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# 1-(4-Dimethylaminobenzyl)-2-(4-dimethylaminophenyl)-benzimidazole: Synthesis, X-ray crystallography and density functional theory calculations

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#### Abstract

The product of the reaction between *o*-phenylenediamine and 4-dimethylaminobenzaldehyde, mp=179°, is unambiguously shown to be 1-(4-dimethylaminobenzyl)-2-(4-dimethylaminophenyl)-benzimidazole by X-ray crystallography. It crystallises in the monoclinic space group  $P2_1/c$ , with a=18.327(5) Å, b=6.318(15) Å, c=18.204(4) Å,  $\beta=110.73(2)^\circ$ ,  $R_1=0.0647$ . Quantum chemical calculations [density functional theory, B3LYP/6-31G(d)] are used to propose a reaction mechanism for the rearrangement of the initially formed bis-Schiff base via a two-step process involving cyclization (**TS1**,  $\Delta G^{\neq}=32$  kcal mol<sup>-1</sup>) to a tetrahedral intermediate (**3**,  $\Delta G_{\text{react}}=30$  kcal mol<sup>-1</sup>). A formal (1,3)-shift (**TS2**,  $\Delta G^{\neq}=38$  kcal mol<sup>-1</sup> with respect to **3**) then yields in a strongly exothermic reaction ( $\Delta G_{\text{react}}=-17$  kcal mol<sup>-1</sup>) the rearranged product, 1-(4-dimethylaminobenzyl)-2-(4-dimethylaminophenyl)-benzimidazole (**2**). © 2006 Elsevier B.V. All rights reserved.

Keywords: X-ray; Schiff base rearrangement; Density functional calculations; Mechanism

### 1. Introduction

Aromatic Schiff bases form complexes with a variety of metal ions [1] with a number of possible applications, e.g. as liquid crystal or non-linear optic materials, as catalysts in stereoselective organic transformations and multielectron redox reactions, and for analytical applications [1-7]. Of special interest are multidentate Schiff base ligands, e.g. those derived by reaction of aromatic aldehydes with o-phenylenediamines (1 in Scheme 1). Surprisingly, although formation of such bis-Schiff bases by the 'standard' synthetic procedure (see Section 2) has been described by several authors [8–14], others have instead observed cyclisation to benzimidazole derivatives [15,16]. Such benzimidazoles, which also can be obtained by microwave-assisted condensation of aromatic aldehydes and o-phenylenediamines in the presence of montmorillonite catalysts [17] or indium-mediated reductive coupling of o-nitroaniline with aromatic aldehydes [18], easily form-like their Schiff base isomers-complexes with a number of metal cations [19]. In an attempt to prepare N,N'-bis(4-dimethylaminobenzylidene)-benzene-1,2-diamine 1,  $R = N(CH_3)_2$ , by reaction of o-phenylenediamine with p-dimethylaminobenzaldehyde, a colourless compound,  $mp = 179^\circ$ , was obtained. On the basis of its <sup>1</sup>H NMR spectrum the Schiff base structure immediately could be ruled out (see Section 2). On the other hand, however, the melting point significantly differed from that reported for the also possible benzimidazole derivative 2 (252–255° [15,17]). However, a value of 168° for the mp of this very same compound can also be found in Ref. [18]. Thus, the identities of the products formed by reacting o-phenylenediamine with aromatic aldehydes are still not completely clear. Consequently, in the present paper we show unambiguously by X-ray crystallography that despite this difference in melting points, the compound obtained by us is 1-(4-dimethylaminobenzyl)-2-(4-dimethylaminophenyl)benzimidazole 2. In addition, by density functional theory computations [B3LYP/ 6-31G(d)], we propose a detailed reaction mechanism for the formation of 2 from *o*-phenylenediamine and 4-dimethylaminobenzaldehyde.

### 2. Experimental section

## 2.1. Synthesis of 2

A mixture of 1,2-phenylenediamine (1 mmol), and 4-dimethylaminobenzaldehyde (2 mmol) in hot ethanol

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Scheme 1. Structures of the *o*-phenylendiamine-4-dimethylaminobenzaldehyde bis-Schiff base 1 and the rearrangement product 1-(4-dimethylaminobenzyl)-2-(4-dimethylaminophenyl)-benzimidazole 2.

(30 mL) was stirred and refluxed for 4 h, the formed yellow precipitate was filtered and washed sparingly with hot ethanol several times to give 0.23 mg (63%) of 2: mp=179°; The assignment of NMR resonances has been done by the heteronuclear multiple-bond connectivity (HMBC) procedure [20], the atom numbering corresponds to that in Fig. 1: <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) & 2.95 (6H, s, N14(CH<sub>3</sub>)<sub>2</sub>), 3.02 (6H, s, N24(CH<sub>3</sub>)<sub>2</sub>), 5.39 (2H, s, CH<sub>2</sub>), 6.65 (2H, d, J=8.68 Hz, C13(15)–H), 6.71 (2H, d, J=8.84 Hz, C23(25)–H), 7.00 (2H, d, J=8.68 Hz, C12(16)–H), 7.14 (1H, t, J=7.88 Hz, C6–H), 7.18 (1H, d, J=7.38 Hz, C7–H), 7.24 (1H, t, J=7.99 Hz, C5– H), 7.63 (2H, d, J=8.84 Hz, C22(26)–H), 7.82 (1H, d, J= 7.98 Hz, C4–H); <sup>13</sup>C NMR (500 MHz, CDCl<sub>3</sub>) δ 40.0 (C27,C28), 40.3 (C17,C18), 47.9 (C10), 110.2 (C7), 111.7 (C23, C25), 112.6 (C13, C15), 116.9 (C21), 119.0 (C4), 122.1 (C5,C6), 124.1 (C11), 126.7 (C12, C16), 130.2 (C22, C26), 136.2 (C8), 142.9 (C9), 149.9 (C14), 151.0 (C24), 155.0 (C2); Anal. Calcd for C<sub>24</sub>H<sub>26</sub>N<sub>4</sub>: C, 77.83; H, 7.02; N, 15.13. Found: C, 77.02; H, 7.98; N, 15.11. Single crystals of 2 were obtained from a solution of CHCl<sub>3</sub>/ethylacetate (1:1,  $mp = 182.2^{\circ}$ ).

#### 2.2. X-ray diffraction data of 2

All the measurements were performed using graphitemonochromatised Mo K<sub> $\alpha$ </sub> radiation at 100 K: C<sub>24</sub>H<sub>26</sub>N<sub>4</sub>, M<sub>r</sub> 370.49, monoclinic, space group  $P2_1/c$ , a = 18.327(5) Å, b =6.3188(15) Å, c = 18.204(4) Å,  $\beta = 110.73(2)^{\circ}$ , V =1971.6(9) Å<sup>3</sup>, Z=4,  $d_{calc} = 1.248 \text{ g cm}^{-3}$ ,  $\mu = 0.075 \text{ mm}^{-1}$ . A total of 4423 reflections were collected ( $\Theta_{\text{max}} = 25.30^{\circ}$ ), from which 3591 were unique ( $R_{int}=0.0421$ ), with 2364 having  $I > 2\sigma(I)$ . The structure was solved by direct methods (SHELXS-97 [21]) and refined by full-matrix least-squares techniques against  $F^2$  (SHELXL-97 [22]). The non-hydrogen atoms were refined with anisotropic displacement parameters without any constraints. The H atoms of the CH<sub>2</sub> group were refined with common isotropic displacement parameters for the H atoms and idealized geometry with approximately tetrahedral angles and C-H distances of 0.99 Å. The H atoms of the phenyl rings were put at the external bisector of the C-C-C angle at a C-H distance of 0.95 Å and common isotropic displacement parameters were refined for the H atoms of the same phenyl group. The H atoms of the methyl group C28 are disordered over two orientations and were refined with site occupation factors of 0.5 at two positions rotated from each other by 60°. The H atoms of the methyl groups were refined with common isotropic displacement parameters for the H atoms of the same group and idealized geometry with tetrahedral angles, enabling rotation around the X-C bond, and C-H distances of 0.98 Å. For 265 parameters final R indices of R = 0.0647 and  $wR^2 = 0.1324$  (GOF = 1.034) were obtained. The largest peak in a difference Fourier map was  $0.202 \text{ e} \text{ Å}^{-3}$ . Crystal data and structure refinement for 2 are provided in Table 1. CCDC 297274 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/ retrieving.html (or from the Cambridge Crystallographic



Fig. 1. Stereoscopic ORTEP [28] plot of **2** showing the atomic numbering scheme. The probability ellipsoids are drawn at the 50% probability level. The H atoms of the methyl group C28 are disordered over two sites.

| Table 1          |           |                  |   |
|------------------|-----------|------------------|---|
| Crystal data and | structure | refinement for 2 | 2 |

| Crystal data                              |  |
|---|--|
| Identification code                       | 400a   |
| Empirical formula                         | $C_{24}H_{26}N_4$  |
| Formula weight                            | 370.49   |
| Crystal description                       | Needle, colourless   |
| Crystal size                              | 0.40×0.38×0.22 mm  |
| Crystal system, space group               | Monoclinic, $P2_1/c$   |
| Unit cell dimensions                      |  |
| <i>a</i>                                  | 18 327(5) Å  |
| b   | 6.3188(15) Å   |
| C   | 18 204(4) Å  |
| B   | 110.73(2)°   |
| Volume                                    | $1971.6(9) \text{ Å}^3$  |
| Z   | 4  |
| Calculated density                        | $1.248 \text{ Mg/m}^3$   |
| F(000)                                    | 792  |
| Linear absorption coefficient $\mu$       | $0.075 \text{ mm}^{-1}$  |
| Absorption correction                     | None   |
| Unit cell determination                   | $18.12 < \Theta < 21.36^{\circ}$   |
|   | 42 reflections used at 100 K   |
| Data collection                           |  |
| Temperature                               | 100 K  |
| Diffractometer                            | Stoe   |
| Radiation source                          | Fine-focus sealed tube   |
| Radiation and wavelength                  | Mo K., 0.71069 Å   |
| Monochromator                             | Graphite   |
| Scan type                                 | $\omega - 2\Theta$ scans   |
| Standard reflections                      | 3 every 100 reflections  |
| Intensity decay                           | 9.4%   |
| Theta range for data collection           | 2.71–25.30°  |
| Index ranges                              | $0 \le h \le 22, -7 \le k \le 1, -21 \le l \le 20$   |
| Reflections collected/unique              | 4423/3591  |
| Significant unique reflections            | 2364 with $I > 2\sigma(I)$   |
| R(int), R(sigma)                          | 0.0421, 0.0874   |
| Completeness to $\Theta = 25.30^{\circ}$  | 99.9%  |
| Refinement                                |  |
| Refinement method                         | Full-matrix least-squares on $F^2$   |
| Data/parameters/restraints                | 3591/265/0   |
| Goodness-of-fit on $F^2$                  | 1.034  |
| Final <i>R</i> indices $[I > 2\sigma(I)]$ | $R_1 = 0.0647, wR_2 = 0.1156$  |
| <i>R</i> indices (all data)               | $R_1 = 0.1069, wR_2 = 0.1324$  |
| Extinction expression                     | None   |
| Weighting scheme                          | $w = 1/[\sigma^2(F_2^2) + (aP)^2 +$  |
|   | <i>bP</i> ] where $P = (F^2 + 2F^2)/3$   |
| Weighting scheme parameters               | <i>a</i> , <i>b</i> 0.0236, 0.7910   |
| Largest $\Delta/\sigma$ in last cycle     | 0.000  |
| Largest difference peak and hole          | $0.202 \text{ and } -0.255 \text{ e/}Å^3$  |
| Structure solution program                | SHELXS – 97 Sheldrick [21]   |
| Structure refinement program              | shelxL-97 Sheldrick [22]   |
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#### 2.3. Computational details

All density functional theory (Becke's hybrid HF-DFT procedure [23] with the Lee-Yang-Parr [24] correlation functional [B3LYP/6-31G(d)]) calculations were done with GAUSSIAN 03 [25]. Geometries were completely optimized and characterized as true minima or transition states (TSs) by frequency calculations. For transition states, in addition intrinsic reaction coordinate calculations have been performed.

Bulk solvent effects were estimated by B3LYP/6-31G(d) single point calculations using the polarizable continuum method (IEF-PCM [26]) with ethanol as solvent. The electronic structures of the various minima and TSs were analyzed with the aid of the NBO method [27].

# 3. Results and discussion

### 3.1. X-ray crystal structure

The crystal structure analysis of 2 showed that the compound is 1-(4-dimethylaminobenzyl)-2-(4-dimethylaminophenyl)-benzimidazole. Fig. 1 shows a stereoscopic ORTEP plot [28] of 2 with the atom numbering scheme; the packing of 2 is depicted in Fig. 2. Selected bond lengths, bond angles and dihedral angles are listed in Table 2. Also given there are the corresponding calculated [B3LYP/6-31G(d)] geometric parameters. Whereas the phenyl ring bonded to C2 is only slightly twisted out of the plane of the benzimidazole ring [the angle between their leastsquares planes is 24.01(11)°,  $\tau_1 = \tau$  (N1–C2–C21–C26) = – 22.6°], the benzyl group is oriented almost perpendicular to the benzimidazole ring [87.83(11)°,  $\tau_2 = \tau$  (C8–N1–C10–C11) = – 84.5°] (Fig. 1). The dimethylamino groups are nearly co-planar to the phenyl rings they are bonded to [the angles between their least-squares planes are 8.76(17)° for N14 and 13.49(17)° for N24;  $\tau_3 = \tau$  (C15–C14–N14–C18)=12.6°,  $\tau_4 = \tau$  (C15–C14– N14–C17) = 166.6°;  $\tau_5 = \tau$  (C25–C24–N24–C28 = 18.8°,  $\tau_6 = \tau$  $(C25-C24-N24-C27) = -170.0^{\circ}$  and essentially trigonal as evidenced by the corresponding sum of angles ( $w_1 = 354.9^\circ$  for N14;  $w_2 = 354.5$  for N24). The corresponding calculated [B3LYP/6-31G(d)] structural parameters are  $\tau_1 = -33.7^\circ$ ,  $\tau_2 = -81.4^{\circ}, \ \tau_3 = 11.6^{\circ}, \ \tau_4 = 170.0^{\circ}, \ \tau_5 = 9.1^{\circ}, \ \tau_6 = 172.4^{\circ},$  $w_1 = 359.4^\circ$ ,  $w_2 = 357.8^\circ$ . The T shaped molecules are packed in a herringbone pattern (see Fig. 2).

#### 3.2. Quantum chemical calculations

For the formation of 2 by reaction of o-phenylenediamine with 4-diaminobenzaldehyde a mechanism involving cyclisation of the initially formed bis-Schiff base 1  $[R = N(CH_3)_2]$  to a zwitterionic intermediate **3**, followed by 1,3-H shift (Scheme 2), has been proposed [16]. In the following, a detailed mechanistic study of this reaction sequence using quantum chemical methods [B3LYP/6-31G(d)] density functional theory calculations] is presented. To assess the appropriateness of the chosen model chemistry, selected structural parameters calculated by the B3LYP/6-31G(d) procedure for compound 2 are compared with the corresponding experimental data in Table 2 (for atom numbering, see Fig. 1). Agreement is generally very good, with the largest deviations between experimental X-ray and calculated data found for the C2-N1-C10-C11 torsional angle,  $100^{\circ}$  (X-ray) vs.  $123^{\circ}$  (calcd). Intermolecular interactions in the crystal (see Fig. 2 for an ORTEP plot of the packing of 2) easily can account for this discrepancy. Thus, we are confident that the chosen computational procedure will be of sufficient reliability.



Fig. 2. Stereoscopic ORTEP [28] plot of the packing of 2. The atoms are drawn with arbitrary radii.

A detailed conformational analysis with respect to rotation around the aryl-N formal single bonds resulted in four distinct structures **1a–d**, characterized by the respective torsional angles C4–C9–N3–C2 and C7–C8–N1–C10 (Table 3, the atom numbering corresponds to that given in Fig. 1 for compound **2**; the conformation shown in Scheme 2 corresponds approximately to that of **1d**). Conformer **1d**, where the reacting centres, N1 and C2, are in an arrangement particularly favourable for cyclisation, is the lowest one among **1a–1d**. The reaction commences by attack of the nitrogen lone pair lp(N1) at C2 with a concomitant 90° rotation (breaking) of the C2=N3 double bond. In the cyclisation transition state **TS1** the phenyl ring on C2 is almost perpendicular to the plane formed by N1–C2–N3,  $\tau$ (C9–N3–C2–C21)=94° (Table 3). The newly forming N1–C2 single bond is already quite short, r(N1-C2) = 1.823 Å, compared to 2.863, 1.532, 1.503 and 1.397 Å in **1d**, **3**, **TS2**, and **2**, respectively. Calculated structures of **TS1** and **TS2** are shown in Fig. 3.

The NBO analysis indicates the presence of a  $\sigma$ -type N1–C2 single bond with an occupancy of 1.756; that of the corresponding antibonding  $\sigma^*$  is 0.268. The electron pair of the C2=N3 double bond in **1d** becomes a partial N3=C9  $\pi$ -bond (occupancy=1.869; that of the corresponding antibonding  $\pi^*$  orbital is 0.495) in **TS1** and the  $\pi$ -type lone pair lp(N3) in the cyclic intermediate **3**. The barrier for this first step is ca. 30 kcal mol<sup>-1</sup>, substantially higher than those normally found in pseudopericyclic reactions [29–32]. Although formally there is one orbital disconnection, i.e. a switch from

Table 2

Selected geometric parameters of 2 (bond lengths in Å, bond angles and dihedrals in °) obtained by X-ray crystallography and B3LYP/6-31G(d) calculations

|           | X-ray    | B3LYP |                 | X-ray    | B3LYP |  |
|-----------|----------|-------|-----------------|----------|-------|--|
| N1-C2     | 1.380(3) | 1.397 | N1-C8-C7        | 131.6(3) | 132.1 |  |
| N1-C8     | 1.386(3) | 1.388 | N1-C8-C9        | 105.4(2) | 105.4 |  |
| N1-C10    | 1.457(3) | 1.457 | C7-C8-C9        | 123.0(3) | 122.6 |  |
| C2-N3     | 1.331(3) | 1.320 | N3-C9-C8        | 110.5(2) | 110.2 |  |
| C2-C21    | 1.473(3) | 1.468 | N3-C9-C4        | 129.7(3) | 130.0 |  |
| N3-C9     | 1.393(3) | 1.382 | C8-C9-C4        | 119.7(3) | 119.8 |  |
| C8–C9     | 1.398(4) | 1.414 | N1-C10-C11      | 114.1(2) | 115.0 |  |
| C10-C11   | 1.524(4) | 1.521 | C14-N14-C17     | 119.3(3) | 119.2 |  |
| C14-N14   | 1.390(3) | 1.391 | C14-N14-C18     | 118.1(3) | 119.2 |  |
| N14-C17   | 1.445(4) | 1.453 | C17-N14-C18     | 117.5(2) | 118.1 |  |
| N14-C18   | 1.452(4) | 1.453 | C24-N24-C27     | 121.0(2) | 119.6 |  |
| C24-N24   | 1.379(3) | 1.386 | C24-N24-C28     | 121.5(2) | 119.5 |  |
| N24-C27   | 1.440(4) | 1.453 | C27-N24-C28     | 116.9(2) | 118.7 |  |
| N24-C28   | 1.443(3) | 1.452 | C2-N1-C10-C11   | 99.5(3)  | 112.8 |  |
| C2-N1-C8  | 106.9(2) | 106.2 | N1-C10-C11-C12  | -9.2(4)  | -18.5 |  |
| C2-N1-C10 | 130.1(2) | 128.9 | C13-C14-N14-C17 | -14.2(4) | -10.8 |  |
| C8-N1-C10 | 122.9(2) | 123.7 | C15-C14-N14-C18 | 12.6(4)  | 11.6  |  |
| N3-C2-N1  | 112.5(2) | 112.6 | N3-C2-C21-C22   | -19.5(4) | -30.7 |  |
| N3-C2-C21 | 121.7(2) | 122.9 | C23-C24-N24-C27 | 7.6(4)   | -8.3  |  |
| N1-C2-C21 | 125.7(2) | 124.6 | C25-C24-N24-C28 | 18.8(4)  | 9.1   |  |
| C2-N3-C9  | 104.7(2) | 105.7 |                 |          |       |  |



Scheme 2. Reaction mechanism for the rearrangement  $1 \rightarrow 2$ .

the  $\pi$ -system comprising C2–N3–C9–C8 to the orthogonal  $\sigma$ -type lone pair on N1-the prerequisite for a pseudopericyclic reaction to occur-formation of the N1-C2 single bond requires rotation of the C2=N3 double bond with a concomitant cost in energy. Furthermore, formation of the intermediate 3 is strongly endothermic/endergonic ( $\Delta G_{\text{react}} = +30 \text{ kcal mol}^{-1}$ ) and **3** is barely stable with a barrier for ring opening of  $\Delta G^{\neq} =$  $2 \text{ kcal mol}^{-1}$ . Thus, the reverse reaction, ring opening of the intermediate 3, meets the criteria for low-barrier pseudopericyclic reactions [31,32]. Surprisingly, despite the formal zwitterionic character of 3, polar solvents (EtOH) do not appreciably stabilise this structure (Table 3). Although, according to the natural population analysis (NPA) there is a decrease and increase of negative charge on N1 and N3, respectively, in **3** [-0.3082 (N1), -0.5417 (N3)] as compared to 1 [-0.4601 (N1), -0.4663 (N3)], actually the charge separation is considerably smaller than suggested by the zwitterionic formula of Scheme 2. The N1-C10 bond is quite short, r(N1-C10) = 1.330 Å, compared to 1.285 Å in 1d and 1.457 Å in 2, but the NBO analysis does not indicate a substantial double bond character. Yet, nitrogen N1 is trigonal and the pendant moiety, 4-(CH<sub>3</sub>)<sub>2</sub>N-C<sub>6</sub>H<sub>4</sub>-CH, is planar  $[\tau(C7-C8-N1-C10) = -5.8^{\circ},$  $\tau$ (C8–N1–C10–C11) =  $-171.9^{\circ}$ ]. Apparently, **3** is characterized by a rather delocalised, polymethine-like electronic structure of the N3- $C_6H_4$ -N1-C10H-C<sub>6</sub>H<sub>4</sub>-N(CH<sub>3</sub>)<sub>2</sub> moiety without significant charge separation. Rearrangement of the intermediate 3 to the final product 2 via a formal 1,3-H shift is found to be the rate determining step and has a quite substantial barrier (TS2, Table 3), in line with the reaction conditions, i.e. refluxing EtOH. It is, however, strongly exothermic/exergonic ( $\Delta G_{\text{react}}$ = -16 kcal mol<sup>-1</sup> in EtOH). Thus, although ring-opening of **3** back to the starting material has an almost negligible Gibbs free activation energy ( $\Delta G^{\neq} = 3 \text{ kcal mol}^{-1}$  in EtOH), the title compound 1-(4-dimethylaminobenzyl)-2-(4-dimethylaminophenyl)-benzimidazole 2 is the product formed under thermodynamic control. As a consequence, one would expect formation of the bis-Schiff base under milder reaction conditions. For instance, formation of 4,5-dichloro-N,N'-bis-(4-diethylamino-benzylidene)-benzene-1,2-diamine has been observed in the room temperature reaction of 4,5-dichlorobenzene-1,2-diamine with 4-(diethylamino)salicylaldehyde [33].

(1,3)-Sigmatropic rearrangements would involve antarafacial movements of the hydrogen atom and are seldom observed in thermal reactions [34]. However, as described above, the double bond character of the N1-C10 bond in 3 is very small and, thus, the usual frontier orbital (orbital symmetry) rules will not apply. Viewing 3 as an immonium ion, C10 is expected to have partial carbonium ion character  $[q(C10)_{NPA}=0.05]$ , and all pericyclic reactions are allowed. Just counting electrons, yields six electrons involved in the rearrangement; thus, it is suprafacially allowed. Furthermore, transition state TS2 has some unusual features: (i) the moving hydrogen atom is still quite strongly bound to C2, bond order = 0.640, r(C2-H) = 1.238 Å and an occupancy of 1.744 of the C2–H NBO. (ii) Despite the planar arrangement of the N1 substituents in both intermediate 3 and product 2, in TS2 N1 is strongly pyramidalised (sum of angles  $= 316^{\circ}$ ) with the aryl rings at N1 and C2 pointing in opposite directions ( $\tau$ (C10–N1–C2– C21 =  $-103.3^{\circ}$ ). As a consequence of this distortion, the H atom approaches C10 suprafacially in contrast what is expected for a formal 1,3 H-shift. In fact, the four atoms involved in this rearrangement, H-C2-N1-C10, lie in a common plane forming a distorted rectangle (Fig. 3). Thus, TS2 shows some

Table 3

B3LYP/6-31G(d) calculated relative Gibbs' free energies (kcal mol<sup>-1</sup>) in the gas phase and ethanol solution and selected geometrical parameters for reactants 1a-1d, transition states TS1 and TS2, intermediate 3 and product 2 of the Schiff base  $\rightarrow$  benzimidazole rearrangement

|     | $\Delta G$ (gas phase) | $\Delta G$ (EtOH) |                    |   |
|-----|------------------------|-------------------|--------------------|---|
| 1a  | 0.0                    | 0.0               | 44.1 <sup>a</sup>  | -44.4 <sup>b</sup>                      |
| 1b  | 1.7                    | 3.2               | $-129.0^{\rm a}$   | $-129.0^{b}$                            |
| 1c  | 0.5                    | 1.6               | $-131.7^{\rm a}$   | $-38.5^{b}$                             |
| 1d  | -1.1                   | 0.0               | 146.4 <sup>a</sup> | $-38.2^{b}$                             |
| TS1 | 31.6                   | 31.2              | 298 <sup>c</sup>   | 1.823 <sup>d</sup> , 94.1 <sup>e</sup>  |
| 3   | 29.6                   | 28.6              |                    |   |
| TS2 | 67.7                   | 66.3              | 900 <sup>c</sup>   | 1.238 <sup>f</sup> , 1.705 <sup>g</sup> |
| 2   | -16.9                  | -15.7             |                    |   |

<sup>a</sup>  $\tau$ (C4–C9–N3–C2).

<sup>b</sup>  $\tau$ (C7–C8–N1–C10).

<sup>c</sup> Imaginary frequency (cm<sup>-1</sup>).

<sup>d</sup> *r*(N1–C2).

<sup>e</sup> τ(C9–N3–C2–C21).

<sup>f</sup> r(C2–H).

<sup>g</sup> r(C10–H).



Fig. 3. Calculated [B3LYP/6-31G(d)] structures and pertinent structural data (distances in Å, angles in °) of transition states TS1 and TS2.

resemblance to the pseudopericyclic 1,3-shifts observed in  $\alpha$ -oxo-ketenes and related heterocumulenes (lone-pair-LUMOmediated pericyclic reactions [35,36]). (iii) The rather high barrier calculated for the rearrangement  $3 \rightarrow 2$  can be attributed to the substantial geometrical reordering accompanying this transformation. (iv) The moving hydrogen atom carries a positive charge (+0.248) which is comparable to that in the intermediate 3 (+0.250) and TS1 (+0.232). (v) The carbon atom C10, which becomes sp<sup>3</sup>-hybridised in the product is still trigonal in TS2 (sum of angles=358°). (vi) Although there is some interaction between C10 and H15 via lp(C10), or, more precisely, the bonding and antibonding linear combinations of lp(N2) and lp(C10) with  $\sigma$ (C2–H) and  $\sigma^*$ (C2–H), respectively, the C10–H bond is still quite weak, bond order <0.2, r(C10–H)=1.705 Å.

#### 4. Conclusion

X-ray crystallography shows that the compound obtained in the reaction of o-phenylenediamine with 4-dimethylaminobenzaldehyde in refluxing EtOH is 1-(4-dimethylaminobenzyl)-2-(4-dimethylaminophenyl)-benzimidazole 2 rather than N, N'-bis(4-dimethylaminobezylidene)-benzene-1,2-diamine **1**. The benzyl group is almost perpendicular oriented with respect to the heterocyclic ring system. In contrast, the 2-aryl moiety is nearly coplanar. <sup>1</sup>H and <sup>13</sup>C NMR spectra have been completely assigned by the heteronuclear multiple-bond connectivity (HMBC) procedure [20]. The melting point of this compound is  $mp = 182^\circ$ , much closer to that reported in [18],  $mp = 168^{\circ}$ , than those given in other previous reports  $(252-255^{\circ} [15,17])$ . Thus, the present results allow to establish the true identity of the compounds obtained by reaction of o-phenylenediamine with 4-dimethylaminobenzaldehyde. Density functional theory calculations [B3LYP/6-31G(d)] indicate facile cyclisation of the initially formed Schiff base 1 to a tetrahedral intermediate 3. Rearrangement of this intermediate has a rather high barrier, the product of this rearrangement, 1-(4-dimethylaminobenzyl)-2-(4-dimethylaminophenyl)-benzimidazole 2, however, is considerably more stable than 1. Despite the formal zwitterionic character of 3, polar solvents are calculated (polarizable continuum model) to have only a marginal stabilising effect. Analysis of the electronic structures of the various minima and transition states involved in the reaction  $1 \rightarrow 2$  with the aid of the NBO method helps to rationalise the unusual features of this process, especially those of TS2. Here, in contrast to what one would expect for a formal (1,3)-sigmatropic rearrangement, movement of the hydrogen occurs in a suprafacial manner.

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