

Form III of 2,2',4,4',6,6'-hexanitro-
azobenzene (HNAB-III)Mark A. Rodriguez,^{a*} Charles F. Campana,^b A. David
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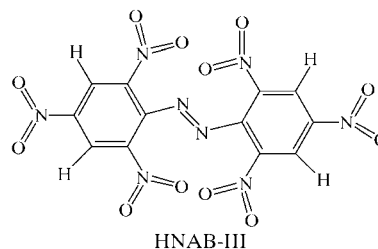
The crystal structure of form III of the title compound, HNAB [systematic name: bis(2,4,6-trinitrophenyl)diazene], $C_{12}H_4N_8O_{12}$, has finally been solved as a pseudo-merohedral twin (monoclinic space group $P2_1$, rather than the orthorhombic space group $C222_1$ suggested by diffraction symmetry) using a dual space recycling method. The significant differences in the room-temperature densities of the three crystalline forms allow examination of molecular differences due to packing arrangements. An interesting relationship with the stilbene analog, HNS, is discussed. Interatomic separations are compared with other explosives and/or nitro-containing compounds.

Comment

2,2',4,4',6,6'-Hexanitroazobenzene (HNAB) is employed as an explosive and is extremely complex in its crystallographic behavior, as evidenced by the relationships among the various phases and their transformations. There are at least five crystallographic polymorphs of HNAB. Two of these structures, stable at ambient conditions, were solved over 30 years ago (HNAB-I and -II; Graeber & Morosin, 1974), while the third, the subject of the present study, eluded sporadic structure solution attempts over that time frame. The five crystalline polymorphs were initially identified by hot-stage optical microscopy (McCrone, 1967). Forms I and III are stable from room temperature to 458 K, and form II from room temperature to 478 K; above these temperatures, solid–solid transformations begin to occur. The very unstable forms IV and V are formed only from the melt on supercooling during recrystallization. Forms II and III also transform rapidly through the solution phase into form I. Bulk samples of HNAB, regardless of the polymorphic forms present, melt at 496 K.

Historically, precession and Weissenberg photography were used to determine preliminary unit-cell dimensions and space-group extinctions, and to inspect the diffraction images for

satellites. These methods appeared to show very slight splitting at high diffraction angles for reflections down the short axis. There was a remarkable similarity with the precession photographs also taken along the short axis of a crystal of HNS (2,2',4,4',6,6'-hexanitro-*trans*-1,2-diphenylethene), with the exception of the $h0l$ reflections with odd l , as required by the c -glide in the latter compound. HNS is also known as 2,2',4,4',6,6'-hexanitrostilbene [$P2_1/c$, $a = 22.351 \text{ \AA}$, $b = 5.572 \text{ \AA}$, $c = 14.668 \text{ \AA}$ and $\beta = 110.05^\circ$ (Duke, 1977); Duke commented on the remarkable structure similarities of his HNS results to those of the monoclinic form of TNT]. Systematic absences and the symmetry of the reciprocal lattice indicated the space group to be consistent with orthorhombic $C222_1$ [$a = 15.4015(8) \text{ \AA}$, $b = 41.471(18) \text{ \AA}$, $c = 5.5240(3) \text{ \AA}$, $V = 3528.3(3) \text{ \AA}^3$ and $Z = 8$], but possibly of monoclinic $P2_1$ or $P2_1/m$ symmetry. Attempts to solve the structure using this orthorhombic cell with disordered molecules using various molecular packing models were unsuccessful.



The structure of HNAB-III was finally solved and refined as a pseudo-merohedral twin (monoclinic space group $P2_1$ emulating orthorhombic space group $C222_1$) using a dual space recycling method (Sheldrick & Gould, 1995). Since $Z = 4$, space group $P2_1$ requires two structurally independent molecules, labeled *A* and *B* below, in the cell. The structure was also refined independently by one of us (ADR) using *RAELS2000* (Rae, 2000), with essentially identical results. The *SHELXTL* (Bruker, 1998) results are principally given in the present report, with the *RAELS2000* results also indicated where appropriate. The twin ratio for reflections h, k, l and $h, h - k, l$ related by a twofold axis parallel to the c axis, was refined to 0.551 (1)/0.449 (1) using the program *RAELS2000* and can be compared with 0.552/0.448 determined by *SHELXTL*. Reflections with even $h + k$ values were approximately three times more intense than the others.

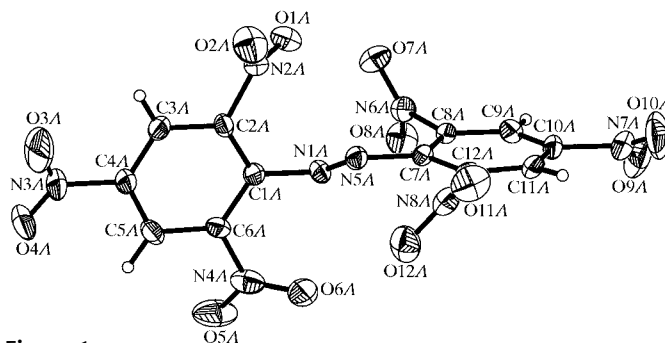


Figure 1
The atom-labeling scheme used for molecule *A* of HNAB-III. Displacement ellipsoids are shown at the 50% probability level.

Reflections were monitored according to the parity of h and k , and showed a consistently good fit over all such classes.

Fig. 1 shows our labeling scheme for molecule *A*; that for molecule *B* is identical. In this regard, even the displacement ellipsoids of the nitro groups of the two molecules appear very similar; in fact, the absolute structures of the two independent molecules are inverted with respect to one another. The shorter intermolecular contacts include, but are not limited to,

possible hydrogen-bond interactions, with H···O distances of 2.462, 2.491 and 2.516 Å, C···O contacts of 2.954, 2.969 and 2.979 Å, and N···O contacts of 2.919, 2.935 and 2.969 Å.

Fig. 2(a) shows the packing of the molecules as viewed along the b axis. The a and c axes are interchanged relative to those given above, and the cell contents are shifted from the normal placement of the 2_1 axes by $a/4$, so that the remarkable similarity (noted earlier) with the corresponding projection for HNS can be shown (Fig. 2b; Gérard & Hardy, 1988). Note that HNS belongs to $P2_1/c$ and each of its molecules resides on an inversion center. Examination of the dihedral angles for the HNAB molecules shows significant differences between not only those molecules in HNS but also that for HNAB-I. In HNAB-III, the phenyl planes form smaller angles with respect to the linkage (C–N–N–C) planes [$\varphi_1 = 27.7$ (3), 32.0 (3), 50.8 (3) and 57.4 (3)°] and the phenyl planes are twisted with respect to one another [$\varphi_p = 82.7$ (3) and 84.9 (3)° for *A* and *B*], while in HNS, the phenyl planes form larger angles with respect to the linkage (C–C–C–C) planes [$\varphi_1 = 67.1$ (4) and 72.0 (4)°] and the phenyl planes are in parallel alignment as required by the inversion center ($\varphi_p = 0^\circ$). Interestingly, HNAB-I also shows this parallel disposition for the phenyl planes ($\varphi_p = 0^\circ$, with a phenyl–linkage angle of $\varphi_1 = 43.2$ (4)°], while in HNAB-II, the phenyl planes are twisted, but to a smaller degree than in HNAB-III [$\varphi_p = 81.1$ (5)°, with phenyl–linkage angles of $\varphi_1 = 48.0$ (5) and 51.3 (5)°]. Table 1 summarizes the angles between the appropriate planes formed by various entities of the molecules in these crystal structures.

HNS shows pseudosymmetry (Fig. 2b), and imposing a mirror at $y = \frac{1}{4}$ creates a 1:1 disordered structure of approximate $Pnma$ symmetry in the cell $a' = a + c/2$, $b' = b$, $c' = c/2$, but with $\beta' = 90.87^\circ$. Upon ordering this structure to create the B-centered cell $2a'$, b' , $2c'$, equivalent to the real structure, the symmetry elements associated with the a' and c' directions must be destroyed. However, they suggest a mechanism for stacking faults and twinning if β' had been 90° . The structure of HNAB-III has $\beta' = 90.00^\circ$ within the estimated error for the cell $a' = a/2 + c$, $b' = -b$, $c' = a/2$, but although the structure looks similar to that of HNS in projection, the centers of non-equivalent molecules now differ in y by about $\frac{1}{4}$. However, a twofold screw operation parallel to the a axis is the likely twin operation, as it leaves NO₂ groups adjacent to the twin plane at $z = \frac{1}{4}$ unchanged to a first approximation.

The most striking differences between the three HNAB forms are in the C_{ring}–N_{azo} bond lengths, which increase with the corresponding decrease in the crystal densities (1.795, 1.744 and 1.703 Mg m⁻³ forms I, II and III). These differences are not considered significant by the usual statistical criteria (Hamilton, 1964); however, the increasing values of 1.426 (5) Å for HNAB-I, 1.430 (5) and 1.438 (5) Å for HNAB-II, and 1.441 (7), 1.442 (6), 1.447 (6) and 1.457 (7) Å for HNAB-III, together with the increasing phenyl ring twisting from the parallel configuration, must contribute toward the packing contributions responsible for the density differences.

The examination of various specific bond lengths led to a further comparison with other nitro-containing and other aromatic energetic materials, considering how the electron-

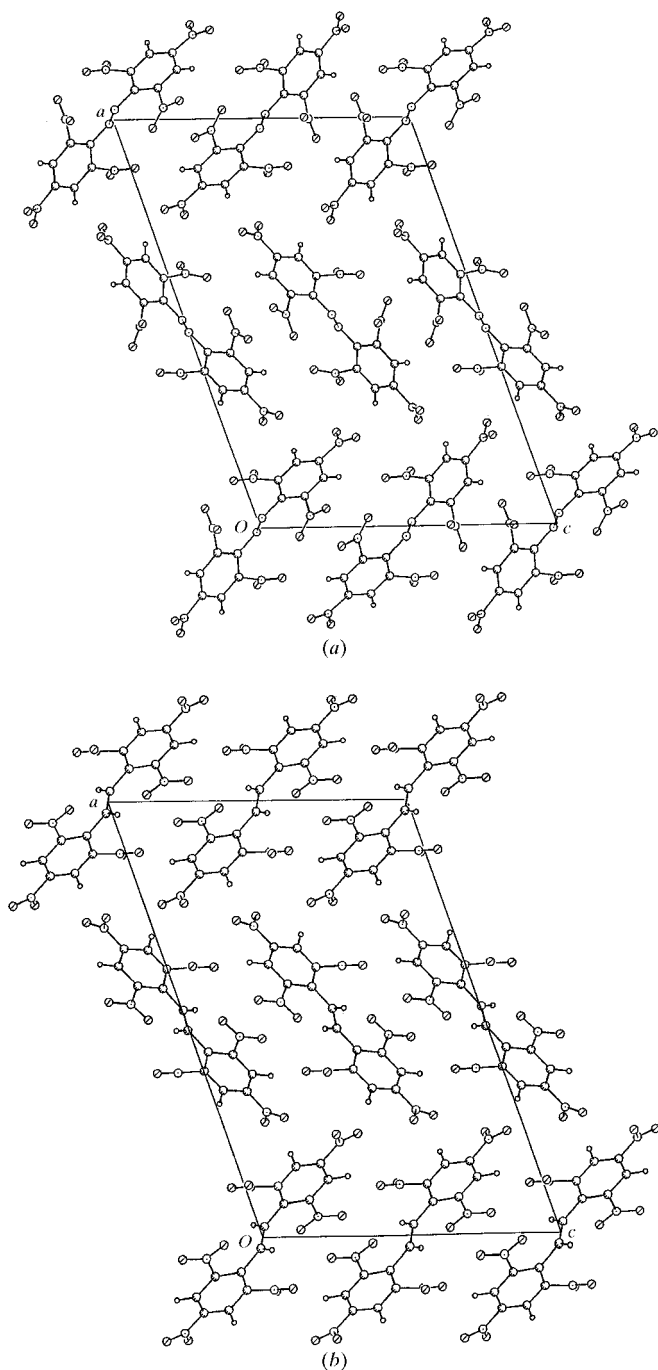


Figure 2
(a) A packing diagram, viewed down the b axis, for HNAB-III. The a and c axes are interchanged, and the cell contents are shifted from the normal placement of the 2_1 axes by $a/4$ (see *Comment*). (b) A packing diagram, viewed down the b axis, for HNS.

withdrawing characteristics of various substituting groups might impose on the ring bond lengths. The variation of the C—C_{ring} bond lengths in other related nitro-containing and aromatic explosive materials, particularly the long values, were initially attributed to steric effects of the crowded substituents; other reports have since related this variation to electronic effects associated with resonance structures, as well as the quinonoid contribution involving the ring. This led Holden *et al.* (1972) to demonstrate an inverse correlation between the lengths of the ring bonds and the length of the C—N bond in various aromatic amine compounds. Fig. 3 shows this relationship and includes the values for the different HNAB forms, as well as some other recent structure determinations. The C—N values range from 1.310 to 1.466 Å. [The C—N value of 1.497 Å for an average ring bond of 1.391 Å found in tetryl (Cady, 1967) is an exception to this linear relationship and is probably due to steric intramolecular interactions.] In decreasing order the values are 1.457, 1.447, 1.442 and 1.441 Å (HNAB-III), 1.438 Å (HNAB-II), 1.433 Å (azotoluene; Brown, 1966*a*), 1.434 Å (azobenzene; Brown, 1966*b*), 1.430 Å (HNAB-II), 1.426 Å (HNAB-I), 1.426 Å (2,4,6-tribromoaniline; Christensen & Stromme, 1969), 1.412 Å (1,3,5-triaminobenzene 1,3,5-trinitrobenzene or TAB-TNB; Iwasaki & Saito, 1970), 1.407 Å (2,5-dichloroaniline; Sakurai *et al.*, 1963), 1.40 Å (4-chloroaniline; Palm, 1966), 1.392 and 1.391 Å for TAB-TNB, 1.386 Å (2-chloro-4-nitroaniline; McPhail & Sim, 1965), 1.371 Å (4-nitroaniline; Trueblood *et al.*, 1961), 1.367 Å (2-amino-3-methylbenzoic acid; Brown & Marsh, 1963), 1.358 Å (2,6-dichloro-4-nitroaniline; Hughes & Trotter, 1971), 1.340 Å (2,4,6-trinitroaniline or

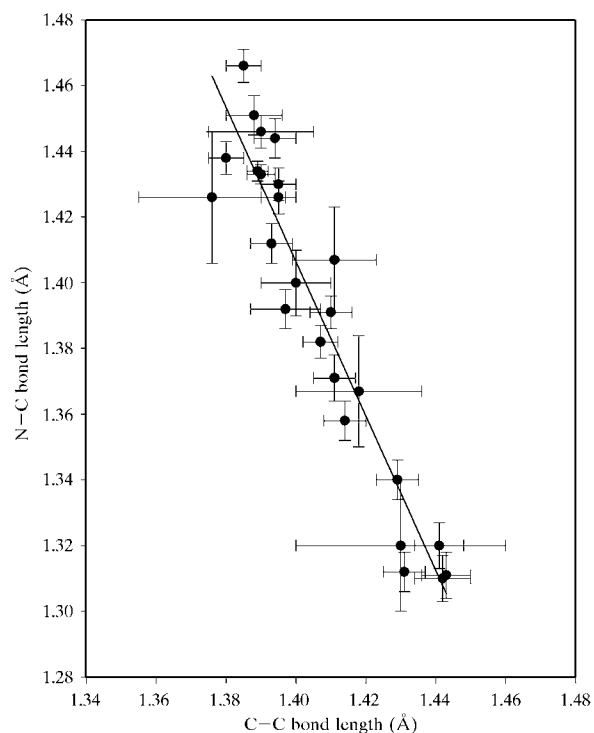


Figure 3
C—N_{amine} bond lengths versus average adjacent C—C_{ring} bond lengths (see *Comment*).

TNA; Holden *et al.*, 1972), 1.32 Å (1,3-diamino-2,4,6-trinitrobenzene or DATB; Holden, 1967), 1.320 Å (1,3,5-triamino-2,4,6-trinitrobenzene or TATB; Cady & Larson, 1965), 1.312 Å (2,3,4,6-tetranitroaniline; Dickinson *et al.*, 1966), and 1.311 and 1.310 Å (TATB). The interesting result of this plot is the relative position of the values for the nitro-containing HNAB molecules. The C—N lengths are longer than those for aromatic amines containing no nitro groups; a possible reason for the shortened values is the electron-withdrawing properties of the nitro group. It had previously been noted from the position of 2-amino-3-methylbenzoic acid that the acid group also functions in such a capacity. This suggests that the azo linkage must be an even greater electron-withdrawing group in order to neutralize the affect of the nitro groups.

The benzene ring is also distorted by the increase in the C—C lengths given in the above inverse correlation. This is achieved in part by the C—C—C ring angles increasing at the location of the corresponding nitro groups. Other uncorrelated and minor contributions to the distortion of the ring are the quinonoid and resonance shortening of the other C—C lengths (details available from authors).

Experimental

A sample of hexanitroazobenzene was obtained from the Explosive Component Division of (our) Sandia National Laboratories; the compound was prepared by reacting purified picryl chloride with hydrazine and potassium acetate in ethanol followed by acidification with hydrochloric acid. The yield of crude hexanitrohydrazobenzene was subsequently oxidized with nitric acid to give orange crystals of HNAB. About 70% of the crystals from this preparation were form I crystals, the balance being form II. Larger crystals of forms I and II may be obtained by recrystallization from nitromethane at room temperature, and those of form III from hot nitromethane. Morphological characteristics for forms I and II were described previously. Equant crystals of form I consist of rhombohedra with monoclinic symmetry, and well developed dipyrmaid {111} faces and {100} basal pinacoids; form II crystals consist of long obliquely truncated rods with {110} prism and {001} basal pinacoids; form III mostly consists of flat bladed crystals of apparent orthorhombic symmetry bound by {100} and {110} prism and {101} basal pinacoids along the long direction.

Crystal data

C₁₂H₄N₈O₁₂
M_r = 452.23
Monoclinic, P2₁
a = 15.4015 (8) Å
b = 5.5240 (3) Å
c = 22.1182 (11) Å
β = 110.367 (2)°
V = 1764.13 (16) Å³
Z = 4

D_x = 1.703 Mg m⁻³
Mo Kα radiation
Cell parameters from 770 reflections
θ = 2.8–22.2°
μ = 0.16 mm⁻¹
T = 298 (2) K
Acicular, orange
0.40 × 0.10 × 0.08 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: empirical, using intensity measurements (SADABS; Sheldrick, 1999)
T_{min} = 0.94, T_{max} = 0.99
10 081 measured reflections

6076 independent reflections
4219 reflections with I > 2σ(I)
R_{int} = 0.028
θ_{max} = 26.0°
h = -19 → 10
k = -6 → 6
l = -26 → 27

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.004P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.038$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.086$	$(\Delta/\sigma)_{\max} = 0.004$
$S = 1.02$	$\Delta\rho_{\max} = 0.16 \text{ e } \text{Å}^{-3}$
6076 reflections	$\Delta\rho_{\min} = -0.17 \text{ e } \text{Å}^{-3}$
578 parameters	Extinction correction: <i>SHELXTL</i>
H-atom parameters constrained	Extinction coefficient: 0.0028 (6)

Table 1

Angles (°) between various molecular entities for HNAB and HNS molecules.

HNAB-I			
	C1–N1–N1 ⁱ –C1 ⁱ	C1–C6	
C1–C6	43.2		
O1–N2–O2			129.6
O3–N3–O4			126.1
O5–N9–O6			148.3
HNAB-II			
	C1–N1–N11–C11	C1–C6	C11–C61
C1–C6	48.0		
C11–C61	51.3	81.1	
O1–N2–O2		87.5	
O3–N4–O4		1.4	
O5–N6–O6		151.2	
O11–N21–O21			52.4
O31–N41–O41			21.3
O51–N61–O61			143.4
HNAB-III (two molecules)			
	C1A–N1A–N5A–C7A	C1A–C6A	C7A–C12A
C1A–C6A	50.8		
C7A–C12A	32.0	97.3	
O1A–N2A–O2A		130.0	
O3A–N3A–O4A		160.0	
O5A–N4A–O6A		148.1	
O7A–N6A–O8A			67.7
O9A–N7A–O10A			31.6
O11A–N8A–O12A			47.1
	C1B–N1B–N5B–C7B	C1B–C6B	C7B–C12B
C1B–C6B	57.4		
C7B–C12B	27.7	95.1	
O1B–N2B–O2B		41.1	
O3B–N3B–O4B		16.7	
O5B–N4B–O6B		155.1	
O7B–N6B–O8B			70.8
O9B–N7B–O10B			26.7
O11B–N8B–O12B			123.3
HNS (two molecules)			
	C11–C17–C17 ⁱ –C11 ⁱ	C11–C16	
C11–C16	67.1		
O12–N12–O13			5.5
O14–N14–O15			18.4
O16–N16–O17			48.7
	C21–C27–C27 ⁱ –C21 ⁱ	C21–C26	
C21–C26	72.0		
O22–N22–O23			43.8
O24–N24–O25			21.7
O26–N26–O27			13.5

Note: The labeling schemes are those of the original publications. Labels including the superscript *i* signify inversion-symmetry-related atoms.

Atom N1B was fixed at $y = 1.0$. H atoms were constrained ($C-H = 0.93 \text{ Å}$), with their $U_{\text{iso}}(\text{H})$ values set at $1.2U_{\text{eq}}(\text{C})$. An independent refinement (conducted by ADR) used similarly constrained H atoms at 0.93 Å ; however, in this case, these H atoms were given the same atomic displacement parameters as the atom to which they were attached. In the refinement of ADR, the origin along y was fixed by setting the mean y coordinate of the two pairs of central N atoms to $y = 0.625$.

Data collection: *SMART* (Bruker, 1997); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1997) and *SADABS* (Sheldrick, 1999); program(s) used to solve structure: *XM* in *SHELXTL* (Bruker, 1998); program(s) used to refine structure: *XL* in *SHELXTL*; molecular graphics: *XP* and *XSELL* in *SHELXTL*; software used to prepare material for publication: *XCIF* in *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GA1037). Services for accessing these data are described at the back of the journal.

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