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## SHORT COMMUNICATIONS

*Acta Cryst.* (1995). **B51**, 1097–1102

**Structure of 2,2,3,3-tetranitrobutane** BY L. L. KOH, K. Y. SIM, H. H. HUANG,\* Y. L. LAM and E. P. LIANG, *Department of Chemistry, National University of Singapore, Lower Kent Ridge Road, Singapore 0511, Singapore*

(Received 23 December 1994; accepted 20 July 1995)

### Abstract

In two crystalline polymorphs, 2,2,3,3-tetranitrobutane adopts a conformation in which the two methyl groups are *gauche* to each other and the nitro groups are staggered to minimize steric interactions in the crystal lattice.

### Introduction

From dipole moment data, supported by IR and Raman spectroscopic measurements, it was concluded that 2,2,3,3-tetranitrobutane exists as a mixture of 66% of the *trans* and 34% of the *gauche* rotamer in carbon tetrachloride solution at 298 K (Tan, Chia & Huang, 1986). It was also suggested that some of the observed weak spectral bands of the solid could be attributed to the presence of the *trans* rotamer in the solid state in addition to the *gauche* form. The suggested presence of the *trans* rotamer was based mainly on the fact that no additional bands were seen on dissolving the solid in organic solvents. Furthermore, three bands were observed in the solid-state IR spectra at 847 (weak) 860 (strong) and 877 (weak)  $\text{cm}^{-1}$  in the region where C—N stretching vibrations are expected (Lin-Vien, Colthup, Fately & Graselli; 1991). In his IR study of solid 2,2,3,3-tetranitrobutane, Diallo (1974) assumed that only two IR-active bands due to the C—N stretching modes of the *trans*-rotamer would appear in the 800–900  $\text{cm}^{-1}$  region. Since three bands attributable to the C—N stretching vibrations instead of two were observed, Diallo concluded that 2,2,3,3-tetranitrobutane exists as a mixture of *gauche* and *trans* conformers in the solid state, the additional band being due to the *gauche* conformer. However, our X-ray crystal diffraction study of two different crystalline forms of the compound show that in both cases, 2,2,3,3-tetranitrobutane has a structure in which the two methyl groups are *gauche*. Although this does not rule out the possibility of other existing forms of the solid which may contain *trans* rotamers, it appears that the *gauche* rotamer is the preferred conformer in the crystalline state. Consequently, the earlier inference that both the *gauche* and *trans* rotamers are present in the solid state needs to be reviewed. On the assumption that the crystals chosen for our X-ray studies are representative of the bulk material, all the IR and Raman bands in the solid-state spectra must therefore be assigned to vibrations of the *gauche* rotamer. We have also re-examined

the IR and Raman spectra of the dry compound taken from the same batch of carefully dried crystals that was used for our X-ray study and measured some depolarization ratios, paying particular attention to the 800–900  $\text{cm}^{-1}$  region. The measurements were carried out using the JASCO NR-1800 Laser Raman spectrophotometer (resolution  $\pm 0.15 \text{ cm}^{-1}$ ) and the Perkin–Elmer 1725X spectrophotometer (resolution  $\pm 1 \text{ cm}^{-1}$ ). We believe the spectra thus obtained are more accurate than our earlier measurements in terms of observed frequencies. We have also remeasured the IR spectra in solution and in the vapour phase up to a temperature of 433 K to investigate the possibility of occluded solvent. However, the new IR spectra still remained the same, exhibiting the same three bands with practically the same relative intensities at the frequencies observed earlier. Furthermore, the new Raman spectra also show that the three bands of interest occur at frequencies of 845 (weak), 862 (weak) and 874 (strong)  $\text{cm}^{-1}$ . Although these bands are slightly different from the earlier Raman observations, they are now virtually identical to the IR frequencies; all three are clearly depolarized. Thus, we can now see that these results are incompatible with the existence of the *trans* ( $C_{2h}$ ) rotamer in the solid state for two reasons. (1) The three Raman shifts clearly coincide with the three IR bands observed. This correspondence is incompatible with the *trans* ( $C_{2h}$ ) conformation, but is expected for the *gauche* ( $C_2$ ) rotamer. (2) The fact that all three Raman lines are depolarized and the same lines are IR active suggest that they belong to vibrations of the *B*-type of *gauche* molecules. This conclusion is based on the selection rules shown in Table 1. Here we are assuming that the *gauche* molecules have strictly  $C_2$  symmetry, although the X-ray structure shows that the *gauche* molecules have only approximate  $C_2$  symmetry as the nitro groups are staggered in such a way as to lower the symmetry of the molecule as a whole.

Nevertheless, we feel that these rules provide a useful guide for drawing some general conclusions. We have also reconsidered the number of bands expected for the C—N stretching vibrations. A careful analysis shows that in theory, there can be four types of such vibrations for the *gauche*  $C_2$  molecule and also four for the *trans*  $C_{2h}$  molecule. In fact a vibrational frequency computation based on SAM1 parameterization gives the following results in  $\text{cm}^{-1}$ .

<i>trans</i>	$\nu_{\text{CN}}(\text{sym})$	$A_g$ 790.7	$B_u$ 839.4
conformer	$\nu_{\text{CN}}(\text{asym})$	$A_u$ 770.7	$B_g$ 820.3
<i>gauche</i>	$\nu_{\text{CN}}(\text{sym})$	$A$ 727.4	$B$ 819.9
conformer	$\nu_{\text{CN}}(\text{asym})$	$A$ 779.6	$B$ 795.4

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Table 1. *Vibrational species of 2,2,3,3-tetranitrobutane*

Point group	Vibrational species	Activity		Total number of fundamentals
		IR	Raman	
$C_{2h}$	$A_g$	ia	p	17
	$A_u$	a	x	14
	$B_g$	ia	dp	13
	$B_u$	a	x	16
$C_2$	$A$	a	p	31
	$B$	a	dp	29

ia = inactive; a = active; p = polarized; dp = depolarized; x = forbidden.

However, although the selection rules and the fact that the observed three lines are depolarized would exclude the *trans* conformer, they can account for only two of the three observed bands with regard to the C—N stretching vibrations. These are the two depolarized *B*-type bands, the *A*-type being polarized and therefore excluded by the selection rules. The third band thus remains unassigned. Nevertheless, the important conclusion can be drawn that our spectroscopic data can now be shown to be consistent with the X-ray findings. It should be noted that in the Raman spectrum, the band at  $874\text{ cm}^{-1}$  is much more intense than the other two. This band is probably associated with the symmetric *B*-type vibration. On the other hand, the IR band at  $860\text{ cm}^{-1}$  is much more intense than the other two bands. It is therefore likely to be associated with the asymmetric *B*-type vibration. The band around  $845\text{ cm}^{-1}$  is very weak in both the IR and Raman spectra. Its origin is uncertain, but could be a mixture of C—N stretch and other skeletal vibrations.

In view of the above, it is a little surprising to find from the dielectric data that in solution the proportion of *trans* rotamer is quite high, 66% in carbon tetrachloride and 28% in benzene at 298 K. The fact that no additional bands were seen on dissolving the solid in an organic solvent would seem to mean that the *trans* bands in solution are not distinguishable from the *gauche* bands within the limits of resolution of the spectrophotometer, *i.e.* they may be masked by or coincide in frequency with the *gauche* bands. The latter explanation receives strong support from the experimental observation that the Raman shifts in carbon tetrachloride and acetonitrile solution at  $845$ ,  $860$  and  $874\text{ cm}^{-1}$  are all polarized in contrast to the solid-state shifts which are all depolarized.

#### X-ray structure determination

Two types of crystals were found after recrystallization: monoclinic (1), space group  $P2_1/c$ ; triclinic (2), space group  $P1$ . Both types of crystal consist of the *gauche* rotamer. The structures of the molecules in the two types of crystal are very similar in terms of bond lengths and angles.\* The molecular conformations are almost identical, as can be seen in Figs. 1(a) and (b). The monoclinic form, having a higher density, is better packed. For structure (2) it has been noted that the  $F_o$  values of some of the stronger  $0kl$  reflections tend to be smaller than the  $F_c$  values. Disorder was suspected, but electron-density and difference electron-density calculations showed no signs of

\* Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BK0023). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

disorder. The discrepancy might be due to imperfection in the packing of the crystal. The results for the monoclinic form appear to be better ( $R = 0.040$  and  $wR = 0.042$ , with no unusual discrepancy between  $F_o$  and  $F_c$  values). The following discussion is thus based on the structural parameters of the monoclinic form.

#### Comparison of 2,2,3,3-tetranitrobutane (TNB) with 2,3-dinitro-2,3-dimethylbutane (DNDMB)

There are no unusual bond lengths in TNB. The central C—C bond at  $1.548(5)\text{ \AA}$  is normal, but appreciably shorter than the unusually long central C—C bond length of  $1.575\text{ \AA}$  for DNDMB (Kai, Knochel, Kwiatkowski, Dunitz, Oth, Seebach & Kalinowski, 1982). In DNDMB the nitro groups adopt almost perpendicular conformation with respect to the central C—C bond, the C—C—N—O torsion angles being  $-86$  and  $-99^\circ$ , respectively. In TNB there is more congestion and the nitro groups are therefore more twisted to avoid O...O contacts: C(3)—C(2)—N(2)—O(2b)  $-150.2(3)$ , C(3)—C(2)—N(2')—O(2'b)  $-70.9(3)$ , C(2)—C(3)—N(3)—O(3a)  $-58.7(4)$  and C(2)—C(3)—N(3')—O(3'a)  $-25.5(4)^\circ$ . In DNDMB, there is considerable distortion of bond angles at the central C atoms. The three N—C—C bond angles are  $2-3^\circ$  less than the tetrahedral value, while the three C—C—C bond angles are greater; the largest at both ends of the molecule are those between the central C—C and C—H bond that is synclinal to the opposite  $\text{NO}_2$  substituent. Similarly, TNB also exhibits distortion of the bond angles at the central C atoms; the bond angles around C(2) and C(3) ranging from  $102.6(3)$  to

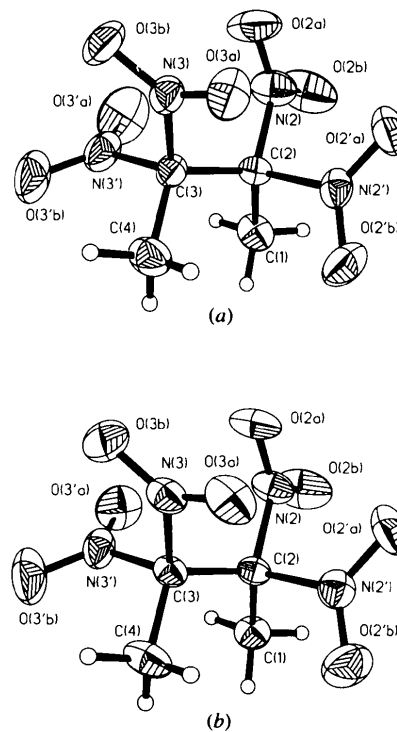


Fig. 1. Atomic numbering and thermal ellipsoid diagram (35% probability) of (a) (1) and (b) (2).

Table 2. *Experimental details*

	(1)	(2)
<b>Crystal data</b>		
Chemical formula	C <sub>4</sub> H <sub>6</sub> N <sub>4</sub> O <sub>8</sub>	C <sub>4</sub> H <sub>6</sub> N <sub>4</sub> O <sub>8</sub>
Chemical formula weight	238.1	238.1
Cell setting	Monoclinic	Triclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 1
<i>a</i> (Å)	6.224 (13)	6.152 (3)
<i>b</i> (Å)	10.344 (13)	7.216 (2)
<i>c</i> (Å)	14.55 (2)	11.622 (4)
$\alpha$ (°)	90.0	76.17 (3)
$\beta$ (°)	101.32 (15)	76.93 (6)
$\gamma$ (°)	90.0	69.27 (5)
<i>V</i> (Å <sup>3</sup> )	919 (3)	462.8 (3)
<i>Z</i>	4	2
<i>D<sub>x</sub></i> (Mg m <sup>-3</sup> )	1.722	1.709
Radiation type	Mo <i>K</i> $\alpha$	Mo <i>K</i> $\alpha$
Wavelength (Å)	0.71073	0.71073
No. of reflections for cell parameters	18	12
$\theta$ range (°)	3.3–11.3	4.5–12.7
$\mu$ (mm <sup>-1</sup> )	0.169	0.168
Temperature (K)	298	297
Crystal form	Prism	Prism
Crystal size (mm)	0.40 × 0.35 × 0.30	0.40 × 0.30 × 0.30
Crystal colour	Colourless	Colourless
<b>Data collection</b>		
Diffractometer	Siemens <i>R3m/V</i>	Siemens <i>R3m/V</i>
Data collection method	$\omega$	$\omega$
Absorption correction	Empirical	None
<i>T</i> <sub>min</sub>	0.809	–
<i>T</i> <sub>max</sub>	0.830	–
No. of measured reflections	1788	1494
No. of independent reflections	1632	1353
No. of observed reflections	982	1062
Criterion for observed reflections	<i>F</i> > 4 $\sigma$ ( <i>F</i> )	<i>F</i> > 4 $\sigma$ ( <i>F</i> )
<i>R</i> <sub>int</sub>	0.0185	0.0187
$\theta$ <sub>max</sub> (°)	25	24.0
Range of <i>h</i> , <i>k</i> , <i>l</i>	0 → <i>h</i> → 7 0 → <i>k</i> → 12 –17 → <i>l</i> → 16	0 → <i>h</i> → 6 –7 → <i>k</i> → 8 –12 → <i>l</i> → 13
No. of standard reflections	3	3
Frequency of standard reflections	Every 97 reflections	Every 97 reflections
Intensity decay (%)	±2	±1.5
<b>Refinement</b>		
Refinement on	<i>F</i>	<i>F</i>
<i>R</i>	0.0403	0.050
<i>wR</i>	0.0421	0.050
<i>S</i>	1.52	2.90
No. of reflections used in refinement	982	1062
No. of parameters used	164	164
H-atom treatment	Only coordinates of H atoms refined	Only coordinates of H atoms refined
Weighting scheme	$w = 1/[\sigma^2(F) + 0.0002F^2]$	$w = 1/\sigma^2(F)$
( $\Delta/\sigma$ ) <sub>max</sub>	0.042	0.036
$\Delta\rho$ <sub>max</sub> (e Å <sup>-3</sup> )	0.19	0.25
$\Delta\rho$ <sub>min</sub> (e Å <sup>-3</sup> )	–0.13	–0.22
Extinction method	$F^* = F[1 + 0.002\chi F^2/\sin(2\theta)]^{-1/4}$	
Extinction coefficient	$\chi = 0.0021$ (4)	$\chi = 0.0007$ (8)
Source of atomic scattering factors	<i>International Tables for X-ray Crystallography</i> (1974, Vol. IV)	<i>International Tables for X-ray Crystallography</i> (1974, Vol. IV)
<b>Computer programs</b>		
Data collection	<i>P3</i> (Siemens, 1989)	<i>P3</i> (Siemens, 1989)
Cell refinement	<i>P3</i> (Siemens, 1989)	<i>P3</i> (Siemens, 1989)
Data reduction	<i>SHELXTL-Plus</i> (Sheldrick, 1991)	<i>SHELXTL-Plus</i> (Sheldrick, 1991)
Structure solution	<i>SHELXTL-Plus</i> (Sheldrick, 1991)	<i>SHELXTL-Plus</i> (Sheldrick, 1991)
Structure refinement	<i>SHELXTL-Plus</i> (Sheldrick, 1991)	<i>SHELXTL-Plus</i> (Sheldrick, 1991)
Preparation of material for publication	<i>SHELXTL-Plus</i> (Sheldrick, 1991)	<i>SHELXTL-Plus</i> (Sheldrick, 1991)

Table 3. Fractional atomic coordinates and equivalent isotropic displacement parameters ( $\text{\AA}^2$ )
$$U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j.$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>eq</sub>
(1)				
C(1)	0.4948 (5)	0.2560 (3)	0.0362 (3)	0.053 (1)
C(2)	0.7347 (4)	0.2472 (3)	0.0777 (2)	0.036 (1)
C(3)	0.7833 (4)	0.1795 (3)	0.1744 (2)	0.039 (1)
C(4)	0.7040 (6)	0.0422 (4)	0.1748 (3)	0.061 (1)
N(2)	0.8453 (5)	0.3804 (3)	0.0795 (2)	0.064 (1)
N(2')	0.8427 (4)	0.1704 (3)	0.0066 (2)	0.048 (1)
N(3)	1.0288 (4)	0.1769 (3)	0.2167 (2)	0.050 (1)
N(3')	0.6792 (4)	0.2612 (4)	0.2428 (2)	0.070 (1)
O(2a)	1.0182 (4)	0.3948 (2)	0.1324 (2)	0.087 (1)
O(2b)	0.7525 (4)	0.4599 (2)	0.0249 (2)	0.102 (1)
O(2'a)	0.9931 (4)	0.2184 (3)	-0.0207 (1)	0.073 (1)
O(2'b)	0.7583 (4)	0.0672 (3)	-0.0180 (2)	0.072 (1)
O(3a)	1.1398 (3)	0.1231 (2)	0.1691 (2)	0.066 (1)
O(3b)	1.0899 (3)	0.2210 (3)	0.2935 (1)	0.080 (1)
O(3'a)	0.6526 (5)	0.3749 (4)	0.2262 (2)	0.119 (2)
O(3'b)	0.6320 (4)	0.2035 (3)	0.3081 (2)	0.105 (1)
(2)				
C(1)	0.5306 (6)	0.0969 (6)	0.6671 (3)	0.048 (2)
C(2)	0.2836 (5)	0.1958 (5)	0.7272 (2)	0.036 (1)
C(3)	0.2617 (5)	0.3814 (5)	0.7790 (3)	0.037 (1)
C(4)	0.4141 (7)	0.3403 (8)	0.8729 (4)	0.059 (2)
N(2)	0.1032 (5)	0.2430 (5)	0.6430 (2)	0.052 (1)
N(2')	0.2120 (5)	0.0345 (5)	0.8287 (3)	0.051 (1)
N(3)	0.0058 (4)	0.4849 (5)	0.8368 (3)	0.046 (1)
N(3')	0.3173 (5)	0.5430 (4)	0.6745 (3)	0.055 (1)
O(2a)	-0.0876 (4)	0.3663 (4)	0.6660 (2)	0.066 (1)
O(2b)	0.1631 (5)	0.1521 (6)	0.5609 (3)	0.094 (2)
O(2'a)	0.0299 (5)	0.0031 (4)	0.8309 (3)	0.075 (1)
O(2'b)	0.3515 (5)	-0.0554 (5)	0.8969 (3)	0.083 (1)
O(3a)	-0.0725 (4)	0.3748 (4)	0.9202 (2)	0.062 (1)
O(3b)	-0.0876 (4)	0.6575 (4)	0.8006 (3)	0.073 (1)
O(3'a)	0.2766 (5)	0.5447 (5)	0.5768 (3)	0.081 (1)
O(3'b)	0.3991 (5)	0.6565 (5)	0.6971 (3)	0.095 (2)

115.1(3)°. The two C—C—C angles are much greater than the tetrahedral value [115.1(3) and 113.3(2)°], while the two N—C—N angles are much smaller [102.6(3) and 105.3(2)°]. However, the N—C—C angles are close to the tetrahedral angle. The deviations from the tetrahedral value are due to steric congestion arising from having two nitro groups at one C atom. This deviation is also seen in 2-methyl-2,3,3-trinitrobutane and 2-methyl-2,3,3-trinitropentane, where the N—C—N angles range from 103 to 104° (Lee, Koh, Lam & Huang, 1992). The C—N bond lengths of TNB (1.532–1.557 Å) are comparable with those of DNDMB. The long C—N bond lengths [compared with 1.46 Å in nitromethane (Brockway, Beach & Pauling, 1935)] and the general pattern of bond angle deformations in both DNDMB and TNB appear to be consistent with Bent's Rule concerning the effects of electron-withdrawing substituents on hybridization (Bent, 1961).

The N—C—C—N torsion angle in DNDMB is 52.5°. The four nitro groups in TNB are staggered with N—C—C—N torsion angles shown in Fig. 2. The difference in torsion angles for the orientation of the nitro groups is linked to the corresponding difference in the non-bonded distances between the NO<sub>2</sub> groups. In DNDMB the O(2)···N(2) distance is 3.03 Å, while the O(3)···N(1) distance is only 2.83 Å with the O(2)···O(3) distance (between the two overlapping O atoms) exactly half way between them. In TNB the intramolecular non-bonding distances between different NO<sub>2</sub> groups are O(3b)—N(3') 2.552(4), N(2)—O(2'a) 2.512(5),

Table 4. Selected geometric parameters (Å, °) for (1)

C(1)—C(2)	1.499 (5)	C(2)—N(2)	1.539 (5)
C(2)—C(3)	1.548 (5)	C(3)—C(4)	1.504 (6)
C(2)—N(2')	1.557 (5)	C(3)—N(3')	1.542 (6)
C(3)—N(3)	1.532 (5)	N(2)—O(2a)	1.203 (4)
N(2)—O(2b)	1.209 (5)	N(2')—O(2'a)	1.195 (4)
N(2')—O(2'b)	1.212 (5)	N(3)—O(3a)	1.205 (4)
N(3)—O(3b)	1.198 (4)	N(3')—O(3'a)	1.205 (6)
N(3')—O(3'b)	1.205 (5)		
C(1)—C(2)—C(3)	113.3 (3)	C(1)—C(2)—N(2)	111.0 (3)
C(3)—C(2)—N(2)	112.5 (2)	C(1)—C(2)—N(2')	106.8 (2)
C(3)—C(2)—N(2')	109.9 (2)	N(2)—C(2)—N(2')	102.6 (3)
C(2)—C(3)—C(4)	115.1 (3)	C(2)—C(3)—N(3)	112.0 (2)
C(4)—C(3)—N(3)	106.5 (3)	C(2)—C(3)—N(3')	107.9 (3)
C(4)—C(3)—N(3')	109.6 (3)	N(3)—C(3)—N(3')	105.3 (2)
C(2)—N(2)—O(2a)	117.6 (3)	C(2)—N(2)—O(2b)	116.3 (3)
O(2a)—N(2)—O(2b)	126.0 (3)	C(2)—N(2')—O(2'a)	118.6 (3)
C(2)—N(2')—O(2'b)	115.3 (3)	O(2'a)—N(2')—O(2'b)	126.1 (3)
C(3)—N(3)—O(3a)	114.6 (2)	C(3)—N(3)—O(3b)	118.5 (3)
O(3a)—N(3)—O(3b)	126.8 (3)	C(3)—N(3')—O(3'a)	117.6 (3)
C(3)—N(3')—O(3'b)	115.8 (4)	O(3'a)—N(3')—O(3'b)	126.6 (4)
C(1)—C(2)—C(3)—C(4)	60.4 (4)		
N(2)—C(2)—C(3)—C(4)	-172.6 (3)		
N(2')—C(2)—C(3)—C(4)	-59.0 (3)		
C(1)—C(2)—N(2)—O(2a)	160.3 (3)		
C(3)—C(2)—N(2)—O(2b)	-150.2 (3)		
C(1)—C(2)—N(2')—O(2'a)	125.2 (3)		
C(3)—C(2)—N(2')—O(2'b)	70.9 (3)		
C(2)—C(3)—N(3)—O(3a)	-58.7 (4)		
C(4)—C(3)—N(3)—O(3b)	-108.3 (3)		
C(2)—C(3)—N(3')—O(3'a)	-25.5 (4)		
C(4)—C(3)—N(3')—O(3'b)	28.2 (3)		
C(1)—C(2)—C(3)—N(3)	-177.7 (3)		
N(2)—C(2)—C(3)—N(3)	-50.7 (3)		
N(2')—C(2)—C(3)—N(3)	62.9 (3)		
C(1)—C(2)—N(2)—O(2b)	-22.1 (4)		
N(2')—C(2)—N(2)—O(2a)	-85.9 (3)		
C(1)—C(2)—N(2')—O(2'b)	-52.5 (3)		
N(2)—C(2)—N(2')—O(2'a)	8.4 (3)		
C(2)—C(3)—N(3)—O(3b)	125.0 (3)		
N(3')—C(3)—N(3)—O(3a)	-175.7 (3)		
C(2)—C(3)—N(3')—O(3'b)	154.3 (3)		
N(3)—C(3)—N(3')—O(3'a)	94.2 (3)		
C(1)—C(2)—C(3)—N(3')	-62.3 (3)		
N(2)—C(2)—C(3)—N(3')	64.7 (3)		
N(2')—C(2)—C(3)—N(3')	178.3 (2)		
C(3)—C(2)—N(2)—O(2a)	32.1 (4)		
N(2')—C(2)—N(2)—O(2b)	91.7 (3)		
C(3)—C(2)—N(2')—O(2'a)	-111.5 (3)		
N(2)—C(2)—N(2')—O(2'b)	-169.3 (3)		
C(4)—C(3)—N(3)—O(3a)	68.0 (3)		
N(3')—C(3)—N(3)—O(3b)	8.0 (4)		
C(4)—C(3)—N(3')—O(3'a)	-151.6 (3)		
N(3)—C(3)—N(3')—O(3'b)	-86.0 (3)		

O(2a)—N(3) 2.561(4), O(2a)—O(2'a) 2.861(4) and O(3'a)—O(2a) 2.881(5) Å. These values are a consequence of both the affinity between the nitro groups and steric congestion. The NO<sub>2</sub> groups are, however, all quite planar. N(2), N(2') and N(3) are slightly displaced from the least-squares planes away from the O atoms by 0.0122, 0.0119 and 0.0188 Å, respectively. N(3') does not show such displacement.

### Experimental

2,2,3,3-Tetranitrobutane was prepared as described in the literature (Gabriel, Bisgrove & Clapp, 1955) and recrystallized from absolute alcohol to give a waxy product. Recrystallization of this product from toluene gave transparent prisms which crumbled easily. This product turned out to have the triclinic form. A second form of crystal was obtained by recrystallizing

Table 5. Selected geometric parameters (Å, °) for (2)

C(1)—C(2)	1.516 (4)	C(2)—N(2)	1.540 (5)
C(2)—C(3)	1.548 (5)	C(3)—C(4)	1.507 (6)
C(2)—N(2')	1.553 (4)	C(3)—N(3')	1.539 (4)
C(3)—N(3)	1.554 (4)	N(2)—O(2a)	1.214 (3)
N(2)—O(2b)	1.201 (5)	N(2')—O(2'a)	1.213 (5)
N(2')—O(2'b)	1.205 (4)	N(3)—O(3a)	1.222 (4)
N(3)—O(3b)	1.188 (4)	N(3')—O(3'a)	1.214 (5)
N(3')—O(3'b)	1.202 (6)		
C(1)—C(2)—C(3)	113.2 (3)	C(1)—C(2)—N(2)	110.9 (3)
C(3)—C(2)—N(2)	112.5 (2)	C(1)—C(2)—N(2')	107.6 (2)
C(3)—C(2)—N(2')	110.2 (2)	N(2)—C(2)—N(2')	101.8 (3)
C(2)—C(3)—C(4)	115.2 (3)	C(2)—C(3)—N(3)	112.6 (3)
C(4)—C(3)—N(3)	106.1 (3)	C(2)—C(3)—N(3')	108.5 (2)
C(4)—C(3)—N(3')	109.7 (3)	N(3)—C(3)—N(3')	104.3 (2)
C(2)—N(2)—O(2a)	117.3 (3)	C(2)—N(2)—O(2b)	116.9 (3)
O(2a)—N(2)—O(2b)	125.8 (3)	C(2)—N(2')—O(2'a)	118.9 (3)
C(2)—N(2')—O(2'b)	115.5 (3)	O(2'a)—N(2')—O(2'b)	125.5 (3)
C(3)—N(3)—O(3a)	113.5 (2)	C(3)—N(3)—O(3b)	118.9 (3)
O(3a)—N(3)—O(3b)	127.5 (2)	C(3)—N(3')—O(3'a)	117.6 (3)
C(3)—N(3')—O(3'b)	116.8 (3)	O(3'a)—N(3')—O(3'b)	125.6 (3)
C(1)—C(2)—C(3)—C(4)	-60.0 (3)		
N(2)—C(2)—C(3)—C(4)	173.4 (3)		
N(2')—C(2)—C(3)—C(4)	60.5 (3)		
C(1)—C(2)—N(2)—O(2a)	-161.2 (3)		
C(3)—C(2)—N(2)—O(2b)	147.6 (3)		
C(1)—C(2)—N(2')—O(2'a)	-126.4 (4)		
C(3)—C(2)—N(2')—O(2'b)	-73.1 (3)		
C(2)—C(3)—N(3)—O(3a)	60.2 (4)		
C(4)—C(3)—N(3)—O(3b)	110.7 (4)		
C(2)—C(3)—N(3')—O(3'a)	28.3 (3)		
C(4)—C(3)—N(3')—O(3'b)	-24.7 (4)		
C(1)—C(2)—C(3)—N(3)	178.2 (2)		
N(2)—C(2)—C(3)—N(3)	51.5 (3)		
N(2')—C(2)—C(3)—N(3)	-61.3 (3)		
C(1)—C(2)—N(2)—O(2b)	19.7 (5)		
N(2')—C(2)—N(2)—O(2a)	84.6 (3)		
C(1)—C(2)—N(2')—O(2'b)	50.7 (4)		
N(2)—C(2)—N(2')—O(2'a)	-9.7 (4)		
C(2)—C(3)—N(3)—O(3b)	-122.5 (4)		
N(3')—C(3)—N(3)—O(3a)	177.6 (3)		
C(2)—C(3)—N(3')—O(3'b)	-151.3 (3)		
N(3)—C(3)—N(3')—O(3'a)	-91.8 (3)		
C(1)—C(2)—C(3)—N(3')	63.4 (3)		
N(2)—C(2)—C(3)—N(3')	-63.3 (3)		
N(2')—C(2)—C(3)—N(3')	-176.1 (2)		
C(3)—C(2)—N(2)—O(2a)	-33.3 (4)		
N(2')—C(2)—N(2)—O(2b)	-94.5 (3)		
C(3)—C(2)—N(2')—O(2'a)	109.8 (3)		
N(2)—C(2)—N(2')—O(2'b)	167.4 (3)		
C(4)—C(3)—N(3)—O(3a)	-66.6 (4)		
N(3')—C(3)—N(3)—O(3b)	-5.1 (5)		
C(4)—C(3)—N(3')—O(3'a)	154.9 (3)		
N(3)—C(3)—N(3')—O(3'b)	88.5 (3)		

## Calculations

Semi-empirical molecular orbital calculations were performed using the program AMPACS.0 with AM1 and SAM1 parameterization (Dewar, Stewart, Ruiz, Liotard, Kealy & Dennington, 1994). Full geometry optimization was performed for each incremental value of the C—C—C—C torsion angle. The calculations were carried out starting from a C—C—C—C torsion angle of 60°, with the bond lengths and angles obtained by the X-ray study and working incrementally towards 0 and 180° for the other values of the torsion angle. The energy profile of the compound as a function of the C—C—C—C torsion angle is shown in Fig. 3. Calculations were performed on a VAX 6430 computer using Fortran operating under VMS. The variation of the heat of formation with the torsion angle shown in Fig. 3 shows that the *trans* rotamer has a slightly lower energy than the *gauche* form. From the Boltzmann distribution and the difference in energy between the two rotamers, the compound is predicted to exist in the gas phase as an equilibrium mixture of 37% *gauche* and 63% *trans*. This compares well with the 34% *gauche* and 66% *trans* found for carbon tetrachloride solution at 298 K (Tan, Chia & Huang, 1986).

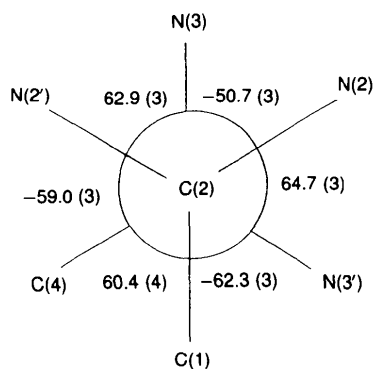


Fig. 2. Newman projection of 2,2,3,3-tetranitrobutane (1) with bond angles in °.

the waxy product from hexane. This turned out to have the monoclinic form. From each, a suitable crystal for X-ray determination was wedged and sealed in a quartz capillary for data collection (see Table 2).

Both structures were solved by direct methods using the SHEXTL-Plus programs (Sheldrick, 1991). On refinement the final structure was found to be *gauche* with an *R* value of 0.040 for the monoclinic form and 0.050 for the triclinic form.

A plot of the molecular structure was produced using XP (Siemens, 1989). The atomic coordinates for the two crystals are given in Table 3 and the atomic numbering scheme shown in Figs. 1(a) and (b). Selected bond lengths, angles and torsion angles are listed in Tables 4 and 5. The C—H bond lengths for the monoclinic form ranged from 0.931 (23) to 0.969 (23) Å, while those for the triclinic form ranged from 0.875 (39) to 0.961 (37) Å.

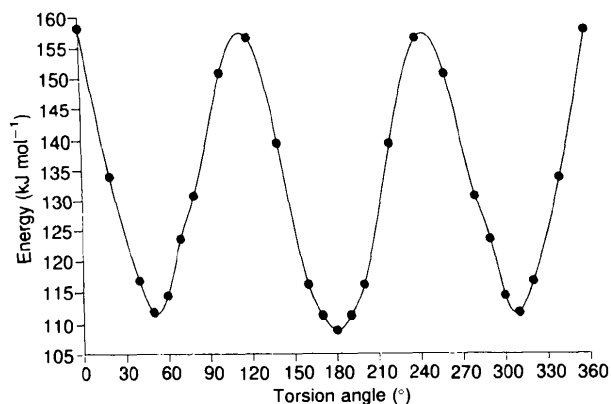


Fig. 3. Energy of 2,2,3,3-tetranitrobutane (1) as a function of the C—C—C—C torsion angle calculated using AM1 parametrization.

We thank JASCO International for assistance with the Raman depolarization ratio measurements.

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