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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 porphyrinazines [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′-bithiazolidinylidene 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-amino-nitriles contain both a nucleophilic amino group and an electrophilic cyano group [32]. As the use of DAMN as an α-amino-nitrile for the synthesis of heterocycles has not been reported, the aim of this investigation is to use amine 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 K2CO3 in DMF afforded the corresponding 4,4′-bithiazolidinylidenes 4a–e in moderate to good yields (Scheme 1).
The structures of the products 2a,b and 4a−e were determined using elemental analysis and IR, 1H, 13C 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 1H 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 D2O, the broad band signals at 5.27 and 8.60 disappear. The 13C NMR spectrum of 2a reveals three signals at δ 147.4, 152.5, and 158.3 due to the olefinic C=C, iminic C≡N 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. 1H NMR (300 MHz or 500 MHz) and 13C NMR (75 MHz or 125 MHz) spectra were recorded on Bruker instruments using tetramethylsilane (TMS) as the internal standard and dimethyl sulfoxide-d6 (DMSO-d6) 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 washed with EtOH/H2O (1:1). 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 washed with EtOH/H2O (1:1).

5,5′-Diamo-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=C) cm−1; 1H NMR (500 MHz): δ 5.27 (2(1H), br s, 2NH, imine), 6.93 (2(1H), t, J = 7.5 Hz, 2CH2phen of Ph-N), 7.24 (2(2H), t, J = 7.5 Hz, 4CH2phen of Ph-N), 7.41 (2(2H), d, J = 7.5 Hz, 4CH2phen of Ph-N), 8.60 (2(1H), br s, 2NH, amidine); 13C NMR (75 MHz): δ 118.2, 121.8, 128.8 (2(5C), 2Ph), 139.7 (2Cphen of Ph-N), 1474 (2C=), 152.5 (2C=NH), 158.3 (2C=O); El-MS: m/z (%) 346 (M+; 4), 160 (52), 133 (34), 106 (20), 88 (21), 60 (51), 44 (100). Anal. Calcd for C54H39N3O6: C, 73.62; H, 4.19; N, 9.32. Found: C, 73.73; H, 4.18; N, 9.27.

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;
IR: 3379 (NH), 3049 (CH, aromatic), 1669, 1600, 1476 (C=N, C=C); 13C NMR (125 MHz): 141.7 (2(4C), 2Ph), 131.3 (2C ipso of Ph-N), 148.3 (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 + 1), 280 (13), 153 (13), 127 (100), 111 (10), 99 (11), 75 (8), 63 (10). Anal. Calcd for C6H4Cl2N6O2 (233–235): C, 40.18; H, 2.91; N, 20.54. Found: C, 40.17; H, 3.04; N, 20.54.

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

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