



The *Pseudo* Symmetric Crystal Structure of 1,4-Diazabicyclo[2.2.2]octane-1,4-dium bis(5-hydroxy-2,4-dinitrophenolate)

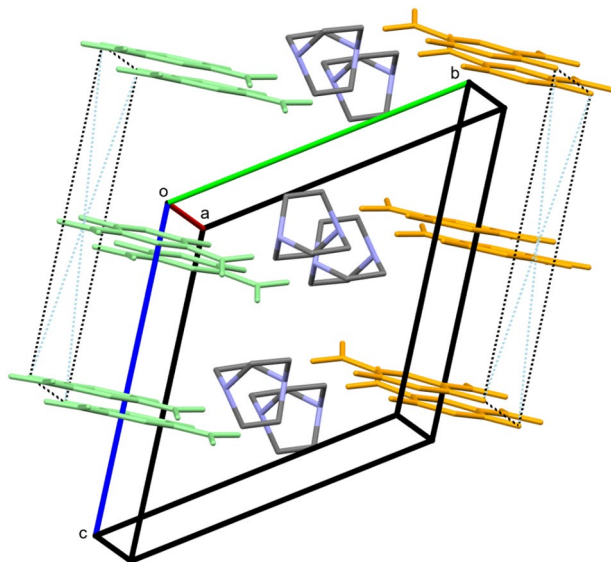
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Abstract

Reaction of 4,6-dinitroresorcinol (**1**) and the nitrogen base 1,4-diazabicyclo[2.2.2]octane (**2**) affords the 1:2 salt and proton-transfer compound 1,4-diazabicyclo[2.2.2]octane-1,4-dium bis(5-hydroxy-2,4-dinitrophenolate) (**3**). Compound **3** crystallizes in the triclinic crystal system (space group *P*-1) with $a = 8.3242(5)$ Å, $b = 11.9915(7)$ Å, $c = 12.4595(7)$ Å, $\alpha = 116.282(2)^\circ$, $\beta = 100.576(3)^\circ$, $\gamma = 101.051(2)^\circ$, $1042.30(11)$ Å³ and $Z = 2$. The dication 2-H_2^{2+} forms charge assisted donating bifurcated $\text{N}^+ - \text{H} \cdots \text{O}^-$ hydrogen bonds to the phenolate moieties of two monoanions of **1**. The latter exhibit an intramolecular $\text{O} - \text{H} \cdots \text{O}$ hydrogen bond between the hydroxy group and the nitro group in *ortho* position. The crystal structure of **3** features *pseudo* *B*-centering of the lattice, which relates the two crystallographically distinct monoanions of **1** by a *pseudo* translation. The possible *B*-centring is broken by the ethylene groups of 2-H_2^{2+} , which are related in neighbouring molecules by centres of symmetry.

Graphical Abstract



The 1:2 proton-transfer compound 1,4-diazabicyclo[2.2.2]octane-1,4-dium bis(5-hydroxy-2,4-dinitrophenolate) features *pseudo* *B*-centering of the lattice.

Keywords 1,4-diazabicyclo[2.2.2]octane · 4,6-dinitroresorcinol · *Pseudo* symmetry · Proton-transfer · Hydrogen bonding · Crystal structure

Dedicated to Professor Carl Krüger on the occasion of his 90th birthday.

Extended author information available on the last page of the article

Introduction

4,6-Dinitroresorcinol (systematic name: 4,6-dinitrobenzene-1,3-diol, **1**, Fig. 1) is a useful precursor to 4,6-diaminoresorcinol for the production of the synthetic polymer material poly(*p*-phenylene-2,6-benzobisoxazole) (PBO) [1], which is marketed under the tradename Zylon®. Crystallographic data for **1** were published for the first time in 1952, albeit without atom positions [2]. A full crystal structure determination of the compound was reported by Kolev et al. in 2000 [3]. In the crystal, the molecules feature two intramolecular O–H⋯O hydrogen bonds, each formed between a hydroxy group and the nitro group in *ortho* position, as previously observed in the gas-phase [4].

The electron-withdrawing effect of the nitro groups in *ortho* and *para* position of each hydroxy group in **1** significantly increase the acidity ($pK_{a1} = 3.71$; $pK_{a2} = 7.49$ [5]) in comparison with resorcin ($pK_{a1} = 9.48$; $pK_{a2} = 12.08$ [6]), but reports on structurally characterized salts of **1** are surprisingly scarce. To the best of our knowledge and based on a search of the Cambridge Structural Database (CSD; version 5.43 with November 2022 updates [7]), the sole example is the crystal structure of the monocesium salt [8], whereas structurally characterized organic salts of **1** appear to be unknown. For salt formation, the nitrogen base 1,4-diazabicyclo[2.2.2]octane (**2**, Fig. 1) attracted our interest. Compound **2** is a versatile reagent, which has found many applications in organic chemistry [9]. It exhibits two protonation sites (2-H_2^{2+} ; $pK_{a1} = 3.2$; $pK_{a2} = 9.0$ [10]), which are readily accessible owing to the bicyclic structure of the molecule.

The molecular structure of **2** lacks a centre of symmetry. Its capability to form non-centrosymmetric crystalline salts with achiral anions has been demonstrated, for example, in the dihydrate of the 1:2 proton transfer compound with chloranilic acid (CSD refcode: BOXJOQ) [11] or in the 1:1 salt of 2,4-dinitrobenzoic acid (CSD refcode: CERRUN) [12]. Such materials are potentially interesting for applications in non-linear optics (NLO). In this context, we investigated salt formation of **2** with **1**. Herein, we describe the crystal

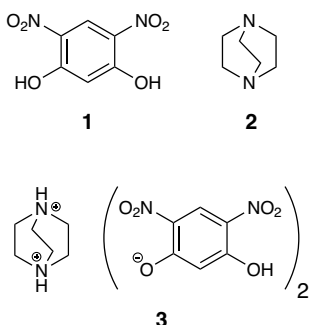


Fig. 1 Chemical diagrams of 1–3

structure of the 1:2 salt and proton-transfer compound of **1** and **2**, namely 1,4-diazabicyclo[2.2.2]octane-1,4-dium bis(5-hydroxy-2,4-dinitrophenolate) (**3**), the title compound (Fig. 1). As far as we are able to ascertain, compound **3** represents the first structurally characterized organic salt of **1**.

Experimental Section

Synthesis and Crystallisation

Reagent grade 1,4-diazabicyclo[2.2.2]octane (**2**) was purchased and used as received, and 4,6-dinitroresorcinol (**1**) was prepared as described previously [3]. Compound **2** (224 mg, 2 mmol) dissolved in 40 mL of methanol was mixed with **1** (400 mg, 2 mmol) dissolved in 60 mL of methanol under continuous stirring. The mixture was stirred for four hours and then left undisturbed at ambient conditions. Orange-yellow crystals of **3** suitable for single-crystal X-ray diffraction analysis were obtained after two weeks.

X-ray Crystallography

Diffraction data were collected on a Bruker AXS X8 Proteum diffractometer with a FR591 rotating anode X-ray source. The data were processed with the SAINT software [13]. The crystal structure was solved with SHELXS-97 [14] and initial independent atom model refinement (IAM) was carried out with SHELXL-2019/3 [15]. The final structure refinement was carried out by Hirshfeld atom refinement with non-spherical atomic form factors using NoSpherA2 [16, 17] partitioning in Olex2 [18] based on electron density from iterative single-determinant SCF single-point DFT calculations using ORCA (version 5.0) [19] with a B3LYP functional [20, 21] and a def2-TZVPP basis set [22]. The hydrogen atom positions were refined with isotropic atomic displacement parameters. For carbon-bound hydrogen atoms, $U_{\text{iso}}(\text{H})$ was constrained to $1.2 U_{\text{eq}}(\text{C})$. Structure pictures were drawn with Diamond [23] and Mercury [24]. Root mean square (r.m.s.) deviations of atomic positions (hydrogen atoms excluded) were calculated with Mercury. Table 1 lists crystal data and refinement details for **3**.

Results and Discussion

Reaction of equimolar amounts of the base 1,4-diazabicyclo[2.2.2]octane and 4,6-dinitroresorcinol in methanol afforded thin orange-yellow plate-shaped crystals of the proton-transfer compound **3**, as revealed by X-ray crystallography. The compound crystallizes in the centrosymmetric space group *P*-1. The asymmetric unit comprises one 2-H_2^{2+} cation and two 5-hydroxy-2,4-dinitrophenolate anions

Table 1 Crystal data and refinement details for **3**

Empirical formula	C ₁₈ H ₂₀ N ₆ O ₁₂
<i>M_r</i>	512.393
<i>T</i> (K)	200.15
λ (Å)	1.54178
Crystal system	Triclinic
Space group	<i>P</i> -1
<i>a</i> (Å)	8.3242(5)
<i>b</i> (Å)	11.9915(7)
<i>c</i> (Å)	12.4595(7)
α (°)	116.282(2)
β (°)	100.576(3)
γ (°)	101.051(2)
<i>V</i> (Å ³)	1042.30(11)
<i>Z</i> , ρ_{calc} (mg m ⁻³)	2
μ (mm ⁻¹)	1.212
<i>F</i> (000)	534.341 [532] ^a
Crystal size (mm)	0.29 × 0.12 × 0.01
θ range (°)	4.16–67.11
Reflections collected/unique	23,926/3562
<i>R</i> _{int}	0.0620
Data/restraints/parameters	3562/0/390 [342] ^a
Observed data [<i>I</i> > 2 σ (<i>I</i>)	2693
Goodness-of-fit on <i>F</i> ²	0.9454 [1.028] ^a
<i>R</i> 1 [<i>I</i> > 2 σ (<i>I</i>)	0.0351 [0.0429] ^a
<i>wR</i> 2 (all data)	0.0927 [0.1196] ^a
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ (eÅ ⁻³)	0.2316/−0.2285 [0.248/−0.244] ^a

^aThe numbers in square brackets result from the IAM refinement (carbon-bound hydrogen atoms constrained).

(Fig. 2). The transfer of a phenolic acidic proton of **1** to both nitrogen atoms of **2** was evident from the $F_{\text{obs}} - F_{\text{calc(IAM)}}$ difference map (Fig. 3). Moreover, the average C9–O1 bond length is shorter than the average C11–O2 bond length by 0.09 Å, consistent with deprotonation of O1. The C–N–C

bond angles of **2** are increased by 1.7° upon protonation compared with the crystal structure of the free base (polymorph II, CSD refcode: TETDAM08) [25]. With the above-mentioned *pK_a* values for **1** and **2**, we calculate $\Delta pK_{\text{a}} = pK_{\text{a}}[\text{protonated base}] - pK_{\text{a}}[\text{acid}] = 3.2 - 3.71 = -0.51$ for the second protonation step of **2**. This suggests that predicting the location of the proton based on aqueous *pK_a* values alone would be difficult [26]. It is assumed that the environment in the crystal has a bearing on the position of the acidic hydrogen atom.

The 2-H₂²⁺ ion in **3** exhibits approximate molecular *D*_{3h} point group symmetry (r.m.s. deviation: 0.041 Å). The two protonated tertiary amino groups form charge-assisted N⁺–H···O[−] hydrogen bonds with the two crystallographically distinct 5-hydroxy-2,4-dinitrophenolate anions. These hydrogen bonds are best described as donating asymmetrically bifurcated (three-centred). The graph set descriptor for the pattern is R₁²(6) [27]. Such a hydrogen bond pattern was, for example, also encountered in the bis(2,4,6-trinitrophenolate) salt of **2** (CSD refcode: QUYPQQ) [28]. Table 2 lists hydrogen bond parameters in **3**. These suggest that the N1–H1···O1₁ and N4–H4···O1₂ interactions involving the phenolate oxygen atoms are, as expected, stronger than the N1–H1···O6₁ and N4–H4···O6₂ interactions with the nitro oxygen atoms. The nitro group in *ortho* position to the phenolate oxygen atom is markedly tilted out of the plane of the benzene ring, as revealed by the C9–C14–N2–O6 torsion angles of 19.2(2)° for anion 1 and −10.4(2)° for anion 2. In contrast, the nitro group in *ortho* position to the hydroxy group is virtually coplanar with the benzene ring in both unique anions and serves as acceptor for an intramolecular O–H···O hydrogen formed by the hydroxy group, resulting in a six-membered ring. The graph set notation for this ring is S(6). The hydrogen bond pattern encountered in **3** agrees with Etter's hydrogen bond rules for organic crystals [29], especially rule 2 stating that six-membered ring intramolecular hydrogen bonds form in preference to

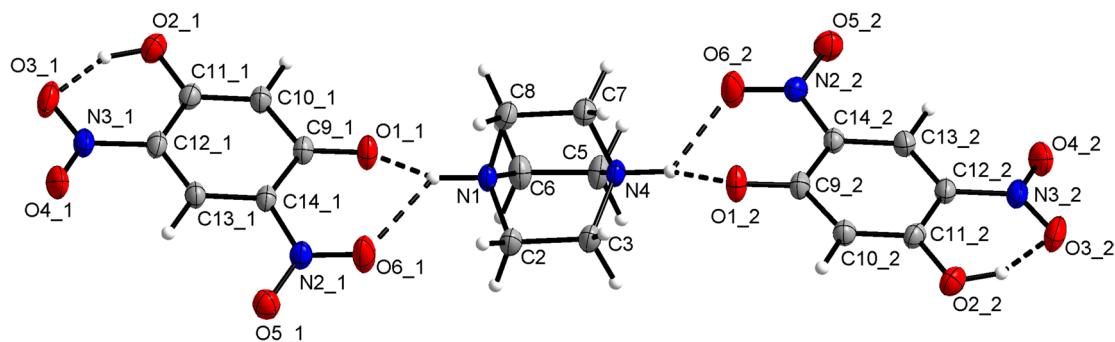


Fig. 2 Asymmetric unit of **3**. Displacement ellipsoids are drawn at the 50% probability level. Hydrogen atoms are represented by small spheres of arbitrary radius. Dashed lines illustrate hydrogen bonds.

The numbers after the underscore indicate the two crystallographically unique 5-hydroxy-2,4-dinitrophenolate anions

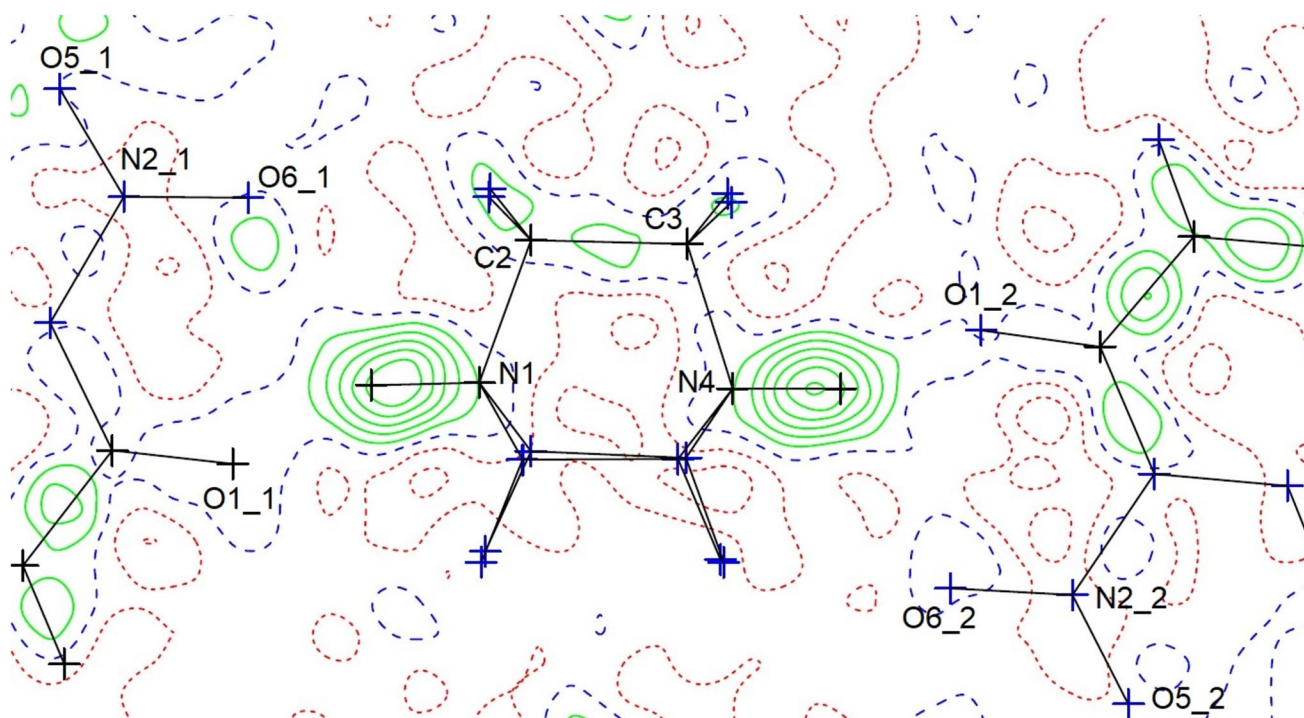


Fig. 3 $F_{\text{obs}} - F_{\text{calc(IAM)}}$ difference map in a plane through the nitrogen atoms and one of the ethylene bridges in the 2-H_2^{2+} cation in **3**. Contours are drawn from $-0.30 \text{ e}\text{\AA}^{-3}$ (red dotted line) through zero (blue dashed line) to $0.60 \text{ e}\text{\AA}^{-3}$ in $0.10 \text{ e}\text{\AA}^{-3}$ intervals. The hydrogen atoms

bonded to N1 and N4 were omitted from the structure factor calculations and thus show up as positive difference electron density close to the parent nitrogen atoms (Color figure online)

intermolecular hydrogen bonds. In accord with this rule, the parent neutral **1** features two such six-membered ring intramolecular hydrogen bonds between hydroxy and nitro groups with the latter being virtually coplanar with the benzene ring [3, 30].

In the chosen asymmetric unit, as shown in Fig. 2, the two crystallographically unique 5-hydroxy-2,4-dinitrophenolate anions are approximately related by local inversion symmetry, which is not fulfilled by the non-centrosymmetric cation. In the crystal, neutral hydrogen-bonded assemblies forming **3** (coinciding with the chosen asymmetric unit) are stacked along the [101] direction via $\pi \cdots \pi$ stacking of the 5-hydroxy-2,4-dinitrophenolate anions (Fig. 4). Details of the of the $\pi \cdots \pi$ interactions in the crystal between the rings defined by and C9_1-C14_1 (plane 1) and C9_2-C14_2 (plane 2) are given in Table 3. The sheets so formed are layered in alternating fashion so that no voids remain and are associated via weak van der Waals forces. The crystal structure features *pseudo* symmetry, namely *pseudo* B-centering of the lattice with 83% fit, as calculated with ADDSYM in PLATON [31]. This is reflected in the mean intensity of the lattice exceptions for B-centering in the diffraction data, which is half those of possible A-, C-, I- or F-centering, although this difference is less significant when the errors of the intensities are taken into account. As shown in Fig. 5,

Table 2 Hydrogen bond parameters (\AA , $^\circ$) for **3**

$D\text{-H}\cdots A$	$d(D\text{-H})$	$d(\text{H}\cdots A)$	$d(D\cdots A)$	$\angle(D\text{-H}\cdots A)$
N1-H1 \cdots O1_1	1.06 (2)	1.60 (2)	2.571 (2)	150 (2)
N1-H1 \cdots O6_1	1.06 (2)	2.24 (2)	2.938 (2)	122 (1)
N4-H4 \cdots O1_2	1.07 (2)	1.56 (2)	2.554 (2)	152 (2)
N4-H4 \cdots O6_2	1.07 (2)	2.27 (2)	2.929 (2)	118 (1)
O2_1-H2_1 \cdots O3_1	1.00 (2)	1.62 (2)	2.535 (2)	150 (2)
O2_2-H2_2 \cdots O3_2	0.99 (2)	1.65 (2)	2.550 (2)	148 (2)

two crystallographically distinct 5-hydroxy-2,4-dinitrophenolate anions are related by a *pseudo* translation by the vector $0.5\mathbf{c} + 0.5\mathbf{a}$. The additional translational symmetry is, however, not fulfilled by the 2-H_2^{2+} ions. These are related by crystallographic inversion symmetry, as can be seen in Fig. 5.

Conclusions

We have structurally characterized the 1:2 proton-transfer compound **3**, resulting from reaction of equimolar amounts of **2** and **1**, by X-ray crystallography. Cations and

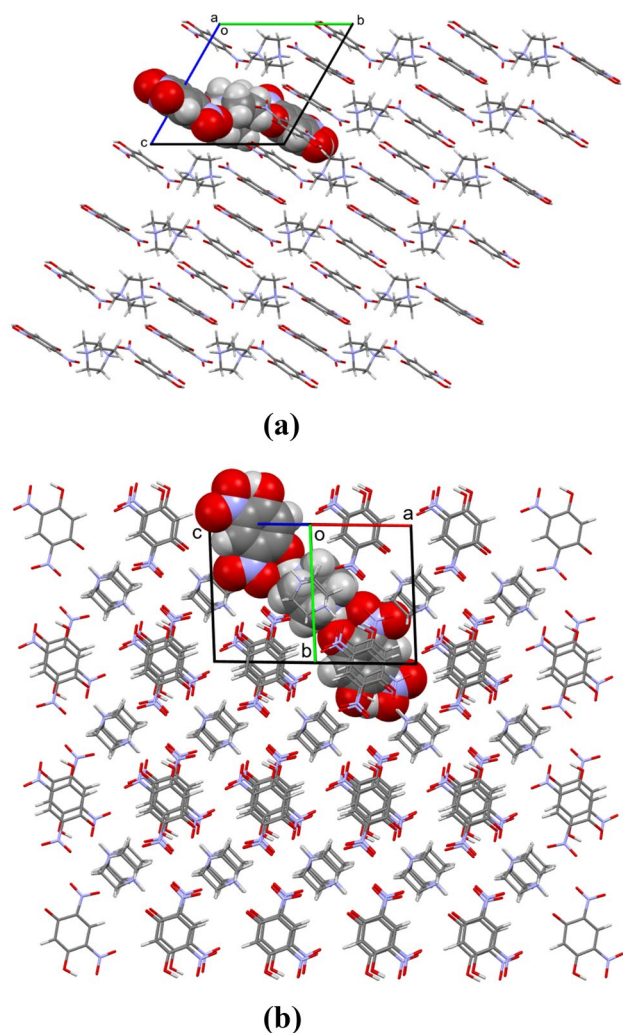


Fig. 4 Packing diagram of **3** **a** viewed along the *a* axis direction and **b** along the [101] direction, showing the $\pi\cdots\pi$ stacking of the 5-hydroxy-2,4-dinitrophenolate anions on neighbouring neutral hydrogen-bonded assemblies forming **3** (one such unit is highlighted as a space filling model) Colour scheme: carbon, grey; hydrogen, white; nitrogen, blue; oxygen, red. Hydrogen atoms are omitted for clarity (Color figure online)

anions are linked through charge-assisted intermolecular $N^+-H\cdots O^-$ hydrogen bonds, and the anions exhibit intramolecular $O-H\cdots O$ hydrogen bonds. In the crystal, neighbouring neutral hydrogen-bonded assemblies forming **3** are held together by a combination of $\pi\cdots\pi$ stacking in a zip fastener fashion and van der Waals forces between adjacent layers. Since the second protonation can hardly be predicted from aqueous pK_a values alone and we have no evidence that the structure is disordered, we conclude that the crystal environment has a bearing on the proton-transfer. The crystal structure of **3** features *pseudo B*-centering of the lattice. The centrosymmetry of the crystal structure renders **3** unsuitable for NLO applications.

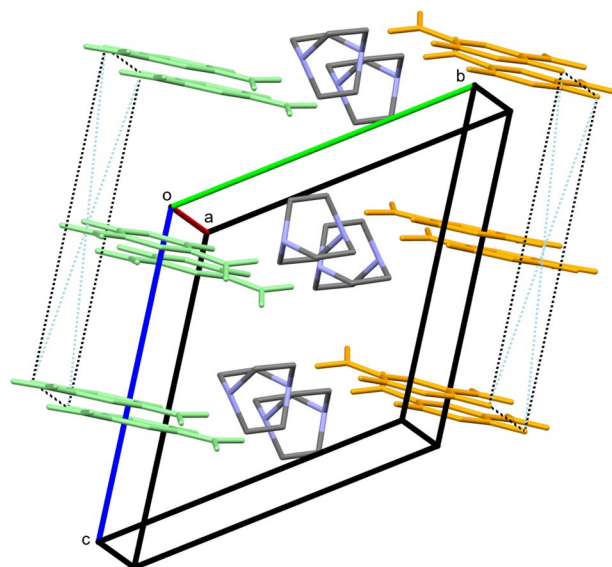


Fig. 5 Packing diagram of **3**. The orange and the green highlightings of the crystallographically unique 5-hydroxy-2,4-dinitrophenolate anions illustrate their respective relation by *pseudo* symmetry (see text). Neighbouring $2-H_2^+$ cations are related by translation centres of symmetry. Colour scheme: carbon, grey; nitrogen, blue; oxygen, red. Hydrogen atoms are omitted for clarity (Color figure online)

Table 3 Summary of the $\pi\cdots\pi$ interactions in the crystal structure of **3** between the rings defined by C9_1-C14_1 (plane 1) and C9_2-C14_2 (plane 2)

Plane	Symmetry relation	Angle (°)	Centroid-centroid distance (Å)	Shift distance (Å)
2-2	$2-x, 2-y, 1-z$	0.00	3.54	1.24
1-1	$-1-x, -y, -z$	0.00	3.58	1.34
1-2	$-1+x, -1+y, +z$	4.94	3.40	0.97

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Author Contributions Conceptualization, RWS and TMK; methodology, RWS and RG; validation, RWS and RG; formal analysis, RWS and RG; investigation, RG and TMK; resources, RG and TMK; data curation, RWS and RG; writing—original draft preparation, RWS; writing—review and editing, RG and TK; visualization, RWS and RG; supervision, TMK; project administration, RWS and TMK.

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Data Availability CCDC 2304129 contain the supplementary crystallographic data for this paper. The data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures.

Declarations

Competing interests The authors declare no competing interests.

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