organic papers

4,4,8,8-Tetranitro-2,6-dioxabicyclo[3.3.0]octane

Judith L. Flippen-Anderson,* Jeffrey R. Deschamps, Clifford George and Richard D. Gilardi

Laboratory for the Structure of Matter, Code 6030, Naval Research Laboratory, Washington, DC 20375, USA

Correspondence e-mail: flippen@nrl.navy.mil

The title compound, $C_6H_{26}N_4O_{10}$, was synthesized as part of the Office of Naval Research Energetic Materials Research Program. When first studied in the mid-1980s, a solution was obtained which had two molecules in the asymmetric unit, one of which was severely disordered. A new look at this compound in 2002 has revealed a structure with six molecules in the asymmetric unit with no disorder. Five of the six unique molecules are essentially identical. This deceptively simple molecule presents an interesting case study to show how much data-collection hardware and software have improved since the middle-1980s.
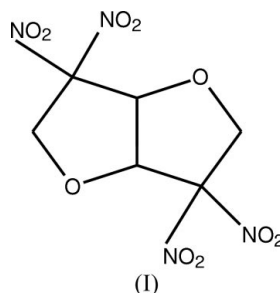
Comment

Data on 4,4,8,8-tetranitro-2,6-dioxabicyclo[3.3.0]octane (TNBO), (I) (Fig. 1), were originally collected in 1984 on what was then a Nicolet P3-F diffractometer using Cu $K\alpha$ radiation.

(I)

The monoclinic unit cell was a = 9.631 (1) Å, b = 11.538 (20) Å, c = 10.205 (1) Å and β = 105.30 (1)°. The structure was solved, with difficulty, in space group $P2_1$ and
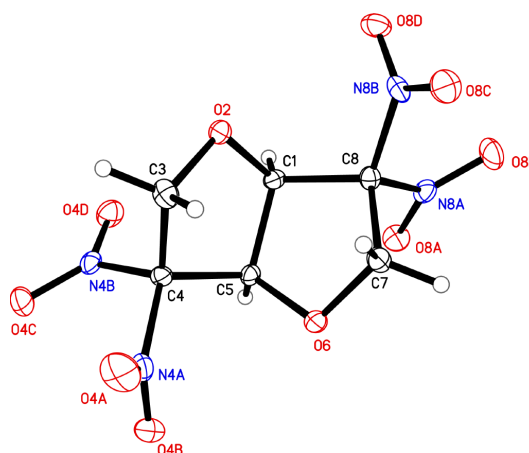

Figure 1

A view of one molecule of TNBO, with displacement ellipsoids at the 50% probability level (from the 2002 data set).
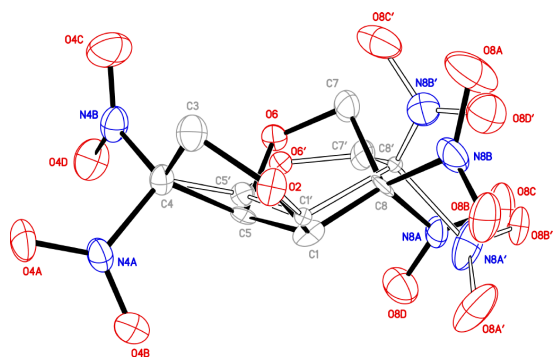
Figure 2
The disordered molecule of TNBO from the small unit cell of the 1984 determination. Displacement ellipsoids are at the 20% probability level. Anisotropic displacement parameters for six atoms (C1′, C5′, C8′ O6′, N8B′ and O8D′) were constrained to be approximately isotropic.
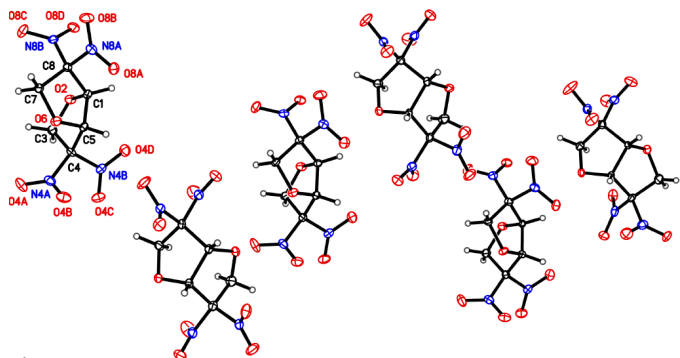

Figure 3
The asymmetric unit of TNBO, in the larger 'true' cell, with displacement ellipsoids at the 50% probability level.

larger than that of the original cell. In this 'super' cell, two thirds of the data were quite weak, but too strong to be ignored. The distribution of intensities also made it difficult for direct-methods programs to solve the structure automatically. A partial structure was obtained using *SnB* (Weeks & Miller, 1999), which was developed into the full structure using difference Fourier maps (Fig. 3).

There are six molecules in the asymmetric unit with no disorder. There is a *cis* junction between the two five-membered rings, both of which have normal envelope conformations, with C7 and C5 being the flap atoms. Five of the six unique molecules are essentially identical (Fig. 3). In the sixth molecule, the envelope flips for one of the two five-membered rings, such that atom C7 is on the opposite side of
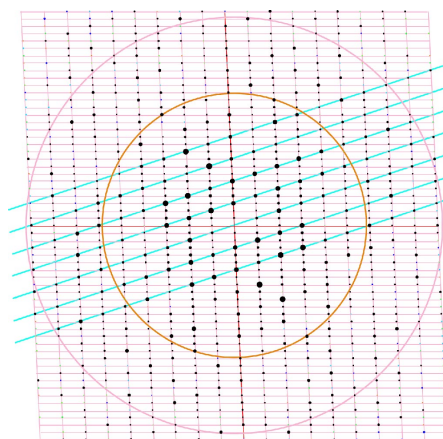

Figure 4
Relative intensity plot for the $k = 3$ layer in TNBO. The circles represent 1.5 and 1.0 Å resolution, l is down and h is to the right. The plot was generated by *XPREP* (Bruker, 2001). The blue diagonal lines were added to highlight the strong intensities that led to the smaller cell in 1984.

refined to an R factor of 0.042 for the 1160 observed reflections (R for all 1601 unique data was 0.063). There were two molecules in the asymmetric unit, one of which was disordered (Fig. 2). The structure answered the questions posed by the chemist who synthesized the material. TNBO was the expected product and the solid-state density was 1.847 Mg m^{-3}. However, crystallographically, the results were unsatisfactory. Many constraints were required to keep the bond lengths and angles chemically reasonable, and a number of atoms required constraints to prevent the anisotropic displacement parameters from going negative during the refinement. Results were essentially the same for at least three different crystals from the same sample. The results were filed away and forgotten.

The availability of more powerful data-collection systems prompted a reinvestigation of this problem in 2002. Fortunately, the material was still available so we decided to grow new crystals and try again. This time, data were collected on a Bruker SMART 1000 CCD with Mo $K\alpha$ radiation at 93 K. The autoindexing routine selected a similar, but different, cell from that obtained in 1984. The new cell had a volume three times
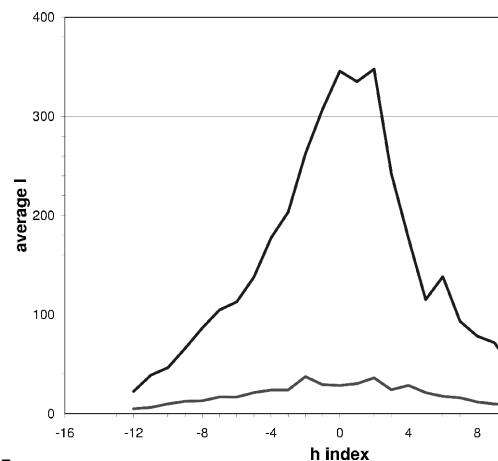

Figure 5
Intensity distribution for the TNBO CCD data. The upper line shows the distribution for the strong data and the lower line is the intensity distribution for the remaining two-thirds of the data set (*i.e.* the weak data).

the plane formed by the other four ring atoms, and, as a result, the two nitro groups on C8 are also displaced from the positions they occupy in the other five molecules. In the small cell, the non-disordered molecule and the major component of the disordered molecule have the same conformation and the disorder is present at ~18%, which correlates quite well with the finding that one molecule out of six is different in the larger cell.

Now that the correct structure is in hand, it is obvious that two-thirds of the data were missed in 1984. An examination of the new data set clearly shows why that happened. Fig. 4 shows the density distribution in the $h3l$ layer. The transformation from the smaller cell to the larger, $(100, 0\overline{1}0, \overline{1}0\overline{3})$, is more complicated than a simple tripling of the l axis. However, the regular pattern of strong and weak data is obvious in Fig. 4. Once this pattern was understood, it was possible to calculate the average intensities for both the strong and weak data within each layer (Fig. 5). On average, the strong data were approximately eight times more intense than the weak data. It is not surprising that the larger cell went undiscovered in 1984.

Experimental

Crystals of (I) were grown from 2-butanone octane. The sample was provided by Kurt Baum of Fluorochem, Inc.

Crystal data

$C_6H_6N_4O_{10}$	$D_x = 1.847$ Mg m^{-3}
$M_r = 294.15$	Mo $K\alpha$ radiation
Monoclinic, $P2_1$	Cell parameters from 7125
$a = 9.5746$ (9) Å	reflections
$b = 11.347$ (1) Å	$\theta = 2.3–28.3°$
$c = 29.241$ (3) Å	$\mu = 0.18$ mm^{-1}
$\beta = 92.546$ (2)°	$T = 93$ (2) K
$V = 3173.8$ (5) Å^3	Irregular, colorless
$Z = 12$	$0.45 \times 0.22 \times 0.12$ mm

Data collection

Bruker SMART 1000 CCD area-detector diffractometer	13 028 independent reflections
	10 983 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{int} = 0.029$
Absorption correction: by integration (*SHELXTL*; Bruker, 2001)	$\theta_{max} = 28.3°$
	$h = -12 \rightarrow 12$
$T_{min} = 0.922$, $T_{max} = 0.979$	$k = -14 \rightarrow 14$
25 608 measured reflections	$l = -35 \rightarrow 38$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.098P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.049$	$+ 0.5756P]$
$wR(F^2) = 0.130$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.89$	$(\Delta/\sigma)_{max} = 0.001$
13 028 reflections	$\Delta\rho_{max} = 0.52$ e Å^{-3}
1081 parameters	$\Delta\rho_{min} = -0.26$ e Å^{-3}
H-atom parameters constrained	

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SnB* (Weeks & Miller, 1999); program(s) used to refine structure: *SHELXTL* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2001) and *MidasPlus* (Ferrin *et al.*, 1988; Huang *et al.*, 1991); software used to prepare material for publication: *SHELXTL* (Bruker, 2001) and *XPREP* (Bruker, 2001).

References

Bruker (2001). *SMART* (Version 5.624) and *SAINT* (Version 6.04) for Windows NT, and *SHELXTL* (Version 5.10) and *XPREP* (Version 6.12) for UNIX. Bruker AXS Inc., Madison, Wisconsin, USA.

Ferrin, T. E., Huang, C. C., Jarvis, L. E. & Langridge, R. (1988). *J. Mol. Graphics*, **6**, 13–27.

Huang, C. C., Pettersen, E. F., Klein, T. E., Ferrin, T. E. & Langridge, R. (1991). *J. Mol. Graphics*, **9**, 230–236.

Sheldrick, G. M. (1997). *SHELXTL*. Version 5.10. Bruker AXS Inc., Madison, Wisconsin, USA.

Weeks, C. M. & Miller, R. (1999). *J. Appl. Cryst.* **32**, 120–124.