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Crystal Structure of 2-[(1*E*)-2-(4-Fluorophenyl)diazenyl]-1*H*-imidazole

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Abstract: The molecule of the title compound adopts a twisted geometry with a rotation of approximately 30° between the mean planes of the imidazole and phenyl rings. The crystal structure displays hydrogen bonded chains as a result of N–H···N interactions between the imidazole rings of neighboring molecules. These H-bonded chains are assembled into flat molecular layers parallel to the (121) plane. Two intermolecular interactions, involving inversion-related molecules belonging to adjacent molecular layers, contribute significantly to the stabilization of the crystal.

Keywords: crystal structure; hydrogen bonding; 2-arylazoimidazoles

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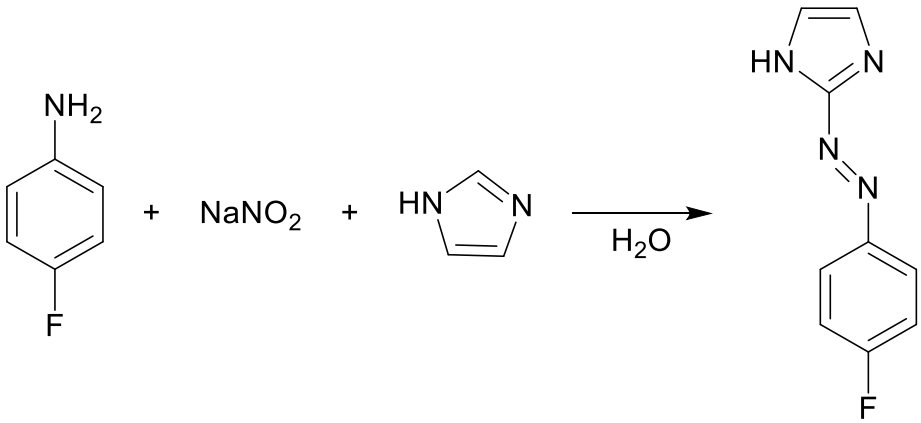
1. Introduction

2-[(1*E*)-2-(4-Fluorophenyl)diazenyl]-1*H*-imidazole, **F-Ph-N=N-Im** (Scheme 1), represents a member of highly versatile late stage intermediates for the divergent synthesis of direct dyes [1], which are characterized by their insolubility in the aqueous diazotizing mother liquor, hence allowing for their isolation with great ease (Scheme 1). When the imidazole core is subsequently quarternized, such 2-(Arylazo)-imidazoles have long been described in the literature as valuable reactive chromophores [2], but they are also relevant for commercial applications [3], as well as for academic research in the field of materials science [1].



Scheme 1. Synthesis of 2-[(1*E*)-2-(4-fluorophenyl)diazenyl]-1*H*-imidazole.

When industrial researchers from BASF started to explore the reactive behavior of quarternized 2-arylazoimidazolium salts containing halogenated phenyl moieties, it was

first established that quaternary salts of 2-(4-chlorophenylazo)-imidazole react very readily with amines, exchanging the chlorine atom for the amine residues, and usually yielding red dyes [4]. These SN_{AR} reactions turned out to proceed particularly smoothly with the 4-fluorophenyl relative and secondary aliphatic amines, thus allowing for very mild staining procedures of keratin or polyamide fibers. Consequently, the subsequent functionalization at the halogenated sites of haloaryl-azoimidazolium salts represents a synthetic permutation toolkit in its own right.

2. Results and Discussion

Crystal data and parameters of the crystal structure refinement for **F-Ph-N=N-Im** are collected in Table 1. The crystal structure has the space group symmetry $P\bar{1}$, and its asymmetric unit contains a single molecule (Figure 1). It displays a 1:1 disorder with regard to the location of the NH group of the imidazole ring, which can be either at N1 or N2. As expected, the central C1–N3=N4–C4 bridge between its imidazole and phenyl rings is almost planar, displaying a torsion angle of −179.08(10)°. The bond distances C1–N3, N3–N4, and N4–C4 are 1.3960(16), 1.2575(15), and 1.4294(17) Å, respectively. These values agree well with the parameters observed in the unsubstituted analogs (1*H*-imidazol-2-yl)phenyldiazene (CDS code HIPXAF) [5], 2-(*p*-tolylazo)imidazole (KEGMAL) [6], and a third structurally related compound (BUQRAH) [7]. With regard to the N–C=N unit of the imidazole ring, one expects the bond between the central carbon atom and the unprotonated nitrogen atom to be significantly shorter than that between the carbon and protonated nitrogen atoms, as is the case in two reference structures (HIPXAF: 1.324 vs. 1.353 Å; KEGMAL: 1.313/1.314 vs. 1.346/1.353 Å). By contrast, the corresponding C1–N1 and C1–N2 bond distances in **F-Ph-N=N-Im** appear to be roughly equal, i.e., C1–N1 = 1.3423(17) Å and C1–N2 = 1.3356(17) Å. This apparent equality is an averaging effect due to the random distribution of **F-Ph-N=N-Im** molecules with respect to the location of their protonated imidazole N atom in the crystal, whereas each individual molecule displays a characteristic difference in length between its two imidazole C-N bonds. Attempts to establish an alternative structure model, with split positions for N1 and N2, that would reflect this distinction were not successful. The imidazole and phenyl rings are both slightly rotated against the central planar unit of the molecule, as indicated by the corresponding torsion angles N4–N3–C1–N1 = 13.09(19)° and N3–N4–C4–C5 = 16.89(17)°. As a result, the overall molecular geometry is characterized by a significant twist between the mean planes of the imidazole and phenyl rings of 30.24(5)°.

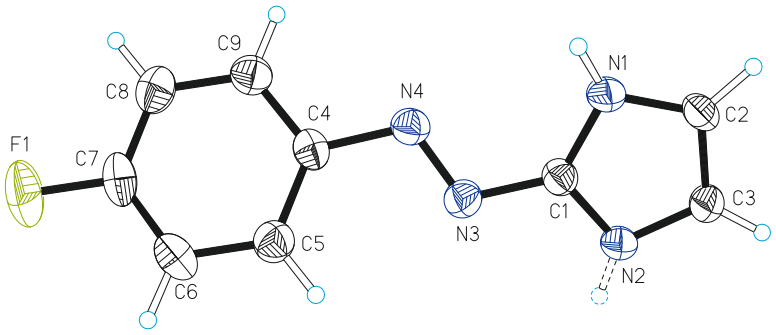


Figure 1. Molecular structure with non-H atoms depicted as ellipsoids at the 50% probability level and H atoms drawn as spheres of random size. The location of the NH group is either at N1 or N2 (1:1 disorder).

F-Ph-N=N-Im molecules are arranged in chains along the $[\bar{1}01]$ direction. Each individual chain along $[\bar{1}01]$ is perfectly ordered, in that successive imidazole rings in the chain show an alternation with respect to the location of their NH group between N1 and N2. This alternation induces a directionality and results in the formation of an infinite one-dimensional structure based on N1–H1N···N1^{i} and N2–H2N···N2^{ii} bonds (see Figure 2

and Table 2). H-bonded chains of this kind are packed into layers parallel to the (121) plane, with a random parallel/antiparallel mode of arrangement. The two most significant molecule/molecule interactions are formed between molecules belonging to adjacent layers of this type. In both cases, the two molecules concerned are related by an inversion operation and display an antiparallel arrangement with a large contact area between their flat van der Waals surfaces. This situation is illustrated in Figure 3. The centroid of the phenyl ring of the central molecule is at a distance of 3.64 Å to the central N3=N4 unit of a molecule in the adjacent layer below, and at a distance of 3.86 Å to the C1 atom of the imidazole ring of a molecule in the neighboring layer above. Another notable intermolecular interaction, resulting in an H3$\cdots$F1($x-1$, y+1, $z-1$) distance of 2.50 Å, involves a CH group of the imidazole ring and the fluoro substituent of the phenyl ring.

Table 1. Crystal data and structure refinement.

Empirical formula	$C_9H_7FN_4$
Formula weight	190.19
Temperature (K)	183
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	$P\bar{1}$
a (Å)	7.0756(4)
b (Å)	7.7929(5)
c (Å)	8.8199(6)
α (°)	70.801(2)°
β (°)	74.9153(19)°
γ (°)	83.689(2)°
Unit cell volume (Å^3)	443.29(5)
Z/Z′	2/1
Reflections collected/R_{int}	10418/0.0405
Data/restraints/parameters	1632/2/136
Goodness-of-fit on F^2	1.036
$R1$ [$I > 2\ \sigma(I)$]	0.0344
$wR2$ (all data)	0.0943
Largest diff. peak and hole (e · Å^{-3})	0.216 and −0.199
CCDC no.	2229643

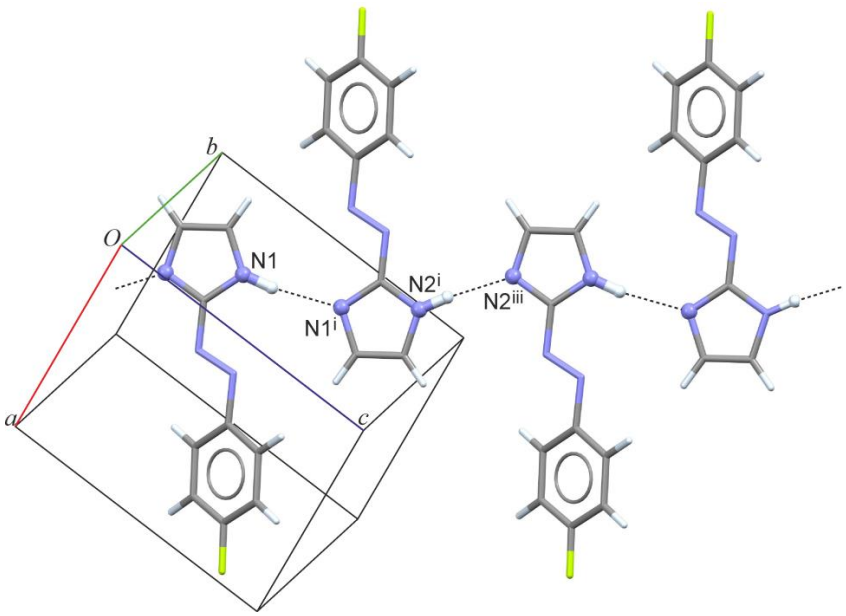


Figure 2. H-bonded chain structure displaying an ordered sequence of alternating locations for the NH group at either N1 or N2. Symmetry codes: (i) −x, −y + 1, −z + 1; z + 1; (iii) x − 1, y, z + 1., y, z + 1.

Table 2. Hydrogen-bond geometry (Å, °).

D–H···*A*	*d*(*D*–H)	*d*(H···*A*)	*d*(*D*···*A*)	*D*–H···*A*
N1–H1N···N1 [i]	0.873(10)	2.011(11)	2.876(2)	171(3)
N2–H2N···N2 [ii]	0.870(10)	1.944(10)	2.810(2)	174(3)

Symmetry codes: (i) $-x, -y + 1, -z + 1$; (ii) $-x + 1, -y + 1, -z$.

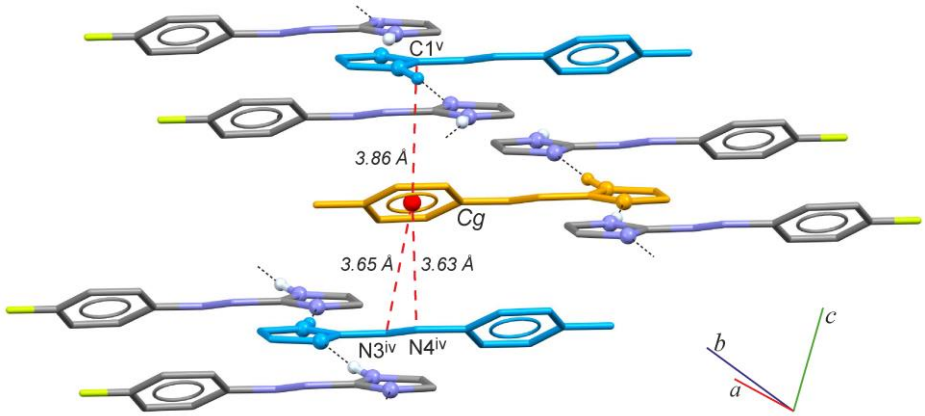


Figure 3. Intermolecular interactions between a central molecule (orange) and two neighboring molecules (blue) belonging to two adjacent molecular layers parallel to the (121) plane. Symmetry codes: (iv) −x + 1, −y, −z + 1; (v) −x + 1, −y + 1, −z + 1.

3. Materials and Methods

2-[(1*E*)-2-(4-fluorophenyl)diazenyl]-1*H*-Imidazole [210180-24-0] was prepared following a published procedure [2,8] as shown in Scheme 1. It is noteworthy that this protocol resulted in the neutral product rather than its hydrochloride as described in the literature. The NMR and IR data were in agreement with known literature or patent data [8].

FT-IR (ATR, neat) ν = 3072, 2975, 2869, 2761, 2696, 2572, 2525, 2439, 2325, 2111, 1901, 1722, 1591, 1494, 1366, 1222, 1107, 1000, 901, 840, 767 cm^{-1}. ^1H NMR (300 MHz, DMSO-*d6*) δ = 13.02 (s, 1H), 7.91 (dd, *J* = 8.8, 5.5 Hz, 2H), 7.46–7.33 (m, 4H). NMR spectra were recorded on a Bruker Avance DPX 300 MHz spectrometer (Supplementary Materials). IR spectra were obtained with a Bruker ALPHA Platinum FT-ATR instrument (Supplementary Materials).

Single crystals suitable for X-ray structure determination were grown from a saturated solution of **F-Ph-N=N-Im** in toluene. Intensity data for the single crystal structure determination were recorded with a Bruker D8 Quest Photon 100 diffractometer using MoKα radiation (λ = 0.71073 Å). The crystal structure was solved by Direct Methods with SHELXT [9] and refined with least-squares techniques using SHELXL [10]. H atoms were identified in difference-Fourier maps and those bonded to carbon atoms were refined using a riding model with U_{iso} parameters set to $1.2U_{eq}$(C). The H atom positions at N1 and N2 were both found to be half-occupied and were each refined with a distance restraint, N–H = 0.88(1) Å. Their U_{iso} parameters were refined freely. CCDC 2229643 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures.

Supplementary Materials: The following are available online, spectra data, cif data and check cif report.

Author Contributions: Conceptualization, H.S.; methodology, T.G.; writing—original draft preparation, T.G., S.N. and H.S.; writing—review and editing, P.M.—recording spectra and repeating published synthesis; H.S. and S.N.; visualization, crystal structure determination, K.W. and T.G.; supervision, H.S. and S.N.; funding acquisition, S.N. All authors have read and agreed to the published version of the manuscript.

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