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Intermolecular N₃···N₃ interactions in the crystal of pentaerythrityl tetraazide

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The peculiarities of intermolecular interactions in a crystal of the title compound are analysed within topological analysis of electron density function and their influence on the molecular geometry and charge distribution is discussed.

Polyazido compounds are of great interest as potential energetic materials.[1] Although there are numerous X-ray diffraction (XRD) investigations of this class of compounds [the Cambridge Structural Database (CSD)[2] contains about 480 entries (92 organic compounds)], there are no data concerning intermolecular contacts in such crystals. In order to get more information about the supramolecular organization in the crystals of polyazido compounds and to distinguish from all N₃···N₃ contacts the attractive ones, we performed experimental (XRD)[†,‡] and theoretical (DFT)[§] investigations of neopentane tetraazide **1** (Figure 1). Note that **1** is a powerful explosive[3] with impact sensitivity (H_{50}) equal to 2 cm[3(a)] (for comparison, the corresponding values for cyanuric azide and pentaerythritol tetranitrate are 6.2 and 14.5 cm).[1] In addition, **1** is the best candidate for the analysis of N₃···N₃ contacts as far as its surface is built up only by azido groups.

The peculiarities of chemical bonding pattern, as well as crystal packing in **1**, were analysed using Bader's 'Atom in Molecule' (AIM) theory.[4] In the case of weak interactions, the application of this approach makes it possible not only to find
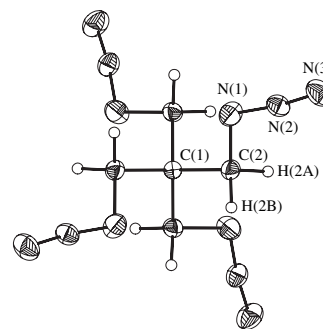

Figure 1 The general view of **1** in representation of atoms by thermal ellipsoids at $p = 50\%$. The bond lengths (Å) and angles (°), calculated by XRD and according to B3LYP/6-311G* are N(1)–N(2) 1.2299(5)/1.230, N(2)–N(3) 1.1310(5)/1.134, C(2)–N(1) 1.4837(5)/1.481, C(1)–C(2) 1.5307(4)/1.539; N(1)–N(2)–N(3) 173.05(4)/173.7, N(2)–N(1)–C(2) 114.77(3)/116.0, C(1)–C(2)–N(1) 109.06(2)/109.3.

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† Pentaerythrityl tetraazide (neopentane tetraazide) was synthesised according to ref. 10, mp 45–50 °C. ¹H NMR (CDCl₃) δ: 3.33 (s, 4CH₂), a crystal for XRD was prepared from melt at –15 °C.
Crystallographic data: crystals of **1** (C₅H₈N₁₂, $M = 236.23$) are tetragonal, space group $I4_1/a$, at 200 K, $a = b = 10.357(1)$, $c = 9.738(2)$ Å, $V = 1044.4(3)$ Å³, $Z = 4$ ($Z' = 1/4$), $d_{calc} = 1.502$ g cm⁻³, μ(MoKα) = 1.14 cm⁻¹, $F(000) = 472$. Intensities of 4056 reflections were measured with a Syntex P2₁ diffractometer [λ(MoKα) = 0.71072 Å, θ/2θ-scans, 2θ < 90°] and 2132 independent reflections [$R_{int} = 0.0240$] were used in a further refinement. The structure was solved by a direct method and refined by the full-matrix least-squares technique against F^2 in the anisotropic-isotropic approximation. Hydrogen atoms were located from the Fourier synthesis of the electron density and refined in the isotropic approximation. For **1**, the refinement converged to $wR_2 = 0.0971$ and GOF = 0.971 for all independent reflections [$R_1 = 0.0334$ was calculated against F for 1549 observed reflections with $I > 2\sigma(I)$]. All calculations were performed using SHELXTL PLUS 5.0.
Atomic coordinates, bond lengths, bond angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). These data can be obtained free of charge *via* www.ccdc.cam.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or deposit@ccdc.cam.ac.uk). Any request to the CCDC for data should quote the full literature citation and CCDC reference number 289403. For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2005.

‡ The multipole refinement was carried out within the Hansen-Coppens formalism[11(a)] using the XD program package[11(b)] with the core and valence electron density derived from wave functions fitted to a relativistic Dirac-Fock solution. Before the refinement, C–H bond distances were normalised to the values obtained in the B3LYP/6-311G(d,p) calculation. The level of multipole expansion was octopole for carbon, nitrogen and sulfur atoms and dipole for hydrogens. The multipole occupancies of the C(1) atom were refined with the $\bar{4}$ symmetry restrains, respectively, according to ref. 11(c). The refinement was carried out against F and converged to $R = 0.02139$, $wR = 0.0202$ and GOF = 0.84 for 1528 merged reflections with $I > 3\sigma(I)$. All bonded pairs of atoms satisfy the Hirshfeld rigid-bond criteria[11(d)] (difference of the mean square displacement amplitudes along the bond were not larger than 8×10⁻⁴ Å²). The residual electron density was no higher than 0.05 eÅ⁻³. Analysis of topology of the $\rho(r)$ function was carried out using the WINXPRO program package.[12]

§ DFT calculations of **1** were performed with the Gaussian 98 program package[13] at the B3LYP/6-311G* level of theory. As convergence criteria the normal threshold limits of 2×10⁻⁶ and 6×10⁻⁶ were applied, for the maximum force and displacement, respectively. To enhance the B3LYP calculation accuracy, the pruned (99590) grid was used. Topological analysis of the $\rho(r)$ function was performed using the MORPHY 98 program,[14] based on wave functions obtained from the B3LYP calculations.
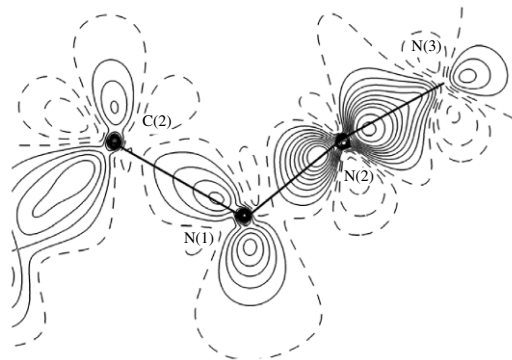
Figure 2 The section of deformation electron density in the CN_3 plane of **1**. Contours are drawn with 0.1 e$Å^{-3}$ step, the negative contours are dashed.

all attractive intermolecular interactions but also to estimate their energy and thus the overall lattice energy of a crystal.[5]

The XRD study of **1** has revealed that site symmetry [$I4_1/a$, C(1) atom is located in the special position $\overline{4}$] in a crystal coincides with molecular one (S_4). The geometry of **1** in either a crystal or an isolated molecule is strictly the same, thus indicating that the influence of intermolecular contacts, as well as the polarity of a medium (crystal field effects), is negligible (Figure 1). The azide moiety in **1** consists of longer N(1)–N(2) [1.2299(5) Å] and shorter N(2)–N(3) bonds [1.1310(5) Å]; the angle N(1)N(2)N(3) is slightly bent. The bond angles at the C(1) atom deviate from the ideal tetrahedral values and equal 108.63(2) and 111.16(3)°. Assuming that the same flattening of a tetrahedron is observed in the isolated molecule (109.1 and 110.3°), we can consider this effect as an intramolecular one.

The deformation electron density (DED) distribution function[‡] for **1** in a crystal is characterised by expected features (see ref. 6). The DED accumulation is observed in the areas of N–N and N–C bonds. The DED peaks, which can be attributed to a lone electron pair, are located in the vicinity of the N(1) and N(3) atoms, in particular, the maxima located along the N(2)–N(3) bond line indicate the *sp* hybridization of the N(3) atom and, as a consequence, the triple character of the N(2)–N(3) bond.

The topological analysis of electron density distribution function has revealed that, in addition to the geometry, the topological parameters of $\rho(r)$ in the critical points (3,–1) [CP (3,–1)] in crystals and isolated molecules of **1** are nearly identical. In particular, the difference in the values of $\rho(r)$ in CP (3,–1) for the N_3 fragment is no more than 0.1 e$Å^{-3}$ (2.5%) for the N(2)–N(3) bond (3.83 and 3.94 e$Å^{-3}$). The values of ellipticity are also close to each other: the maximum deviation is observed for the N(1)–N(2) bond and equal 0.07 (0.22 and 0.15). The distinction of the ellipticity values for N(1)–N(2) and N(2)–N(3) bonds both in the crystal and isolated molecule (*ca.* 0.07) indicates a considerable contribution of resonant forms with the formal triple character of the N(2)–N(3) bond, which is in agreement with the above DED distribution for the N_3 moiety.

The atomic basins (Ω) in the crystal and isolated molecule of **1** were localised as subspaces surrounded by a zero-flux surface. For the Langrangian [$L(r) = -1/4\nabla^2\rho(r)$] integrated over the every Ω (which must be exactly zero according to theory[4]), the relatively small numbers (with averaged values equal to 6×10^{-5} and 2×10^{-5} a.u. for a crystal and an isolated molecule, respectively) were obtained. The sum of the atomic volumes for **1** (260.2 e$Å^{-3}$) in a crystal reproduces well the unit cell volume per molecule [261.1(3) $Å^3$] with a 0.4% error.

Surprisingly, the sum of atomic volumes for 0.001 a.e. envelope of $\rho(r)$ in the isolated molecule of **1** (272.1 $Å^3$) is nearly the same as that for the molecule in a crystal. Furthermore, differences in the atomic volumes of the outward nitrogen atoms of the N_3 fragment in the crystal and in the isolated molecule are merely absent (0.29–0.70 $Å^3$). It should be noted that such a constancy of the atomic volume, when going from the isolated molecule to the molecule in a crystal, in particular, for terminal groups, is a unique feature of **1** (*e.g.*, see ref. 7).
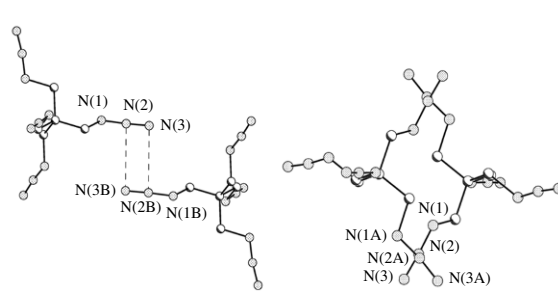

Figure 3 Two types of $N_3\cdots N_3$ contacts with (*a*) antiparallel and (*b*) perpendicular arrangement of azide fragments.

The same constancy is observed for charges obtained by the integration of $\rho(r)$ over Ω. Both in the crystal and in the isolated molecule, the N(1) and N(2) atoms are characterised by negative charges (–0.31, –0.15e and –0.39, –0.14e, respectively) while the N(3) atom is positively charged (0.10 and 0.10 e).

The similarity of charges, as well as of the atomic volumes (which is even more surprising) for crystal and isolated molecules of **1** definitely designates that specific intermolecular contacts in the crystal are fully absent or extremely weak.

Indeed, the intermolecular contacts in **1** are respectively long, so we cannot fetch out the specific interactions only on the basis of van der Waals radii.[8] As a consequence, the density of the crystal of **1** is small (1.502 g cm^{-1}) for explosive materials (*e.g.*, see ref. 1) in spite of high impact sensitivity.[3(a)] However, these 'long' $N_3\cdots N_3$ intermolecular contacts in **1** (3.124–3.369 Å) are characterised by specific directionality and can be divided into two groups with antiparallel [N(2)$\cdots$N(3B) 3.141(1) Å)] [Figure 3(*a*)] and perpendicular [N(2)$\cdots$N(2A) 3.261(1) Å] [Figure 3(*b*)] arrangements of azide fragments. Note that the 'skewed' N(2)$\cdots$N(3C) contact with N(2)$\cdots$N(3C) distances and the N(1)N(2)N(3C) angle equal to 3.273(1) Å and 105.7°, respectively, are also observed.

It is important that such contacts with this specific arrangement of azide groups is not a unique characteristic of **1**, they are also observed in other polyazides. Indeed, the analysis of CSD has revealed that the antiparallel arrangement of azide groups (with N$\cdots$N distances of 2.9–3.5 Å) is more frequently observed (127 structures) while the perpendicular one is rather rare (32 structures).

In order to check whether or not these long interatomic contacts between N_3 groups correspond to specific interactions, we performed a search for CP (3,–1) in the area of said contacts. Unexpectedly, the CP (3,–1) were located not only for the above N$\cdots$N contacts (Figure 3) but also for extremely long N–H contacts, namely, H(2B)$\cdots$N(1′) (H$\cdots$N 2.80 Å, CHN 130°) and H(2B)$\cdots$N(3′) (H$\cdots$N 2.84 Å and 105°). The topological parameters of $\rho(r)$ for N$\cdots$N contacts and N$\cdots$H in CP (3,–1) are close to each other. In particular, $\rho(r)$ varies in the range 0.030(2)–0.043(2) e$Å^{-3}$. The estimation of the energy of the said contacts using Lecomte's correlation scheme[9] has revealed that its values are small (0.56–0.97 kcal mol^{-1}). However, the total lattice energy calculated by energy summation for all independent contacts and multiplied by 4 (due to site symmetry) for **1** is high and equal to 14 kcal mol^{-1}.

Thus, we can conclude that the formation of the short $N_3\cdots N_3$ contacts in polyazide crystals is uncharacteristic. Therefore, the assembling of pentaerythrityl tetraazide molecules in a solid state for such a rigid molecular framework (the constancy of geometry and atomic volumes) leads to a structure with high impact sensitivity because even small deformations of the crystal structure cause a shortening of favourable intermolecular contacts.

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