerable interest in the development of reliable and simple preparative methods for the production of quinazolines [2], because they and their ring-fused derivatives display a broad spectrum of biological activities [3-5], like *e. g.* antitubercular, analgesic, antiinflammatory, and anti-bacterial, analgesic, and many other properties. These examples clearly demonstrate the remarkable potential of quinazoline derivatives as a source of useful pharmacophores for new drug development. Substituted quinazolines have been synthesized by a number of methods involving several substrates such as 2-amino-N'-aryl-benzamidines [6-8] and 2aminobenzylamine [9, 10]. A further important class of heterocycles is furnished by benzodiazepines [11]. Benzodiazepine derivatives are widely distributed in nature, and they represent a class of heterocycles which possesses a wide range of biological applications. Many of them are for example widely used as antileukaemic, antiplatelet, anticonvulsant, and neuroleptic agents [12]. Some heterocycles containing benzodiazepine moieties were also found to have anti-inflammatory, antiviral, anti-HIV-1, antimicrobial, and antitumour activities [13]. Apart from their biological importance, benzodiazepines are valuable synthons for the preparation of fused ring compounds, such as triazolo, thiazolo, imidazo and pyrimidobenzo-diazepines [14]. Although many methods for synthesizing benzodiazepine ring systems have been reported, they continue to receive much attention [11]. We found that reaction of either 2,3-dichloro-1,4-naphthoquinone (DCHNQ) or 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) with 2-amino-N'-arylbenzamidines led to the formation of benzodiazepine derivatives via charge-transfer (CT) complexes [15]. The formation of CT complexes has long been recognized as an important phenomenon in many chemical processes [16], and this approach led us to synthesize several heterocyclic systems that could not be obtained by usual methods [17].

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Results and Discussion

On continuing our studies in electron donoracceptor interactions (EDA) as well as developing conventional approaches for the synthesis of Nheterocycles, we reported very recently highly efficient approaches for the synthesis of quinazoline [6-8] and benzodiazepine [12] derivatives. The study was initiated by investigating the reaction of 2aminobenzylamine (1) with the acceptors 2, 5, 8, and 11. We have found that treatment of 1 with TCNE 5 and/or TCNQ 11 in anhydrous ethyl acetate leads to the formation of deep-red or green complexes. The color gradually disappears to give rise to the formation of the quinazoline derivatives 6, 7 and 12, respectively, in excellent yield (Scheme 1). The assigned molecular structures of the new compounds were based on spectroscopic analysis including IR, NMR, MS, and elemental analysis data.

The product **6** displayed in its IR spectrum strong absorption maxima at v = 3272 and 3218 cm^{-1} indicating the presence of two different NH groups; the CN groups absorb at v = 2207 and 2175 cm^{-1} .

Furthermore, the IR spectrum reveals no absorption bands characteristic of NH₂ groups. The ¹H NMR spectrum of **6** exhibits, besides the signals from the aromatic protons, two sharp singlets at $\delta = 10.26$ and 8.32 ppm for the two different NH groups, and a doublet at $\delta = 4.38$ ppm is assigned to the aliphatic CH₂ protons with a coupling constant of J = 1.00 Hz. The ¹³C NMR spectrum showed signals from eleven distinct carbon atoms, two of them at $\delta = 119.16$ and 117.62 ppm characteristic of cyano groups. The signal at $\delta = 41.12$ ppm was assigned to the carbon atom of the CH₂ group. Both MS and elemental analysis confirm the molecular formula of **6** as C₁₁H₈N₄.

The ¹H NMR of compound 7 reveals, in addition to the three multiplets assignable to the NH group and aromatic protons, a singlet at $\delta = 4.73$ ppm for the two aliphatic methylene protons. The IR spectrum shows bands at v = 3278 and 2180 cm^{-1} characteristic for NH and CN, respectively. Formation of the quinazolines 6 and 7 is suggested to proceed according to the mechanism outlined in Schemes 2 and 3. In this case the reaction sequence would start by the formation of the adducts 13-15. Losing a molecule of either HCN or malononitrile furnishes the quinazolines 6 and 7, respectively.

Addition of the electron donor 1 to the electron acceptor 11 in anhydrous ethyl acetate at room temperature led to an EDA complex with a deep-red color, which gradually disappeared to give a single new reaction product 12 (TLC analysis). The mass spectrum and elemental analysis suggest the molecular formula of 12 as $C_{17}H_{12}N_4$. The IR spectrum of 12 shows sharp absorptions characteristic of differ-



Scheme 1. Reaction of 2-aminobenzylamine (1) with π -electron-deficient compounds.



Scheme 2. Mechanism for the formation of quinazoline derivative 6.



Scheme 3. Mechanism for the formation of quinazoline derivative 7.

ent cyano groups at v = 2185 and 2133 cm^{-1} , and of the NH groups at v = 3271, 3245 cm^{-1} . Its ¹H NMR spectrum reveals, apart from the aromatic protons, two broad singlets at $\delta = 11.51$ and 10.12 ppm for the two different NH groups; the cyclohexadiene protons appear as two doublets at $\delta = 7.60$ and 6.90 ppm with similar coupling constants of J = 8.81 Hz, and the two aliphatic methylene protons as a singlet at $\delta =$ 4.76 ppm.

Benzonaphthodiazepine derivative **3** rather than **4** is formed on stirring compound **1** with DCHNQ **2** in ethyl acetate at room temperature. One indication of this is the coupling between the methylene protons (doublet at $\delta = 4.33$ ppm with J = 5.25 Hz) and the adjacent *sp*³ NH proton (triplet at $\delta = 8.38$ ppm with J = 5.10 Hz); in **4** both of the NH and methylene protons should appear as two different singlets. The IR spectrum of **3** displayed absorptions at v = 3284 (NH) and 1630 cm⁻¹ (CO). In its ¹³C NMR spectrum, the C=O and C=N carbon atoms appear at $\delta = 174.59$ and 151.14 ppm, respectively, while the methylene carbon

bon appears at $\delta = 44.80$ ppm. The brutto formula C₁₇H₁₁ClN₂O of **3** was confirmed by the mass spectrum, which exhibited the molecular ion at m/z = 294 (100%).

Treatment of **1** with DDO **7** in ethyl acetate led to the dibenzodiazepine 8 rather than to its isomer 9, the evidence for which is related to the case of 3 and 4 (see above). The IR spectrum of compound 8 showed three strong absorptions at v = 3296, 2209 and 1663 cm⁻¹, indicating the presence of NH, CN and CO groups, respectively. In the ¹H NMR spectrum the NH group appeared as a triplet at $\delta = 9.85$ ppm with J = 5.16 Hz, whereas the methylene protons form a doublet at $\delta =$ 4.37 ppm with J = 5.27 Hz. The ¹³C NMR spectrum of 8 showed fourteen distinct resonances, of which those at $\delta = 172.15$ and 45.24 ppm are assigned to the carbonyl and the methylene carbon atoms, respectively. The molecular formula of dibenzodiazepine 8 is supported by elemental analysis and the mass spectrum with the expected molecular ion peak as the base peak.

Heating of 1 with NQ 16 and/or BQ 18 in anhydrous ethyl acetate produced 17 and 19, respectively (Scheme 4). The ¹H NMR spectrum showed all the expected signals; in addition to the aromatic signals a triplet at $\delta \approx 8.14$ ppm for the NH protons, and a singlet of two protons at $\delta \approx 5.00$ ppm for the NH₂ protons were observed. In addition, a characteristic doublet at $\delta \approx 4.20$ ppm with a coupling constant $J \approx$ 6.00 Hz for the methylene protons was noted. The IR spectra showed bands at $v \approx 3420, 3390, 3220 \,\mathrm{cm}^{-1}$ for the NH₂ and NH groups, whereas the carbonyl groups absorbed at $v \approx 1670$ and 1629 cm^{-1} . Furthermore, the structure assigned for the products 17 and 19 were fully supported by their mass spectra, which showed their molecular formulae C₁₇H₁₄N₂O₂ and C₂₀H₂₀N₄O₂, respectively.

Heating of **1** with dimethyl acetylenedicarboxylate (DMAD, **20**) in anhydrous chloroform provides quinazoline derivative **22**, which might be in equilibrium with its diazepine isomer **21** (Scheme 4). The results obtained from elemental microanalysis and the IR, ¹H NMR, ¹³C NMR and mass spectroscopic data are in agreement with the assigned structure. The IR spectrum showed two strong absorptions at v = 3362 and 1729 cm^{-1} , indicating the presence of NH and CO groups, respectively. However, the ¹H NMR spectrum shows two broad resonances at $\delta = 4.88$ and 2.60 ppm for the two exchangeable protons of the two NH groups. Moreover, there are two singlets at $\delta =$ 3.76 and 3.70 ppm for the methyl ester protons and a doublet at $\delta = 3.94$ ppm for the -NH–CH₂- protons with J = 4.35 Hz. The ¹H NMR spectrum of **21** displayed two doublets at $\delta = 3.05$ and 2.85 ppm with similar coupling constants J = 15.63 Hz referred to the AB spin system, along with characteristic resonances for the four aromatic protons. The presence of the AB spin system in the ¹H NMR spectrum indicates the formation of the product 21. As the result of the expected instability of the benzodiazepine derivative 21, due to its angle strain, one can expect its rearrangement into the more stable quinazoline derivative 22. Isomerization between 21 and 22 has been noticed and confirmed by measuring the NMR spectrum of the sample after 1 h. The data reveals the presence of a quaternary carbon atom resonating in the ¹³C NMR spectrum at $\delta = 70.63$ ppm characteristic for the NH-C-NH carbon atom, in addition to the presence of a signal at $\delta = 43.24$ ppm for the methylene carbon of the $CH_2CO_2CH_3$ group. The two carbonyl groups of the product have been recorded in the ¹³C NMR spectrum at $\delta = 172.31$ and 170.22 ppm. Furthermore, the methylene carbon atom of the CH₂NH group resonates at $\delta = 42.48$ ppm, and the methyl ester carbon atoms at $\delta = 52.92$ and 51.93 ppm. The mass spectrum of this sample gives the molecular ion peak at m/z = 264 which is in accordance with the molecular mass (264.11) of compound 22.



Scheme 4. Reactions of 1 with CHL-p, NQ, BQ and DMAD.

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Scheme 5. Reactions of compound 1 with selected anhydrides.

The substituted quinone 24 was obtained in excellent yield by the reaction of 2-amino-benzylamine (1)with CHL-p 23 in absolute ethyl acetate at room temperature (Scheme 4). The deep-green solution initally formed rapidly turned to yellowish green while a precipitate was formed. The structure of 24 was confirmed by elemental analysis and spectral data. Three IR bands at $v = 3421, 3349, 3326 \text{ cm}^{-1}$ are assignable to NH₂ and NH groups, while the carbonyl group appeared at $v = 1638 \text{ cm}^{-1}$. In the ¹H NMR spectrum the NH and NH₂ protons appeared at $\delta = 8.18$ and 5.11 ppm, respectively; six multiplets in the region at $\delta = 7.17 - 6.50$ ppm are assigned to aromatic protons, and a singlet at $\delta = 4.80$ ppm to the methylene protons. In the ¹³C NMR spectrum signals of most of the carbon atoms of CH_2 , CH, C = O and the aromatic system could be assigned and were in agreement with the proposed structure (see spectral data in the Experimental Section). Both mass spectrum and elemental analysis confirm the molecular formula of the product 24 as C₂₀H₁₈Cl₂N₄O₂.

Recently, we have reported that diamino compounds can be employed as key starting materials for the synthesis of diverse nitrogen bridgehead compounds [6-8, 15]. This prompted us to investi-

gate the reactivity of 1 towards electrophilic reagents such as naphthalic anhydride, tetrahydrophthalic anhydride, diphenic anhydride, and tetrachlorophthalic anhydride (Scheme 5). The conditions for the reaction between the reactant 1 and the anhydrides 25, 27, 29, and 31 were investigated in a number of trials, and the optimized conditions were identified by varying the reagent concentrations, the reaction time and/or temperature. We found that the optimum conditions for this reaction involve mixing both reaction partners in equimolar amounts and heating them at 200 °C for 5 min. This reaction sequence is conveniently performed in one-pot procedures without isolation of the intermediates. Previous studies on refluxing 1 with anhydride 27 in absolute EtOH afforded a mixture of two products in low yields [18]. Thus when a mixture of **1** and anhydride **25** were dry heated at 200 °C for 5 minutes, the quinazoline derivative 26 was formed as colorless crystals in excellent yield (Scheme 5).

The structure of product **26** was corroborated by its elemental analysis and IR, ¹H and ¹³C NMR spectroscopic data. The mass spectrum of **26** displayed the molecular ion (M⁺) at m/z = 238 as the base peak. The ¹H NMR spectrum of **26** exhibited four differ-



Fig. 1. The molecular structure of **26** in the solid state with the crystallographic numbering scheme adopted.

ent multiplets at $\delta = 7.24 - 7.00$ ppm for the aromatic protons, along with five different characteristic multiplets for the six protons of the cyclohexene moiety at $\delta = 3.38 - 2.24$ ppm. Furthermore, the methylene proton resonated as a sharp singlet at $\delta = 4.79$ ppm. The proton-decoupled ¹³C NMR spectrum of **26** showed 14 distinct resonance lines in agreement with the proposed structure. Unambiguous evidence for the proposed structure of **26** was finally obtained by singlecrystal X-ray-diffraction analysis as shown in Fig. 1.

Similarly, heating of **1** with naphthalic anhydride (NA, 27) in the absence of solvents for 5 minutes at 200 °C afforded the quinazoline derivative 28 as orange crystals in excellent yield as shown in Scheme 5. The structure of the quinazoline derivative 28 was established by conventional spectroscopic methods as well as elemental analysis. It exhibits two strong IR absorption bands at 1694 and 1623 cm⁻¹ for the CO and C=N groups, respectively. The same carbon atoms resonated in the ¹³C NMR at $\delta = 171.16$ and 160.73 ppm, respectively. The ¹H NMR spectrum of **28** shows characteristic signals in the aromatic region at $\delta =$ 8.51–6.26 ppm. A singlet at $\delta = 5.06$ ppm was assigned to the methylene protons. The carbon atom of this methylene group resonated in the $\ensuremath{^{13}\text{C}}$ NMR at $\delta = 40.33$ ppm. The mass spectrum exhibits the molecular ion peak at m/z = 284. Moreover, the structure of 28 was confirmed by an X-ray diffraction study (Fig. 2).

The quinazoline derivative **30** was formed when one equivalent of **1** was fused with one equivalent of the anhydride **29**; its structure was fully supported by elemental analysis and its mass spectrum, which



Fig. 2. The molecular structure of **28** in the solid state with the crystallographic numbering scheme adopted.

confirmed the molecular formula $C_{15}H_6Cl_4N_2O$ (369.92).

The reactivity of 1 towards the anhydride 31 was also studied; as illustrated in Scheme 5 the reaction furnishes the dibenzoazepinoquinazoline 32. Its structure was assigned on the basis of the NMR data and was supported by IR data. The ¹H NMR spectrum of the quinazoline derivative 32 revealed six characteristic multiplets at $\delta = 7.68 - 6.55$ ppm assigned to the twelve aromatic protons. Furthermore, a singlet was present at $\delta = 4.14$ ppm due to the methylene protons. The methylene carbon signal of 32 appeared in the ¹³C NMR spectrum at $\delta = 40.78$ ppm, and the carbonyl carbon atom resonated at $\delta = 175.11$ ppm. The molecular formula of compound 32 is supported by elemental analysis and a mass spectrum that gave the expected molecular ion peak and fragmentation patterns (see Experimental Section).

Conclusion

Herein, we have reported a facile and efficient synthesis of substituted quinazoline and benzodiazepine derivatives by using a one-pot reaction of diverse π acceptors and anhydrides with 2-aminobenzylamine. In all cases the reaction of two components proceeded rapidly to afford the corresponding desired products in excellent yields. The reaction conditions are mild, the work-up is simple, and the steps are automation-friendly. The structures of two selected examples (**26** and **28**) were elucidated by single X-ray diffraction analysis. The mechanism of formation of the obtained products **5**, **6**, **36**, and **37** has been rationalized.

Compound	26	28
Formula	C ₁₅ H ₁₄ N ₂ O	C ₁₅ H ₁₄ N ₂ O
M _r	238.28	278.33
Habit	colorless tablet	colorless tablet
Crystal size, mm ³	$0.35 \times 0.3 \times 0.2$	$0.3\times0.15\times0.1$
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$
Temperature, °C	-133	-173
a, Å	6.1268(2)	5.2041(6)
<i>b</i> , Å	10.5576(3)	17.6877(16)
<i>c</i> , Å	18.0859(5)	14.1232(16)
β , deg	90.357(3)	90.03(2)
V, Å ³	1169.85	1300.0
Ζ	4	4
$D_{\rm calcd.}$, Mg m ⁻³	1.35	1.45
μ (Mo K_{α}), mm ⁻¹	0.1	0.1
<i>F</i> (000), e	504	592
$2\theta_{\rm max}$, deg	60	56.6
Refl. measured / unique / R_{int}	41055 / 3412 /	30329 / 3215 /
	0.028	0.044
Ref. parameters	163	200
$R[F > 4\sigma(F)]$	0.041	0.041
$wR(F^2, \text{ all refls.})$	0.107	0.106
S	1.02	1.06
$\Delta \rho_{\rm max}$, e Å ⁻³	0.35	0.31

Table 1. Crystallographic data for compounds 26 and 28.

Experimental Section

General. All reagents were purchased from Acros and Aldrich companies and were used without further purification. The melting points were measured in capillary tubes without corrections using a Büchi 530 melting point apparatus. The NMR spectra were recorded on a Bruker AM 400 MHz spectrometer with TMS as internal standard; the coupling constants are given in Hz. The mass spectra (EI) were performed using a Finnigan MAT 8430 spectrometer. IR spectra were run from KBr discs using a Bruker Tensor 27 instrument. Chromatography columns were prepared from Merck silica gel 230–240 mesh.

Synthesis of 6-chloro-7,8-dihydro-5H-benzo[e]naphtho[2,1b][1,4]diazepin-5-one (**3**)

To 227 mg (1.0 mmol) of **2** in anhydrous ethyl acetate (10 mL) at room temperature was added dropwise a solution of **1** (122 mg, 1.0 mmol) in anhydrous ethyl acetate (10 mL). The color of the reaction mixture changed to deep red. The mixture was stirred at room temperature for 9 h. A red precipitate separated. The resulting precipitate was filtered, washed with ethyl acetate, dried and recrystallized from EtOH to give the diazepine derivative **3**.

Red powder (yield: 259 mg, 88%), m. p. > 240 °C. – IR (film): v = 3284 (NH), 3066, 2923, 2853 (CH), 1630 (CO), 1590 (C=N), 1539 (C=C) cm⁻¹. – ¹H NMR (400 MHz, [D₆]DMSO): δ = 4.33 (d, 2H, CH₂, *J* = 5.25 Hz), 7.41 – 7.56 (m, 4H), 7.96 – 7.98 (dd, 1H, *J* = 1.72, 7.54 Hz), 7.66 – 7.73 (m, 2H), 8.12 – 8.14 (dd, 1H, *J* = 1.70, 7.66 Hz), 8.38 (t, 1H, NH, *J* = 5.10 Hz). – ¹³CNMR (100 MHz, [D₆]DMSO): δ = 44.80 (CH₂), 103.41 (C), 106.04 (C), 124.61 (CH), 125.74 (CH), 127.14 (CH), 129.06 (CH), 129.11 (C), 129.15 (CH), 130.85 (CH), 131.55 (CH), 132.03 (CH), 135.11 (C), 145.44 (C), 149.41 (C), 151.14 (C=N), 174.59 (CO). – MS (EI, 70 eV): m/z(%) = 297 (5), 296 (30), 294 (100) [M]⁺, 293 (16), 268 (5), 260 (10), 259 (16) [M – HCI]⁺, 251 (4), 233 (2), 232 (8), 231 (9), 229 (18), 217 (4), 203 (10), 190 (2), 176 (5), 165 (4), 156 (4), 134 (2), 128 (4), 115 (10), 102 (16), 89 (12), 77 (4). – C₁₇H₁₁ClN₂O (294.06): calcd. C 69.28, H 3.76, N 9.50; found C 69.17, H 3.75, N 9.43.

Reaction of 2-aminobenzylamine (1) with 1,1,2,2-tetracyanoethylene (5)

To 128 mg (1.0 mmol) of **5** in anhydrous ethyl acetate (20 mL), 122 mg (1.0 mmol) of **1** in 10 mL of anhydrous ethyl acetate was added with stirring within 1/2 h. The mixture was stirred for 7 h at room temperature, during which time a crystalline colorless product separated. The resulting solid material was filtered, and the precipitate was washed with ethyl acetate, dried and recrystallized from ethanol to give the quinazoline derivative **6**. The filtrate was concentrated to dryness, and the residue was subjected to column chromatography using CH₂Cl₂ as an eluent to give the quinazoline derivative **7**.

2-(3,4-Dihydroquinazolin-2(1H)-ylidene)malononitrile (6)

Colorless powder (yield: 147 mg, 75%), m. p. > 240 °C. – IR (film): v = 3272, 3218 (NH), 3168, 3059, 2944, 2870 (CH), 2207, 2175 (CN), 1596, 1552 (C=C) cm⁻¹. – ¹H NMR (400 MHz, [D₆]DMSO): $\delta = 4.38$ (d, 2H, CH₂, J =1.00 Hz), 7.04–7.09 (m, 1H), 7.15 (d, 1H, J = 7.41 Hz), 7.19–7.25 (m, 2H), 8.32 (s, 1H, NH), 10.26 (s, 1H, NH). – ¹³CNMR (100 MHz, [D₆]DMSO): $\delta = 41.12$ (CH₂), 115.95 (CH), 117.62 (C), 119.16 (C), 124.08 (CH), 125.91 (CH), 128.16 (CH), 133.71 (C), 158.05 (C). – MS (EI, 70 eV): m/z(%) = 197 (7) $[M+1]^+$, 196 (75) $[M]^+$, 195 (100) $[M-1]^+$, 168 (22) $[M - \text{HCN}]^+$, 141 (10), 129 (7), 116 (4), 104 (6), 97 (4), 89 (2), 77 (8). – C₁₁H₈N₄ (196.07): calcd. C 67.34, H 4.11, N 28.55; found C 67.25, H 4.13, N 28.49.

1,4-Dihydroquinazolin-2-carbonitrile (7)

Deep-red powder (yield: 35 mg, 22%), m.p. 121–123 °C. – IR (film): v = 3278 (NH), 3135, 3059, 2976, 2864 (CH), 2180 (CN), 1695, 1619, 1575 (C=N, C=C) cm⁻¹. – ¹H NMR (400 MHz, CDCl₃): $\delta = 4.73$ (s, 2H, CH₂), 6.91 (d, 1H, J = 7.41 Hz), 7.09–7.13 (m, 2H), 7.20–7.24 (m, 1H), 7.31–7.37 (m, 1H). – ¹³C NMR (100 MHz, CDCl₃): δ = 42.02 (CH₂), 108.83 (C), 126.01 (CH), 126.41 (CH), 128.12 (C), 128.55 (CH), 128.59 (CH), 129.68 (CH), 147.49 (C). – MS (EI, 70 eV): m/z(%) = 158 (5) [M+1]⁺, 157 (40) [M]⁺, 156 (100) [M-1]⁺, 129 (22) [M–HCN]⁺, 102 (6), 77 (10). – C₉H₇N₃ (157.06): calcd. C 68.78, H 4.49, N 26.74; found C 68.61, H 4.44, N 26.60.

Synthesis of 6,7-dichloro-8-oxo-10,11-dihydro-8Hdibenzo[b,e][1,4]diazepine-9-carbonitrile (9)

To 227 mg (1.0 mmol) of **8** in anhydrous ethyl acetate (15 mL) was added dropwise a solution of compound **1** (122 mg, 1.0 mmol) in anhydrous ethyl acetate (10 mL) at room temperature. The color of the reaction mixture changed to deep red. The mixture was stirred at room temperature for 4 h. A red precipitate separated, which was filtered and washed with ethyl acetate, dried and recrystallized from EtOH to give the diazepine derivative **9**.

Deep-red powder (yield: 264 mg, 87%), m.p. 201-204 °C. – IR (film): v = 3296 (NH), 3015, 2921, 2875 (CH), 2209 (CN), 1663 (CO), 1559 (C=C) cm⁻¹. $- {}^{1}$ H NMR (400 MHz, [D₆]DMSO): $\delta = 4.37$ (d, 2H, J = 5.27 Hz, CH₂), 7.34 - 7.39 (m, 1H), 7.45 - 7.49 (m, 1H), 7.59 (d, 2H, J = 2.96 Hz), 9.85 (t, 1H, NH, J = 5.16 Hz). – ¹³CNMR (100 MHz, $[D_6]$ DMSO): $\delta = 45.24$ (CH₂), 79.75 (C), 114.79 (C), 127.59 (CH), 128.94 (CH), 129.57 (CH), 130.22 (C), 134.57 (C), 131.46 (CH), 140.11 (C), 144.51 (C), 147.35 (C), 155.60 (C=N), 172.15 (CO). - MS (EI, 70 eV): m/z(%) = 307 (30) $[M+4]^+$, 305 (75) $[M+2]^+$, 303 (100) [M]+, 289 (35), 277/275 (35/55) [M-HCN]+, 269 (20), 255 (10), 240 (35) [M - (HCN + HCl)]⁺, 213 (10), 204 (10) $[M - (HCN + 2HCl)]^+$, 179 (10), 177 (12), 163 (4), 153 (6), 137 (8), 104 (6), 77 (8). - C₁₄H₇Cl₂N₃O (303.00): calcd. C 55.29, H 2.32, N 13.82; found C 55.18, H 2.34, N 13.70.

Synthesis of 2-(4-(3,4-dihydroquinazolin-2(1H)ylidene)cyclohexa-2,5-dien-1-ylidene)malononitrile (12)

To 204 mg (1.0 mmol) of **11** in anhydrous ethyl acetate (30 mL) was added dropwise a solution of **1** (122 mg, 1.0 mmol) in anhydrous ethyl acetate (10 mL) at room temperature. The color of the reaction mixture changed to green. The mixture was stirred at room temperature for 3 h. A yellowish-green precipitate separated, which was filtered and washed with ethyl acetate, dried and recrystallized from DMF to give the quinazoline derivative **12**.

Yellowish-green powder (yield: 261 mg, 96%), m. p. > 240 °C. – IR (film): v = 3271, 3245 (NH), 3155, 3025, 2937,

2871 (CH), 2185, 2133 (CN), 1598, 1566 (C=C) cm⁻¹. – ¹H NMR (400 MHz, [D₆]DMSO): δ = 4.76 (s, 2H, CH₂), 6.90 (d, 2H, *J* = 8.81 Hz), 7.20–7.27 (m, 3H), 7.32–7.38 (m, 1H), 7.60 (d, 2H, *J* = 8.81 Hz), 10.12 (br s, 1H, NH), 11.51 (br s, 1H, NH). – ¹³CNMR (100 MHz, [D₆]DMSO): δ = 41.62 (CH₂), 112.14 (C), 116.84 (CH), 117.38 (2CH), 118.55 (C), 122.93 (C), 126.07 (CH), 126.46 (CH), 128.63 (CH), 128.85 (2CH), 132.61 (C), 149.92 (C), 156.48 (C). – MS (EI, 70 eV): m/z(%) = 273 (15) [M+1]⁺, 272 (100) [M]⁺, 243 (30) [M – HCN]⁺, 215 (10), 205 (6), 178 (10), 164 (2), 151 (5), 141 (10), 129 (12), 122 (10), 114 (5), 104 (25), 95 (3), 85 (3), 76 (20). – C₁₇H₁₂N₄ (272.11): calcd. C 74.98, H 4.44, N 20.58; found C 74.87, H 4.41, N 20.47.

Reactions of 2-aminobenzylamine (1) with 1,4-naphthoquinone (16) and/or 1,4-benzoquinone (18)

In a typical experiment, reactant 1 (122 mg, 1.0 mmol) was added dropwise to a well-stirred solution of 1,4-naphthoquinone (16) (158 mg, 1 mmol) and/or 1,4-benzoquinone (18) (108 mg, 1.0 mmol) in anhydrous ethylacetate (15 mL) at room temperature. The color of the parent quinone disappeared, and the solution turned brown. The solution was heated under reflux conditions for 3-5 h. The progress of the reaction was monitored *via* TLC. The volume of the solution was reduced to half under reduced pressure. A brown precipitate appeared which was filtered, dried at room temperature and recrystallized from EtOH to obtain the desired products 17 and 19.

2-((2-Aminobenzyl)amino)naphthalene-1,4-dione (17)

Deep-brown powder (yield: 220 mg, 79%), m.p. 132 - 134 °C. – IR (film): v = 3425, 3393, 3223 (NH₂,NH), 3074, 3028, 2959, 2827 (CH), 1671, 1601 (CO), 1568 (C=C) cm⁻¹. – ¹H NMR (400 MHz, [D₆]DMSO): δ = 4.22 (d, 2H, CH₂, J = 6.03 Hz), 5.08 (br s, 2H, NH₂), 6.50 (t, 1H, J = 6.46 Hz), 6.61 - 6.64 (dd, 1H, J = 1.16, 8.52 Hz), 7.22(s, 1H), 6.94–6.98 (m, 2H), 7.63 (t, 1H, J = 7.47 Hz), 7.73 (t, 1H, J = 7.51 Hz), 8.04 (t, 2H, J = 5.60 Hz), 8.13 (t, 1H, NH, J = 6.12 Hz). - ¹³CNMR (100 MHz, [D₆]DMSO): $\delta = 41.74$ (CH₂), 115.67 (CH), 119.01 (C), 122.82 (C), 125.37 (C), 126.58 (CH), 127.02 (CH), 127.11 (CH), 128.00 (C), 128.46 (CH), 130.74 (CH), 131.66 (CH), 133.12 (CH), 142.16 (C), 151.10 (C), 172.54 (CO), 182.53 (CO). -MS (EI, 70 eV): m/z(%) = 280 (4) $[M+2]^+$, 279 (16) $[M+1]^+$, 278 (54) $[M]^+$, 261 (6) $[M-NH_3]^+$, 185 (12), 172 (32), 156 (6), 121 (10), 106 (68), 93 (5), 76 (10). -C17H14N2O2 (278.11): calcd. C 73.37, H 5.07, N 10.07; found C 73.19, H 5.03, N 9.93.

2,5-Bis((2-aminobenzyl)amino)cyclohexa-2,5diene-1,4-dione (**19**)

Brown powder (yield: 327 mg, 94%), m. p. 219-222 °C. - IR (film): v = 3429, 3403, 3352, 3329 (NH₂,NH), 3074, 3028, 2917, 2873 (CH), 1629 (CO), 1583 (C=C) cm⁻¹. -¹H NMR (400 MHz, [D₆]DMSO): $\delta = 4.20$ (d, 4H, 2CH₂, J = 6.24 Hz), 5.14 (s, 4H, NH₂), 5.19 (s, 2H), 6.50 (t, 2H, J = 6.46 Hz), 6.61 - 6.64 (dd, 2H, J = 1.16, 8.52 Hz), 6.94-6.98 (m, 4H), 8.15 (t, 2H, 2NH, J = 6.20 Hz). -¹³CNMR (100 MHz, $[D_6]$ DMSO): $\delta = 42.46$ (2CH₂), 93.06 (2CH), 114.94 (2CH), 115.74 (2CH), 119.18 (2C), 128.00 (2CH), 128.46 (2CH), 146.16 (2C), 151.10 (2C), 177.53 (2CO). – MS (EI, 70 eV): m/z(%) = 350 (2) $[M+2]^+$, 349 (10) $[M+1]^+$, 348 (40) $[M]^+$, 331 (6) $[M-NH_3]^+$, 314 (4), 295 (5), 282 (2), 242 (48), 225 (30), 198 (5), 181 (2), 169 (5), 121 (5), 106 (100), 93 (5), 77 (12). - C₂₀H₂₀N₄O₂ (348.16): calcd. C 68.95, H 5.79, N 16.08; found C 68.79, H 5.71, N 15.89.

Synthesis of dimethyl 2,3,4,5-tetrahydro-1Hbenzo[e][1,4]diazepine-2,3-dicarboxylate (**21**)/methyl 2-(2-methoxy-2-oxoethyl)-1,2,3,4-tetrahydroquinazoline-2carboxylate (**22**)

Into a 250 mL two-necked round bottom flask containing a solution of **20** (142 mg, 1.0 mmol) in absolute CHCl₃ (10 mL), a solution of **1** (122 mg, 1.0 mmol) in absolute CHCl₃ (10 mL) was added dropwise with stirring. The mixture was stirred at room temperature for 1 h, and at reflux for 3 h monitored by TLC. The solvent was evaporated under vacuum, and the residue was purified by dissolving in CH₂Cl₂ (5 mL) and then subjected to preparative plate chromatography (silica gel, diethyl ether). The obtained products **21** and/or **22** were detected by spectral analyses.

Colorless oil (yield: 214 mg, 81%). – IR (film): v =3362 (NH), 3008, 2953, 2894 (CH), 1729 (CO), 1609, 1592 (C=C) cm⁻¹. – ¹H NMR (400 MHz, CDCl₃): $\delta = 2.60$ (br s, 1H, NH), 2.85 (d, 1H, J = 15.63 Hz, -CH–CO₂CH₃), 3.05 (d, 1H, J = 15.63 Hz, -CH-CO₂CH₃), 3.70 (s, 3H, $-CH_3$), 3.94 (d, 2H, J = 4.35 Hz, $-CH_2$), 3.76 (s, 3H, $-CH_3$, 4.84 (br s, 1H, 1NH), 6.60–6.57 (dd, 1H, J = 0.92, 7.97 Hz, 6.72 - 6.67 (ddd, 1H, J = 1.14 Hz), 6.89 - 6.86 (dd, J = 1.14 Hz), 6.80 - 6.86 (dd, J = 1.14 Hz), 6.80 - 61H, J = 1.02, 7.50 Hz), 7.00 (t, 1H, J = 7.00 Hz). - ¹³C NMR (100 MHz, CDCl₃): $\delta = 42.48$ (CH₂), 43.24 (CH₂), 51.93 (CH₃), 52.92 (CH₃), 70.63 (C), 115.18 (CH), 118.47 (CH), 119.93 (C), 125.83 (CH), 127.38 (CH), 141.10 (C), 170.22 (CO), 172.31 (CO). – MS (EI, 70 eV): m/z(%) = 265(4) $[M+1]^+$, 264 (18) $[M]^+$, 232 (7), 206 (14), 205 (96), 199 (6), 191 (18), 190 (62), 173 (10), 157 (38), 145 (10), 130 (40), 129 (100), 106 (46), 77 (20).

Synthesis of 2,5-bis((2-aminobenzyl)amino)-3,6dichlorocyclohexa-2,5-diene-1,4-dione (24)

A solution of compound 1 (122 mg, 1.0 mmol) in anhydrous ethyl acetate (10 mL) was added to a magnetically stirred solution of 2,3,5,6-tetrachloro-1,4-benzoquinone (23) (246 mg, 1.0 mmol) in anhydrous ethyl acetate (20 mL). The yellow color of the solution changed to deep green and then to yellowish green. The reaction mixture was stirred at room temperature for 5 h. After completion of the reaction (followed by TLC), the formed precipitate was collected by filtration, washed and recrystallized from EtOH to afford the product 24.

Pale-brown powder (yield: 408 mg, 98%), m.p. $164 - 167 \degree C. - IR (film): v = 3421, 3349, 3326 (NH₂,NH),$ 3025, 2996, 2921, 2849 (CH), 1638 (CO), 1564 (C=C) cm^{-1}. – $^1\mathrm{H}$ NMR (400 MHz, [D_6]DMSO): $\delta=4.80$ (s, 4H, 2CH₂), 5.11 (br s, 4H, 2NH₂), 6.50-6.59 (m, 2H), 6.64-6.69 (m, 1H), 6.70-6.72 (m, 1H), 6.86-6.90 (m, 1H), 6.95-6.99 (m, 1H), 7.03-7.07 (m, 1H), 7.15-7.17 (dd, 1H, J = 1.20, 7.49 Hz), 8.18 (br s, 2H, 2 NH). – ¹³CNMR (100 MHz, [D₆]DMSO): $\delta = 39.49$ (CH₂), 114.90 (C), 115.62 (CH), 116.05 (CH), 116.18 (CH), 117.28 (CH), 122.06 (C), 121.37 (C), 126.91 (C), 127.30 (CH), 127.87 (CH), 129.39 (CH), 130.52 (CH), 144.43 (C), 146.95 (C). – MS (EI, 70 eV): m/z(%) = 420/418/416(2/4/6) [M⁴⁺/M²⁺/M⁺], 380 (4) [M-HCl]⁺, 362 (2) $[M - (HCl + H_2O)]^+$, 346 (2), 313/311/309 (10/16/12), 277/275 (5/8), 259 (7), 208 (6), 179 (3), 171 (4), 143 (3), 131 (4), 118 (7), 106 (100), 93 (5), 77 (12). $- C_{20}H_{18}Cl_2N_4O_2$ (416.08): calcd. C 57.57, H 4.35, N 13.43; found C 57.47, H 4.33, N 13.35.

General procedures for the reaction of **1** with anhydrides **25**, **27**, **29**, and **31**

In a fusion tube provided with a condenser, a mixture of compound 1 (122 mg, 1.0 mmol) and 1.0 mmol of the anhydride (either 25, 27, 29 or 31) was heated in an oil bath at 200 °C for 5 min. Then the mixture was cooled to room temperature and poured into 20 mL Et_2O . The obtained solids were collected and recystallized from EtOH or DMF to give the products 26, 28, 30 and 32.

1,4,4a,12a-Tetrahydroisoindolo[1,2-b]quinazolin-12(10H)one (**26**)

Colorless crystals (yield: 226 mg, 95%), m. p. 154–156 °C. – IR (film): v = 3039, 2944, 2898 (CH), 1730 (CO), 1641 (C=N), 1599, 1578 (C=C) cm⁻¹. – ¹H NMR (400 MHz, CDCl₃): $\delta = 2.24-2.30$ (m, 1H), 2.34–2.40 (m, 1H), 2.61–2.69 (m, 2H), 3.01–3.06 (m, 1H), 3.32–3.38 (m, 1H), 4.79 (s, 2H, CH₂), 5.90–5.93 (m, 2H), 7.00–7.03 (m, 1H), 7.10–7.14 (m, 1H), 7.21–7.24

(m, 2H). $-{}^{13}$ CNMR (100 MHz, CDCl₃): $\delta = 23.25$ (C H₂), 25.27 (C H₂), 37.36 (CH), 38.66 (CH), 41.55 (CH₂), 126.09 (CH), 126.40 (CH), 126.42 (CH), 127.73 (CH), 128.06 (CH), 128.75 (CH), 140.39 (C), 160.73 (C=N), 178.36 (CO). - MS (EI, 70 eV): m/z(%) = 240 (3) [M+2]⁺, 239 (12) [M+1]⁺, 238 (100) [M]⁺, 233 (2), 223 (10), 209 (25), 195 (8), 183 (18), 168 (6), 155 (5), 144 (6), 132 (12), 116 (3), 104 (12), 97 (4), 91 (6), 76 (14). - C₁₅H₁₄N₂O (238.11): calcd. C 75.61, H 5.92, N 11.76; found C 75.50, H 5.90, N 11.67.

Benzo[4,5]isoquinolino[1,2-b]quinazolin-7(9H)-one (28)

Orange crystals (yield: 210 mg, 74%), m. p. 211-215 °C. - IR (film): v = 3064, 2967 (CH), 1737, 1694 (CO), 1623 (C=N), 1588, 1560 (C=C) cm⁻¹. – ¹H NMR (400 MHz, $[D_6]DMSO$: $\delta = 5.06$ (s, 2H, CH₂), 6.46 (t, 1H, J = 7.60 Hz), 6.69 (d, 1H, J = 7.47 Hz), 6.96 – 7.02 (m, 1H), 7.18-7.28 (m, 1H), 7.68-7.91 (m, 3H), 8.36-8.51 (m, 3H). – ¹³CNMR (100 MHz, $[D_6]$ DMSO): $\delta = 40.33$ (CH₂), 114.33 (CH), 115.98 (CH), 118.84 (C), 119.71 (C), 121.68 (C), 125.76 (CH), 126.60 (CH), 127.15 (CH), 127.21 (CH), 127.87 (CH), 128.28 (C), 130.95 (CH), 132.38 (CH), 134.45 (CH), 135.30 (C), 146.14 (C), 160.73 (C=N), 171.16 (CO). - MS (EI, 70 eV): m/z(%) = 286 (3) $[M+2]^+$, 285 (14) [M+1]⁺, 284 (65) [M]⁺, 283 (100), 255 (12), 227 (5), 198 (4), 180 (2), 152 (8), 142 (6), 127 (10), 114 (2), 99 (2), 76 (5). - C₁₉H₁₂N₂O (284.09): calcd. C 80.27, H 4.25, N 9.85; found C 80.21, H 4.26, N 9.78.

1,2,3,4-Tetrachloroisoindolo[*1,2-b*]*quinazolin-12*(*10H*)*-one* (**30**)

Yellow powder (yield: 336 mg, 91%), m. p. 159–161 °C. – IR (film): v = 3054, 2916 (CH), 1722 (CO), 1633 (C=N), 1601 (C=C) cm⁻¹. – ¹H NMR (400 MHz, [D₆]DMSO): $\delta = 4.37$ (s, 2H, CH₂), 6.27–6.29 (dd, 2H, J = 1.18, 7.96 Hz), 7.58–7.60 (dd, 2H, J = 1.57, 7.60 Hz). – ¹³CNMR (100 MHz, [D₆]DMSO): $\delta = 38.82$ (CH₂), 116.39 (CH), 118.31 (CH), 119.75 (C), 126.83 (C), 127.92 (C), 128.67 (C), 128.98 (C), 129.21 (C), 129.50 (C), 130.25 (CH), 133.27 (CH), 139.07 (C), 146.31 (C), 163.54 (C). – MS (EI, 70 eV): m/z(%) = 374 (15), 372 (52), 370 (100), 368 (68) [M]⁺, 336 (8), 308 (6), 299 (5), 271 (6), 236 (6), 209 (3), 186 (6), 172 (2), 153 (5), 135 (3), 119 (4), 102 (5), 76 (4). - C $_{15}H_6Cl_4N_2O$ (369.92): calcd. C 48.43, H 1.63, N 7.53; found C 48.29, H 1.60, N 7.42.

Dibenzo[3,4:5,6]azepino[2,1-b]quinazolin-9(11H)-one (32)

Colorless powder (yield: 214 mg, 69%), m. p. 88–91 °C. – IR (film): v = 3059, 2929, 2872 (CH), 1709 (CO), 1596 (C=N), 1540 (C=C) cm⁻¹. – ¹H NMR (400 MHz, CDCl₃): $\delta = 4.14$ (s, 2H, CH₂), 6.50–6.55 (m, 3H), 6.57–6.85 (m, 1H), 6.99–7.18 (m, 3H), 7.28–7.37 (m, 3H), 7.46–7.51 (m, 1H), 7.62–7.68 (m, 1H). – ¹³CNMR (100 MHz, CDCl₃): $\delta = 40.78$ (CH₂), 116.18 (CH), 118.42 (CH), 127.10 (CH), 127.71 (CH), 127.83 (CH), 128.96 (CH), 129.89 (CH), 130.00 (CH), 130.19 (CH), 130.67 (CH), 134.65 (C), 139.48 (C), 175.11 (CO). – MS (EI, 70 eV): m/z(%) = 312 (2) [M+2]⁺, 311 (8) [M+1]⁺, 310 (26) [M]⁺, 309 (15) (M– 1]⁺, 282 (30), 281 (65), 254 (10), 223 (4), 206 (4), 197 (8), 181 (18), 152 (22), 144 (10), 121 (60), 106 (30), 76 (12). – C₂₁H₁₄N₂O (310.11): calcd. C 81.27, H 4.55, N 9.03; found C 81.12, H 4.51, N 8.90.

X-Ray structure determinations

Numerical details are presented in Table 1. *Data collection and reduction*: Crystals were mounted in inert oil on glass fibers and transferred to the cold gas stream of an Oxford Diffraction Xcalibur E diffractometer. Measurements were performed using monochromated Mo K_{α} radiation ($\lambda = 0.71073$ Å). Absorption corrections were applied for **28** using the multi-scan method. *Structure refinement*: The structures were refined anisotropically against F^2 (program SHELXL-97) [19]. Hydrogen atoms were included using a riding model. Compound **28** was refined as a non-merohedral twin (by 180° rotation about the *a* axis).

CCDC 922329 (26) and 922330 (28) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/ cif.

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