

On the influence of weak intermolecular interactions on the molecular crystal density of 1,3,5-triazine trinitroalkyl derivatives

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SUPPLEMENTARY INFORMATION

Δ_{OED} -based densification approach

It is assumed that upon crystal formation, molecules interact with each other by means of overlap of their electron densities. It means that volume of isolated molecule is larger than that of the molecule in a crystal. Similarly, density of an isolated molecule (d_{mol}) is lower than that in a crystal (d_{cryst}). The latter is the density of the crystal structure obtained from X-ray experiment. In the other words, upon crystal structure formation, molecule is densified. The value of d_{mol} can be estimated by analysis of the electron density of optimized isolated molecule in terms of the AIM theory. It is defined as a ratio of molecular mass per molecular volume (the latter is presented as the sum of atomic volumes)

$$d_{\text{mol}} = m_{\text{mol}}/V_{\text{mol}}; \quad m_{\text{mol}} = M_{\text{mol}}/N_{\text{A}}; \quad V_{\text{mol}} = \sum_i V_{\text{at}}^{(i)}$$

Here, M_{mol} and m_{mol} are molar and molecular masses, respectively, N_{A} is Avogadro number, V_{mol} and V_{at} are molecular and atomic volumes, respectively. It is convenient to present d_{mol} in g/cm^3 units. Evidently, the volume and density of any molecular fragment can be calculated in a similar way. For estimation of V_{mol} , isodensity surface of $0.0004 \text{ e}/a_0^3$ (a_0 – Bohr radius) was utilized for integration procedure. So estimated molecular volume comprises about 99.8% of all electrons (nearly whole molecule), and charge leakage does not exceed $0.002 \text{ e}/\text{\AA}^3$ that approximately corresponds to numerical error of integration of calculated electron density. It is evident, that difference between crystal and molecular density can be served as a measure of how pronounced is the overlap of molecular electron densities upon crystal structure formation. Therefore, the Δ_{OED} criterion defined as $\Delta_{\text{OED}} = d_{\text{cryst}} - d_{\text{mol}}$ would characterize a degree of molecular densification and, therefore, tightness of crystal packing. Combined analysis of d_{mol} and Δ_{OED} values would clarify an origin of the observed crystal density.

In the case of salts, co-crystals and solvates (with two or more different structural units) one needs to define a way of estimation of the volume of the structural unit in a crystal. This is also necessary for investigation of molecular fragments or functional groups that is the case of the present study. To calculate contributions from each type of structural unit, fragment or atom into the crystal density, the QTAIM partitioning of promolecular electron density defined on supramolecular clusters was carried out using the MultiWFN program (T. Lu, F. Chen, *J. Comput. Chem.* **2012**, *33*, 580-592). The supramolecular clusters were generated such as each symmetry independent atom forms all geometric contacts within the sphere of 5\AA radii. After that volume in crystal of any molecular fragment, structural unit or atom (and, therefore, density) can be calculated as it is done for isolated molecule. Difference between crystal and molecular density of any fragment will give Δ_{OED} criterion for this particular fragment.

Table 1S. Pair intermolecular interaction energies (kcal/mol) and shortened contacts (Å) of molecule of compound **3** with its closest environment in the crystal obtained at M052X/6-311G(df,pd) level of approximation

Entry	Atomic pair			Distance	Symmetry code	Type of interaction	Energy
1	No shortened contacts				2-x,1-y,2-z	vdW	-0.1
2	No shortened contacts				1.5-x,2-y,-1/2+z	vdW	-0.4
3	No shortened contacts				1.5-x,2-y,1/2+z	vdW	-0.4
4	N2	O6	3.321	1/2+x,y,1.5-z	weak O... π	-3.3	
	N3	O6	3.271				
	C3	O6	3.005				
5	O6	N2	3.321	-1/2+x,y,1.5-z	weak O... π	-3.3	
	O6	N3	3.271				
	O6	C3	3.005				
6	C4	O8	3.206	2-x,-1/2+y,1.5-z	H-bond	-8.8	
	H4A	O8	2.577				
	H4A	N2	2.599				
7	O8	C4	3.206	2-x,1/2+y,1.5-z	H-bond	-8.8	
	O8	H4A	2.577				
	N2	H4A	2.599				
8	No shortened contacts				x,1.5-y,1/2+z	vdW	-1.6
9	No shortened contacts				x,1.5-y,-1/2+z	vdW	-1.6
10	No shortened contacts				-1/2+x,1.5-y,1-z	vdW	-1.5
11	No shortened contacts				1/2+x,1.5-y,1-z	vdW	-1.5
12	No shortened contacts				-1/2-x,-1/2+y,z	vdW	-0.4
13	No shortened contacts				-1/2-x,1/2+y,z	vdW	-0.4
14	O6	O3	3.027	1.5-x,1/2+y,z	weak O... π NO ₂ ...NO ₂	-6.0	
	O6	N3	3.117				
	O6	C1	3.162				
	O6	C2	3.370				
	O6	C3	3.143				
15	O3	O6	3.027	1.5-x,-1/2+y,z	weak O... π NO ₂ ...NO ₂	-6.0	
	N3	O6	3.117				
	C1	O6	3.162				
	C2	O6	3.370				
	C3	O6	3.143				

Table 2S. Pair intermolecular interaction energies (kcal/mol) and shortened contacts (Å) of molecule A of compound **2** with its closest environment in the crystal obtained at M052X/ M052X/6-311G(df,pd) level of approximation

Entry	Atomic pair		Distance	Symmetry code	Type of interaction	Energy
1	No shortened contacts			-1+x,1+y,z	vdW	-0.8
2	No shortened contacts			1+x,-1+y,z	vdW	-0.8
3	No shortened contacts			x,-1+y,z	vdW	-2.4
4	No shortened contacts			x,1+y,z	vdW	-2.4
5	O1	O9	2.927	-1+x,y,z	O...NO ₂ NO ₂ ...NO ₂	-7.0
	O2	O9	2.948			
	O4	O9	3.013			
	O8	N9	3.001			
	O8	O14	2.961			
6	O9	O1	2.927	1+x,y,z	O...NO ₂ NO ₂ ...NO ₂	-7.0
	O9	O2	2.948			
	O9	O4	3.013			
	N9	O8	3.001			
	O14	O8	2.961			
7	N5	O12	2.854	1-x,-y,2-z	NO ₂ ...NO ₂	-7.1
	O4	O12	3.02			
	O5	O12	3.033			
	O7	O12	2.966			
	O12	N5	2.854			
	O12	O4	3.02			
	O12	O5	3.033			
	O12	O7	2.966			
8	C1	O4	3.021	-x,-y,2-z	O...π	-9.4
	N1	O4	3.243			
	C2	O5	3.101			
	N2	O5	3.269			
	O4	C1	3.021			
	O4	N1	3.243			
	O5	C2	3.101			
	O5	N2	3.269			
9	No shortened contacts			-x,1-y,2-z	vdW	-2.3
10	O1	O10'	2.853	-x,-y,1-z	O...π weak H-bond	-6.8
	C1	O10'	2.87			
	N1	O10'	3.283			
	C2	O13'	3.113			
	N1	O13'	3.216			
	O3	C4'	3.421			
	O3	H4'B	2.491			
11	No shortened contacts			-x,1-y,1-z	vdW	-0.5
12	No shortened contacts			1-x,-1-y,1-z	vdW	-0.4
13	O10	C1'	3.017	1-x,-y,1-z	O...π	-8.2
	O10	N1'	3.083			
	O10	N3'	3.214			
	O10	C2'	3.254			
	O10	C3'	3.361			

Table 3S. Pair intermolecular interaction energies (kcal/mol) and shortened contacts (Å) of molecule A' of compound **2** with its closest environment in the crystal obtained at M052X/ M052X/6-311G(df,pd) level of approximation

Entry	Atomic pair		Distance	Symmetry code	Type of interaction	Energy
1	O7'	C7'	3.386	-1+x,1+y,z	vdW	-0.6
2	C7'	O7'	3.386	1+x,-1+y,z	vdW	-0.6
3	C6'	O6'	3.425	x,-1+y,z	vdW	-2.5
4	O2'	C7'	3.656	x,1+y,z	vdW	-2.5
5	O9'	O1'	2.955	-1+x,y,z	O...NO ₂ NO ₂ ...NO ₂	-6.7
	O9'	O2'	2.873			
	O9'	O4'	3.018			
	O14'	O8'	3.016			
	N9'	O8'	3.036			
6	O1'	O9'	2.955	1+x,y,z	O...NO ₂ NO ₂ ...NO ₂	-6.7
	O8'	N9'	3.036			
	O8'	O14'	3.016			
	O2'	O9'	2.873			
	O4'	O9'	3.018			
7	N5'	O12'	2.845	-x,-y,1-z	NO ₂ ...NO ₂	-7.4
	O5'	O12'	3.0			
	O7'	O12'	3.015			
	O12'	N5'	2.845			
	O12'	O5'	3.0			
	O12'	O7'	3.015			
8	C2'	O5'	3.069	1-x,-y,1-z	O...π NO ₂ ...NO ₂	-9.5
	N2'	O5'	3.187			
	O4'	O4'	2.849			
	O5'	C2'	3.069			
	O5'	N2'	3.187			
9	C8'	C8'	3.779	1-x,-1-y,1-z	vdW	-1.0
10	C4'	O3	3.421	-x,-y,1-z	O...π weak H-bond	-6.8
	H4'B	O3	2.491			
	O10'	O1	2.853			
	O10'	C1	2.87			
	O10'	N1	3.283			
	O13'	N1	3.216			
	O13'	C2	3.113			
11	N6'	C7	3.734	-x,1-y,1-z	vdW	-0.5
12	C7'	O6	3.18	1-x,-1-y,1-z	vdW	-0.4
13	C1'	O10	3.017	1-x,-y,1-z	O...π	-8.2
	N1'	O10	3.083			
	N3'	O10	3.214			
	C2'	O10	3.254			
	C3'	O10	3.361			