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Diaminomaleonitrile as a versatile building block for the synthesis of 4,4′-biimidazolidinylidenes and 4,4′-bithiazolidinylidenes

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Abstract: Ring closure reactions of diaminomaleonitrile (DAMN) with electrophilic aryl isocyanates and aryl isothiocyanates lead to the formation of the target 5,5′-diimino-1,1′-diaryl-4,4′-biimidazolidinylidene-2,2′-diones **2a,b** and 2,2′-diarylimino-4,4′-bithiazolidinylidenes **4a–e**, respectively. The protocol provides a new strategy for the synthesis of a wide range of alkenes with two electron-donating and two withdrawing substituents of DAMN in moderate to good yields.

Keywords: 4,4′-biimidazolidinylidene; 4,4′-bithiazolidinylidene; aryl isocyanate; aryl isothiocyanate; diaminomaleonitrile.

Introduction

Diaminomaleonitrile (DAMN), a tetramer of hydrogen cyanide, is a weakly basic diamine with reactivity similar to *o*-phenylenediamine. It is an important precursor for the synthesis of heterocyclic compounds [1–3]. For instance, DAMN has been used to synthesize purines [4, 5], pyrimidines [4–6], pyrazines [7, 8], pyrroles [9], imidazoles [10], pyrazoles [11], oxazoles [12], 1,2,3-triazoles [13], 1,4-diazepines [14], 1,3,5-triazepines [15] and porphyrazines [16]. The reaction of DAMN with substituted aromatic aldehydes produces monoimines [17], which are important synthetic intermediates in the synthesis of drugs [18], conjugated linear polymers [19], optical materials [20] and diimines [21]. Moreover, Schiff bases derived from DAMN are employed as fluorescent materials [22] and ligands for metal complexes [23].

The chemical behavior of the carbon-carbon double bond in tetrasubstituted ethylene derivatives is greatly influenced by the electron-donating or withdrawing power of the four substituents. Alkenes with four electron-donating substituents such as 1,1′,3,3′-tetraalkyl-2,2′-biimidazolidinylidene are powerful reducing reagents [24, 25] and they react as strong nucleophiles [26]. The sulfur-rich π-electron acceptors derived from 5,5′-bithiazolidinylidenes are used in the preparation of charge transfer salts [27, 28] and air-stable *n*-channel organic transistors [29]. Synthesis of related 4,4′-bis[3-alkyl(aryl)-2-alkyl(aryl) imino-5-oxothiazolidinylidenes] [30] and 2,2′-dithioxo-[5,5′]bithiazolidinylidene-4,4′-dione (birhodanine) derivatives [31] have been reported. Bifunctional α-aminonitriles contain both a nucleophilic amino group and an electrophilic cyano group [32]. As the use of DAMN as an α-aminonitrile for the synthesis of heterocycles has not been reported, the aim of this investigation is to use amino and cyano groups on DAMN for the synthesis of five-membered bis-heterocycles. Herein, we report a simple synthetic method for the preparation of 4,4′-biimidazolidinylidene **2a,b** and 4,4′-bithiazolidinylidene **4a–e** systems from DAMN starting with either aryl isocyanates **1a,b** or aryl isothiocyanates **3a–e** (Scheme 1).

Results and discussion

The reaction of DAMN with aryl isocyanates **1a,b** in the presence of KOH in dimethylformamide(DMF) gave the 4,4′-biimidazolidinylidene derivatives **2a,b** in good yields as shown in Scheme 1. In addition, treatment of DAMN with aryl isothiocyanates **3a–e** in the presence of K_2CO_3 in DMF afforded the corresponding 4,4′-bithiazolidinylidenes **4a–e** in moderate to good yields (Scheme 1).

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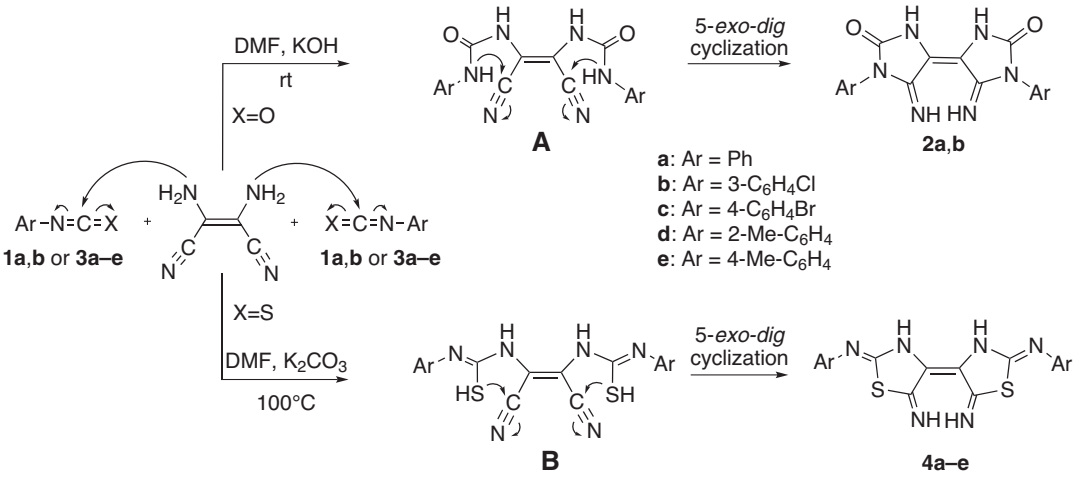

Scheme 1

The structures of the products **2a,b** and **4a–e** were determined using elemental analysis and IR, ^{1}H, ^{13}C NMR spectroscopic and mass spectrometric data. In the IR spectra of the products **2a,b** and **4a–e**, the absorptions of C≡N groups are absent. The IR spectrum of compound **2a** shows five characteristic absorption bands at 3411, 3310, 1651, 1593 and 1554 cm^{-1} for the NH, amidic C=O, C=N and C=C functions, respectively. Its ^{1}H NMR spectrum displays two signals at δ 5.27 and 8.60 due to the protons of iminic NH and amidic NH groups, respectively. On shaking **2a** with D_2O, the broad band signals at δ 5.27 and 8.60 disappear. The ^{13}C NMR spectrum of **2a** reveals three signals at δ 147.4, 152.5 and 158.3 due to the olefinic C=C, iminic C=NH and amidic C=O carbons, respectively. Mechanistically, the reactions start with the formation of the intermediates **A** and **B** from the nucleophilic addition of DAMN to aryl isocyanate **1** or aryl isothiocyanate **3**. Then, these intermediate products undergo 5-*exo-dig* cyclization to yield the target products **2** and **4** (Scheme 1) [33].

Conclusion

A new addition-cyclization process that offers direct access to 4,4′-biimidazolidinylidenes **2a,b** and 4,4′-bithiazolidinylidenes **4a–e** *via* the reaction of DAMN with aryl isocyanates and aryl isothiocyanates was developed.

Experimental

All reagents were purchased from Merck and used without further purification. Melting points were measured using an Electrothermal 9100 apparatus and were uncorrected. Elemental analyses were performed using a Heraeus CHN-O-Rapid analyzer. IR spectra were measured in KBr disks using a Thermo Nicolet 8700 FT-IR spectrometer. ^{1}H NMR (300 MHz or 500 MHz) and ^{13}C NMR (75 MHz or 125 MHz) spectra were recorded on Bruker instruments using tetramethylsilane(TMS) as the internal standard and dimethyl sulfoxide-d_6 (DMSO-d_6) as the solvent. Thin layer chromatography (TLC) was performed using precoated silica gel plates (0.2 or 0.5 mm thickness). Mass spectra were obtained by using an Agilent HP 5973 mass spectrometer operating at an ionization potential of 70 eV.

General procedure for the synthesis of 4,4′-biimidazolidinylidene derivatives 2a,b

To a cold suspension of KOH (0.056 g, 1.0 mmol) in DMF (10 mL), DAMN (0.054 g, 0.5 mmol) was added, followed by aryl isocyanate (**1a,b**, 1.0 mmol). The mixture was stirred for 6 h at room temperature. The progress of the reaction was monitored by TLC eluting with AcOEt/hexane (4:1). The mixture was cooled, poured into 20 g of ice/10 g of water and acidified using 1 M HCl. Then, the organic layer was extracted with CH_2Cl_2 (3 × 50 mL), dried (5.0 g of Na_2SO_4) and concentrated under reduced pressure to afford the crude product, which was washed with EtOH/H_2O (1:1).

5,5′-Diimino-1,1′-diphenyl-4,4′-biimidazolidinylidene-2,2′-dione (2a) Brown powder; yield 0.24 g (68%); mp >200°C (decomposition); IR: 3411, 3310 (NH), 1651 (C=O), 1593, 1554 (C=N, C=C) cm^{-1}; ^{1}H NMR (500 MHz): δ 5.27 (2(1H), br s, 2NH, imine), 6.93 (2(1H), t, ^3J = 7.5 Hz, 2CH$_{para}$ of Ph-N), 7.24 (2(2H), t, ^3J = 7.5 Hz, 4CH$_{meta}$ of Ph-N), 7.41 (2(2H), d, ^3J = 7.5 Hz, 4CH$_{ortho}$ of Ph-N), 8.60 (2(1H), br s, 2NH, amide); ^{13}C NMR (75 MHz): δ 118.2, 121.8, 128.8 (2(5C), 2Ph), 139.7 (2C$_{ipso}$ of Ph-N), 147.4 (2C=), 152.5 (2C=NH), 158.3 (2C=O); EI-MS: *m/z* (%) 346 (M$^{+\cdot}$, 4), 160 (52), 133 (34), 106 (20), 88 (21), 60 (51), 44 (100). Anal. Calcd for $C_{18}H_{14}N_6O_2$ (346.34): C, 62.42; H, 4.07; N, 24.27. Found: C, 62.71; H, 3.85; N, 24.53.

1,1′-Di(3-chlorophenyl)-5,5′-diimino-4,4′-biimidazolidinylidene-2,2′-dione (2b) Pale brown powder; yield 0.31 g (75%); mp 221–223°C; IR: 3291 (NH), 1634 (C=O), 1586, 1551 (C=N, C=C) cm^{-1};

^{1}H NMR (500 MHz): δ 7.02–7.70 (2(4H), m, 2Ph), 8.98 (2(1H), br s, 2NH, amide), signals for 2NH protons of imine are not seen; ^{13}C NMR (125 MHz): δ 116.8, 117.8, 121.7, 130.4 (2(4C), 2Ph), 133.2 (2C_{ipso} of Ph-Cl), 141.0 (2C_{ipso} of Ph-N), 148.3 (2C=), 152.3 (2C=NH), 157.5 (2C=O); EI-MS: *m/z* (%) 417 (M^++2, 1), 415 (M^+, 3), 280 (13), 153 (13), 127 (100), 111 (10), 99 (11), 75 (8), 63 (10). Anal. Calcd for $C_{18}H_{12}Cl_2N_6O_2$ (415.23): C, 52.07; H, 2.91; N, 20.24. Found: C, 52.28; H, 3.14; N, 20.02.

General procedure for the synthesis of 4,4′-bithiazolidinylidene derivatives 4a–e

A mixture of DAMN (0.054 g, 0.5 mmol), aryl isothiocyanate (**3a–e**, 1.0 mmol) and K_2CO_3 (0.28 g, 2.0 mmol) in DMF (10 mL) was heated at 100°C under reflux for 12–15 h. The progress of the reaction was monitored by TLC eluting with AcOEt/hexane (3:1). The mixture was cooled and poured into 20 g of ice/10 g of water. Then, the organic layer was extracted with CH_2Cl_2 (3×50 mL), dried (5.0 g of Na_2SO_4) and concentrated under reduced pressure to afford the crude product **4a–e**, which was purified by preparative TLC eluting with AcOEt/hexane (3:1).

5,5′-Diimino-2,2′-diphenylimino-4,4′-bithiazolidinylidene (4a) Yellow powder; yield 0.24 g (64%); mp 221–223°C; IR: 3390 (NH), 1650, 1608, 1487 (C=N, C=C) cm^{-1}; ^{1}H NMR (500 MHz): δ 6.94–7.24 (2(5H), m, 2Ph), 9.10 (2(1H), br s, 2NH, imine), 9.69 (2(1H), br s, 2NH, amidine); ^{13}C NMR (125 MHz): δ 124.3, 125.2, 128.3 (2(5C), 2Ph), 137.7 (2C_{ipso} of Ph-N), 149.3 (2C=), 160.0 (2C=NH), 165.0 (2C=NPh); EI-MS: *m/z* (%) 378 (M^+, 88), 352 (59), 334 (20), 289 (76), 274 (100), 200 (79), 150 (30), 104 (23), 76 (19). Anal. Calcd for $C_{18}H_{14}N_6S_2$ (378.47): C, 57.12; H, 3.73; N, 22.21. Found: C, 56.87; H, 3.48; N, 22.54.

2,2′-Bis(3-chlorophenylimino)-5,5′-diimino-4,4′-bithiazolidinylidene (4b) Yellow powder; yield 0.27 g (60%); mp 240–242°C; IR: 3386 (NH), 3056 (CH, aromatic), 1608, 1581, 1484 (C=N, C=C) cm^{-1}; ^{1}H NMR (500 MHz): δ 7.19–7.65 (2(4H), m, 2Ph), 9.10 (2(1H), br s, 2NH, imine), 10.05 (2(1H), br s, 2NH, amidine); ^{13}C NMR (125 MHz): δ 122.1, 123.2, 124.3, 130.2 (2(4C), 2Ph), 132.6 (2C_{ipso} of Ph-Cl), 140.8 (2C_{ipso} of Ph-N), 148.8 (2C=), 159.7 (2C=NH), 165.4 (2C=NAr); Anal. Calcd for $C_{18}H_{12}Cl_2N_6S_2$ (447.36): C, 48.33; H, 2.70; N, 18.79. Found: C, 48.56; H, 2.93; N, 18.51.

2,2′-Bis(4-bromophenylimino)-5,5′-diimino-4,4′-bithiazolidinylidene (4c) Yellow powder; yield 0.35 g (65%); mp 258–260°C; IR: 3379 (NH), 3049 (CH, aromatic), 1669, 1600, 1476 (C=N, C=C) cm^{-1}; ^{1}H NMR (500 MHz): δ 7.75 (2(2H), d, ^3J = 7.4 Hz, 4CH_{ortho} of Ph-N), 7.85 (2(2H), d, ^3J = 7.4 Hz, 4CH_{ortho} of Ph-Br), 9.25 (2(1H), br s, 2NH, imine), 9.97 (2(1H), br s, 2NH, amidine); ^{13}C NMR (125 MHz): δ 116.6, 125.7, (2(4C), 2Ph), 131.3 (2C_{ipso} of Ph-Br), 138.7 (2C_{ipso} of Ph-N), 151.0 (2C=), 159.6 (2C=NH), 165.1 (2C=NAr); Anal. Calcd for $C_{18}H_{12}Br_2N_6S_2$ (536.27): C, 40.31; H, 2.26; N, 15.67. Found: C, 63.89; H, 3.34; N, 20.92.

5,5′-Diimino2,2′-bis(2-methylphenylimino)-4,4′-bithiazolidinylidene (4d) Yellow powder; yield 0.21 g (51%); mp 235–237°C; IR: $\bar{\nu}$ = 3389 (NH), 3084 (CH, aromatic), 2915 (CH, aliphatic), 1651, 1613, 1483 (C=N, C=C) cm^{-1}; ^{1}H NMR (500 MHz): δ 7.22 (2(1H), d, ^3J = 8.2 Hz, 2CH_{ortho} of Ph-N), 7.35 (2(1H), d, ^3J = 8.2 Hz, 2CH_{ortho} of Ph-CH_3), 7.47 (2(1H), t, ^3J = 8.2 Hz, 2CH_{para} of Ph-N), 7.53 (2(1H), t, ^3J = 8.2 Hz, 2CH_{para} of Ph-CH_3), 9.15 (2(1H), br s, 2NH, imine), 9.85 (2(1H), br s, 2NH, amidine); ^{13}C NMR (125 MHz): δ 17.8 (2CH_3), 126.2, 126.7, 128.3, 130.4 (2(4C), 2Ph), 135.1 (2C_{ipso} of Ph-CH_3), 137.8 (2C_{ipso} of Ph-N), 150.1 (2C=), 158.6 (2C=NH), 161.2 (2C=NAr); Anal. Calcd for $C_{20}H_{18}N_6S_2$ (406.53): C, 59.09; H, 4.46; N, 20.67. Found: C, 58.86; H, 4.25; N, 20.91.

5,5′-Diimino2,2′-bis(4-methylphenylimino)-4,4′-bithiazolidinylidene (4e) Yellow powder; yield 0.24 g (60%); mp 233–235°C; IR: 3383 (NH), 3056 (CH, aromatic), 2917 (CH, aliphatic), 1608, 1573, 1480 (C=N, C=C) cm^{-1}; ^{1}H NMR (500 MHz): δ 7.18 (2(2H), d, ^3J = 8.0 Hz, 4CH_{ortho} of Ph-N), 7.39 (2(2H), d, ^3J = 8.0 Hz, 4CH_{ortho} of Ph-CH_3), 9.20 (2(1H), br s, 2NH, imine), 9.59 (2(1H), br s, 2NH, amidine); ^{13}C NMR (125 MHz): δ 20.5 (2CH_3), 124.0, 128.9 (2(4C), 2Ph), 133.7 (2C_{ipso} of Ph-CH_3), 136.8 (2C_{ipso} of Ph-N), 148.1 (2C=), 159.7 (2C=NH), 163.3 (2C=NAr); EI-MS: *m/z* (%) 406 (M^+, 5), 303 (9), 279 (39), 200 (87), 149 (100), 113 (23), 91 (18), 71 (48), 57 (70). Anal. Calcd for $C_{20}H_{18}N_6S_2$ (406.53): C, 59.09; H, 4.46; N, 20.67. Found: C, 59.32; H, 4.66; N, 20.41.

Supplementary material: IR, ^{1}H NMR, ^{13}C NMR and MS spectra of the products.

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