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The importance of charge-charge interactions in shaping supramolecular hybrid compounds adeninium based

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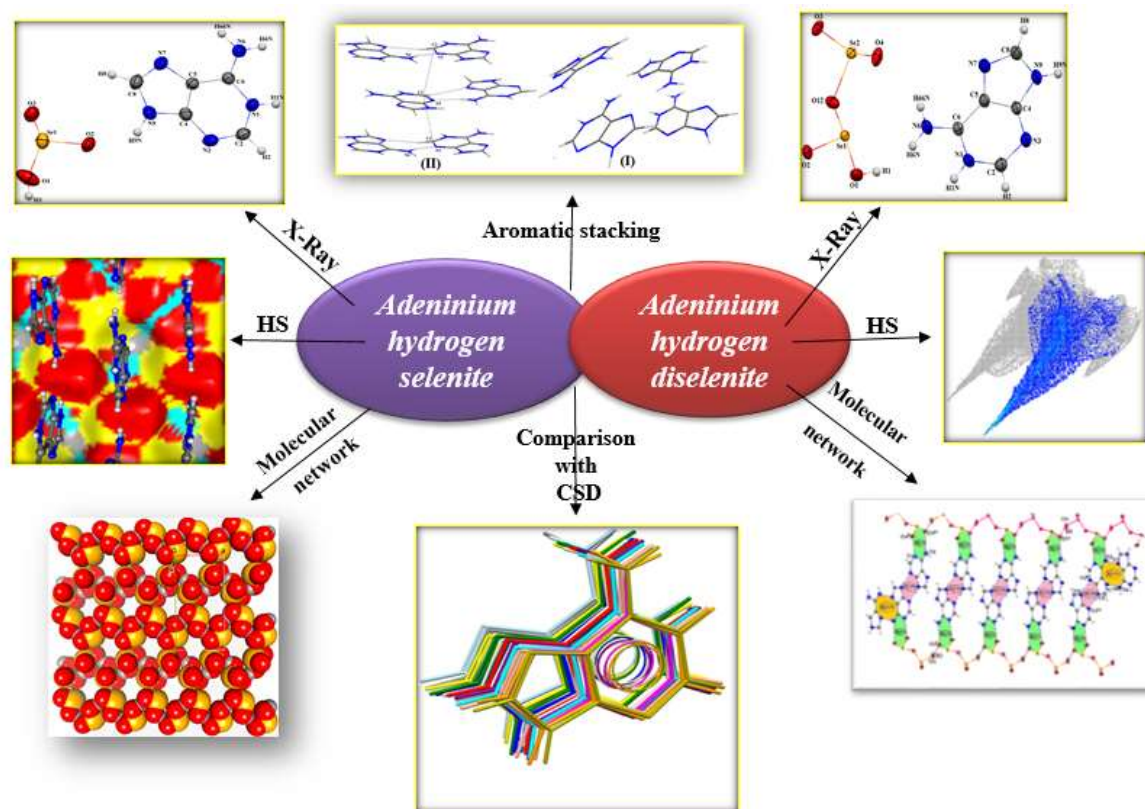
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LASPI²A

The importance of charge-charge interactions in shaping supramolecular hybrid compounds adeninium based



Graphical Abstract



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Abstract:

The new organic-inorganic hybrid compounds adeninium hydrogen diselenite (I) and adeninium hydrogen selenite (II), were prepared from adenine and selenious acid. Our initial products were selected based on the multifold non covalent interactions of adenine through the Watson–Crick, Hoogsteen and sugar-face N atoms or N—H bonds, with small molecules.

The inspection of hydrogen bonding network in both compounds shows direct interactions between the cations and the anions. Furthermore, supramolecular homo and hetero-synthons found play an important role in shaping these supramolecular compounds. Moreover, the 1H,9H-adeninium in both structures generate cationic ribbons. In addition to the N—H \cdots N and C—H \cdots N hydrogen bonds connecting the bases in (I) and (II), weak stacking interactions are observed between the aromatic rings of the adeninium base in both compounds. The stacking of cations is stabilized in the crystal packing of (I) and (II) by the ionic bridges with the surrounding anions; indeed, anions play an important role in maintaining the three-dimensional network through hydrogen bonds and charge-charge interactions. In (I) the anions exercise their role in solo while in (II) they do it as hexamers. Further, the connectivity between these hexamers in (II) generates a three-dimensional honeycomb-like inorganic framework. This effect should be considered as important in crystal engineering. There is an interesting electrostatic association, seen only in (I), between the SeOH oxygen electron lone pairs and the aromatic cation.

Keywords: Adeninium hybrid compounds; Aromatic stacking interactions; Charge transfer; Intermolecular interactions; Supramolecular synthons.



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Introduction

The ability of small molecules to interact with DNA via an intercalative, groove-binding or electrostatic mode has led to the development of many novel anticancer [1-3] and antimicrobial agents [4]. In this context, nucleobases are key structure directing agents due to their rich combination of hydrogen bond donor and acceptor positions. Their propensity to self-assemble through hydrogen-bonding interactions has led to a plethora of supramolecular structures. As a significant nucleobase of DNA, adenine is an important naturally occurring nitrogen heterocycle present in nucleic acids. Such studies have helped us better understand the role of DNA association with small molecules.

Adenine is one of the key components in the DNA double helix. Cocrystals between The 9H tautomer of adenine (shown Fig. 1) or protonic adenine and some selected small molecules have been reported

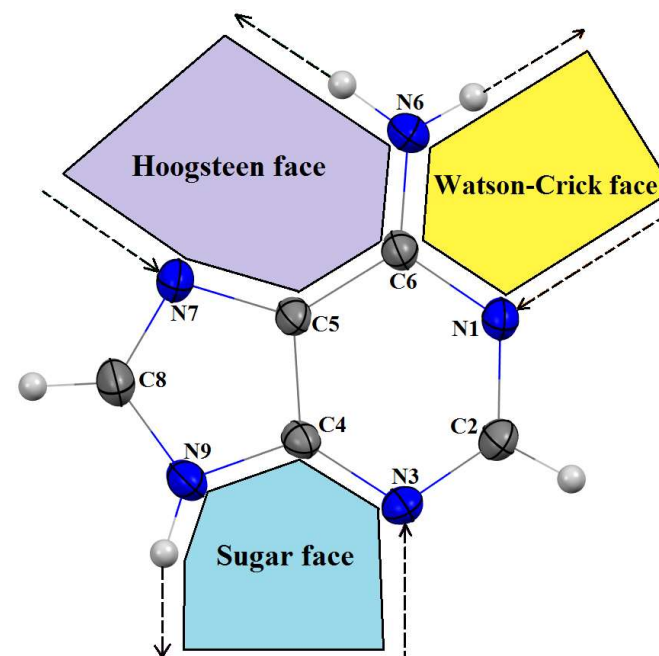


Fig. 1. Adenine structure showing the numbering scheme and characterized by three pairing edges: Watson–Crick, Hoogsteen and sugar.

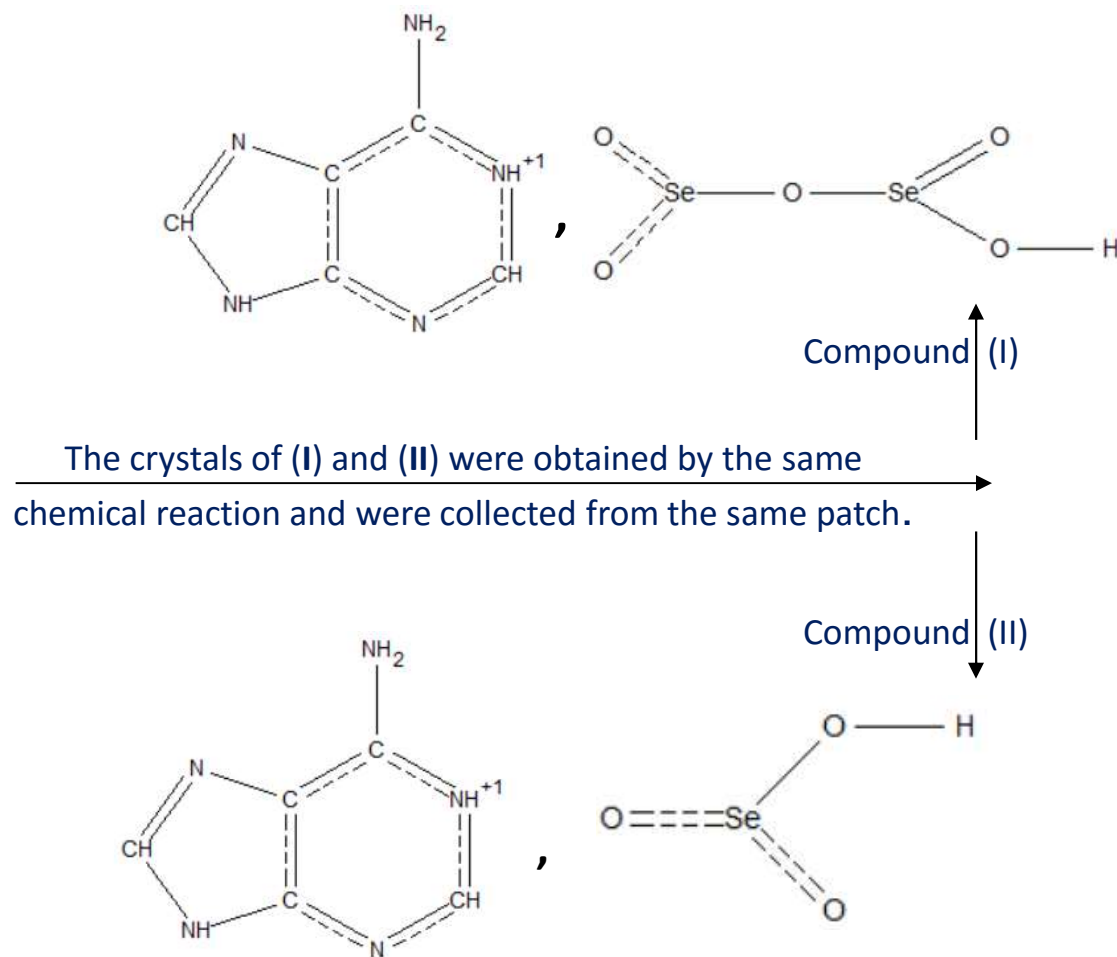
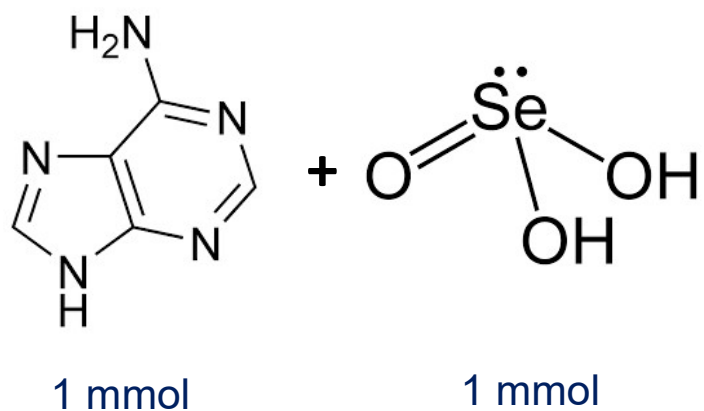


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Results and discussion

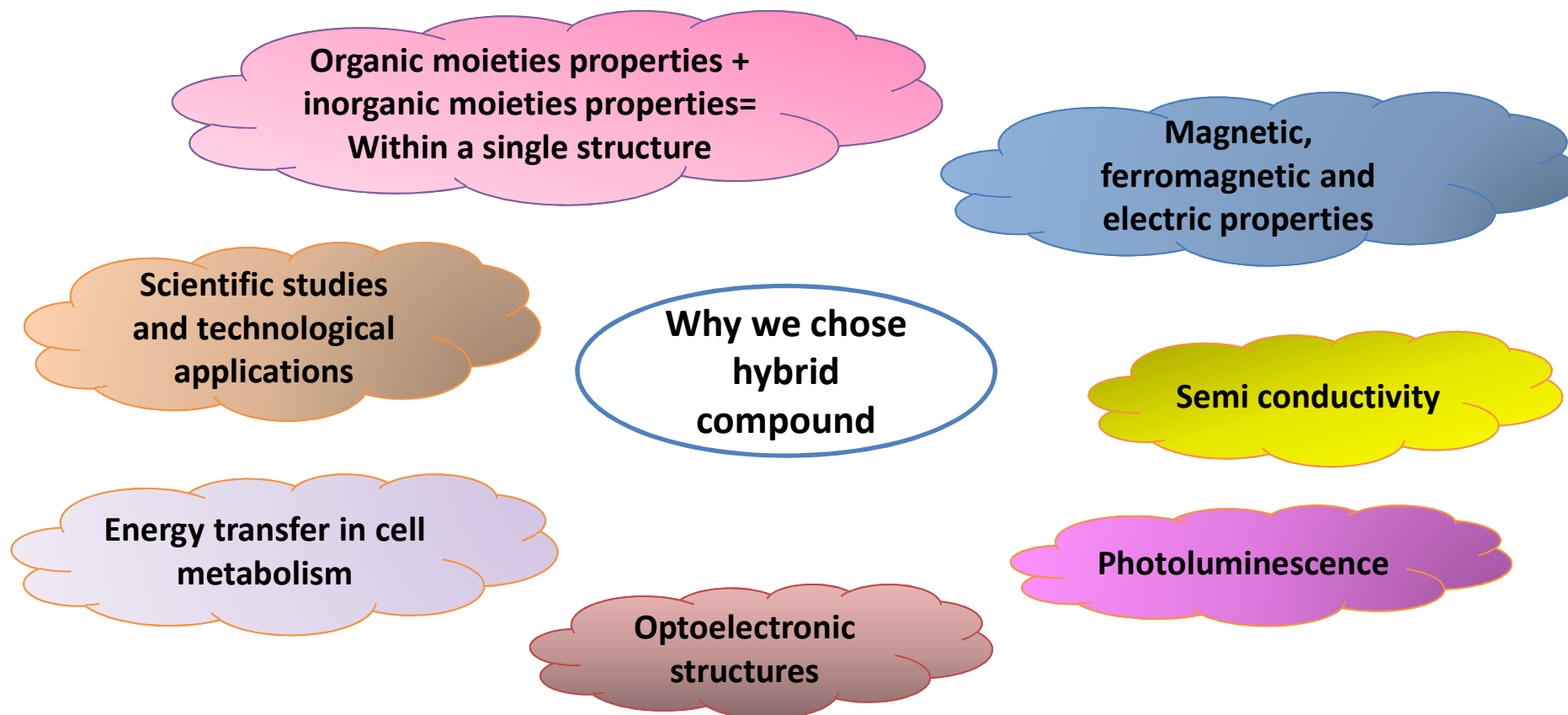
Chemical preparation



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Results and discussion



Organic-inorganic hybrid materials can generate new functionalities from this association



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Results and discussion

Structural analyzes

A- Adeninium hydrogen diselenite (I)

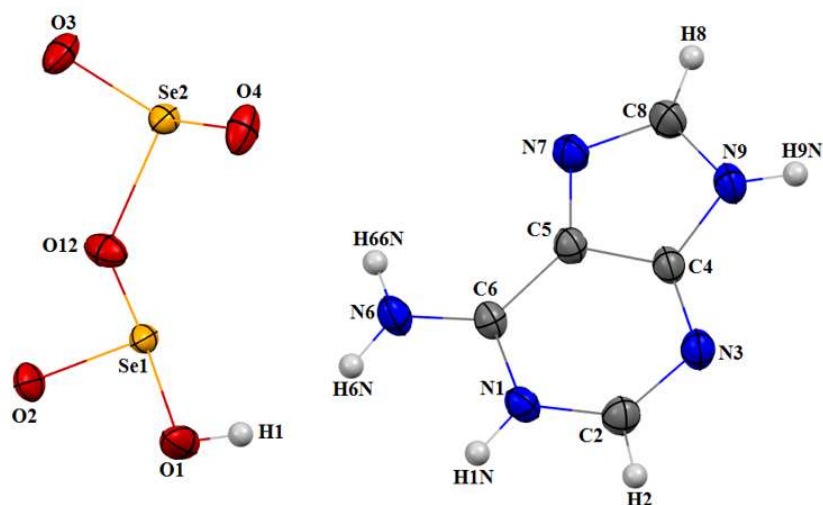


Fig. 2. The asymmetric unit of adeninium hydrogen diselenite (I)

Crystal data	(I)
Empirical Formula	C ₅ H ₇ N ₅ O ₅ Se ₂
Molecular weight (g/mol)	375.08
Crystal system	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> (Å)	6.2851 (3)
<i>b</i> (Å)	21.0046 (2)
<i>c</i> (Å)	8.1402 (2)
β (°)	105.838 (1)
<i>V</i> (Å ³)	1033.84 (6)
<i>Z</i>	4
<i>R</i> _(int) Refinement	0.044
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)] ^b , <i>wR</i> (<i>F</i> ²) ^c , <i>S</i> ^d	0.033, 0.087, 1.07
No. of unique reflections	5116



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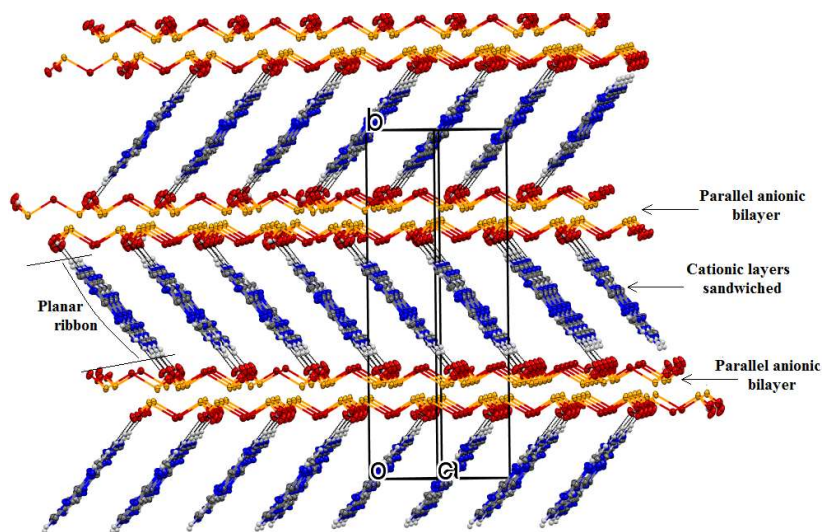


Fig. 3. A view of the crystal packing of (I)

In (I), the adeninium cations are arranged into; a centrosymmetric homosynthon $R_2^2(10)$ ring motifs through a double N6—H6N \cdots N7 interaction that mimics the Hoogsteen pattern and a centrosymmetric homosynthon $R_2^2(8)$ ring motif via two N9—H9N \cdots N3 interactions that mimics the sugar pattern (Fig. 4).

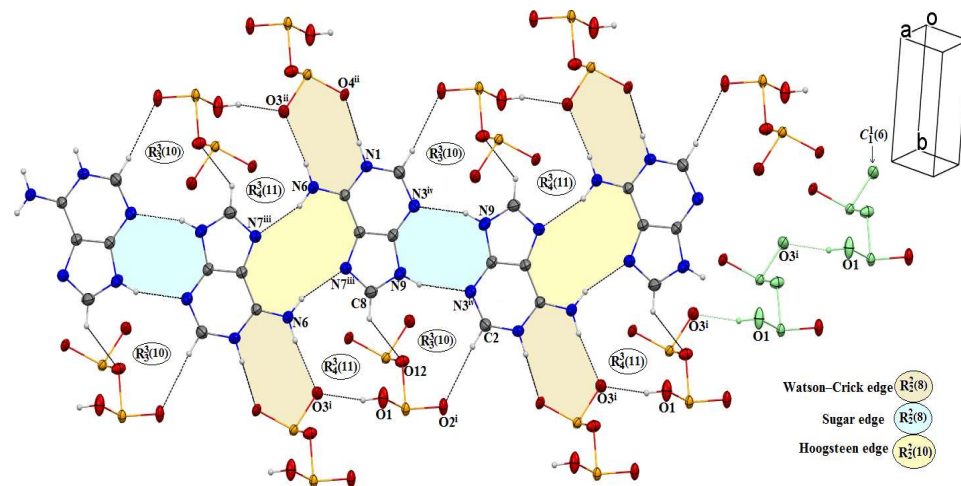


Fig. 4. Part of packing diagram of (I)



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Adeninium base pairs are stacked together through an inversion center and the interplanar distance is 3.361(14) Å (Fig. 5) to form Å planar ribbons

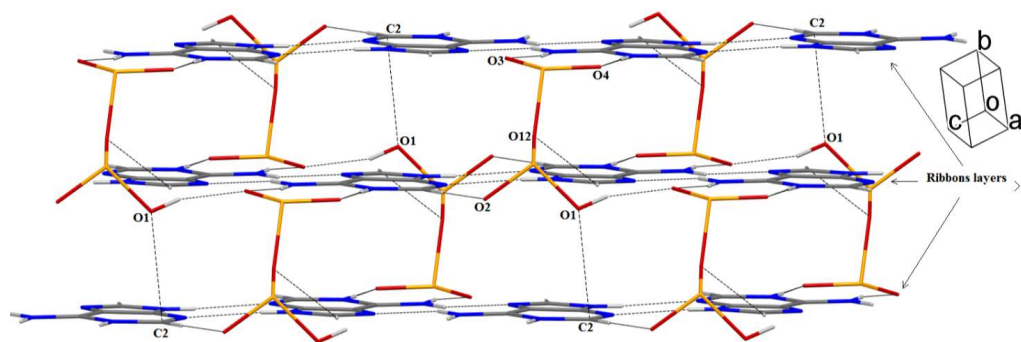


Fig. 6. Electrostatic interaction between the O1 atom and the adeninium cation.

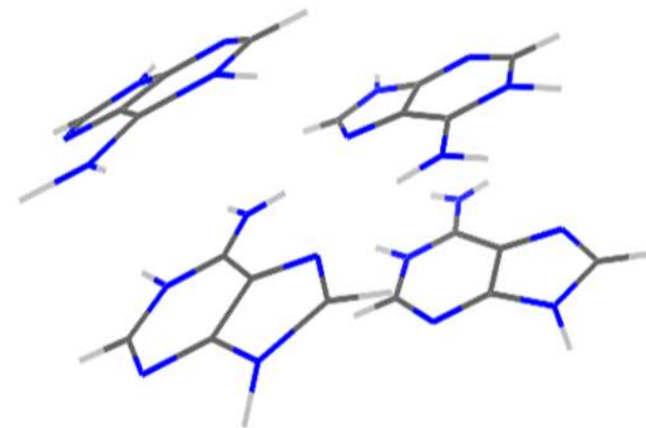


Fig. 5. Crystallographic autostereogram of the stacking interaction between adeninium cations contributing to the maintenance of the organic layers.

The OH oxygen atom O1 of anions molecules exhibits an electrostatic contacts with the π – hole of C2 carbon atom of the pyrimidine ring, resulting in a very short O1—C2_{ring} contact, the distance of O1 to the ring plane is only 2.94(2) Å°. This cation ... O^{δ-} supramolecular association contributes to the stabilization of the molecular structure of (I) (Fig. 6)



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Structural analyzes

B- Adeninium hydrogen selenite (II)

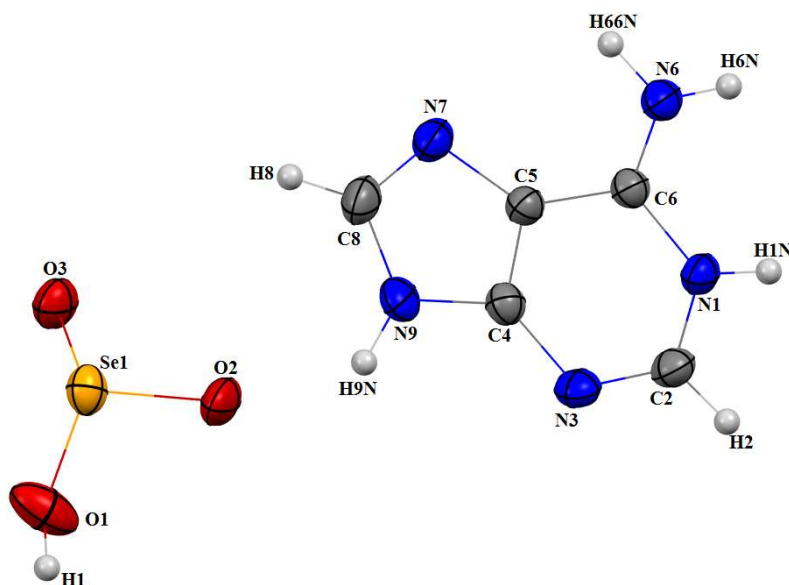


Fig. 7. The asymmetric unit of adeninium hydrogen selenite (II)

Crystal data	(II)
Empirical Formula	C ₅ H ₇ N ₅ O ₃ Se
Molecular weight (g/mol)	264.12
Crystal system	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>a</i>
<i>a</i> (Å)	6.5612 (2)
<i>b</i> (Å)	12.7621 (2)
<i>c</i> (Å)	10.4529 (3)
β (°)	99.846 (3)
<i>V</i> (Å ³)	862.38 (4)
<i>Z</i>	4
<i>R</i> _(int)	0.085
Refinement	
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)] ^b , <i>wR</i> (<i>F</i> ²) ^c , <i>S</i> ^d	0.034, 0.091, 1.03
No. of unique reflections	2507



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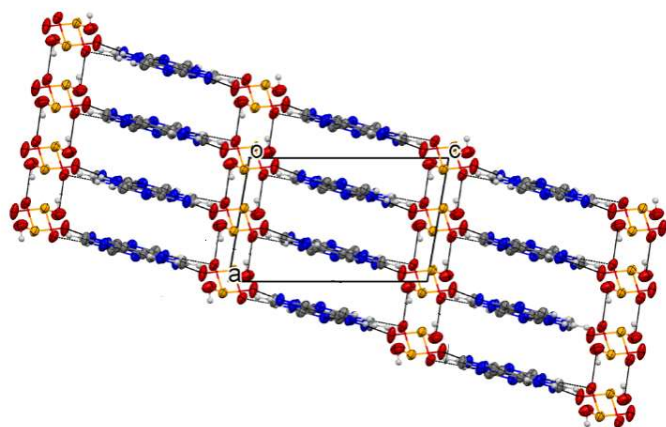


Fig. 8. (a) The crystal packing of (II)

In (II), the adeninium cations form together a non centrosymmetric Hoogsteen/sugar edge pair interactions thereby generating a heterosynthon motif. Adeninium moieties are located in layers parallel to the (a,b) plane around $z=n$, with the stacking occurring in the a direction. The ribbon edges are bordered by anions which form together a supramolecular homo-synthon dimer assembled with two centro-symmetric related $\text{Se1} \cdots \text{O3}$ ionic interactions (Fig. 9)

The structure is built up from tunnels, prolonged along the **b** -axis at $(\frac{1}{2}, y, \frac{1}{2})$ and $(0, y, 1)$. These tunnels are formed by the intersections of two types of chains. (Fig. 8)

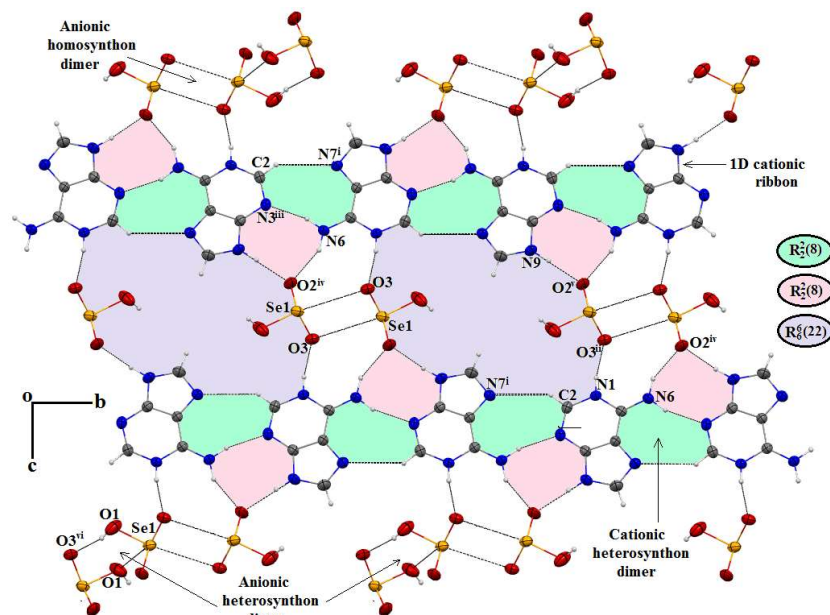


Fig. 9. The supramolecular synthons and the graph set describing intermolecular interactions



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The connectivity between these dimers generates a three-dimensional honeycomb-like inorganic framework (Fig. 10). The O1 oxygen atom (from the SeOH moiety) does not form any hydrogen bond, but is involved in three long distance H \cdots O electrostatic interactions ($d_{\text{H} \cdots \text{O}} > 2.7\text{\AA}$).

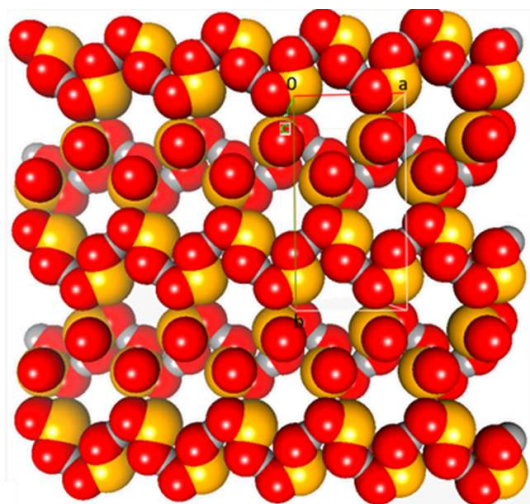


Fig. 10. Molecular packing of (II) showing honeycomb-like molecular network

Similarly to (I), the cationic ribbons in (II) stack together to form two-dimensional layers running in the *a*-direction (Fig. 11). These layers are held together through aromatic stacking interactions established between, one via an inversion centre and one via a 2-fold axis

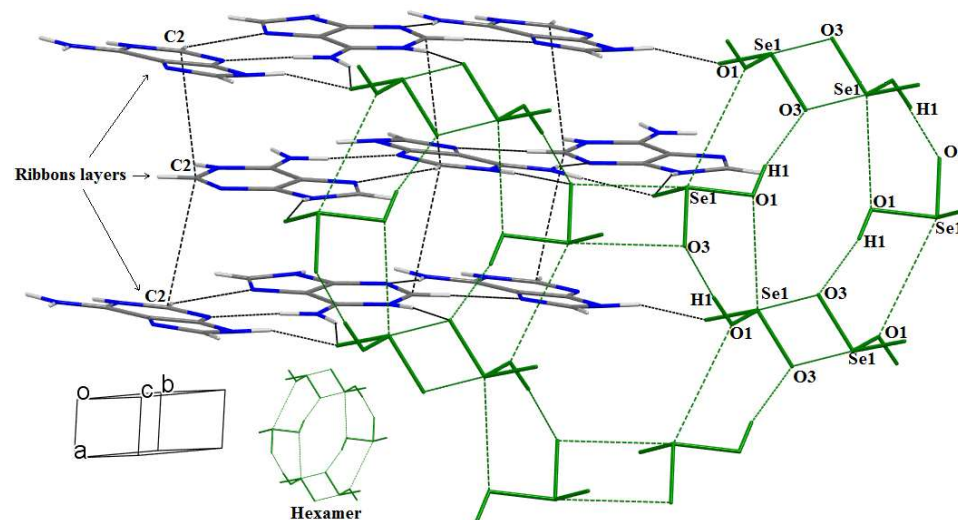


Fig. 11. Three dimensional crystal structure of (II) showing the role of selenite hexamers and aromatic stacking in stabilizing the crystal packing.



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The distance of the C2 ...C2 interaction around the 2-fold rotation axis centre is $d_{C2 \cdots C2} = 3.364(4) \text{ \AA}$. Each adeninium cation forms a total of four aromatic stacking interactions, i.e. two on each side of the moiety

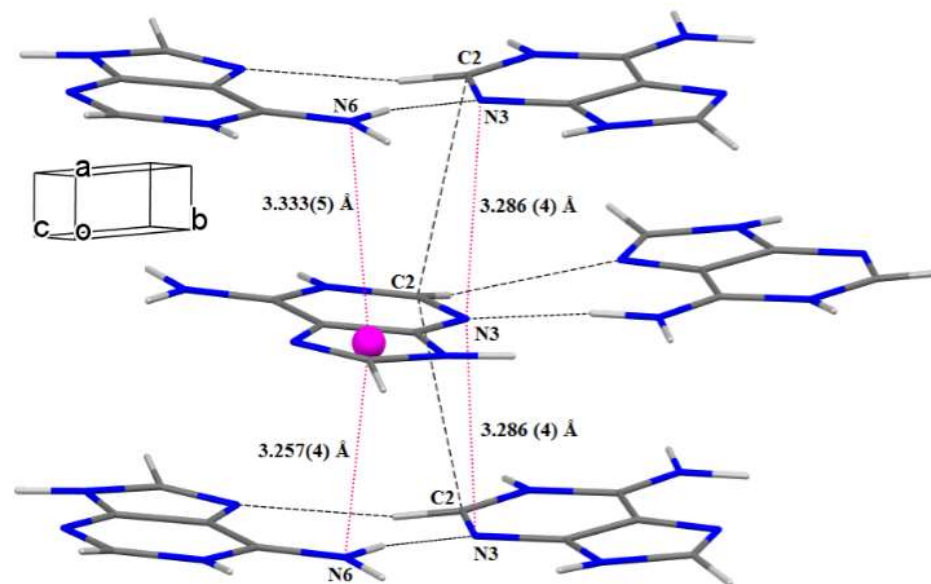


Fig. 12. Charge-charge interactions between cationic layers in (II)



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The enrichment ratios (E)

Overall, hydrogen occupies the largest proportion of the Hirshfeld surfaces, reaching 28.9% for (I) and 34% for (II) most of which is constituted by the polar Hn/o type (Table 1). For both compounds, the major contacts are constituted by strong O \cdots H—N/O and N \cdots H—N hydrogen bonds. The Ho/n \cdots O contacts are enriched ($E=1.46$ for (I) and $E=2.37$ for (II)); the difference corresponds to the presence of three strong N—H \cdots O hydrogen bonds in (II) and only two in (I) .

Table 1: Analysis of contacts on the Hirshfeld surface.

(I)	O	N	Ho/n	Se	Hc	C	(II)	O	N	Hn/o	Se	Hc	C
surf%	23.8	13.4	20.4	18.4	8.5	15.6	%	18.7	15.9	22.6	13.3	11.4	18.1
O	0.0						O	0.0					
N	2.4	1.8					N	1.0	3.3				
Ho/n	14.9	12.4	0.5				Hn/o	21.2	6.5	2.7			
Se	15.9	1.1	5.8	4.6			Se	7.6	1.5	5.1	1.9		
Hc	8.6	0.4	3.0	2.7	0.0		Hc	5.6	4.7	2.2	7.0	0.6	
C	7.5	5.5	4.5	2.3	2.2	4.1	C	2.8	10.2	6.3	2.8	0.9	6.1
O	0.00						O	0.00					
N	0.38	1.11					N	0.17	1.41				
Ho/n	1.46	2.36	0.11				Hn/o	2.37	0.92	0.50			
Se	1.75	0.24	0.75	1.34			Se	1.44	0.36	0.79	0.97		
Hc	2.06	0.17	0.86	0.87	0.00		Hc	1.35	1.43	0.43	2.33	0.54	
C	1.01	1.44	0.71	0.41	0.87	1.81	C	0.41	1.91	0.77	0.56	0.24	1.98



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DFT quantum chemical calculations

The MEP surfaces of the studied compounds (Fig. 13) show that the interaction region between the adeninium cation and the protonated hydrogen diselenite are very attractive.

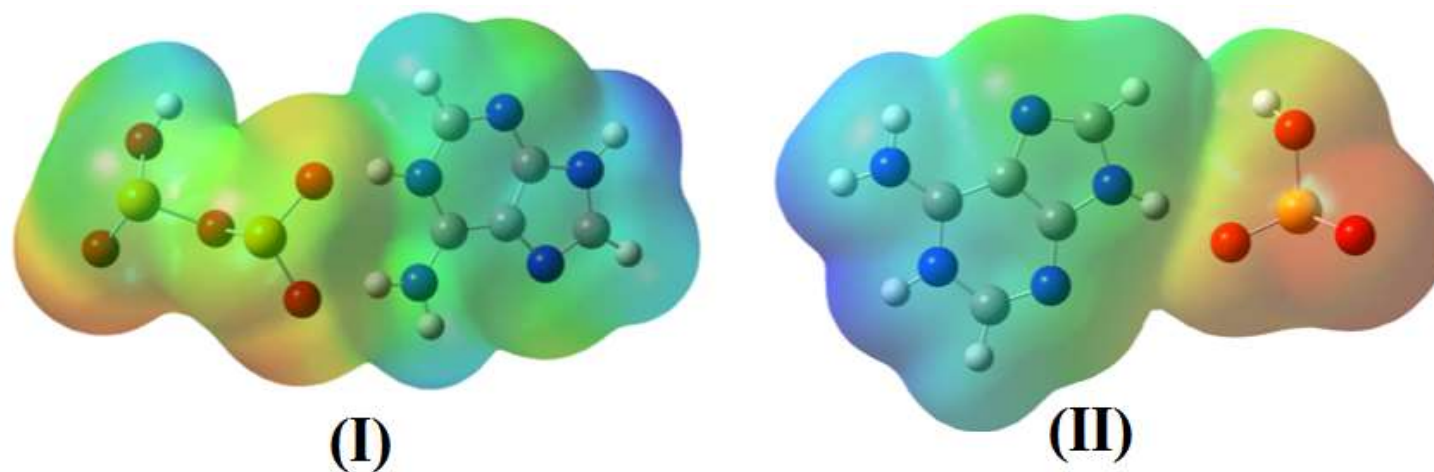


Fig. 13. Molecular electrostatic potential (MEP)



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As appear from Fig.14 , the HOMO orbitals of the two compounds are exclusively delocalised on the atoms of anions, when these later have small contributions in the LUMO orbitals that are mainly located over all adeninium atoms.

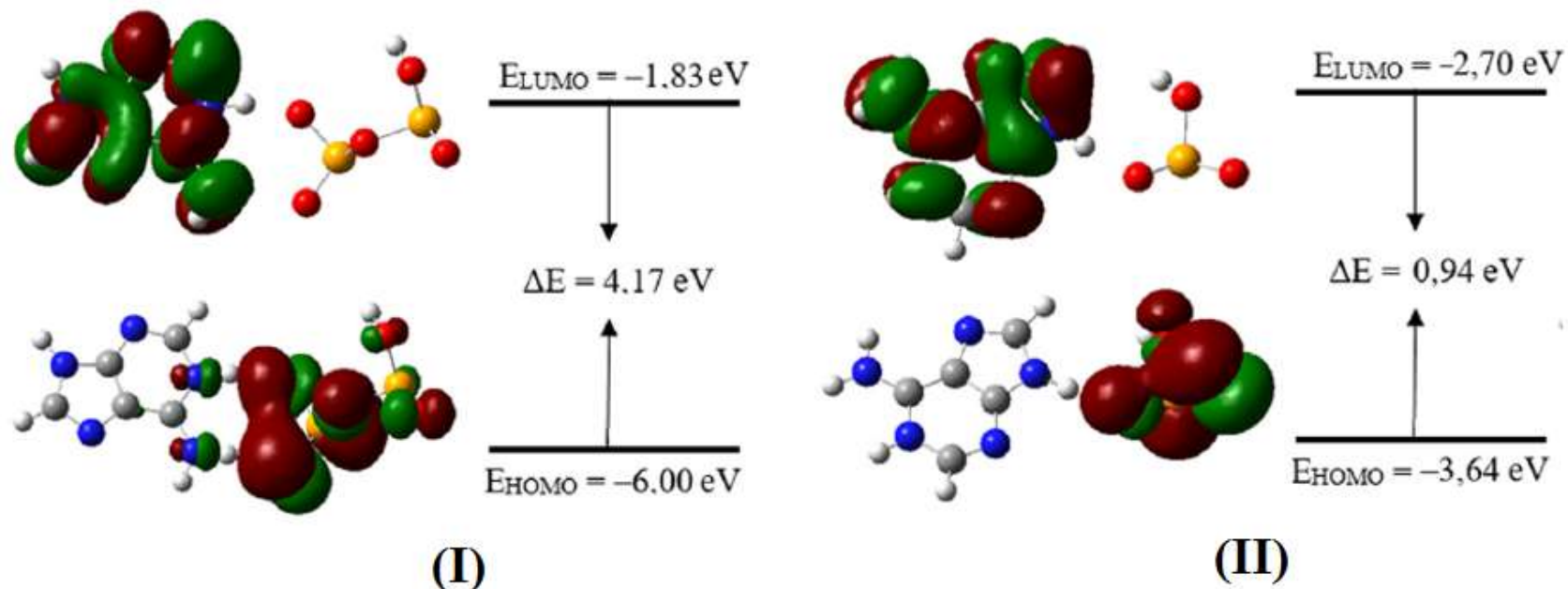


Fig. 14. HOMO and LUMO plots for (I) and (II)



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Conclusions

The molecular structures of the studied compounds were determined by single crystal X-ray diffraction study. The structural investigation reveals the ability of the 1H,9H adeninium cations to exhibit a variety of hydrogen bonding motifs with hydrogen selenite/diselenite anion. Furthermore, supramolecular homo and hetero-synthons found in (I) and (II) play an important role in shaping these supramolecular compounds. The stacking of organic cations is stabilized in the crystal packing of (I) and (II) by the ionic bridges with the surrounding anions; this effect should be considered as important in crystal engineering. There is an interesting electrostatic association, seen only in compound (I), between the SeOH oxygen electron lone pairs and the aromatic cation. In addition, the complementary enrichment ratios (E) were used to investigate the relative proportions of intermolecular close contacts existing within the compounds. Moreover, HOMO/LUMO energy gaps and MEP surfaces have been computed using DFT calculations to get a close insight into the studied compounds.

The results discussed in this work can be useful for investigating the bioactive process of similar molecular materials through, for example, docking approaches.



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