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Short Note

N,N′-Di(*p*-tolyl)-1,4-benzoquinonediimine (*N,N′*-Di-*p*-tolylcyclohexa-2,5-diene-1,4-diimine)

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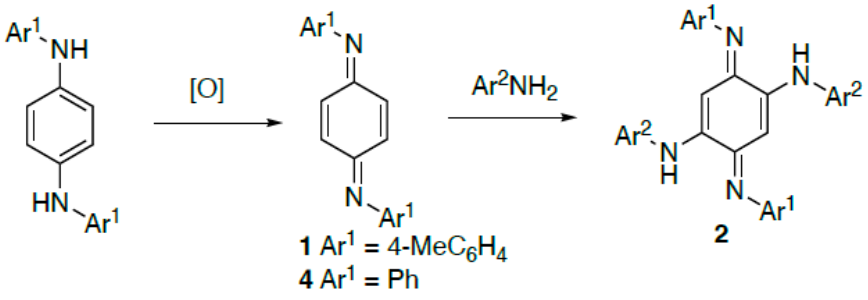
Abstract

The title compound has been fully characterised using ^{1}H and ^{13}C NMR spectroscopy, which reveals (*E*) to (*Z*) isomerisation upon dissolution. In the solid state, X-ray diffraction shows exclusively the (*E*)-isomer with two geometrically near-identical independent molecules each with the outer rings tilted with respect to the central ring.

Keywords: quinonediimines; NMR spectra; X-ray structures

1. Introduction

The title compound **1** was first described in the literature in 1956 [1], when it was prepared by oxidation of the corresponding diamine using mercuric oxide and subsequently reacted with a large excess of different anilines to give substituted azophenines (Scheme 1). This route provides perhaps the most efficient route to unsymmetrically substituted azophenines **2** which have been of recent interest as potential molecular switches when adsorbed onto a metal surface [2]. Because of the early date of the previous work, the degree of characterisation of **1** is limited with only the melting point, elemental analysis, and UV and IR spectra being reported [1].



Scheme 1. General formation of *N,N′*-diaryl-1,4-benzoquinonediimines and their reaction to give azophenines.

We recently prepared compound **1** on a large scale for new studies on the molecular switching behaviour of derived azophenines, and in this paper we describe a detailed ^{1}H and ^{13}C NMR analysis of **1** as well as its X-ray structure determination.

2. Results

The required starting diamine *N,N′*-di-*p*-tolyl-*p*-phenylenediamine **3** is reported to be readily accessible from the inexpensive starting materials hydroquinone and *p*-toluidine. However, the earliest procedures for this reaction used rather harsh conditions involving

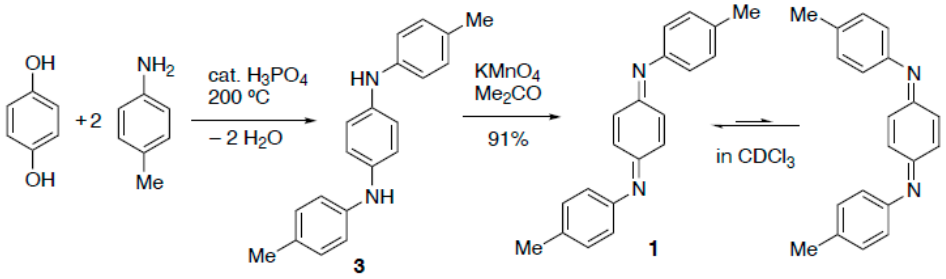
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the prolonged heating of a melt of the neat materials with zinc chloride at over 200 °C [3,4]. A somewhat later procedure replaced the zinc chloride with iodine [5]. In our hands, none of these were satisfactory and so we adapted a patent procedure employing phosphoric acid as a dehydration catalyst [6] (Scheme 2). Using this method, the diamine **3** was reliably obtained in low yield and had a melting point and NMR data in accordance with expectations.



Scheme 2. Synthetic route used to prepare compound **1**.

The original oxidation of **3** to give the target diimine **1** used mercuric oxide in boiling benzene [1], but we found that potassium permanganate in acetone, reported for the synthesis of the corresponding diphenyl compound **4** [7], was less hazardous and just as effective. In this way compound **1** was obtained in high yield as dark red crystals with a melting point in good agreement with expectation.

A study of the compound using ^{1}H and ^{13}C NMR spectroscopy revealed interesting behaviour. Separate signals were observed for (*E*)- and (*Z*)-isomers and, in addition, their ratio varied with time. Specifically, a spectrum run immediately (5 min) after dissolution in $CDCl_3$ showed an (*E*)/(*Z*) ratio of 5:1 but after 15 min this had changed to 3:1 and eventually after >12 h came to an equilibrium value of 1.25:1. When the equilibrated solution was allowed to evaporate, however, the deposited crystals were again the (*E*)-isomer. We conclude that the compound exists in the solid state exclusively as the (*E*)-isomer but this equilibrates in solution to a 55:45 mixture. A similar phenomenon has previously been observed for the diphenyl analogue **4** which was observed to equilibrate from the all-(*E*) solid to a mixture of (*E*)- and (*Z*)-isomers on dissolving in $CDCl_3$ [8], with variable temperature kinetic studies allowing an estimation of the energy barrier to isomerisation. In that case, the full assignment of ^{1}H and ^{13}C signals for both isomers was reported which was in excellent agreement with our independent assignments for **1** (Figure 1). A more recent study also reports ^{1}H and ^{13}C shifts for (*E*)- and (*Z*)-isomers of **4** in CD_3SOCD_3 with the ^{1}H signals fully assigned [9].

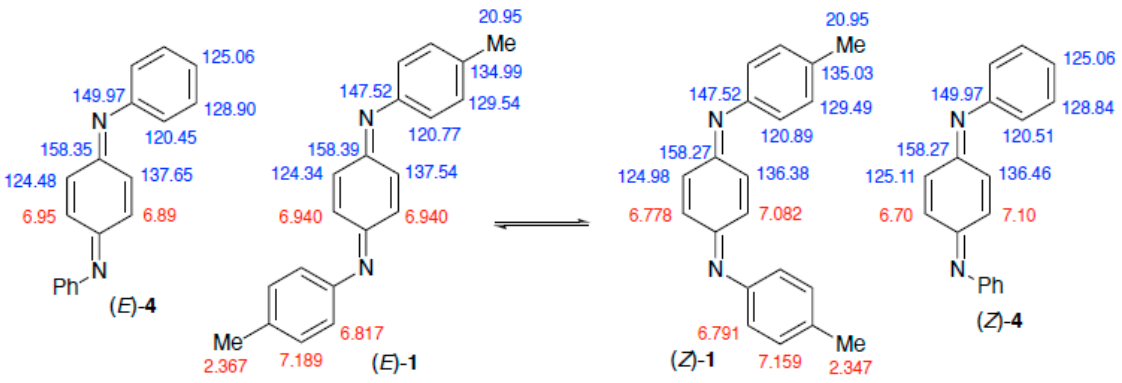


Figure 1. Assignment of ^{1}H (red) and ^{13}C (blue) NMR signals for (*E*)- and (*Z*)-isomers of **1** and comparison with values for **4** [8].

By comparing the spectra at different times after dissolution we were able to unambiguously assign all signals for the (*E*)- and (*Z*)-isomers (see Supplementary Materials). As shown in Figure 1, the data show some unexpected features. First, most chemical shift values are very similar between the two isomers, so we present them with one additional decimal place compared with the normal convention. While the ^{1}H signals for the *p*-tolyl groups are all distinct, the ^{13}C signals for N–C and CH_3 are coincident between the two isomers. Perhaps more surprising is the observation that while the two ^{1}H and ^{13}C signals for the central quinonoid ring are both well separated for the (*Z*)-isomer, distinctly different ^{13}C signals for the (*E*)-isomer correspond to a single ^{1}H environment. A similar phenomenon is also observed for **4** (Figure 1).

For compound **1** the recrystallised material proved to be suitable for X-ray diffraction and the resulting structure features two independent molecules, each symmetrical about an inversion centre located at the centre of the quinonoid ring (Figure 2). We were aware that the crystal initially selected might not have been representative of the bulk material so, to exclude this possibility, six additional crystals were subjected to preliminary crystallographic examination but all gave the same unit cell parameters.

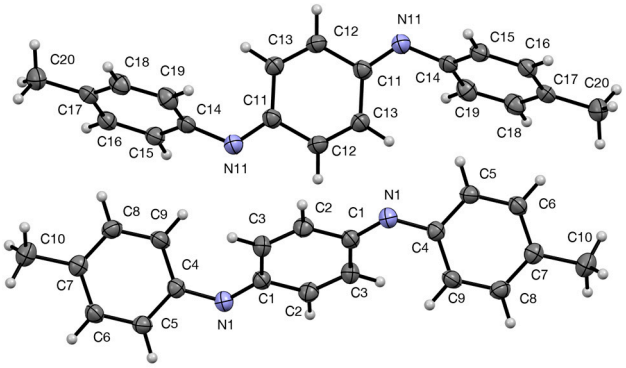


Figure 2. Structures of the two independent molecules of **1** with numbering system used and 50% probability ellipsoids.

The dimensions of the two molecules are very similar (the fit of non-hydrogen atoms of the two independent molecules gives a root-mean-squared deviation of 0.057 Å) but there is a slight difference in the angles between the rings. In each case the two outer tolyl rings are exactly parallel and are tilted with respect to the central quinonediimine plane by 51.47(4)° for the C-1 molecule but 55.34(4)° for the C-11 molecule. In fact this structural feature is also common to most of the analogous *N*,*N*′-diaryl-1,4-benoquinonediimines whose structures have been determined (Figure 3).

Specifically, the diphenyl compound **4** [10], the two independent molecules in the structure of the dinaphthyl compound **5** [11], and the diiodo compound **6** [12] all have angles in a similar range, while the extra methyl groups in **7** [13] lead to a value in that case that is much larger. The exception to this trend is the dibromo compound **8** [12] where the two outer rings are tilted to the same extent with respect to the central ring but in opposite directions, a surprising feature not commented upon by the original authors. In the more hindered monoaryldiimine **9** the angle between planes is again higher in a similar way to **7** [14].

In the crystal, the molecules of **1** are arranged in rows with alternation of the two forms when viewed along the *a*-axis (Figure 4).

In summary, we have found that compound **1** gives very similar NMR data to the diphenyl analogue **4** and exhibits the same (*E*) to (*Z*) isomerisation upon dissolution in $CDCl_3$. In the solid state the X-ray structure shows purely the (*E*)-isomer with the coplanar outer rings tilted with respect to the central one to a similar degree to comparable structures.

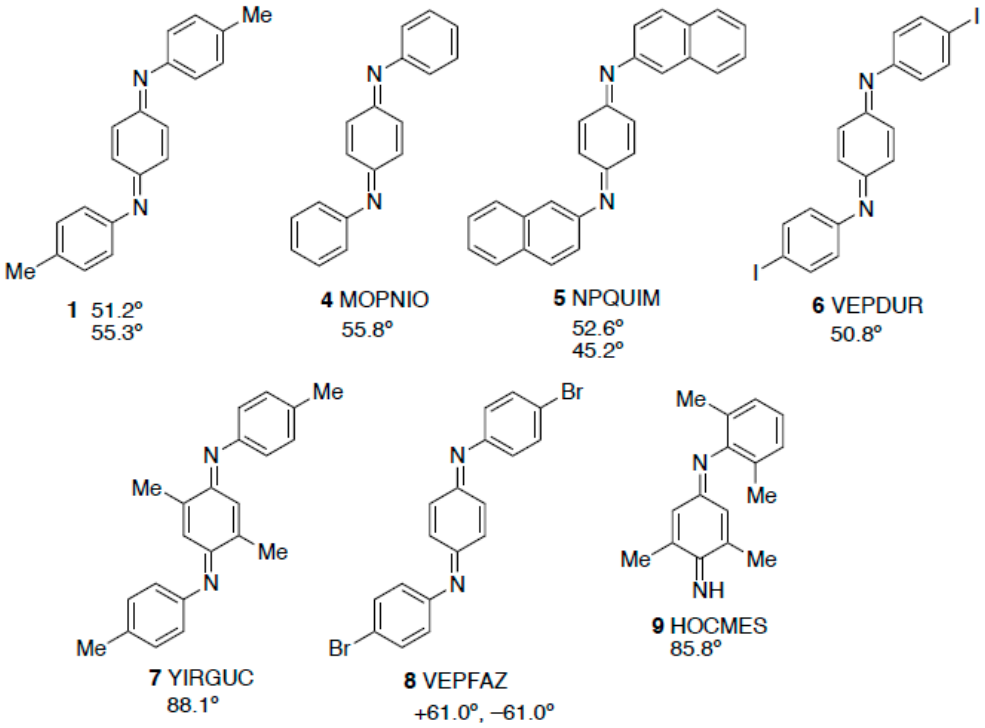


Figure 3. Structure of **1** compared with diarylbenzoquinonediimines that have previously been crystallographically characterised with CSD Refcodes and dihedral angles between the *N*-aryl rings and the central ring.

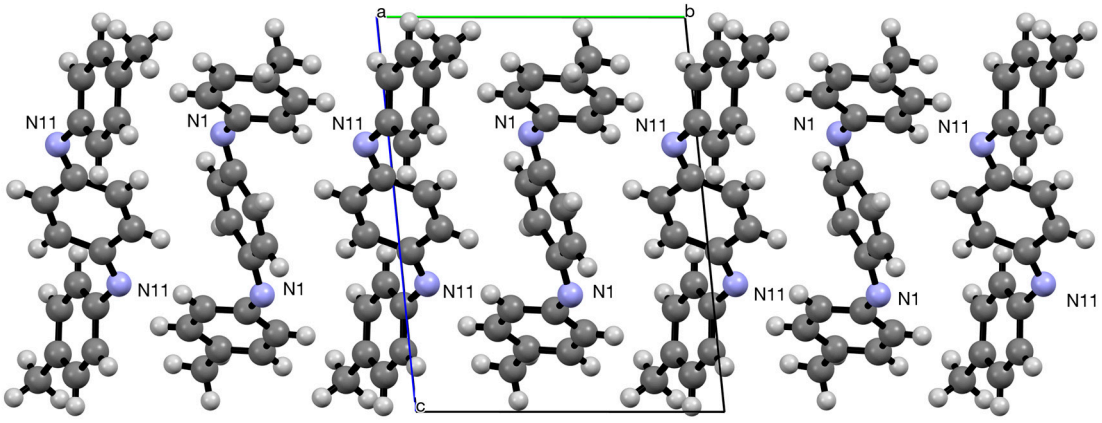


Figure 4. Alternating arrangement of molecules in the crystal viewed along the *a*-axis.

3. Experimental

3.1. General Experimental Details

Melting points were recorded on a Reichert hot-stage microscope (Reichert, Vienna, Austria) and are uncorrected. NMR spectra were obtained using Bruker AVII 400 or AVIII 500 instruments (Bruker, Billerica, MA, USA). Spectra were run in $CDCl_3$ and chemical shifts are reported in ppm to high frequency of the reference and are referenced to internal Me_4Si (δ 0.00) for ^1H and to the solvent signal (δ 77.00) for ^{13}C, and coupling constants are in Hz. NMR spectra were processed using iNMR reader, version 6.3.3 (Mestrelab Research, Santiago de Compostela, Spain).

3.2. N,N′-Di-p-tolyl-p-phenylenediamine **3**

Following a literature procedure [6], a mixture of hydroquinone (27.5 g, 0.25 mol), *p*-toluidine (20.8 g, 0.19 mol), and orthophosphoric acid (1.33 mL, 0.025 mol) was heated in

a sand bath at 200 °C until it melted. With continued heating, additional *p*-toluidine (41.8 g, 0.39 mol) was added through a funnel over 50 min. The mixture was heated with removal of the water produced by distillation for 4.5 h. The molten material was carefully poured into rapidly stirred ethanol (250 mL) and the resulting crystals were filtered off, washed with ethanol and dried to give the product (3.65 g, 5%) as brown crystals, m.p. 182–184 °C (lit. [3,4], 182 °C). ^{1}H and ^{13}C NMR data were in agreement with reported values [15].

3.3. N,N′-Di-(p-tolyl)-1,4-benzoquinonediimine **1**

A solution of diamine **1** (2.01 g, 6.97 mmol) in AR acetone (50 mL) was stirred while a solution of potassium permanganate (0.93 g, 6.0 mmol) in AR acetone (100 mL) was added over a period of 30 min. After a further 30 min, the mixture was filtered to remove MnO_2 and the filtrate evaporated. Recrystallisation of the residue from acetone followed by toluene gave the product (1.82 g, 91%) as dark red crystals, m.p. 121–123 °C (lit. [1], 123–123.5 °C).

E-isomer

^{1}H NMR (500 MHz): δ 7.189 (4 H, d, *J* 8.0), 6.940 (4H, s), 6.817 (4 H, d, *J* 8.0) and 2.367 (6 H, s); ^{13}C NMR (125 MHz): δ 158.39 (2C, C=N), 147.52 (2C, C–N), 137.54 (2CH), 134.99 (2C), 129.54 (4CH), 124.34 (2CH), 120.77 (4CH), and 20.95 ($2CH_3$).

Z-isomer

^{1}H NMR (500 MHz): δ 7.159 (4 H, d, *J* 8.0), 7.082 (2H, d, *J* 1.0), 6.791 (4H, d, *J* 8.0), 6.778 (2 H, d, *J* 1.0) and 2.347 (6 H, s); ^{13}C NMR (125 MHz): δ 158.27 (2C, C=N), 147.52 (2C, C–N), 136.38 (2CH), 135.03 (2C), 129.49 (4CH), 124.98 (2CH), 120.89 (4CH), and 20.95 ($2CH_3$).

3.4. X-Ray Structure Determination of **1**

X-ray diffraction data for compound **1** were collected at 125 K using the St Andrews Automated Robotic Diffractometer (STANDARD) [16], consisting of a Rigaku sealed-tube generator equipped with a SHINE monochromator [Mo Kα radiation (λ = 0.71075 Å)], and a Saturn 724 CCD area detector, coupled with a Microglide goniometer head and an ACTOR SM robotic sample changer. Data for the compound were collected and processed (including correction for Lorentz, polarisation, and absorption) using CrystalClear [17]. The structure was solved by direct methods (SIR2011) [18] and refined by full-matrix least-squares against F^2 (SHELXL-2014/7) [19]. Methyl hydrogens were modelled as disordered across two idealised orientations. All calculations were performed using the CrystalStructure (version 4.1) [20] interface.

Crystal data for $C_{20}H_{18}N_2$: M = 286.38 g mol^{-1}, red prism, crystal dimensions 1.00 × 0.20 × 0.03 mm, triclinic, space group $P\bar{1}$ (No. 2), a = 6.8083(10), b = 9.7827(15), c = 12.2576(19) Å, a = 82.1608(10), b = 80.782(10), g = 74.958(8)°, V = 774.4(2) Å^3, Z = 2, D_{calc} = 1.228 g cm^{-3}, T = 125 K, goodness of fit on F^2 0.947, 11611 reflections measured, 3502 unique (R_{int} = 0.0542), which were used in all calculations. The final R_1 [$I > 2\sigma(I)$] was 0.0412 and wR_2 (all data) was 0.1118. Data have been deposited at the Cambridge Crystallographic Data Centre as CCDC 2482921. The data can be obtained free of charge from the Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/structures.

Supplementary Materials: The following are available online: Figure S1. 500 MHz ^{1}H NMR spectrum of **1** (spectrum after 5 min); Figure S2. 500 MHz ^{1}H NMR spectrum of **1** (spectrum after 5 min, expansion); Figure S3. 500 MHz ^{1}H NMR spectrum of **1** (spectrum after 15 min); Figure S4. 500 MHz ^{1}H NMR spectrum of **1** (spectrum after 15 min, expansion); Figure S5. 400 MHz ^{1}H NMR spectrum of **1** (spectrum after 13 h); Figure S6. 125 MHz DEPTQ ^{13}C NMR spectrum of **1** (after 13 h); Figure S7. 125 MHz DEPTQ ^{13}C NMR spectrum of **1** (after 13 h, expansion); Figure S8. HSQC NMR spectrum of **1**; Figure S9. HMBC NMR spectrum of **1**.

Author Contributions: R.B. prepared the compounds and recorded the spectroscopic data; A.M.Z.S. collected the X-ray diffraction data and solved the structure; R.A.A. designed the study, analysed the data, and wrote the paper. All authors have read and agreed to the published version of the manuscript.

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Conflicts of Interest: The authors declare no conflicts of interest.

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