Review

Spectroscopic Indicators of Diaminomaleonitrile Bisubstitution: A Review

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Abstract: Diaminomaleonitrile (DAMN) is an electron-rich ligand which is commonly used in the synthesis of purines, amides and Schiff base ligands. In the last case lies the interest in this molecule, given its symmetry and apparent facility to form various ligands and complexes of interest in fields such as organic solar cells and catalysis among others. Nevertheless, its bisubstitution with aldehydes displays certain difficulty due to the double conjugated presence of the nitrile group (C≡N) in its structure, which significantly affect its coordination behavior by modulating the chemical reactivity of its amines. In addition to presenting a practical resume of guidelines for the preparation of different bisubstituted compounds from DAMN, this paper reviews the possibility of attaining a precise characterization by simple spectroscopic techniques. We provide an additional discussion for one of these techniques (commonly reported but often overlooked), given its potential to provide both the symmetry and E/Z configuration of the product. We hope the comprehensive evidence discussed and shown in this review will be helpful to further develop and understand the products derived of this interesting molecule in their broad applications.

Keywords: Diaminomaleonitrile; diaminofumaronitrile; monosubstitution, bisubstitution, symmetric, asymmetric, photoisomerization, internal charge transfer.

1. Introduction

Diaminomaleonitrile (DAMN), also known as 2,3-diamino-cis-2-butenedinitrile, is a diamine of relatively small molecular size (Figure 1a), displays a weak Lewis base behavior similar to o-phenylenediamine in reactivity, and can be prepared by oligomerization of HCN and indirectly by hydrogenation of diiminosuccinonitrile [1]. It is a molecule of great interest within organic chemistry, constituted of three groups: amine, nitrile, and a conjugated system in between. The amino group is useful, among other things, to synthesize Schiff base ligands and complexes [2]. Central double bond C=C enables the use of materials derived from DAMN in fields such as organic electronics [3], by forming a conjugated system capable of transferring electrons in internal charge transfer (ICT) processes between donors like the amino group, and acceptors like the nitrile group. Finally, the nitrile group affects the electronic density distribution in the molecule, and with it, the electronic and chemical properties of DAMN, and its derived ligands and complexes [4] [5].

Figure 1: Molecular structure of a) DAMN and b) DAFN.

DAMN has been used in the synthesis of purines, 4,5-dicyanoimidazoles, 5,6-dicyanopyrazines, and amides [1]. Additionally, is a precursor of Schiff base ligands and complexes with applications in: organic solar cells [6] [7], catalysis [8], optoelectronics [9] [10], optical materials [5] [11] [12] [13], fluorescent materials [14] [15] [16], antimicrobial agents [17], heterocyclic synthesis [18], and conjugated polymers [19]. It's known in the literature that DAMN tends to condense monosubstituted ligands even in excess of the precursor aldehyde [20] [21]. This is the case of condensation between DAMN and 2-hydroxybenzaldehyde (2-HBA) whose monosubstituted product 2a is shown in Figure 2. Their bisubstituted complexes 2b whose general structure is shown in Figure 2 are generally obtained *in situ* without going through the characterization of the bisubstituted ligand [22], generally involving a mixture of products with 2a.

Figure 2: Structures of the products between DAMN and 2-HBA: a) monosubstituted ligand and b) bisubstituted complex.

From a practical point of view, the aspects involved in the preparation and characterization of bisubstituted ligands and complexes derived from DAMN are scattered within the literature, and often times are confusing by not having general evaluation criteria that allows discerning the symmetry, E-Z configuration and substitution degree of any the derived products. In this work, we'd like to show the reported advances around this molecule and its derivatives, as well as establishing the spectroscopic evaluation criteria that allow identifying their symmetry and E-Z configuration. Unless explicitly stated otherwise it is worth mentioning that instead of describing most of the molecules as 'bisubstituted' we'll use 'symmetric' given the structural equality between both amino groups of DAMN, its *trans* isomer diaminofumaronitrile (DAFN, Figure 1b) or their respective imine derivatives in the molecules shown and made reference to.

2. Condensation with aldehydes: symmetric or asymmetric

When a primary amino group reacts with the carbonyl group of an aldehyde or ketone, a condensation reaction occurs producing an imine group and a water molecule according to Figure 3. For DAMN, we could expect a double condensation or substitution to occur to produce two imines given the number of basic primary amines that compose the symmetric molecule. However, this does not occur for many of the reported syntheses even in excess of the precursor aldehyde. Much has been discussed in the literature about the reason to which this situation can be attributed, notably the reaction conditions and characteristics of both the aldehyde and DAMN are mentioned.

Figure 3: Synthesis of an imine group.

Given that the reaction products obtained between DAMN with an aldehyde or ketone are hard to predict, a detailed characterization is required to identify the product or products since we often

find a mixture of ligands of unknown E-Z configuration and symmetries. Thus, it is necessary to analyze reported synthesis conditions of ligands and complexes derived from DAMN in conjunction with their products characteristics that allow determining their symmetry and E-Z configuration.

Generally [20], the DAMN condensation with aldehydes is realized using an organic solvent in acid or basic conditions, at a 50-150 °C temperature interval, with water removal by azeotropic distillation or action from a desiccant agent such as phosphorus pentoxide or dicyclohexylcarbodiimide, which favor chemical equilibria towards bisubstituted products. Preferred acids used to perform the condensation are sulfuric acid, phosphoric acid and *p*-toluenesulfonic acid. Organic solvents may be diverse: acetonitrile, THF, DMF, hexamethylphosphoramide, dimethylacetamide, toluene, xylene, benzene and monochlorobenzene are equally useful. After cooling down the reaction mixture to ambient temperature, the bisubstituted product can be isolated by filtration. Recent common options are the use of THF [19] and methanol or ethanol [23] as solvents; acetic acid [5] [8] [24], trifluoroacetic acid [25], HCl [15] or piperidine [25] as catalysts; ambient temperature [23]; and MgSO₄ as desiccating agent.

Given the known nature of DAMN to form almost exclusively asymmetric (monosubstituted) ligands in presence of an aldehyde in soft reaction conditions, two questions arise: ¿Which are the reaction conditions that favor the symmetric ligand or diimine? And once its obtained, ¿How can we differentiate the symmetric product from the asymmetric one, or their E isomers? Is clear that a technique like RMN ¹H would give us an immediate and convincing answer in the symmetry cases, but it is not so obvious in systems with isomer mixtures.

The answer to the first question comes from Johnson [19], Jeux [25] and their respective collaborators. In their work, Johnson and col. Mention that DAMN derivatives carry out Z→E isomerization if the nitrogen substituents are bulky, which of course depends on the precursor aldehyde. They also comment that, while the imines derived from DAMN and conjugated aldehydes seem to form in an irreversible way, the imines derived from aliphatic aldehydes (including formaldehyde, acetaldehyde, propionaldehyde and isobutylaldehyde) appear to be reversible, hindering the pure product isolation.

They attribute the monoimine formation origin in the internal charge transfers (ICT) of DAMN displayed in Figure 4 whose diamina molecular structure is represented using arrows. The unlinked pair of electrons of the amino group is in conjugation with the nitrile group in *trans* position through the central double bond, something that provokes an electronic density delocalization in either NH₂. However, there are two electron pairs with this interaction. This provokes a crossed delocalization effect that lowers electronic density in either of the amines. Additionally, the central double bond allows a direct conjugation between both amines, slightly increasing electronic density in a vinylogous way to hydrazine. Combined with the cross effect, DAMN displays the nucleophilic reactivity of a weak amine instead of null like cyanamide.

Figure 4: Types of possible ICT in DAMN.

According to Figure 5, when DAMN condenses with an unsaturated aldehyde, the crystalline structure suggests a geometric reorientation in the α , β -unsaturated imine, in a way that its π system comes into conjugation with the central double bond and *trans* nitrile of DAMN. On the other hand, the imine lone pair of electrons exists conjugation with the free amine, preventing its participation in the original ICT of DAMN, dramatically reducing the nucleophilic reactivity of the second amine group and consequently, avoiding the second Schiff base formation in a single DAMN molecule. They observed this behavior from the imine lone pair of electrons in the molecular orbitals, where

they do not show contribution to HOMO. This in opposition to the amine's lone pair of electrons, which play a significant role in HOMO [19].

Figure 5: The first imine group condensed between DAMN and an unsaturated aldehyde R 'deactivates' the second NH₂.

On the other hand, using an aromatic aldehyde with donor groups like hydroxy or methoxy, these can align a lone pair of electrons with the conjugated system and participate in the original ICT of DAMN, nucleophilically 'reactivating' the second amine according to Figure 6.

Figure 6: Second amine group 'reactivated' by the participation of an aromatic donor in the ICT of DAMN's derivative.

On their behalf, Jeux y col. [25] confirm the ICT between amine and nitrile groups studying the crystalline structure of products **4** and **5** shown in Figure 7. Their studies indicate a distance reduction in the intermediate bonds between a nitrile group and its *trans* donor group (in **5** either triarylamino group and in **4** the amino group). Said reduction is more remarkable in **4**, which explains the reduction in the amine nucleophilic character and therefore its reactivity.

Figure 7: Synthesis routes of 4 and 5. a) ethanol at reflux; b) toluene at reflux with Dean-Stark; c) toluene, P₂O₅, MW activation, 110 °C, 250 mW, 6 bar; d) toluene, TFA, MW activation, 110 °C, 250 mW, 6 bar. Adapted from ref [25], Copyright 2015, with permission from Elsevier.

Together with the ICT processes, they determined that 4 has a Z configuration and 5 has an E configuration. The synthesis method of 5 was obtained after several attempts (indicated synthesis routes a-d), which allowed them to synthesize the additional ligands 6 and 7 with the same geometric configuration that 5 according to Figure 8. They determined that the second condensation reaction occurs in very specific conditions together with the Z→E isomerization of DAMN, given that they never observed the Z isomer of 4. Thus, they consider this isomerization can be an important obstacle in its bisubstitution.

Figure 8: Symmetric ligands 5, 6, and 7 derived from DAMN with the E configuration of DAFN. Adapted from ref [25], Copyright 2015, with permission from Elsevier.

From these two investigations, we conclude that in addition of displacing the products equilibrium toward bisubstituted species by different means (like using a strong acid or various desiccants) in the reaction conditions, we must also consider the characteristics of the reactants themselves. Two general ideas are the following: using aromatic aldehydes with donor groups that interact in the original ICT of DAMN facilitates the synthesis of symmetric ligands derived from this diamine. However, we must consider the size of the substituents in the precursor aldehyde, given that bulky groups tend to provoke a Z→E isomerization to acquire a lower structural steric hindrance.

Now, the answer to the second question comes from various details in the spectroscopic techniques used to characterize the materials. In 2010, Ho and col. [26] realized the syntheses of the ligands 8Z, 8E, 9Z and 9E (shown in Figure 9) under ambient light.

Figure 9: Structures of and synthetic route to **8Z** and **9Z**, and their proposed photoisomers **8E** and **9E**. Adapted with permission from ref [26], Copyright 2010, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

Using the first route of synthesis as example, they obtained a dark-red precipitate of **8Z** whose color changed to green during the recrystallization stage. X Ray diffraction technique indicated that the green product was **8E**. To obtain the pure **8Z** isomer they repeated the synthesis in absence of ambient light and instead, under dim red light of 700 nm. Once they obtained both pure products, they studied in more detail the origin of the isomerization. After discarding a thermal conversion and considering a photoinduced process, the synthesis was repeated under dim red light with subsequent recrystallization to obtain both products, determining their geometric configuration by X Ray analysis. An additional confirmation was obtained by registering the RMN ^1H and UV-vis spectra's of both isomers. The Figure 10 shows the RMN ^1H spectra (in CDCl_3), where they distinguished the proton signals of the imine groups (**8E**: $\delta=8.52$ ppm, **8Z**: $\delta=8.50$ ppm), the hydroxyl groups (**8E**: $\delta=12.04$ ppm, **8Z**: $\delta=12.55$ ppm) and their mutual changes over time after irradiation from a 406 nm laser. They mention that the long field descent in RMN ^1H for the hydroxyl group also supports a strong intramolecular hydrogen bonding in both isomers.

Figure 10: ^1H NMR spectrum of A) **8Z** and B) **8E** in CDCl_3 . ^1H NMR spectra of **8Z** after irradiation (GaN laser, 406 nm, 5 mW cm^{-2}) for C) 15, D) 45, and E) 100 min. Reproduced with permission from ref [26], Copyright 2010, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

Since the ambient light (mainly the UV radiation as previously seen) affects the geometric configuration of the product during the synthesis stage, they also followed up the $Z \rightarrow E$ photoisomerization of a solution of **8Z** into **8E** through UV-Vis according to the Figure 11. Using the same 406 nm GaN laser as a source of excitation, they registered the spectra of the solution after exposure to the laser each 5 minutes. In **8Z**, they observed a decrease in the bands at 462 y 383 nm, together with an increase in the 582 nm band, attributed to the photoconversion into the isomer **8E**.

The existence of only the isomers **8E** and **8Z** in the solution is supported by the observation of an isosbestic point around 500 nm. Namely, the photoinduced isomerization is confirmed by observing the gradual conversion of the **8Z** spectrum (black solid line) into **8E** spectrum (gray solid line) (line).

Figure 11: Absorption spectra of **8Z** (black solid line) and **8E** (gray solid line) in CH_2Cl_2 . Irradiation (GaN laser, 406 nm) of **8Z** (dashed line) in CH_2Cl_2 as a function of the exposure time at increments of 5 min. Reproduced with permission from ref [26], Copyright 2010, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

Using computational simulation, they determined an energy difference in the **8Z**→**8E** process of -7.70 kcal mol⁻¹ which indicates that the isomerization is exergonic. However, despite its thermally favorable nature, their experiments show that the **8Z**→**8E** isomerization is not kinetically favorable in the ground state, which they attribute to the energy barrier of the central C=C double bond. In addition to this aspect, a work from Takeuchi and col. [27] suggest that the photoisomerization process of stilbene (a DAMN analogous) is a two steps process: a double bond elongation, followed by an out-of-plane rotation. Later, Szabla and col. [28] computationally analyzed this isomerization process for DAMN and DAFN, considering also that the back-photoisomerization process E→Z is less accessible if not prevented in this molecule, given the energy levels involved. Like the ICT's of DAMN, we consider this back- process applies as well to their derivatives.

In conjunction, the irreversible photoisomerization process of **8Z**→**8E** involves the absorption of light in the UV-Vis region from the central bond C=C in **8Z**, which acquires a temporary character of simple bond and rotates around its axis, with a further release of energy as heat after acquiring the structure of **8E**.

Although the energy intensity generated by a laser is not the same as the ambient light that can enter through a window, we consider this fact does not detract from the need to take the necessary precautionary measures when carrying out the synthesis of a pure Z product even when the synthetic route present low yields. This in addition to the importance of the bulkiness of a group in the aldehyde used.

Controlling the molar relation in reagents, Matsuoka and col. [14] realized the synthesis of **10** symmetric and asymmetric ligands derived from DAMN according to the Figure 12.

Figure 12: Five precursor aldehydes of five asymmetric (a) and five symmetric (b) ligands derived from DAMN. Adapted from ref [14], Copyright 2000, with permission from Elsevier.

Physically, the asymmetric ligands displayed a yellow color in different shades (yellow-green, yellow-orange, yellow-dark), with significant variations for their symmetric counterparts (orange, purple, dark blue, bright red, dark green), which suggests the possibility to visually distinguish the symmetry of the condensed products. The authors mention that the symmetric ligands present a higher bathochromic displacement than the asymmetric ligands in UV-Vis ($\delta\lambda \geq 57$ nm), with a remarkable fluorescent effect, attributed to the donor ability of the substituents. In addition, the symmetric cases presented higher molar extinction coefficients than their asymmetric counterparts (around 2-2.7 times greater). These results are in agreement with a comment made by Begland in his patent of 1975 [20], where he indicates that the asymmetric ligands derived from DAMN have a yellow color and don't exhibit the brightness and fluorescence that characterize the symmetric cases.

Up until now, we've mentioned that the symmetry and geometric configuration of the ligands is determined from techniques such as X Ray, NMR ¹H, UV-Vis, dipolar moment and even the color of the obtained ligand. Aside of the last one which, although initially useful is also ambiguous, the techniques of X Ray and NMR are less accessible and UV-Vis has the difficulty of precisely assigning

the bands. Now, during the writing of the present Review we observed that the technique of Infrared spectra (IR), a technique that, to put it in some way is more modest, shows equally capable of providing the symmetry and isomeric configuration of the molecules despite of the almost null importance it has received in the information analyzed to date.

In order to provide more in-depth to this point, we'll begin with a vibrational spectra analysis of DAMN and DAFN.

3. Physical characteristics of DAMN and DAFN

Long y George [29] [30] have reported the vibrational spectra and complete or partial assignments for this molecule and other similar by correlation of Infrared spectra. The authors presented a detailed study of the IR and Raman spectra both in solution as in solid phase. Similarly, Gupta and col. [31] analyzed DAMN and DAFN through computational simulation, with two important points: i) Conformational studies: they found that DAMN is more stable than DAFN by an energetic difference of 0.56 kcal/mol. Related to this, Yamada and col. [32] are the first to prove that DAFN can be obtained from DAMN due to UV radiation, which provokes a π - π^* excitation with further rotation around the C=C bond. This transformation goes over a transition state with an energetic barrier of 58.03 kcal/mol so that, despite the energetic similarity between them, an important potential barrier separates both isomers. Returning to Gupta's team, they calculated the dipolar moment of both molecules, finding that DAMN has a value of 6.8 Debyes (D) and DAFN of 1.49 D. ii) IR spectra vibrational analysis: using computational calculations, they determined the characteristic vibrations of DAMN and DAFN, whose values adjust in a satisfactory way with the values reported by Long and George [29].

According to Gupta, the characteristic bands of DAMN are the following: two experimental vibrations of nitrile in 2209vw and 2264s cm^{-1} visible in IR and Raman spectra, where the first is due to a symmetric stretch mode (present as a very small shoulder), and the second is an asymmetric mode (of greater importance). A C=C stretching band in 1614 cm^{-1} and a scissors mode of NH_2 en 1644 cm^{-1} , where they also found that the NH_2 groups have a significant role in the C=C vibration value. In the region of 3600-3000 cm^{-1} , they report four N-H stretching bands in 3299(w), 3344(s), 3366(sh) y 3436(s) cm^{-1} . The bands of 3344 y 3436 cm^{-1} where assigned respectively to symmetric and asymmetric stretching modes of N-H. These values have difference with those previously reported, and is attributed to hydrogen bonding involving the NH_2 groups in solid state (KBr discs). On the other hand, a molecule of DAMN can form a hydrogen bond from one amino group to the nitrile group of another DAMN molecule, forming a dimer to which the experimental bands at 3299 and 3366 cm^{-1} are assigned and correspond to the symmetric and asymmetric stretching modes of N-H. Just like DAMN, DAFN has two experimental bands at 2198 y 2243 cm^{-1} , assigned respectively to the symmetric and asymmetric stretching modes. A stretching band of C=C in 1618 cm^{-1} and a scissors mode of NH_2 calculated at 1638 cm^{-1} . With respect of the N-H bands, their calculations predict four stretching bands with an approximate difference of 100 cm^{-1} with respect of the values reported by Yamada and col. [32]. Despite considering hydrogen bonding and dimer formation as the case of DAMN, this difference in values could not be fully justified. Additionally, Gupta and col. Found that DAMN and DAFN are separated by a potential barrier of 58.0 kcal/mol related to the C=C bond, which may rotate for a *cis*→*trans* conversion due to UV radiation.

In order to procure utility information in this theme, we attempt to resume the most valuable cases we could find to date in the literature, beginning with the results of Jeux [25]. For the asymmetric ligand **4**, two N-H characteristic bands in 3410 and 3304 cm^{-1} , and two C≡N bands in 2229 y 2208 cm^{-1} where reported. The symmetric ligands **5**, **6** and **7** have a single C≡N band around 2210-2008 cm^{-1} , indicating a structural difference from the asymmetric ligand. From this, we assert that two or more (median or strong) nitrile bands indicate an asymmetric product or a mixture of product, while a single nitrile band indicate the purity of a symmetric or bisubstituted product. A second study in which it is possible to verify this assertion is in the results of Thompson and col. [4], who in 1996 synthesized symmetric and asymmetric complexes with one and two coordination sites as shown in

Figure 13. They mention that DAMN presents three N-H stretching bands in 3440, 3347 and 3206 cm^{-1} , and one $\text{C}\equiv\text{N}$ stretching band in 2213 cm^{-1} with a weak shoulder in 2167 cm^{-1} . Meanwhile, the ligand **2a** (reported by them but not shown in said Figure) presents three similar N-H bands and two $\text{C}\equiv\text{N}$ bands located in 2245 and 2207 cm^{-1} , being the first one of greater magnitude than the second one. All structures shown in Figure 13 follow the explanation found in the results of Jeux. For the products shown in Figure 13, the nitrile bands position (in cm^{-1}) are the following: Cu(L1) **15**: 2221, 2172; Cu₂(M3) **16**: 2235, 2173; Cu(L3)(DMSO) **17**: 2222; [Cu(L2)]₂ **18**: 2236, 2195.

Figure 13: DAMN derived complexes with one and two coordination sites obtained by Thompson. Adapted with permission from [4]. Copyright 1996 American Chemical Society.

A third case comes from the works of Whorle and col. [8] [33], who at the beginning of the eighties where the first to mention (but not discuss nor detail) that the monosubstituted products of DAMN present two $\text{C}\equiv\text{N}$ bands, with respect of the only $\text{C}\equiv\text{N}$ band presented by the bisubstituted products. First, they determined that the asymmetric ligand **2a** is stable at high temperature, in contrast with DAMN who tends to decompose at $T > 70^\circ\text{C}$ according to Takahashi and col [22]. This allowed them to achieve the synthesis of the symmetric complexes of **19** from **2a** and 2-HBA, together with the metallic salt of interest. All in presence of acetic acid. They attribute said achievement to carbonyl group activation from the acid and the template effect of the metallic salt. From both of their works, they report that the yellow-colored ligand **20** can be obtained in two ways shown in Figure 14: *i*) by exposing **19** to an acid medium, and *ii*) from **2a** and 2-HBA by using Chromium (III) or Cobalt (III) acetate as a catalyst.

Figure 14: Routes of synthesis of bisubstituted ligand **20** from DAMN and 2-HBA: catalysis of a metallic salt M^{3+} , or the formation of a symmetric complex and further exposure to an acid. Adapted by permission from Springer Nature [33], Copyright 1985.

Similar to obtaining **20** from **19**, they proceeded to the synthesis of various mono and bisubstituted, symmetric and asymmetric metallic complexes with one or two coordination sites. The general structures of four of these complexes are shown in Figures 15 and 16. On the other hand, Table 1 shows the nitrile bands of the products. The main difference between the molecules **23** and **24** with the rest of those shown in this work is the polymeric structure, which does not seem to affect the number of nitrile bands by comparison with of its monomeric analog **2a**. Additionally, the alkyl polymeric structure seem to have allowed them the asymmetric bisubstitution of DAMN for the ligand and complex cases, for which it would be necessary to determine if this type/kind of aromatic substituents are convenient together with the donor groups.

Figure 15: Bisubstituted complexes derived from DAMN, with one and two coordination sites respectively. For simplicity, R substituents are not shown. Adapted by permission from Springer Nature [8], Copyright 1983.

Figure 16: Conversion route of polymeric ligand **23** to the polymeric complex **24** by Co^{2+} cation coordination. Adapted by permission from Springer Nature [8], Copyright 1983.

Table 1: Nitrile bands of four mono and bisubstituted compounds obtained by Whorle and col. [8].

Product	3	4	5	6
$\text{C}\equiv\text{N}$ (cm^{-1})	2230	2230	2220, 2190	2220

After determining the spectroscopic indicators that allow discerning the symmetry and geometric configuration of DAMN and DAFN derivatives (including simple unexpected evidence for IR through the nitrile bands), we proceed to discuss asymmetric and symmetric cases found in the literature whose symmetry and geometric configuration is confirmed and assigned from the previously discussed evidence.

4. Asymmetric cases

In 2011, Guha and col. [21] synthesized and characterized **2a** and its asymmetric complexes obtained with the $\text{Zn}(\text{II})$ and $\text{Cd}(\text{II})$ cations. The **2a** ligand displayed three N-H bands in 3416, 3307 and 3193 cm^{-1} , in addition of a strong $\text{C}\equiv\text{N}$ band in 2203 cm^{-1} with a sharp and weak shoulder in 2363 cm^{-1} . For **2a**, RMN ^1H showed signals at: δ 10.400 (s, 1H; phenolic O-H), δ 8.548 (s, 1H, imine), δ 7.996 (m, 1H, aromatic), δ 7.803 (s, 2H, NH_2), δ 7.286 (m, 1H, aromatic) and δ 6.876 (m, 1H, aromatic) that corroborate well with their proposed structure. The $\text{Zn}(\text{II})$ complex shows a strong $\text{C}\equiv\text{N}$ band in 2214 cm^{-1} with a weak shoulder in 2374 cm^{-1} . For the $\text{Cd}(\text{II})$ complex, these bands are respectively located in 2214 cm^{-1} and 2381 cm^{-1} with the same strength.

On another work, Devi [34], Hu [7] and their respective collaborators used halogenated aromatic aldehydes (Br and Cl respectively) with DAMN in obtaining the symmetric ligands and complexes. In both cases, the ligands showed a yellow shade of color. The reported IR bands for both ligands are very similar between them: three are located around 3400, 3300 y 3200 cm^{-1} for the amino group and two nitrile bands around 2248 and 2210 cm^{-1} , aside of some similar bands in the fingerprint region. Their values similarity for amino and nitrile bands with the reported values of Thompson [4] suggest that the halogen substituents in the aromatic ring of an aldehyde don't favor the symmetric ligand formation, by matching better with the asymmetric structures shown in Figure 17.

Figure 17: Asymmetric ligands condensed from halogenated aromatic aldehydes and DAMN. X: Cl (Devi) and Br (Hu).

5. Symmetric cases

Matsumoto and col. [9] realized the synthesis of 14 symmetric ligands with different alkoxy-derived substituents. The synthesis process was according to Figure 18 using DAMN as the precursor. According to UV-Vis, all ligands displayed high molar extinction coefficients ($\epsilon_{\text{max}} > 100,000$) around 550 nm, which belong to symmetric ligands with strong ICT processes according to Matsuoka [9] and Kim [35]. IR spectroscopy indicated that the 14 ligands had a single nitrile band in the 2208-2201 cm^{-1} interval. Physically, all products had a purple color except **7b** and **14b**, both of red color. Is remarkable that all products had E configuration, contrary to the DAMN precursor but according to DAFN (hence what is shown in the synthesis process). This fact seem to be in agreement to the observation of Johnson [19] and Jeux [25] where a Z→E isomerization occurs before the second substitution due to the bulkiness of the aldehyde used.

Figure 18: Synthesis scheme of the 14 symmetric ligands of Matsumoto and col. Derived from DAMN. Adapted from ref [9], Copyright 2011, with permission from Elsevier.

On another work, Lacroix and col. [12] realized the synthesis of a dark-green colored symmetric ligand and its Ni^{2+} , Cu^{2+} and Zn^{2+} complexes, as shown in Figure 19. After purifying the ligand **39** by silica chromatography, the ligand and its complexes showed very similar stretching bands in IR spectroscopy for the nitrile group: **39Z** (2210 cm^{-1}), **39-Ni** (2212 cm^{-1}), **39-Cu** (2211 cm^{-1}), **39-Zn** (2210 cm^{-1}). They attribute this similarity of values between compounds to the slight modification of the charge distribution in the π structure by the cationic metals used, in comparison to the free ligand.

Figure 19: Structure of the symmetric ligand **39** and its complexes obtained by Lacroix and col. Adapted with permission from [12]. Copyright 1996 American Chemical Society.

Afterwards, Cheng and col. [10] realized the synthesis of the ligands **39Z** (same color) and **39E** (violet) which were purified by column chromatography and identified by RMN ^1H according to the Figure 20. In it, they showed that the main difference between both isomers comes from the O-H proton localized in $\delta=12.26\text{ ppm}$ for **39Z** and in $\delta=11.71\text{ ppm}$ for **39E**.

Figure 20: ^1H NMR spectrum of **39Z** and **39E** in CDCl_3 . Adapted with permission from [10]. Copyright 1996 American Chemical Society.

Under a similar procedure to Ho [26], Cheng and col. [10] Proved the isomer conversion Z→E by inciting UV radiation in an acetonitrile solution of **39Z**, following the process over time through UV-Vis spectroscopy according to Figure 21. They mention that said conversion was not observed in solid samples.

Figure 21: Change in the absorption spectra of **39Z** under the irradiation of UV lamp. Adapted with permission from [10]. Copyright 1996 American Chemical Society.

On another work, Meng and col. [15] realized the synthesis of two symmetric ligands (**40** and **41**) from DAMN with 2,3-dihydroxybenzaldehyde (2,3-DHBA) or 2,4-dihydroxybenzaldehyde (2,4-DHBA) shown in Figure 22, in which they subsequently introduced the Zn^{2+} cationic metal. The ligands and complexes were characterized in IR, X Ray, fluorescence, UV-Vis and RMN ^1H (available in their Supplementary Information). From IR spectroscopy, the ligand **40** derived from 2,4-DHBA shows two sharp $\text{C}\equiv\text{N}$ bands in 2210s and 2240s cm^{-1} , in addition of three sharp bands in 3199, 3308 and 3400 cm^{-1} , which suggest an asymmetric structure. The ligand **41** derived from 2,3-DHBA shows a single $\text{C}\equiv\text{N}$ band in 2218m cm^{-1} , and four bands in the interval of 3500-3100 cm^{-1} which suggest a symmetric structure. They report single $\text{C}\equiv\text{N}$ bands in 2216 and 2219 cm^{-1} for the Zn^{2+} complexes of both ligands, corresponding to symmetric structures.

Figure 22: General structure of the precursor aldehydes of the ligands **40** and **41**.

In another work, Nemykin and col. [24] realized the synthesis of three complexes derived from DAMN and ferrocenecarbaldehyde using glacial acetic acid as solvent. Of four main products found using thin layer chromatography (TLC), two main products were purified and analyzed in detail: the dark red fraction of **42**, and the dark blue fraction of **43**. They analyzed both using RMN ^1H and ^{13}C , IR, UV-Vis and X Ray spectroscopies. For IR, **42** showed two N-H bands in 3428 and 3320 cm^{-1} , together with two nitrile bands in 2230 and 2199 cm^{-1} ; while **43** showed a single nitrile band in 2212

cm⁻¹. In UV-Vis, both displayed two absorption maxima: for **42** in 512 nm ($\epsilon=3,640 \text{ M}^{-1} \text{ L}^{-1}$) and 355 nm ($\epsilon=22,500 \text{ M}^{-1} \text{ L}^{-1}$), and for **43** in 586 nm ($\epsilon=11,900 \text{ M}^{-1} \text{ L}^{-1}$) and 395 nm ($\epsilon=31,600 \text{ M}^{-1} \text{ L}^{-1}$). They determined the symmetry and geometric configuration of both products using X Ray diffraction together with RMN ¹H and ¹³C, being as follows: **42Z** asymmetric and **43E** symmetric. Before this Review and after almost 40 years from Whorle, they are the second ones to say that the presence of two N-H bands and two nitrile bands may correspond solely to the monosubstituted case, while the absence of N-H bands and a single nitrile band obeys the bisubstituted case. In addition, they consider the E configuration of **43** must occur during the second substitution of DAMN due to the steric hindrance of the ferrocenyl substituent and not a photo-induced type as previously known. Furthermore, they report that the reduction in length of the bonds between a nitrile group and its *trans* amine group in **42** derives on the participation of the amine's lone pair of electrons in the conjugated system. This induces some double bond character between the amine nitrogen and its adjacent carbon atom, and reduces the acidity of the amine hydrogen atoms. From previously shown evidence, we consider it necessary to also emphasize that the difference in ϵ magnitude around 500 nm in UV-Vis is an additional confirmation over the symmetry of their complexes.

Finally, the work done by Rajasekar and col. [17] in 2010 reports the synthesis of an asymmetric bisubstituted ligand obtained in two steps. First, they use 4-methyl-2-hydroxybenzaldehyde together with DAMN for the synthesis of an asymmetric ligand analogous to **2a**, which they use afterwards as a precursor (together with 2-HBA) to realize the second stage of the final ligand. Although they obtained low yields in both stages (Figure 23), together with little spectroscopic information that helps to assert the structure showed using previously shown criteria, they suggest the possibility to extend the explanation obtained from Johnson. Given that the reaction between DAMN and 2-HBA always gives the **2a** product, the presence of an alkyl substituent (methyl) in *para* position with respect of the hydroxyl group allows the double substitution of DAMN similarly to product **24**. On our behalf, we consider the synthesis between DAMN and this type of aromatic aldehydes is something that requires more attention for an appropriate discussion and contribution.

Figure 23: Two step synthetic route (with yields) of the asymmetric and bisubstituted ligand obtained by Rajasekar and col.

6. Infrared Spectroscopy Interpretation, FT-IR

FT-IR characterization requires more than anything a more scrupulous observation of the bands presented by the ligands or complexes obtained from the condensation between different aldehydes and DAMN. As for the interpretation, there are four main regions of interest in a spectra (see Figure 24) indicated by boxes over the IR spectra of DAMN: simple bonds (blue), triple bonds (green), double bonds (yellow) and fingerprint (red) whose complexity increases in any derivative compound.

The analysis for these particular compounds goes as follows: as was mentioned in chapter 3, DAMN displays 3 types of characteristic bands in IR: N-H, C $\equiv$ N and C=C, which is strictly related to

the NH_2 group. First, when DAMN forms an imine group the number of N-H bands should diminish or even disappear in the case of symmetric ligands. Second, the characteristic band of the imine group is very close to the central $\text{C}=\text{C}$ of DAMN [36], opening the possibility of a partial overlapping between them and with it the difficulty of a precise overlapping between them. Third, the fingerprint region's complexity increases in every ligand or complex formed from DAMN. Because of these 3 points, the focus directs towards the last green color region (triple bonds).

Figure 24: Four main band regions of IR over the spectra of DAMN. Original available online [37].

In it, we see that DAMN has two nitrile bands: a very weak band in 2209 cm^{-1} and a strong band at 2264 cm^{-1} , due to symmetric and asymmetric stretching modes respectively. Independently of the aldehyde, when an amine of DAMN realizes the first condensation to form an asymmetric monosubstituted ligand it alters the original ICT processes that involve each nitrile (see Figure 4). Namely, one nitrile group interacts through the conjugated system with the other amine group and the second with the imine group and its structural extension that comes from the precursor aldehyde. This difference of interactions of both nitrile groups with their *trans* structural group in the ligand results in the facile observation of two nitrile bands of different frequency and magnitude, correspondent with their symmetric and asymmetric stretching modes, in which the first (located at lower frequencies) is no longer very low and can even swap magnitude with the second one (as is the reported case of Guha and col. [21]). Afterwards, when the second condensation occurs with the same precursor aldehyde, the structure with which both nitriles interact is the same between them, and we see again a single strong band (with no mention of the symmetric mode, which may still be present as a weak shoulder or may disappear completely, explaining its absence in reports). With respect of the E/Z configuration, the vibration frequency of the nitrile bands in DAFN shows a displacement into lower frequencies with respect of DAMN: The displacement of the symmetric stretching is of $\delta = 11\text{ cm}^{-1}$ and for the asymmetric stretching is of $\delta = 21\text{ cm}^{-1}$ according to the values reported by Gupta [31]. That way, we consider that seeing these changes at an IR spectrum can inform us the symmetry and geometric configuration of the molecule.

7. SUMMARY OF STRATEGIES FOR A SUCCESSFUL DAMN BISUBSTITUTION

In order to achieve a successful DAMN bisubstitution, its necessary to use metallic catalysts that activate the carbonyl group in 2-HBA in order to condense the symmetric ligand with DAMN by mean of the template effect. Another option is to form the symmetric complex and then retire the coordinated cationic metal by acid protonation. An important aspect is the use of aldehydes with donor groups that introduce electronic density to the aromatic ring and, once condensed the imine group, that participate in the original ICT of DAMN to favor its bisubstitution. The effect of size of the aldehyde must be considered for the final product to obtain, since bulky groups favor the rotation of the central $\text{C}=\text{C}$ bond and result in the acquisition of a DAFN bisubstituted derivative, given the

lower steric impediment with the nitrile groups in that structural configuration. On the synthesis methods, is important to start with temperatures lower than 70 °C to avoid decomposing DAMN. After forming the monosubstituted derivative, higher temperatures can be used for further reactions. Solvents choice is up to each case. In the case of a bisubstitution, many cases report the use of desiccants or azeotropic distillation, because it retires any water formed and slowly displaces the equilibrium towards the products. In addition, it must be avoided the exposure of the reaction process and products to visible light due to the irreversible Z→E isomer conversion (mainly due to UV radiation).

Table 2 shows a resume of the main spectroscopic indicators covered that distinguish the symmetry (or substitution degree) and geometric configuration of DAMN derivatives. Additionally, we consider appropriate to include the color of the product (mainly for ligands) as a way to identify both characteristics in the following way: over the symmetry, an asymmetric monosubstituted product should present a yellow shade, while the bisubstituted case should be different to yellow. Over the geometric configuration, a solution of a symmetric bisubstituted product should change of color over exposure to UV radiation due to Z→E conversion. In other words, if a change on color is seen after exposure to radiation, the initial product was Z. Else, its E.

Table 2: Resume of spectroscopic indicators for DAMN derivatives.

Spectroscopy	E/Z configuration	Asymmetric monosubstituted	Symmetric bisubstituted
IR(nitrile group)	Bathochromatic displacement of the bands in E respect of Z	Two bands between 2300-2150 cm ⁻¹	Single strong band 2220 cm ⁻¹
Dipolar moment (Debyes)	E < 4 < Z	Value greater than 4	According to E/Z
UV-vis and ε _{max} (λ/cm ²)	Isosbestic point between isomers when exposing a ligand solution to UV radiation	Low ε _{max} with respect of symmetric	High ε _{max} with a bathochromatic displacement with respect of asymmetric (p.e. ε _{max} >100,000 in 550 nm)
RMN ¹ H	Displacement of Ar-OH proton into High Field from Z→E conversion	Additional signal of NH ₂ group with respect of the symmetric case	According to E/Z

8. CONCLUSIONS

DAMN is a promising molecule in a wide variety of fields of organic and inorganic chemistry due to the presence of three functional groups in its compact structure. The diversity of interactions that it can have provides it with a unique behavior as a reactive and as a formed product. Precisely due to the internal interactions it has, its physical and chemical behavior varies with respect to the expected of an isolated amine. This particularity in its interactions makes it necessary to understand the mechanisms by which it occurs, and at the same time take advantage of its reactivity to achieve the products with desired symmetry and E/Z configuration.

The spectroscopic techniques are of great utility when identifying an obtained product. We make special mention to FT-IR, a relatively modest technique able to help immediately to determine the efficacy of the employed methodology at the moment of the synthesis, when it's not evident the

symmetry and E/Z configuration. Three factors are important when aiming to obtain a Z symmetric derivative of DAMN: donor groups in the aldehyde, its steric hindrance on the ligand, and the ambient light during and after the synthesis, because they all can contribute to an undesired Z→E conversion of the product.

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