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Networks of intermolecular interactions involving nitro groups in the crystals of three polymorphs of 9-aminoacridinium 2,4-dinitrobenzoate · 2,4-dinitrobenzoic acid

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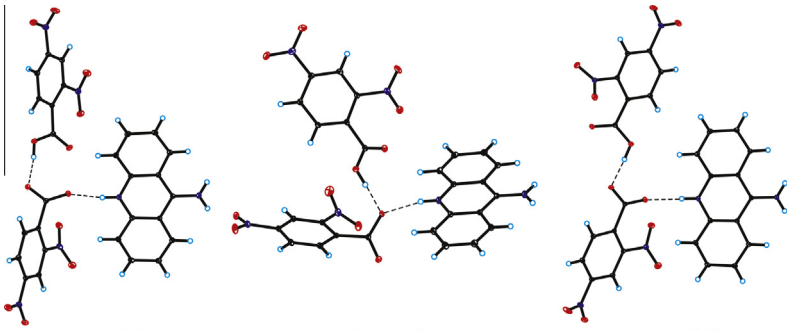
HIGHLIGHTS

- Three polymorphs of 9-aminoacridinium 2,4-dinitrobenzoate · 2, 4-dinitrobenzoic acid have been structurally characterized.
- The N–H···O and O–H···O hydrogen bonds between 9-aminoacridine and carboxylic acid have been analysed.
- The intermolecular interactions involving nitro groups have also been analysed.

GRAPHICAL ABSTRACT



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ABSTRACT

We report on the crystal structures of three polymorphs of 9-aminoacridinium 2,4-dinitrobenzoate · 2,4-dinitrobenzoic acid (**I**, **II** and **III**). Single-crystal X-ray diffraction measurements show that the title compound forms three polymorphs with the space groups $P2_1/n$ (**I**) and $P\bar{1}$ (**II** and **III**). The asymmetric units of all the polymorphs consist of 9-aminoacridinium cation, the 2,4-dinitrobenzoate anion and the 2,4-dinitrobenzoic acid molecule. The neutral and ionic forms of 2,4-dinitrobenzoic acid are linked *via* O–H···O hydrogen bonds with a D graph-set motif, forming monoanionic dimers. The amine and carboxylic acid moieties are linked *via* N–H···O, O–H···O and C–H···O hydrogen bonds. The acridinium skeletons in the crystal packing form π-stacked columns, whereas the monoanionic dimers of 2,4-dinitrobenzoic acid are linked by different types of intermolecular interactions, especially those involving nitro groups. To the best of our knowledge, the crystal structure of 9-aminoacridinium 2,4-dinitrobenzoate · 2,4-dinitrobenzoic acid is the first in which the appearance of monoanionic dimers of 2,4-dinitrobenzoic acid has been documented.

1. Introduction

Crystal engineering – the design and synthesis of functional crystal structures – has become a significant area of interest in solid state chemistry. One of the most important issues in this field relates to polymorphism, which occurs when a chemical compound exists in more than one crystal form [1–4]. Polymorphism is especially interesting in the case of active pharmaceutical ingredients (APIs), which are bioactive components of drugs [5–9]. Such compounds include 9-aminoacridine and its derivatives, a large group of active pharmaceutical ingredients used in the treatment of diseases brought about by various cause, such as mutagens [10], bacteria [11], viruses [12] and prions [13].

Description of the molecular interactions and the supramolecular synthons that they form is the fundamental tool for

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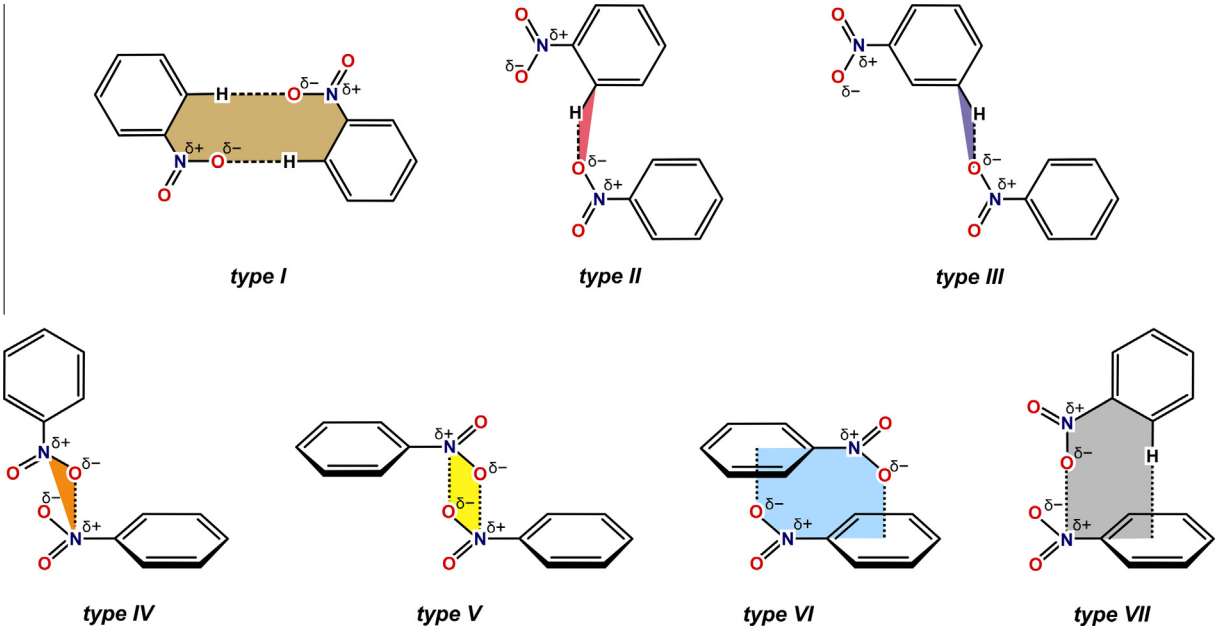

Scheme 1. Types of intermolecular interactions involving nitroarene fragments.

supramolecular chemistry and crystal engineering [14–16]. The analysis of interactions occurring in the crystal structures of organic amine bases and acids, such as the ubiquitous O–H···O, N–H···O, O–H···N hydrogen bonds, has been widely reported owing to their possible occurrence in a variety of biological systems [17–23]. The less well-known examples of such interactions are those involving nitroarene fragments. Several types of such interactions have been described in the literature (Scheme 1) [24–32].

As a continuation of our recent study on the 9-aminoacridinium salts and different aromatic carboxylic acids [33–35], we report on the synthesis, crystal structures and analysis of intermolecular interactions, especially those involving nitro groups occurring in the crystal packing of three polymorphs of 9-aminoacridinium 2,4-dinitrobenzoate · 2,4-dinitrobenzoic acid (**I**, **II** and **III**).

To the best of our knowledge these are the first crystal structures in which the appearance of monoanionic dimers of

Table 1
Crystal data and structure refinement for compounds **I, II** and **III**.

Compound reference	**I**	**II**	**III**
Chemical formula	$(C_{13}H_{11}N_2)^+ \cdot (C_7H_3N_2O_6)^- \cdot C_7H_4N_2O_6$		
M_r	618.47	618.47	618.47
Crystal system	Monoclinic	Triclinic	Triclinic
a (Å)	14.9206(17)	7.7013(1)	8.9319(3)
b (Å)	6.7548(7)	10.735(2)	11.6690(5)
c (Å)	26.005(3)	16.9581(8)	14.0139(6)
α (°)	90	98.202(1)	100.444(4)
β (°)	95.702(9)	102.830(2)	107.521(3)
γ (°)	90	92.750(2)	105.092(3)
Unit cell volume (Å^3)	2608.0(5)	1348.4(3)	1290.2(1)
Temperature (K)	295(2)	295(2)	295(2)
Space group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$
Z	4	2	2
Radiation type	Mo Kα	Mo Kα	Mo Kα
Absorption coefficient, μ (mm^{-1})	0.127	0.123	0.129
No. of reflections measured	10,692	11,124	8806
No. of independent reflections	4686	4859	4657
Reflections collected/unique	10,692/4686	11,124/4859	8806/4657
R_{int}	0.0990	0.0397	0.0370
Data/restraints/parameters	4686/0/406	4859/0/406	4657/0/406
Completeness 2θ = 50.5%	99.5	99.5	99.8
Final $R1$ values ($I > 2\sigma(I)$)	0.0551	0.0489	0.0563
Final $wR(F2)$ values ($I > 2\sigma(I)$)	0.1023	0.0897	0.1302
Final $R1$ values (all data)	0.1382	0.1085	0.0985
Final $wR(F2)$ values (all data)	0.1370	0.1022	0.1608
Goodness of fit on $\|F\|^2$	0.966	0.901	0.995
CCDC number	CCDC 788107	CCDC 788108	CCDC 929446