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A supramolecular assembly formed between phthalimide and 2-guanidinobenzimidazole, containing a short 2.692(4) Å N-H...N hydrogen bond, is reported. The crystal structure of this species was determined by both X-ray and neutron diffraction. The diffraction data reveal that the proton involved in the short hydrogen bond has been transferred from the phthalimide to the guanidinobenzimidazole to form an ion pair. There is also an interesting stacking interaction between the atoms involved in the short hydrogen bond and the π system of a phthalimide molecule that is approximately 3.3 Å away. The structure is compared with the structure of a similar assembly formed between 4-nitrophthalimide and 2-guanidinobenzimidazole.

[†]Dedicated to Professor Jerald S. Bradshaw, a fine chemist and good friend of LFL

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Introduction.

Hydrogen bonds are important intermolecular interactions found in both biochemical and chemical systems [1]. They are responsible for many of the special properties of water, and for the interactions of biological molecules with water. Hydrogen bonds also play important structural roles in nucleic acids and proteins. Within proteins they may form part of the electron conduction pathways [2] and short hydrogen bonds are thought to play important roles at the catalytic sites of particular enzymes, although the exact details of their role tends to remain somewhat uncertain [3]. Hydrogen bonds involving both organic and inorganic species have also often been employed in crystal engineering to form new materials, some of which show potential for acting as functional supramolecular devices [4]. Biological molecules have also been employed to form synthetic systems; for example, hydrogen bonding between complementary strands of DNA has been used in the programmed assembly of nanoscale building blocks [5].

The strengths of hydrogen bonds are less dependent on direction than conventional covalent bonds, and their lengths vary over a greater range [6]. By way of example, N-H...N interactions range from a 'normal' hydrogen bond (the proton essentially remaining on its original nitrogen), through proton-sharing, to an ion-paired hydrogen bond. That is, in a 'normal' hydrogen bond the N-H covalent bond is only slightly extended beyond its usual length and the N—N distance is typically around 3.1 Å. As the N—N distance shortens, the length of the N-H covalent interaction increases until, at an N—N separation of about 2.52 Å, the hydrogen is typically located half-way between the two nitrogen atoms [7]. A 'quasi-symmetric' hydrogen bond [8] is formed if the two nitrogens are not equivalent. Proton-sharing hydrogen bonds, sometimes referred to as 'low barrier hydrogen bonds', are characterised by N-H distances that are considerably longer than a covalent bond

and N—N separations that are significantly less than twice the van der Waals radius for nitrogen. Ion-pair hydrogen bonds form when the proton is essentially transferred from one nitrogen to the other and structurally they are similar to a 'normal' hydrogen bond.

In addition to hydrogen bonding, π -stacking interactions [9] occur in many natural and synthetic assemblies [1]. They contribute to the stability of DNA and to the tertiary structure of proteins, as well as forming the basis for porphyrin aggregation. π -Interactions also play an important role in the binding of particular host-guest complexes [1] as well as in the formation of a range of metal-containing stacked assemblies [10].

In this paper we report the formation of a supramolecular assembly formed between phthalimide and 2-guanidinobenzimidazole, two molecules incorporating potentially complementary hydrogen bonding 'triplets'. (It is of relevance to what follows that neither phthalimide nor 2-guanidinobenzimidazole show any evidence of π -stacking interactions in their crystal structures [11].) The adduct is structurally analysed using both X-ray and neutron diffraction data, with the neutron data providing a more accurate location of the hydrogen atoms. The structure is compared with the structure of a similar assembly formed between 4-nitrophthalimide and 2-guanidinobenzimidazole.

Results and Discussion.

The phthalimide molecule has an acceptor-donor-acceptor motif (ADA) and the 2-guanidinobenzimidazole molecule has the complementary donor-acceptor-donor motif (DAD). The crystal structures establish that the two molecules can accordingly combine to form a dimeric complex linked by a triplet of hydrogen bonds. The outer hydrogen bonds of the triplet have lengths that are typical for N-H...O hydrogen bonds (Tables 1 and 2). However, the central N-H...N hydrogen bond is particularly strong, with

the donor to acceptor separation being just 2.692(4) Å. The N(4)-N(6) (Figure 1, Tables 1 and 2) distance is in fact close to the length expected for a proton-sharing bond. Such hydrogen bonds are seen in proton sponges such as 2,2'-bis(dimethylamino)biphenyl in which the hydrogen bond is intramolecular and the N—N distance is determined by the covalent framework of the molecule[12]. Both the X-ray and neutron data show that the proton has, in fact, been essentially captured by the 2-guanidinobenzimidazole molecule. That is, the hydrogen bonded assembly is formed from complementary AAA and DDD motifs rather than ADA and DAD. All secondary interactions are attractive in AAA-DDD assemblies and increase the stability of the triplet, whereas there is a net destabilising effect of 2-3 kcal/mole in ADA-DAD triplets [13].

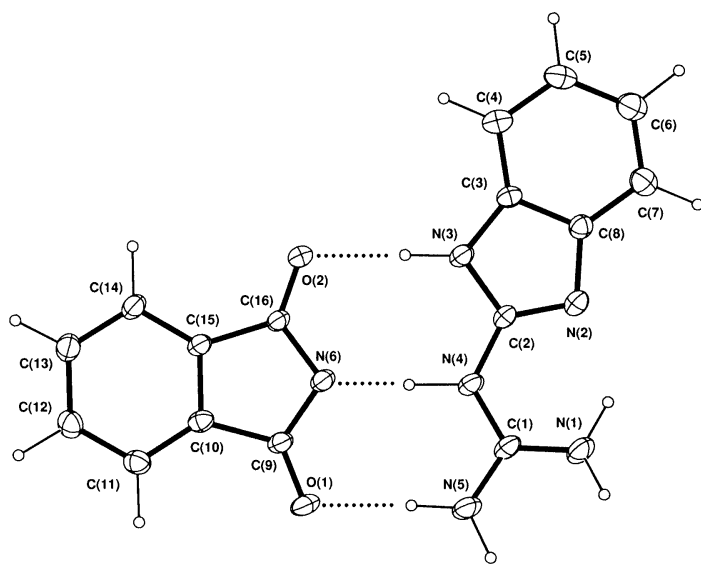


Figure 1. ORTEP depiction of **1** obtained from neutron diffraction data with displacement ellipsoids at the 20% level.

The N—N distance observed lies well outside the range of those used by Steiner [7] in his study of N-H...N hydrogen bonds employing low temperature neutron diffraction data; the shortest bond in his data set was 2.739 Å. Nonetheless, applying his model to the present case gives a calculated length for the N-H covalent bond of 1.091 Å, in accord with the observed value of 1.121(11) Å obtained from the neutron data. The standard errors of the individual N-H lengths used to construct the model vary from 0.001 to 0.02 Å [7]. The proton transfer leaves a formal negative charge on N(6) of phthalimide, and a formal positive charge on N(4) of 2-guanidinobenzimidazole. The electrostatic interaction between the two ions may be the principal influence on the N(4) to N(6) separation. The formal charge on the two molecules also appears to influence the crystal packing. The dimers stack in columns parallel to the *b* axis of the unit cell, with the least squares plane of the molecules forming a dihedral angle of approximately 30° with that axis. Adjacent layers within a column are related by inversion and are separated by approximately 3.3 Å. The nitrogen atoms that form the central hydrogen bond of the triplet are almost directly above the centre of the π electron systems of a phthalimide molecule in an adjacent layer. In particular, the 2-guanidinobenzimidazole N(4) atom is 3.293(2) Å from the least squares plane of the 6 membered ring of the neighbouring phthalimide, and is 3.30 Å from the centroid of that ring. The angle between the line joining N(4) to the centroid of the six membered ring and the normal to the phthalimide least squares plane is 4°. N(6) is 3.293(2) Å from the plane of the neighbouring phthalimide five membered ring and 3.31 Å from the ring's centroid. The angle between the line joining N(6) to the centroid and the normal to the phthalimide five-membered ring least-squares plane normal is 5°. Neighbouring glide related columns of dimers are linked to one another through hydrogen bonding between

Table 1

A Summary of Hydrogen Bond Geometry in **1** (X-ray diffraction)

Donor	Hydrogen	Acceptor	D-H(Å)	H-A(Å)	D-A(Å)	DHAAngle(°)
N(1)	H(1NA)	O(1')	0.930(17)	1.979(18)	2.851(2)	155.6(15)
N(1)	H(1NB)	N(2)	0.968(19)	1.95(2)	2.719(2)	135.1(16)
N(3)	H(3N)	O(2)	0.914(15)	2.024(15)	2.9353(19)	174.5(14)
N(4)	H(4N)	N(6)	1.21(2)	1.48(2)	2.6821(18)	175.3(15)
N(5)	H(5NB)	O(1)	0.984(17)	1.976(18)	2.960(2)	178.7(15)
N(5)	H(5NA)	O(2')	0.897(17)	2.029(17)	2.9196(19)	171.9(15)

Symmetry Operations

(') -x, y-1/2, -z+1/2, (") x, 3/2-y, z-1/2

The 'covalent' N(4)-H(4) distance is the longest of any of the hydrogen bonds in the structure, as would be expected from the short N—N distance (Tables 1 and 2).

donor N(1) and acceptor O(1) atoms on glide related molecules, and between donor N(6) and acceptor O(2) on another glide related molecule (Tables 1 and 2).

Table 2
A Summary of Hydrogen Bond Geometry in **1** (neutron diffraction)

Donor	Hydrogen	Acceptor	D-H(Å)	H-A(Å)	D-A(Å)	DHAAngle(°)
N(1)	H(1NA)	O(1')	1.007(8)	1.914(8)	2.847(4)	152.8(7)
N(1)	H(1NB)	N(2)	1.017(12)	1.934(8)	2.736(4)	133.5(6)
N(3)	H(3N)	O(2)	1.032(10)	1.901(9)	2.929(4)	173.8(6)
N(4)	H(4N)	N(6)	1.121(11)	1.572(10)	2.692(4)	176.7(5)
N(5)	H(5NB)	O(1)	1.018(12)	1.946(11)	2.963(5)	177.1(6)
N(5)	H(5NA)	O(2'')	1.001(8)	1.921(8)	2.909(4)	168.8(7)

Symmetry Operations

(') $-x, y-1/2, -z+1/2$, (") $x, 3/2-y, z-1/2$

The crystal structure of the analogous assembly [2-guanidinobenzimidazole:4-nitrophthalimide], **2**, reported here is of poor quality, but nonetheless it does reveal that the structure has some significant differences to that of **1**. First, although the nitro group has the potential to act as a hydrogen bond acceptor [14], it is not involved in significant hydrogen bonding in **2**. The triplet donor-acceptor distances are similar to those in **1**, and the components of **2** form dimers in a manner analogous to that which occurs in **1** (Figure 2). The central N-H...N hydrogen bond in **2** is, however, somewhat longer [2.788(6)Å] than its counterpart in **1**, and is of a length comparable to those observed in the related nickel-containing assembly [bis(2-guanidi-

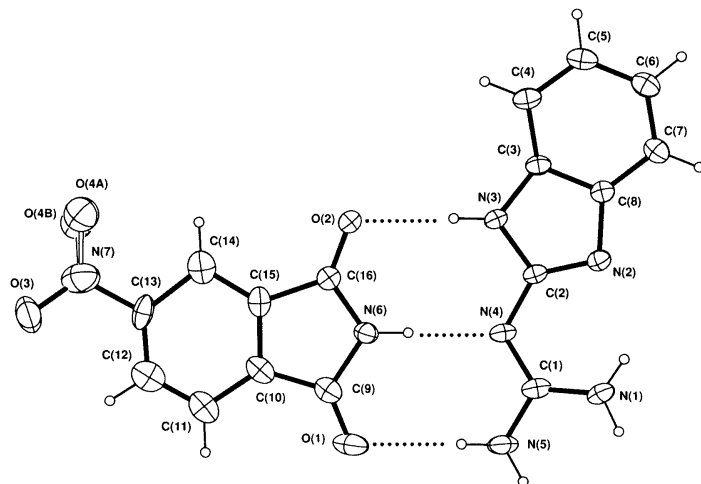


Figure 2. ORTEP depiction of **2** with displacement ellipsoids at the 20% level. As described in the experimental section, atom O(4) is disordered over two sites.

nobenzimidazolo)nickel(II):(phthalimide)₂] [15]. The central N-H...N hydrogen bond appears to be of a somewhat shorter 'normal' type, a conclusion supported by the results of the DFT calculation described below. The two outer N-H...O hydrogen bonds are slightly longer than those in **1**, but are of the length observed between organic amides

[6b]. The dimers are again stacked in columns with inversion related layers; however, the relative orientation of adjacent layers is different to that found for **1**. In **2** the imide nitrogen N(6) of 4-nitrophthalimide lies under the phenylene ring of the 2-guanidinobenzimidazole in an adjacent layer and is 3.365(5) Å from the least squares plane of that ring. The line joining N(6) to the centroid of the phenylene ring forms an angle of 6° with the least squares plane of the ring, and the distance of N(6) from the centroid is 3.38 Å. The N(4) of the 2-guanidinobenzimidazole is not located above either of the 4-nitrophthalimide rings. A molecular model indicates that the crystal packing of **1** is not possible for **2** since, in the latter there would be intermolecular contacts involving the nitro groups of less than 1.7 Å. The local environment of the central N-H...N hydrogen bond in **2** is quite different from its very short equivalent in **1**.

The hydrogen bond links between glide related dimer columns are also different from those in **1**. In **2** N(1) acts as a donor to a carbonyl oxygen O(2) on a neighbouring phthalimide, and N(5) acts as a donor to a neighbouring imidazole N(2). There is also an intramolecular hydrogen bond between N(1) and N(2) (Table 3). The hydrogen bonds that involve N(2) deviate significantly from linearity.

A calculation at the level of DFT, which includes the effects of electron correlation, was carried out for both **1**

Table 3
A Summary of Hydrogen Bonding Geometry in **2** (X-ray diffraction; calculated hydrogen positions)

Donor	Hydrogen	Acceptor	D-A(Å)	DHAAngle(°)
N(1)	H(1A)	N(2)	2.772(6)	127.6
N(1)	H(1B)	O(2')	3.040(5)	162.0
N(3)	H(3)	O(2)	2.981(6)	175.2
N(5)	H(5A)	O(1)	3.098(8)	165.7
N(5)	H(5B)	N(2'')	3.089(6)	129.0
N(6)	H(6)	N(4)	2.796(6)	171.5

Symmetry Operators

(') $x, 3/2-y, z-1/2$ (") $-x, y-1/2, -z+1/2$

and **2**. One 'isolated' dimer was used for the calculation; the bond lengths and angles were set at the values observed in the crystal structures and the atom positions fixed. The N-H-N angle of the central hydrogen bond was held at 180° . An energy profile was calculated by allowing the N(4)-H distance to vary from 0.8 to 1.9 Å in 0.1 Å intervals and the energy of each structure was calculated using the perturbative Becke-Perdew model with the DN* basis set. The energies are expected to be accurate to 0.0002au [16].

The calculated energy profile for **1** shows a minimum corresponding to the observed proton position but, given the size of the zero point energy estimated from the IR stretching frequency (0.005 au), it seems better to describe the potential well as having a broad flat minimum. The latter is what one would expect for a proton-shared or 'quasi-symmetric' hydrogen bond [17]. However, the diffraction data clearly locate the

proton nearer the N(4) nitrogen of the 2-guanidinobenzimidazole molecule, which suggests that the local environment of the hydrogen bond, which was not included in the model, has a role to play in determining the shape of the well (by analogy, this may be an important consideration affecting hydrogen bonds in the active site of an enzyme). Elucidation of the role played by the nearby π -electrons in the structure of the hydrogen bond awaits a more sophisticated calculation. Regrettably, the crystal structure of **2** is not of sufficient quality to locate the hydrogen positions, and a comparison with the computational model cannot be made in this case.

EXPERIMENTAL

Preparation of [2-Guanidinobenzimidazole:phthalimide] **1**.

Phthalimide (0.147 g, 1 mmole) was dissolved in ca. 10 ml of hot ethanol. Solid 2-guanidinobenzimidazole (0.175 g, 1 mmole) was added. Yellow crystals suitable for X-ray crystallography, formed on cooling (yield 25%); a further crop of material can be obtained by evaporation of the filtrate.

Anal. Calcd. for $C_{16}H_{14}N_6O_2$: C, 59.61; H, 4.38; N, 26.06. Found: C, 59.38; H, 4.50; N, 25.91.

Preparation of [2-Guanidinobenzimidazole:4-nitrophthalimide] **2**.

2-Guanidinobenzimidazole (0.176 g, 1 mmole) in absolute ethanol (15 ml) was added to a solution of 4-nitrophthalimide (0.192 g, 1 mmole) in absolute ethanol (30 ml). A bright orange crystalline precipitate formed suddenly in good yield (80%). The product was filtered at the pump and dried.

Anal. Calcd. for $C_{16}H_{13}N_7O_4$: C, 52.32; H, 3.57; N, 26.69. Found: C, 52.24; H, 3.67; N, 26.51.

Structure Determination.

X-Ray Diffraction.

Diffraction data for **1** and **2** were collected using a Bruker SMART 1000 CCD diffractometer employing graphite monochromated MoK α radiation generated from a sealed tube at 297(2) and 294(2) K respectively. Cell constants for **1** were obtained from a least squares refinement against 2201 reflections located between 4.18 and $43.08^\circ 2\theta$. Cell constants for **2** were obtained from a least squares refinement against 501 reflections located between 5.77 and $41.53^\circ 2\theta$. Data were collected with 0.3° increment ω scans to $57^\circ 2\theta$. There was no evidence of crystal decay during the data collection for either sample. The data integration and reduction were undertaken with SAINT and XPREP [18] and subsequent computations were carried out with the teXsan [19] graphical user interface. A Gaussian absorption correction [18,20] was applied to the data obtained from both crystals, and the data reduction included the application of Lorentz and polarisation corrections. The structures were solved in the space group $P2_1/c$ (#14) by direct methods using SIR97 [21] for **1** and SHELXS-97 [22] for **2**. The structure models were extended and refined with SHELXL-97. [23]

[2-Guanidinobenzimidazole:phthalimide] **1**.

Anisotropic thermal parameters were refined for the non-hydrogen atoms and in general a riding atom model was used for the hydrogen atoms included in the model. The N(1), N(3)

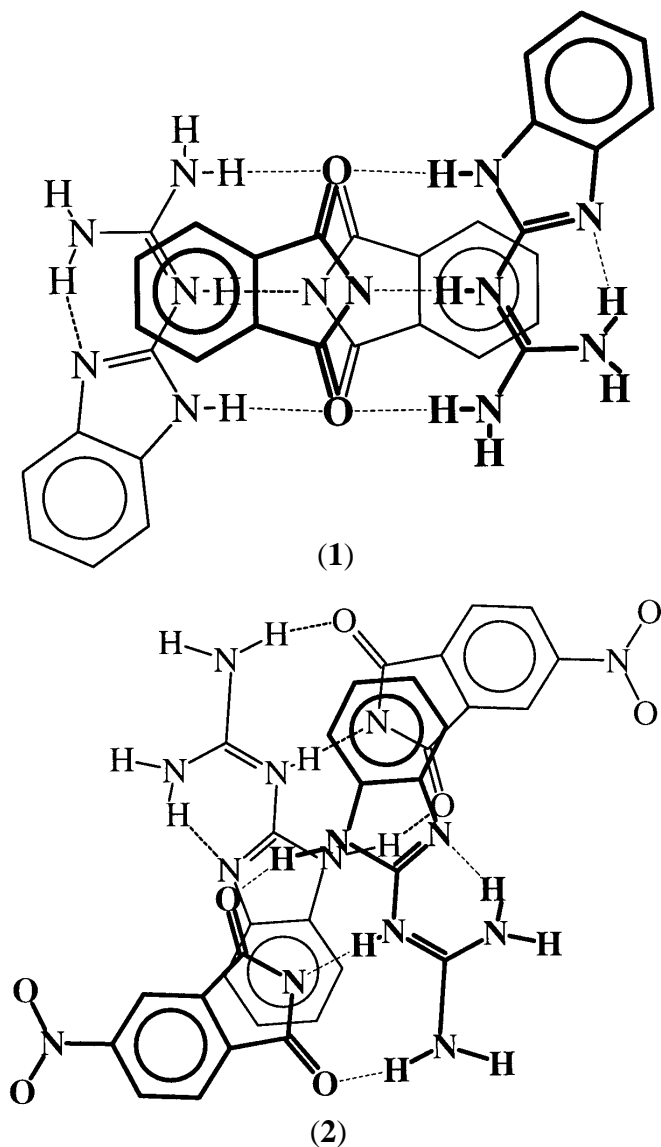


Figure 3. The stacking patterns in the two arrays.

and N(5) hydrogens were located and modelled with isotropic displacement parameters. The asymmetric unit contains two molecules linked by hydrogen bonds. Table 1 summarises the hydrogen bond details.

Crystallographic data; formula $C_{16}H_{14}N_6O_2$, M 322.33, monoclinic, space group $P2_1/c$ (#14), a 12.6822(7), b 7.6192(4), c 16.6270(9) Å, β 109.4400(10), V 1515.04(14) Å³, D_c 1.413 g cm⁻³, Z 4, crystal size 0.492 by 0.074 by 0.041 mm, colour yellow, habit acicular, λ (MoK α) 0.71073 Å, μ (MoK α) 0.099 mm⁻¹, T (analytical)_{min,max} 0.968, 0.994, $2\theta_{max}$ 56.60, hkl range -16 16, -9 10, -21 21, N 14294, N_{ind} 3646(R_{merge} 0.0545), N_{obs} 1620($I > 2\sigma(I)$), N_{var} 241, residuals [26] $R1(F)$ 0.0403, $wR2(F^2)$ 0.0725, GoF(all) 1.017, $\Delta\rho_{min,max}$ -0.139, 0.106 e⁻ Å⁻³.

[2-Guanidinobenzimidazole:4-nitroptthalimide] 2.

Crystals of this material were of particularly poor quality, and this is reflected in the R_{merge} and final model residuals. In general the non-hydrogen atoms were modelled with anisotropic displacement parameters and a riding atom model was used for hydrogen atoms. One of the nitro residue oxygen atoms, O(4), required the use of two sites, with populations refined and then fixed at 0.5. Attempts to resolve O(3) into a matching pair of sites were unsuccessful. Isotropic displacement parameters were used to model the partially occupied sites. An ORTEP [24] depiction of the molecule with 20% displacement ellipsoids is provided in Figure 2, and Table 3 lists some hydrogen bond geometry.

Crystallographic data; Formula $C_{16}H_{13}N_7O_4$, M 367.33, monoclinic, space group $P2_1/c$ (#14), a 12.316(4), b 7.716(2), c 17.680(5) Å, β 97.551(7), V 1665.4(9) Å³, D_c 1.465 g cm⁻³, Z 4, crystal size 0.350 by 0.052 by 0.031 mm, colour orange, habit acicular, λ (MoK α) 0.71073 Å, μ (MoK α) 0.110 mm⁻¹, T (Gaussian)_{min,max} 0.981, 0.997, $2\theta_{max}$ 56.62, hkl range -16 16, -10 10, -23 23, N 16894, N_{ind} 3888(R_{merge} 0.0947), N_{obs} 1340($I > 2\sigma(I)$), N_{var} 244, residuals [26] $R1(F)$ 0.0936, $wR2(F^2)$ 0.3217, GoF(all) 1.017, $\Delta\rho_{min,max}$ -0.393, 1.101 e⁻ Å⁻³.

Neutron Diffraction.

[2-Guanidinobenzimidazole:phthalimide] 1.

The single-crystal neutron-diffraction data were collected at 294(1) K using the 2TANA four-circle diffractometer at ANSTO's HIFAR reactor (Lucas Heights, Australia). The wavelength was 1.236(1) Å as determined from a KCl standard crystal. The sample crystal was an amber coloured prism of approximate dimensions 1 x 1 x 2.5 mm with the long axis along $\langle 001 \rangle$. The crystal was mounted on an aluminium pin with $\langle 100 \rangle$ along the ϕ -axis. Crystal orientation used 21 reflections with the cell dimensions fixed to the values found by x-ray diffraction. Six sets of reflections, consisting of shells of increasing 2θ , were collected over a four week period. The combined data set contained all reflections with $2\theta < 80^\circ$ and half of the reflections with $80^\circ < 2\theta < 90^\circ$. Friedel pairs, which are exact equivalents for neutron diffraction, were only collected for reflections with $2\theta < 55^\circ$. The data sets were measured and converted to intensities using the ANSTO programs DIFF and DIFFPLOT. A correction was made for a small (1.9%) reduction in the standard reflection intensities over the four week data collection period, probably due to degradation of the crystal in air. The WINGX [25] software was used to perform an analytical absorption correction based on the measured shape of the crystal. The structure was refined with SHELXL-97 [23] using the atomic positions determined from the X-ray study. An

ORTEP [24] depiction of the molecule with 20% displacement ellipsoids is provided in Figure 1, and Table 2 lists the hydrogen bond geometry.

Crystallographic data; a 12.6822(7), b 7.6192(4), c 16.6270(9) Å, β 109.4400(10), V 1515.04(14) Å³, D_c 1.413 g cm⁻³, Z 4, crystal size 2.5 by 1.0 by 1.0 mm, colour amber, habit prism, λ (neutron) 1.236 Å, μ (neutron) 0.167 mm⁻¹, T (analytical)_{min,max} 0.703, 0.862, $2\theta_{max}$ 89.96, hkl range -7 13, -8 8, -18 18, N 5384, N_{ind} 2146(R_{merge} 0.0671), N_{obs} 1565($I > 2\sigma(I)$), N_{var} 344, residuals [26] $R1(F)$ 0.0452, $wR2(F^2)$ 0.0969, GoF(all) 1.021, residual_{min,max} -0.390, 0.451 [27].

Density Functional Theory Calculation.

This was performed using *PC Spartan Pro version 1.0.3* (Wavefunction, Inc.). The calculation employed the perturbative Becke-Perdew model with the DN* numerical polarisation basis set (pBP/DN*).

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[26] $R1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ for $F_o > 2\sigma(F_o)$; $wR2 = (\sum w(F_o^2 - F_c^2)^2 / \sum (wF_c^2)^2)^{1/2}$ all reflections $w = 1 / [\sigma^2(F_o^2) + (0.0202P)^2 + 2.2502P]$ where $P = (F_o^2 + 2F_c^2) / 3$.

[27] Residuals as reported by SHELXL-97 with the X-ray atomic scattering factors set to the neutron b values of 6.646, 5.803, 9.360 and -3.739 for atoms C, O, N and H respectively.