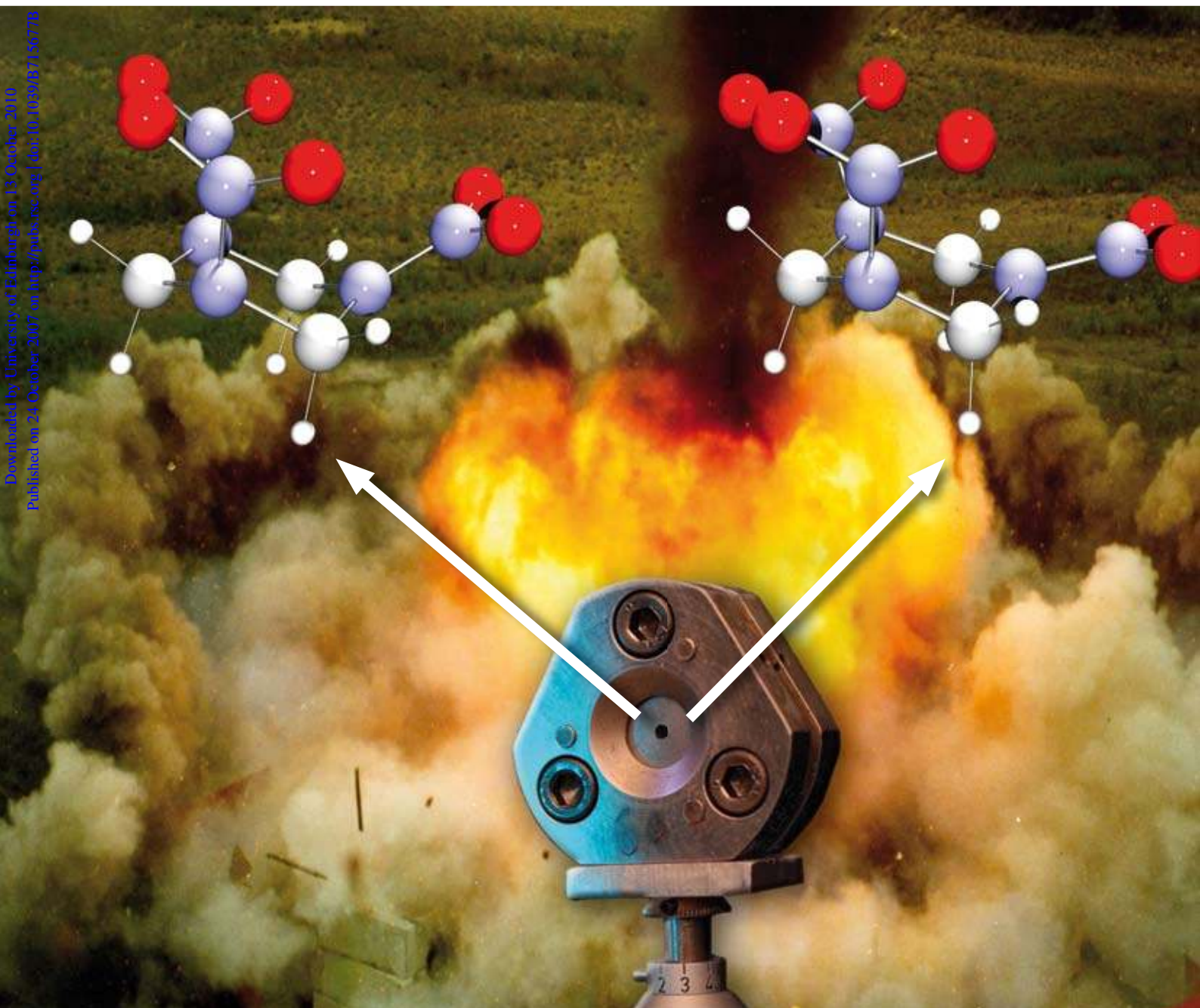


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the crystal structure of  $\gamma$ -RDX as  
determined by high-pressure X-ray  
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Structure of a lead urate complex  
and its effect on the nucleation of  
monosodium urate monohydrate

# Explosives under pressure—the crystal structure of $\gamma$ -RDX as determined by high-pressure X-ray and neutron diffraction†

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Using a combination of X-ray single crystal and neutron powder diffraction, the crystal structure of the high-pressure  $\gamma$ -form of RDX has been determined at 5.2 GPa and shows that the RDX molecules adopt different conformations compared to the conformation found in the ambient-pressure  $\alpha$ -form.

The performance of explosive formulations depends on several factors that include crystal density, detonation velocity, and sensitivity to detonation by stimulus.<sup>1</sup> These in turn are governed by the solid-state structure of the energetic material. In order to model and understand the characteristics and performance of these materials, not only under ambient conditions but also under the extreme conditions of temperature and pressure experienced during detonation, it is essential to obtain detailed structural information. This information can be used to explore aspects of energetic materials that include: sensitivity to shock, heat, and friction; chemical decomposition mechanisms; energy transfer through the solid; detonation velocities; and for testing the efficacy of theoretical modelling techniques. Whilst structural information can be readily obtained under ambient conditions, it is much more difficult to obtain at extreme conditions and to date no high-pressure single crystal studies of energetic materials have been reported.

RDX (1,3,5-trinitrohexahydro-1,3,5-triazine or cyclotrimethylene-trinitramine)‡ is a widely used military explosive that can be compounded with mineral jelly or polymers to form plastic explosives such as C4 and PBX. Two polymorphic forms are known at ambient pressure and were originally designated RDX-I and RDX-II, but are now more usually referred to as the  $\alpha$ - and  $\beta$ -forms, respectively.<sup>2</sup> The structure of the orthorhombic  $\alpha$ -form (space group *Pbca*) has been determined by neutron diffraction,<sup>3</sup> but the structure of the  $\beta$ -form is unknown because of its instability under ambient conditions.<sup>4</sup> Fig. 1 shows the conformation of the RDX molecule in the  $\alpha$ -form with two of the nitro-groups in

pseudo-axial positions and the other in the pseudo-equatorial position—this is denoted as the AAE conformation.

A pressure-induced transition to an orthorhombic  $\gamma$ -form was first reported by Olinger *et al.*<sup>5</sup> at a pressure of  $\sim 4.0$  GPa with a 1.6% reduction in volume and an abrupt increase in the *b*-axis across the transition. Equations of state for both the  $\alpha$ - and  $\gamma$ -forms have been reported based on high-pressure powder X-ray measurements.<sup>6</sup> The pressure–temperature phase diagram for RDX has been determined up to 573 K and 7.0 GPa using powder X-ray diffraction, infrared spectroscopy, and optical polarising microscopy, and the authors demonstrated that an orthorhombic  $\gamma$ -form is produced above 3.8 GPa at ambient temperature.<sup>7</sup> Several theoretical studies have reproduced the effects of hydrostatic compression on the crystallographic lattice parameters of the  $\alpha$ -form,<sup>8–10</sup> but in the absence of experimental structural data, comparisons with molecular geometries were not possible.

Several recent high-pressure spectroscopic studies have attempted to shed light on the nature of the  $\gamma$ -form. A study using Raman spectroscopy up to 15 GPa proposed that the  $\alpha \rightarrow \gamma$  phase transition leads to a rearrangement of the RDX molecules, which in turn significantly changes the intermolecular interaction experienced by the N–O bonds.<sup>11</sup> A compression study up to 26.6 GPa used Raman spectroscopy and far-infrared spectroscopy to identify the  $\alpha \rightarrow \gamma$  transition near 4.0 GPa and presented evidence for a new  $\delta$ -phase at pressures between 17.8 and 18.8 GPa, based on the appearance of new vibrational bands and associated changes in spectral intensities.<sup>12</sup> A very recent structural study used a combination of high-pressure infrared spectroscopy and powder X-ray diffraction in an attempt to determine the crystal structure of  $\gamma$ -RDX.<sup>13</sup> The authors assigned the space group as *Pbca* and used Rietveld refinement to fit their diffraction data to a series of models with the nitro-groups in different conformations.

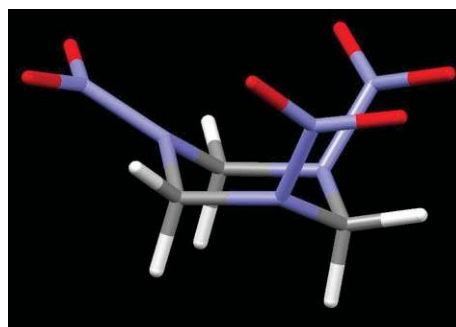


Fig. 1 Conformation of RDX molecule in the  $\alpha$ -form.

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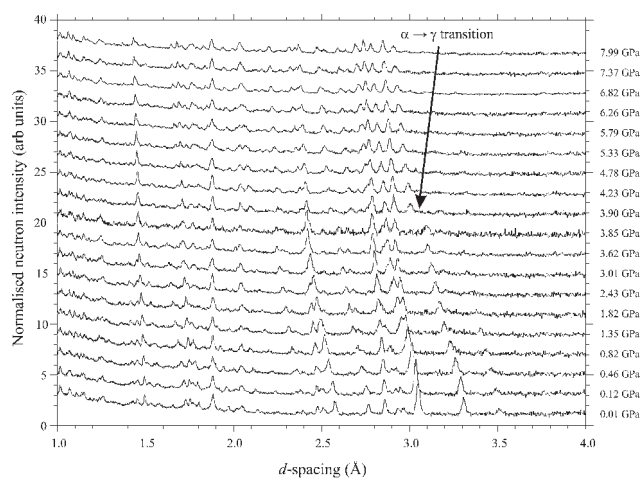


Fig. 2 Sequence of powder neutron diffraction patterns.

The authors concluded that the molecular conformation that best fitted their high-pressure data for  $\gamma$ -RDX was the same as that found for the  $\alpha$ -form (*i.e.* the AAE conformation), but that the N–NO<sub>2</sub> torsion angles had changed marginally.<sup>13</sup>

We have recently initiated a programme to study the effects of high pressure on energetic materials using the techniques and expertise gained in studying other molecular compounds such as polycyclic aromatic hydrocarbons<sup>14</sup> and the drug compounds paracetamol and piracetam.<sup>15</sup> Given the importance and continued interest in RDX, we selected this compound to test our methodologies on energetic compounds.

Fig. 2 shows the sequence of neutron powder diffraction patterns obtained for RDX-*d*<sub>6</sub> as a function of increasing pressure up to 7.9 GPa. Up to 3.85 GPa all of the patterns can be refined using the orthorhombic (*Pbca*) structure of the  $\alpha$ -form. The smooth variation in volume can be fitted to a 3rd order Birch–Murnaghan plot with  $V_0 = 1614.1 \text{ \AA}^3$ ,  $B_0 = 9.8(14) \text{ GPa}$ , and  $B' = 11.4(30)$ . These values are in reasonable agreement with previous studies ( $B_0 = 13.0 \text{ GPa}$ ,  $B' = 6.6$ ;  $B_0 = 13.9 \text{ GPa}$ ,  $B' = 5.8$ ).<sup>5,6</sup> The small differences may reflect the improved precision with which the unit cell volumes have been determined in the current study—neither of the previous studies indicated uncertainties in the derived parameters.

Full-profile Rietveld refinements of the neutron powder diffraction patterns enabled refinement of the crystal structures at a series of pressures up to 3.62 GPa. Over this pressure range, no significant changes were observed in the orientations of the nitro-groups relative to the ring. The most significant changes were observed in the C–D $\cdots$ O–N, N $\cdots$ O, and N $\cdots$ N intermolecular contacts, which decreased by 0.2–0.4 Å. At 3.90 GPa, a dramatic change was observed in the powder diffraction pattern consistent with a phase transition. This phase persisted up to the highest pressure of this study and the peaks were initially indexed to an orthorhombic cell with  $a = 12.669$ ,  $b = 11.048$ , and  $c = 9.610 \text{ \AA}$  at 4.23 GPa. Attempts to refine this pattern using the structure proposed by Goto *et al.*<sup>13</sup> in space group *Pbca* proved unsatisfactory with numerous intensity misfits. After many attempts to fit the data to RDX molecules with different conformations, it became apparent that this was not the correct space group. Assignment of space group can be difficult for high-pressure powder neutron diffraction, particularly for such a

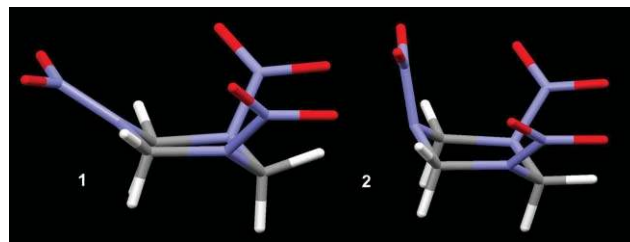


Fig. 3 Conformations of the two independent molecules in  $\gamma$ -RDX.

relatively complex structure, where not only is resolution sacrificed for the sake of high flux, but the constraints of sample environment also restrict the range of *d*-spacing that can be accessed. For this reason we turned to single crystal X-ray diffraction. Earlier optical studies had suggested that hydrostatic compression of a single crystal of RDX through the  $\alpha \rightarrow \gamma$  phase transition did not result in the destruction of the crystal. Further support for this came from the observation that the change in the unit cell volume over the phase transition was small. Hence a single crystal of  $\alpha$ -RDX was initially compressed to 0.1 GPa under hydrostatic conditions in a diamond-anvil cell and, after checking crystal quality, the pressure was then raised slowly to 5.20(5) GPa and single crystal data were collected at this pressure. The reflections were indexed to an orthorhombic cell, space group *Pca*2<sub>1</sub>, with  $a = 12.5650(19)$ ,  $b = 9.4769(6)$ ,  $c = 10.9297(9) \text{ \AA}$ , implying 8 molecules in the unit cell with 2 independent molecules in the asymmetric unit. Owing to the limitations caused by shading from the steel body of the diamond-anvil cell, high-pressure data-sets are frequently incomplete (in this case 73% complete) compared with data-sets recorded at ambient pressure. These factors combined to make structure solution particularly challenging and all attempts using direct methods were unsuccessful. Finally, a data set was solved using the program FOX,<sup>16</sup> which employs direct space global optimisation methods for structure solution. With this solution it proved possible to refine all of the  $\gamma$ -phase neutron powder diffraction patterns extremely well to give typical values for  $\chi^2$  of 1.14 and  $wR_p = 0.026$ , thus providing additional support that the structural model is correct. The two independent molecules, both of which adopt the chair conformation, are shown in Fig. 3.

The orientations of the nitro-groups can conveniently be compared by reference to the angle  $\delta$  (see Fig. 4), which is defined as the angle between the plane of the C–N–C ring atoms and the corresponding N–N bond.<sup>17</sup> Table 1 lists the values of  $\delta$  for the molecules in both crystalline forms, and for *isolated* molecules in a range of conformations calculated by Vladimiroff and Rice<sup>17</sup> using DFT methods. The conformation denoted AAA–AAE (TS-1) represents the transition state between the AAA and AAE conformations, *i.e.* one of the nitro-groups lies midway between

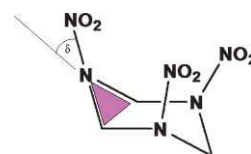


Fig. 4 Definition of parameter  $\delta$  used to describe orientation of nitro-groups in RDX.

**Table 1** Values of  $\delta$  (in  $^\circ$ ) for different conformations of RDX

$\alpha$ -form	$\gamma$ -form (molecule 1)	$\gamma$ -form (molecule 2)	AAA <sup>a</sup>	AAE <sup>a</sup>	AAA-AAE <sup>a</sup> (TS-1)
33.4	39.6	39.6	30.3	34.0	34.1
33.9	17.3	17.3	30.1	34.0	33.8
-19.8	-2.4	9.5	29.9	-37.9	1.5

<sup>a</sup> Calculated structures from ref. 17.

the axial and equatorial positions. Neither of the conformations in  $\gamma$ -RDX corresponds to any of the conformations observed in the calculated structures or in the  $\alpha$ -form. Molecule 1 lies closest to the AAA-AAE (TS-1) conformation and so perhaps could be best described as AAI, where I represents an intermediate orientation of the NO<sub>2</sub> group. On the other hand, with all  $\delta$ -angles being positive, molecule 2 is tending towards the AAA conformation.

Based on the results of the calculations such variability in conformation is perhaps not unexpected, since relative to the AAE conformation the AAA and AAA-AAE (TS-1) conformations are higher in energy by only 0.80 and 3.44 kJ mol<sup>-1</sup>, respectively.<sup>17</sup> Intermolecular interactions within the crystal structure, especially at high pressure, would therefore be expected to modify these conformations. Fig. 5(a) shows the orientations of two adjacent AAA and AAI molecules in the unit cell, illustrating how each molecule effectively “cups” one of the nitro-groups of the other molecule. This interlocking of adjacent molecules results in the formation of interpenetrating chains of AAA and AAI molecules running along a 2<sub>1</sub>-screw axis in the *c*-direction (see Fig. 5(b)). This allows more efficient packing and reduces the number of unfavourable short O...O and N...O contacts.

Across the  $\alpha \rightarrow \gamma$  transition, a 3% decrease in unit cell volume was observed. This is slightly larger than previously reported by Olinger *et al.*<sup>5</sup> but presumably reflects the higher precision of the lattice parameters obtained in the present study. The smooth variation in volume from 3.90 to 7.99 GPa can be fitted to a 3rd order Birch-Murnaghan plot with  $V_0 = 1557.6 \text{ \AA}^3$ ,  $B_0 = 17.6(14) \text{ GPa}$ , and  $B' = 6.8(10)$ , thus demonstrating that  $\gamma$ -RDX is significantly less compressible than the  $\alpha$ -form. The values differ from those reported ( $B_0 = 10.9 \text{ GPa}$  and  $B' = 7.9$ ),<sup>6</sup> but this reflects the greater precision of our measurements.

In conclusion, we have demonstrated that advances in the techniques for the collection and analysis of high-pressure X-ray and neutron diffraction data now permit the accurate determination of the full crystal structure of energetic materials under extreme conditions. These methods have been applied to solve the

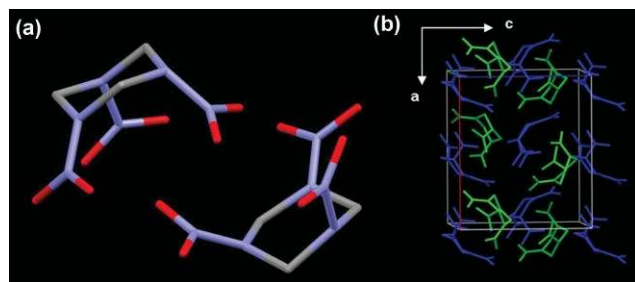
structure of  $\gamma$ -RDX, a long-standing problem of great significance to the energetics community. Such information is crucial not only for the effective prediction of their behaviour under operational conditions, but also to test the efficacy of theoretical modelling techniques applied to energetic materials. The level of complexity of this structure extends significantly the limits to which high-pressure techniques may be applied, and hence opens up opportunities for the study at high pressure of more challenging molecular systems.

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## Notes and references

‡ Crystalline samples of RDX (SME type II; 100–300  $\mu\text{m}$ ) were kindly provided by W. G. Proud and H. Czernski (Cavendish Laboratory, University of Cambridge). The high level of incoherent scattering from hydrogen necessitated the use of fully deuterated RDX for the powder neutron diffraction studies. Powder X-ray diffraction measurements showed no evidence, within experimental uncertainty, of any differences in phase behaviour between deuterated and non-deuterated RDX. RDX-*d*<sub>6</sub> was prepared by nitration of hexamine-*d*<sub>12</sub>.<sup>18</sup> A lightly ground sample (*ca.* 100 mg) of RDX-*d*<sub>6</sub> was loaded into an encapsulated TiZr gasket<sup>19</sup> together with a small quantity of 4 : 1 perdeuterated methanol-ethanol as a pressure-transmitting fluid and a small quantity of lead to act as a pressure calibrant. The resulting capsule assembly was then compressed within a type V3b Paris-Edinburgh (P-E) press.<sup>20</sup> High-pressure neutron powder diffraction data were collected using the PEARL/HiPr diffractometer at the UK spallation neutron source, ISIS, located at the STFC Rutherford Appleton Laboratory. High-pressure X-ray experiments were performed on non-deuterated RDX, RDX-*h*<sub>6</sub>, using a Merrill-Bassett diamond-anvil cell<sup>21</sup> equipped with 600  $\mu\text{m}$  culets and a tungsten gasket with a 300  $\mu\text{m}$  hole. A 4 : 1 mixture of methanol-ethanol was used as a hydrostatic pressure medium with a ruby chip acting as the pressure calibrant. Single crystal and powder diffraction data were collected at the STFC Daresbury Laboratory, UK on Stations 9.8 and 9.5HPT,<sup>22</sup> respectively. Single crystal data were processed according to the procedure described by Dawson *et al.*<sup>23</sup> X-Ray data:  $\gamma$ -phase C<sub>3</sub>H<sub>6</sub>N<sub>6</sub>O<sub>6</sub>  $M = 222.12$ , orthorhombic, space group  $Pca2_1$ ,  $a = 12.5650(19)$ ,  $b = 9.4769(6)$ ,  $c = 10.9297(9) \text{ \AA}$ ,  $V = 1301.5(2) \text{ \AA}^3$ ,  $T = 293(2) \text{ K}$ ,  $P = 5.20(5) \text{ GPa}$ ,  $Z = 8$ ,  $\mu = 0.216 \text{ mm}^{-1}$ ,  $D_c = 2.267 \text{ Mg m}^{-3}$ ,  $\lambda = 0.6710 \text{ \AA}$ ,  $\theta_{\text{max}} = 24.87^\circ$ , 4339 reflections measured, 872 unique ( $R_{\text{int}} = 0.079$ ).  $R_1 = 0.0717$ ,  $wR_2 = 0.1723$  for  $I > 2\sigma(I)$ , and  $R_1 = 0.0893$ ,  $wR_2 = 0.1809$  for all 872 data. CCDC reference numbers 659283 and 663455. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b715677b



**Fig. 5** (a) The relationship between the two independent molecules in  $\gamma$ -RDX (hydrogen atoms omitted for clarity), and (b) packing arrangement of molecules (AAI molecules in blue; AAA molecules in green).

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