DOI: 10.1002/anie.201006000

Pseudosymmetry in Trinitropyrazole: The Cost of Error in Space-Group Determination**

*Yulia V. Nelyubina, Igor L. Dalinger, and Konstantin A. Lyssenko**

electron density distribution · pseudosymmetry · space groups · structure elucidation · X-ray diffraction

With more than 9% of crystal structures having several independent species ($Z' > 1$) in an asymmetric unit[1] (with the number of examples increasing over the years[2]) and 27% of them showing approximate symmetry elements,[3] the pseudosymmetry phenomenon has become a widely recognized disaster in the solid-state world that significantly complicates the scientific efforts of many chemists and crystallographers.[4,5] Although there were episodes of its successful use,[6,7] pseudosymmetry is responsible for many failures to correctly deduce the crystal structure of a chemical substance. Moreover, this occurs more frequently than is often recognized,[5] thus causing the "wrong" structures to regularly appear in the literature.[8]

One of the recent examples is that of 3,4,5-trinitro-1*H*-pyrazole (TNP, Figure 1):[9] its structure was solved in the space group $C2/c$ ($Z' = 1.5$).[9c] The claim of a static disorder at the room temperature together with impossible intermolecular contacts (those between disordered hydrogen atoms) could be indicative of an incorrect (higher symmetry) assignment of the space group.[8,10] We carried out the structure determination at room temperature and 100 K, and in both cases the above symptoms of an erroneous structure persisted when solved in the $C2/c$ space group, but did not appear when solved in the space group $P2_1/c$ ($Z' = 3$).

The revised crystal structure of TNP**[11]** features three independent molecules: O, A, and B (Figure 1); the main parameter that differentiates these molecules is the twist angle of the NO_2 groups at the atoms C(1), C(2), and C(3): 0.89(8), 82.47(2), 2.76(8)° for molecule O; 14.76(6), 63.76(4), 7.47(7)° for molecule A; and 9.71(6), 69.53(4), 7.74(6)° for molecule B. In distinct contrast to molecule O, molecules A and B are related through a pseudo-twofold axis (the distance to the exact symmetry element, which measures the deviation from the ideal high-symmetry structure,[3] is 0.1 Å). This pseudosymmetry caused the above error in the determination

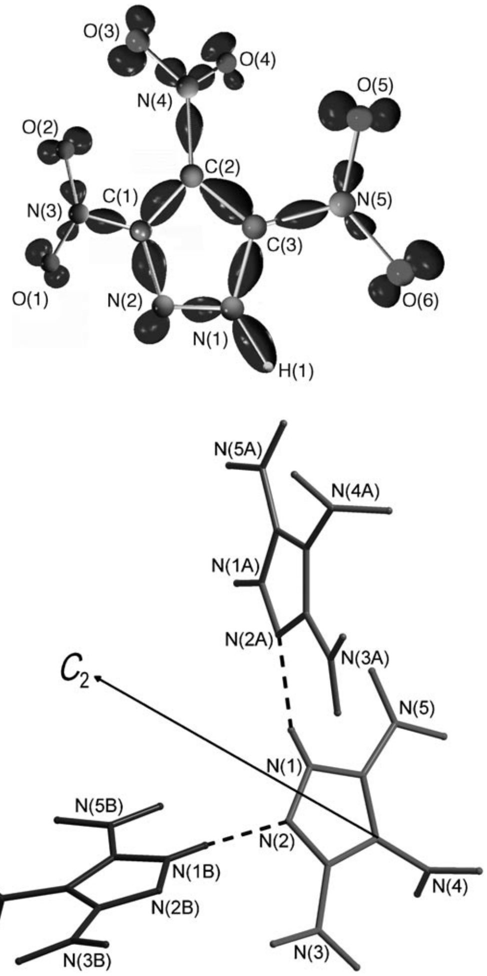

Figure 1. Top: General view of TNP with the 3D surface of deformation electron density (DED) distribution depicted at DED = 0.35 eÅ^{-3}. Bottom: the three indepentent molecules; molecule A is shown with atom number suffixes A, molecule B with suffixes B, and molecule O without suffixes.

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[*] Dr. Y. V. Nelyubina, Prof. K. A. Lyssenko
X-ray Diffraction Center, A.N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences
119991, Vavilov Street, 28, Moscow (Russia)
Fax: (+7) 499-135-5085
E-mail: kostya@xrlab.ineos.ac.ru
Dr. I. L. Dalinger
N.D. Zelinsky Institute of Organic Chemistry
Russian Academy of Sciences
119991, Leninsky prospect, 47, Moscow (Russia)

[**] This study was financially supported by the Russian Foundation for Basic Research (Projects 10-03-00578 and 11-03-92697), the Foundation of the President of the Russian Federation (Federal Program for the Support of Young Doctors, Grant MD-237.210.3), and the Russian Science Support Foundation.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201006000.

of the space group, with molecules A and B merging into one with a disordered hydrogen atom.[9c] With only such a slight disorder resulting (only one hydrogen atom, that is, 0.3 % of $F(000)$), one would think that this easy-to-overlook error is too small to have any measurable consequences. But is it indeed the case?

Herein we aim not simply to reveal one more erroneous structure among the many others (this can be done with standard X-ray diffraction procedures), but rather to illustrate in a quantitative manner how much such a seemingly minor flaw can "cost" a crystal structure. To do this we performed a high-resolution X-ray diffraction study of crystalline TNP at 100 K, followed by a topological analysis of the electron density distribution function $\rho(\boldsymbol{r})$[12,13] by using the "atoms in molecules" (AIM) theory.[14] This approach allows the net properties of molecules and ions, such as charge and volume,[14] as well as the energy of interactions (identified based on the bond critical points (3, −1), or BCP) within a crystal,[15,16] to be assessed accurately, thereby revealing even subtle differences between the independent species and their crystal environments.[7]

Along with the molecular geometries (see above), the electron density distributions within the independent molecules of TNP show that there is a pseudosymmetric relation between molecules A and B: they are rather similar, but have a slight variation in the $\rho(\boldsymbol{r})$ parameters for the bonds (see the Supporting Information). The differences in the $\rho(\boldsymbol{r})$ and $\nabla^2\rho(\boldsymbol{r})$ values in the BCPs within the pyrazole rings of A and B are only 0.02 e Å^{-3} and 2.7 e Å^{-5}, respectively; the bonds involving the nitro groups are, however, less persistent (0.15 e Å^{-3} and 4.4 e Å^{-5}, respectively). This variation can be accounted for by the "natural spread" of $\rho(\boldsymbol{r})$ and $\nabla^2\rho(\boldsymbol{r})$ values, which were shown to vary by 0.1 e Å^{-3} and 3–4 e Å^{-5} for covalent bonds (see Ref. [17] and references therein). At the same time, the $\rho(\boldsymbol{r})$ and $\nabla^2\rho(\boldsymbol{r})$ values for molecule O differ from those of molecules A and B by up to 0.24 e Å^{-3} and 8.3 e Å^{-5}, respectively, which is clearly outside these limits. The same trend is also observed in the bond ellipticities (ε), which serve as a measure of the π-component contribution. In the case of TNP, the ellipticities indicate that all of the covalent bonds ($\varepsilon = 0.10$–0.37) have a partial double-bond character, except for C(2)−N(4) and N(1)−N(2) of molecule O ($\varepsilon = 0.05$–0.07), which are almost single bonds. However, despite the shortened O···N distances between the nitro groups within the molecules (O(2)···N(4) 2.8601(5)–2.9110(5) Å, O(5)···N(4) 2.9034(5)–2.9217(5) Å), no BCPs were found, and only the displacement of the moiety $N(4)O_2$[9c] is due mainly to the conjugation with the pyrazole ring being lacking or negligible. The differences in the bond ellipticities for molecules A and B are not more than 0.05, while those with molecule O amount to 0.12.

The variation in the intramolecular bonding in TNP agrees with the intermolecular binding patterns being different for the independent species (see the Supporting Information). Although in all cases they include the N−H···N hydrogen bonds (N···N 2.9702(5)–3.0631(5) Å, NHN 160–173°; Figure 1) and a plethora of interactions involving the NO_2 groups (all of them located on the basis of the BCP search), the number and the type of the interactions do not coincide—even those for molecules A and B. Nevertheless, the pseudosymmetry between them is reflected in the total energy of the interactions of the independent species with the crystal environment (Table 1). The corresponding values were obtained from the X-ray diffraction data by using the Espinosa correlation, which is equally valid for hydrogen bonds[15,16,18] and weak interactions;[19,20] the energy of the intermolecular interactions in TNP varies in the ranges 4.9–6.0 and 0.3–2.5 kcal mol^{-1}.

Table 1: The net charges and the interaction energies for the independent molecules of TNP.

Molecule	Σq_{at} [e]	ΣE_{int} [kcal mol^{-1}][a]			
		O	A	B	Tot
O	−0.09(1)	0	21.5	23.0	44.5
A	+0.19(1)	21.5	7.2	8.9	37.6
B	−0.09(1)	23.0	8.9	7.1	39.1

[a] The values are given for the interactions with the species O, A, and B and for all the interactions formed by each independent molecule, respectively. The interaction energies were calculated by using the Espinosa correlation (see the Supporting Information).

Molecule O does not interact with its symmetry-related partners—other species of type O—but form a number of contacts with molecules A and B (termed here O–A and O–B interactions). These contacts with molecules A and B show that the concept of the energetic factors favoring the asymmetric pairing suggested in a recent study by Gavezzotti[21] can be extended to systems with more than two independent species in an asymmetric unit.

The O–A and O–B bonding is similar in energy at 21.5 and 23.0 kcal mol^{-1}, as are those of the self-interactions A–A and B–B at 7.1 and 7.2 kcal mol^{-1}. These values result in an energy difference of about 1 kcal mol^{-1} in the interactions involving molecules A and B, thus revealing the "energetic" pseudosymmetry between these species.

The energy of the A–B interactions that were completely ignored in the case of the space group $C2/c$ is 8.9 kcal mol^{-1}. This is approximately how much the error in the space group determination costs the crystal structure of TNP! For comparison, the energy of all the interactions that contribute to the existence of crystalline benzene and 1,3,5-triazine is only 11[22] and 13 kcal mol^{-1},[23] respectively, which is twice the energy of a hydrogen bond in TNP.

Although the geometrical and energetic characteristics of molecules A and B are very similar but very different from those of molecule O, the charge distribution in TNP shows a completely different tendency: molecules O and B rather than A and B appear to be similar (see Table 1). Indeed, the net charges obtained from the X-ray diffraction data for species O, A, and B are −0.09, +0.19, and −0.09 e (the small values of the net Lagrangian, which are 0.001107, 0.00068, and 0.00036 a.u., respectively, indicate the high accuracy of the charges obtained[24]); the nitro groups mostly violate the expected "A = B" relation. Apparently, the relation does not hold in this case because of intermolecular A-to-B charge transfer resulting from interactions between A and B (with an energy of 8.9 kcal mol^{-1}), since the similar energy of the O–A and O–B bonding allows assuming that molecule O receives approximately equal amounts of charge density from A and B. The corresponding difference in the net charges of these pseudosymmetry-related species (0.3 e, which correlates rather well with the interaction energies[7]) can be considered as the cost of the error in determining the space group.

In summary, the high-resolution X-ray diffraction study of crystalline trinitropyrazole has allowed the energetic consequences of overlooked pseudosymmetry between independent molecules therein to be revealed and quantified. It was shown that examining crystals with several independent molecules is a versatile way of analyzing the influence of intermolecular interactions—even those that lead to only a slight perturbation of molecular electron densities—on the charge redistribution between molecules. By using TNP as an example, the interplay between the independent species was measured through the interaction energies and the net charges. These allowed, for the first time, the calculation of how much an error in determining a space group may cost in terms of universal and transferable units—electrons and kilocalories.

Received: September 24, 2010

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