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Rotational Isomerism and Crystal Structures of 2-Methyl-2,3,3-trinitrobutane and 2-Methyl-2,3,3-trinitropentane

Swee Yong LEE, Lip Lin KOH, Yu Lin LAM, and Hsing Hua HUANG*
Chemistry Department, National University of Singapore, Lower Kent Ridge Road, Singapore 0511

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Dielectric data show that in benzene and carbon tetrachloride at 25 °C, 2-methyl-2,3,3-trinitrobutane and 2-methyl-2,3,3-trinitropentane exist as "*trans*":*gauche* rotameric mixtures in the approximate ratios of 68 : 32 and 57 : 43 respectively. These experimental results are compared with those predicted by AMPAC (AM1) calculations. X-Ray structure investigations show that in both compounds, the nitro group at C2 is "*gauche*" with respect to the two nitro groups at C3 in the solid state.

Unlike 2,3-dimethyl-2,3-dinitrobutane and 2,3-dimethyl-2,3-dinitropentane,[1,2] 2-methyl-2,3,3-trinitrobutane and 2-methyl-2,3,3-trinitropentane have three nitro groups attached to the central C2 and C3 atoms, two of which are geminal. In order to investigate the effect of the geminal nitro groups on internal rotation in the latter compounds, their dipole moments were measured. For comparison, semi-empirical molecular orbital calculations of the energies of the molecules were performed. The single crystal structures of these compounds have also been analyzed.

Experimental

Solutes. 2-Methyl-2,3,3-trinitrobutane was synthesized in two steps from 2-methyl-2-butene according to the procedure of Schmidt.[3] The crystals decomposed at 190 °C disappearing by 204 °C (lit, mp 194—195 °C).[4] (Found: C, 29.05; H, 4.35; N, 19.93%; Calcd for $C_5H_9N_3O_6$: C, 28.99; H, 4.35; N, 20.29%).

2-Methyl-2,3,3-trinitropentane was prepared by nitrating isohexane with fuming nitric acid according to the method of Miller[4] with some modifications; mp 95.5 °C (lit, 95—96 °C).[4] (Found: C, 32.54; H, 5.10; N, 19.01%. Calcd for $C_6H_{11}N_3O_6$: C, 32.59; H, 5.01; N, 19.00%.)

Solvents. All solvents were carefully distilled and/or fractionated, and dried before use. Their physical constants required in dielectric measurements have been previously given.[5]

Apparatus and Computations. Dielectric constants were determined with a heterodyne-beat meter.[6] Densities were measured by standard procedures.[7]

Semi-empirical molecular orbital calculations were performed using the program AMPAC.[8] AMI parametrization[9] was used and full geometry optimization was performed for each incremental value of the ethane C-C torsion angle. In the calculations, advantage was taken of the published geometries of two related molecules, 2,3-dimethyl-2,3-dinitrobutane[10] and dipotassium salt of tetranitroethane.[11] Calculations were performed on a Silicon Graphics personal Iris computer using FORTRAN 77 operating under UNIX. Torsion or dihedral angles were defined by the atoms N-C-C-N by the convention of Klyne and Prelog.[12]

X-Ray Data Collection and Structure Determination. X-Ray data were collected using a Siemens R3m/v diffractometer. Absorption correction was not applied as the value of the linear absorption coefficient (Mo *Kα*) was only about 1.3 cm^{-1} for both compounds.

Both structures were determined using the direct method, which led to the locations of all the nonhydrogen atoms. Hydrogen atoms were located either from difference map or placed at calculated positions. In the final least-squares calculations, hydrogen atoms were included but not refined. All calculations were performed with SHELXTL PLUS[13] on a Micro VAX 2000 computer. Essential details of data collection and crystal analysis are given in Table 1. Final nonhydrogen atomic parameters are given in Tables 2 and 3.[14]

Results and Discussion

Table 4 gives the dipole moment results in standard notation. Figure 1 shows the Newman projections of the three likely rotamers of the compounds where the two less polar "*trans*" rotamers, (1) and (3), are mirror images of each other and are in dynamic equilibrium

Table 1. Crystal and Selected Experimental Data for 2-Methyl-2,3,3-trinitrobutane (**I**) and 2-Methyl-2,3,3,-trinitropentane (**II**)

	I	**II**
Formula	$C_5H_9N_3O_6$	$C_6H_{11}N_3O_6$
Formula weight	207.2	221.2
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	Cc
a/Å	6.305(1)	11.292(5)
b/Å	13.106(3)	6.641(3)
c/Å	10.720(2)	13.155(4)
β/°	90.05(2)	101.81(2)
V/Å^3	858.8(3)	965.5(7)
Z	4	4
D_c/g cm^{-3}	1.533	1.522
μ(Mo $K\alpha$)/cm^{-1}	1.34	1.28
Crystal size/mm	0.5×0.45×0.4	0.5×0.4×0.3
Scan mode	ω	ω
$2\theta_{max}$/°	45	45
Reflcns measd	h,k,l	$h,k,\pm l$
No. of reflcns measd	804	781
No. of reflcns used ($F_o>6\sigma(F_o)$)	637	643
$R^{a)}$	0.032	0.072
$R_w^{b)}$	0.053	0.087

a) $R=\sum||F_o|-|F_c||/\sum|F_o|$. b) $R_w=[\sum w(|F_o|-|F_c|)^2/\sum w|F_o|^2]^{1/2}$, $w=[\sigma^2(|F_o|)+aF_o^2]^{-1}$, where a=0.0016 for **I** and 0.017 for **II**.

Table 2. 2-Methyl-2,3,3-trinitrobutane Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients (U_{eq})[a)]

Atom	x	y	z	$10^3 U_{eq}/\text{Å}^2$
C(1)	22(6)	7383(2)	3412(4)	45(1)
C(2)	926(5)	7922(2)	2248(3)	33(1)
C(3)	1029(6)	9101(2)	2393(3)	37(1)
C(4)	−1181(6)	9574(2)	2578(4)	54(1)
C(11)	−272(8)	7621(2)	1117(4)	54(2)
N(1)	3228(5)	7503(2)	2164(3)	39(1)
N(2)	2041(5)	9588(2)	1219(3)	43(1)
N(3)	2452(6)	9474(2)	3455(3)	52(1)
O(11)	3605(4)	6871(2)	1357(2)	62(1)
O(12)	4485(5)	7779(2)	2955(3)	57(1)
O(21)	1509(5)	10441(2)	939(3)	65(1)
O(22)	3380(5)	9089(2)	678(3)	72(1)
O(31)	4053(5)	9956(2)	3194(3)	62(1)
O(32)	1812(6)	9299(2)	4496(3)	68(1)

a) Equivalent isotropic U_{eq} defined as one third of the trace of the orthogonalized U_{ij} tensor.

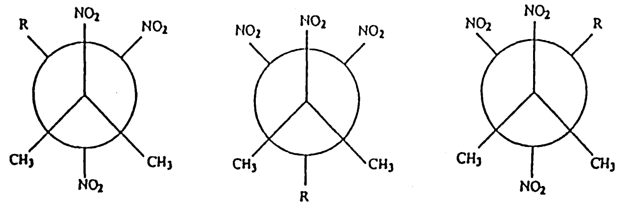
Table 3. 2-Methyl-2,3,3-trinitropentane Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients (U_{eq})[a)]

Atom	x	y	z	$10^3 U/\text{Å}^2$
C(1)	6282(11)	4875(10)	3834(8)	51(3)
C(2)	5823(8)	2694(9)	3814(7)	33(2)
C(3)	5648(8)	2115(9)	4928(6)	30(2)
C(4)	4584(9)	3200(10)	5235(8)	39(2)
C(5)	4202(10)	2422(13)	6217(9)	53(3)
C(11)	4717(11)	2381(15)	2969(8)	55(3)
N(1)	6802(8)	1306(9)	3504(6)	42(2)
N(2)	6832(8)	2567(9)	5687(6)	37(2)
N(3)	5442(8)	−154(9)	5072(7)	39(2)
O(11)	6712(8)	−499(8)	3625(7)	61(2)
O(12)	7565(9)	2071(9)	3106(7)	61(2)
O(21)	7770(8)	1881(9)	5503(6)	55(2)
O(22)	6807(9)	3649(12)	6426(6)	70(2)
O(31)	4553(8)	−846(9)	4509(8)	64(2)
O(32)	6098(8)	−1044(9)	5756(7)	64(2)

a) Equivalent isotropic U_{eq} defined as one third of the trace of the orthogonalized U_{ij} tensor.

with rotamer (2) in solution.

Dielectric Measurements. The observed change of dipole moment with temperature is relatively small, and comparable to experimental errors due to poor solubility. This has prevented us from applying the Lennard Jones method[15)] to determine the energy separating the rotamers and their population distribution. In spite of this, taking advantage of the results provided by AM1 calculations and using the known dipole moments of 2-nitropropane[16)] and 1,1-dinitroethane,[17,18)] it is possible to calculate the dipole moments of the "*trans*" and *gauche* rotamers of the molecule, μ_t and μ_g, respectively and thence the population distribution of these rotamers. This is achieved by taking the group moment of one half of the molecule to be that of 2-nitropropane (μ_1) and the other half to be that of 1,1-dinitroethane (μ_2), and then resolving them vectorially by using the following equation:



(1) "*trans*" (2) *gauche* (3) "*trans*"

Fig. 1. Newman projections of 2-methyl-2,3,3-trinitrobutane ($R=CH_3$) and 2-methyl-2,3,3-trinitropentane ($R=C_2H_5$).

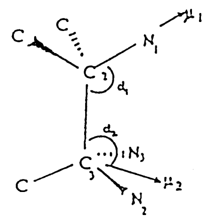
Table 4. Molar Polarizations and Dipole Moments at Infinite Dilution of 2-Methyl-2,3,3-trinitrobutane and 2-Methyl-2,3,3-trinitropentane. (Incremental changes in the relative permittivities and densities, ($\Delta\varepsilon$ and Δd,) were measured for solutions having solute weight fractions w_2. The coefficients α and β were derived from the relations $\alpha\varepsilon_1=\sum\Delta\varepsilon/\sum w_2$, $\beta d_1=\sum\Delta d/\sum w_2$).

Temperature K	Solvent	Concn range (10^5 w_2)	$\alpha\varepsilon_1$	β	P_2/cm^3	$10^{30}\cdot\mu/\text{C m}$[a)]
		2-Methyl-2,3,3-trinitrobutane				
298.2	CCl_4	37—300	16.64	−0.332	415.7	14.18±0.24
318.2	CCl_4	106—303	15.58	−0.135	400.2	14.34±0.27
333.2	CCl_4	95—312	14.21	−0.205	384.4	14.34±0.16
280.2	C_6H_6	492—994	14.03	0.223	580.6	16.53±0.18
298.2	C_6H_6	521—1037	11.74	0.360	502.7	15.76±0.44
318.2	C_6H_6	496—938	10.51	0.376	411.6	15.72±0.32
		2-Methyl-2,3,3-trinitropentane				
298.2	CCl_4	35—183	22.02	−0.210	564.6	16.72±0.47
318.2	CCl_4	85—274	17.57	−0.158	476.6	15.72±0.47
333.2	CCl_4	51—269	15.59	−0.166	444.4	15.46±0.47
280.2	C_6H_6	209—580	15.83	0.474	672.9	17.84±0.47
298.2	C_6H_6	224—665	12.53	0.394	566.6	16.75±0.43
318.2	C_6H_6	322—910	11.79	0.393	557.6	17.15±0.47

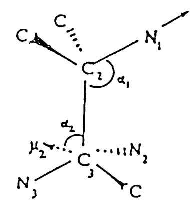
a) Calculated on the basis that ${}_DP=1.05R_D$; R_D(calcd)$=48.92$ cm^3.

$$\mu^2(\theta)=(\mu_1\cos\alpha_1-\mu_2\cos\alpha_2)^2+(\mu_1\sin\alpha_1\cos(\theta/2)+\mu_2\sin\alpha_2\cos(\theta/2))^2$$

The direction of μ_1 as taken to be along the C–NO_2 bond of 2-nitropropane while μ_2 was assumed to be in the direction of the resultant of the two C–NO_2 vectors calculated with the atomic coordinates of the optimized geometry obtained by AMl calculations. μ_2 vectors for the *gauche* and "*trans*" rotamers are shown diagrammatically below:



gauche



"*trans*"

The C_2–C_3–N_1 bond angle, α_1, the angle which vector μ_2 makes with the C_3–C_2 bond, α_2, and the dihedral angle between the planes containing these angles, θ, are calculated and listed in Table 5, together with the calculated dipole moments of the "*trans*" rotamer (μ_t) and *gauche* rotamer (μ_g). The dipole moment of 2-nitropropane, μ_1, in benzene is 11.61×10^{-30} C m and that of 1,1-dinitroethane, μ_2, 11.68×10^{-30} C m.

For an equilibrium mixture of N_t molecules in the "*trans*" conformation having dipole moment μ_t and N_g molecules in the *gauche* conformation with dipole moment μ_g, the mean square dipole moment of the mixture is given by the following equation:

$$\bar{\mu}^2=(\mu_t^2N_t+\mu_g^2N_g)/(N_t+N_g)$$

The root mean square moment $\bar{\mu}$ can be equated to the observed moment (μ_{obsd}); we then have

$$\mu^2_{obsd}=\mu_t^2+x_g(\mu_g^2-\mu_t^2)$$

where

$$x_g=N_g/(N_t+N_g),\quad x_t=N_t/(N_t+N_g)$$

and

$$x_g+x_t=1$$

Thus, using the measured dipole moment of 2-methyl-2,3,3-trinitrobutane in benzene at 25 °C, i.e. 15.76×10^{-30} C m and the above calculated μ_t and μ_g values, the *gauche* and "*trans*" populations of 2-methyl-2,3,3-trinitrobutane are found to be 32% and 68% respectively. Using this isomeric ratio, and applying the Boltzman equation $N_g/N_t=1/2\ \exp(-\Delta E/RT)$, the internal energy difference between the two rotamers in benzene at 25 °C, defined as $\Delta E=E_g-E_t$, is calculated to be 0.174 kJ mol^{-1}. $\Delta G°=-RT\ln K$ where $K=N_g/N_t$ is found to be 1.890 kJ mol^{-1} in benzene at 25 °C. Similarly from the measured dipole moment of 2-methyl-2,3,3-trinitropentane in benzene at 25 °C, i.e. 16.75×10^{-30} C m and the above calculated μ_t and μ_g values, the relative populations of 2-methyl-2,3,3-trinitropentane are found to be *gauche* 43% and "*trans*" 57%. ΔE and $\Delta G°$ of this compound are calculated to be -1.019 and 0.700 kJ mol^{-1} respectively.

For both compounds, these results clearly show that in benzene the "*trans*" rotamers are more stable and their conversion to the *gauche* states is not spontaneous. Essentially the same conclusion may be drawn from the carbon tetrachloride data.

Figure 2 depicts the variation of the heat of formation with the N–C–C–N dihedral angle for 2-methyl-2,3,3-trinitropentane as obtained from AMl calculations. It clearly shows that the "*trans*" rotamer has a lower energy than the *gauche* form, and the energy difference between them is 3.569 kJ mol^{-1}. This is qualitatively consistent with our earlier deductions from the observed

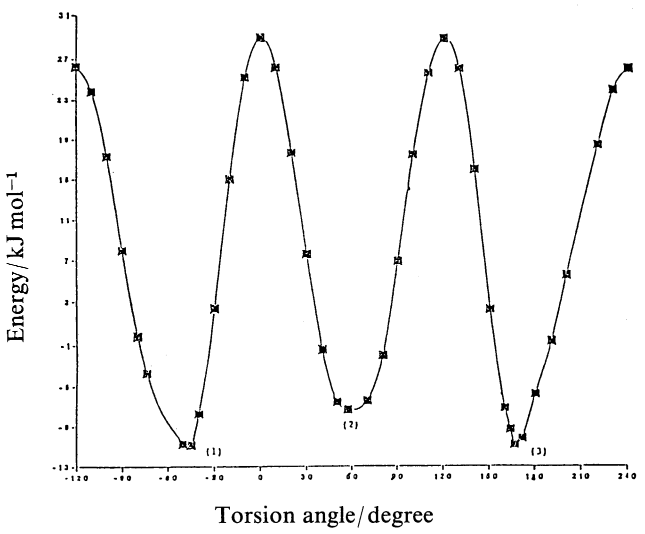


Fig. 2. Energy of 2-methyl-2,3,3-trinitropentane as a function of N–C–C–N torsion angle.

Table 5. Bond Angles (α_1 and α_2), Dihedral Angles (θ), and Calculated Dipole Moments (μ) of 2-Methyl-2,3,3-trinitrobutane and 2-Methyl-2,3,3-trinitropentane

Compound	Rotamer	$\alpha_1/°$	$\alpha_2/°$	$\theta/°$	Calculated $10^{30}\cdot\mu/\mathrm{C\,m}$
2-Methyl-2,3,3-trinitrobutane	"*trans*"	107.8	124.6	106.6	12.73
	gauche	108.4	124.7	4.01	20.82
2-Methyl-2,3,3-trinitropentane	"*trans*"	107.9	124.9	106.5	12.73
	gauche	107.9	124.4	3.11	20.90

Table 6. Comparison between 2-Methyl-2,3,3-trinitrobutane and 2-Methyl-2,3,3-trinitropentane

Compound	*Gauche* population		ΔE/kJ mol^{-1}		$\Delta G°$/kJ mol^{-1}
	Exptl$^{a)}$	AMI	Exptl$^{a)}$	AMI	
2-Methyl-2,3,3-trinitrobutane	32%	23%	0.174	1.234	1.890
2-Methyl-2,3,3-trinitropentane	43%	11%	−1.019	3.569	0.700

a) Based on measured dipole moments in benzene at 25 °C.

dipole moment of the compound in carbon tetrachloride and benzene solution, although the AMI calculated ΔE value of 3.569 kJ mol^{-1} gives a lower population of *gauche* rotamer of 11% and a higher "*trans*" population of 89%. This difference between AMI and experimental results is not unexpected because AMI values represent the situation in vacuo which may be modified in solution.

A similar energy plot was obtained from AMI calculations for 2-methyl-2,3,3-trinitrobutane. It also shows that the "*trans*" rotamer has a lower energy than the *gauche* form and their energy difference is 1.234 kJ mol^{-1}. This AMI calculated ΔE value would give a population of 23% *gauche* and 77% "*trans*" which agrees reasonably well with the rotameric population derived from the measured dipole moment in benzene.

Table 6 summarizes the above by providing a comparison between these two homologous compounds in terms of their *gauche* populations and related physical properties.

The above results are a little surprising when viewed against the fact that in the crystalline state, the favored conformation is the *gauche* as shown by our X-ray diffraction study (vide infra). Intuitively one would expect the *gauche* rotamer to maintain its greater stability after the transition from solid to solution state. However it is possible that the high stability of the highly polar *gauche* rotamer, due to its stabilization by its own reaction field in the close packing of the crystal lattice, would be greatly reduced in a nonpolar solvent of low dielectric constant, like carbon tetrachloride, so that it is no longer more stable than the less polar "*trans*". Similar behavior has been observed in the case of 2,3-dimethyl-2,3-dinitrobutane, which exists in the *gauche* form in the solid state[10] but as a rotameric mixture of 58% "*trans*" and 42% *gauche* in carbon tetrachloride solution.[1]

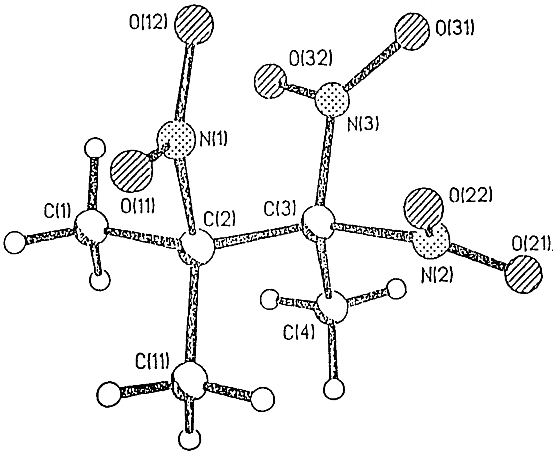


Fig. 3. Perspective view of **I** with atomic numbering.

Crystal Structure of 2-Methyl-2,3,3-trinitrobutane (I). Molecules of **I** are located at general sites. Figure 3 shows the structure and numbering of the atoms of **I**. Important bond lengths and bond angles based on the final atomic positions are given in Table 7.[14]

The molecule as a whole adopts a *gauche* conformation with N(1)–C(2)–C(3)–N(2) and N(1)–C(2)–C(3)–N(3) torsion angles of 63.5(3) and −52.6(4)° respectively. Structural analysis of this molecule shows that unlike its dinitro analogue, 2,3-dimethyl-2,3-dinitrobutane,[1] where the NO_2 groups are in nearly perpendicular conformation with the central C–C bond, the NO_2 groups in **I** show large deviations from this bisected orientation, the torsion angles C(2)–C(3)–N(3)–O(32), C(3)–C(2)–N(1)–O(12), and C(2)–C(3)–N(2)–O(22) being −69.3(4), 50.0(4), and −32.0(4)° respectively. Consideration of Stuart–Briegleb molecular models suggests that it would be impossible to arrange all the NO_2 groups in nearly perpendicular orientation with respect to the central C–C bond without imposing extreme steric congestion on the oxygen atoms of the geminal NO_2 groups. The different torsion angles which the NO_2 groups make with the central C(2)–C(3) bond lead to corresponding differences in the non-bonded interatomic distances between the NO_2 groups. Thus while the O(11)···N(2) distance is 3.698 Å, the O(12)···N(3) distance is only 2.620 Å. In the symmetri-

Table 7. Selected Bond Lengths (l) and Bond Angles (ϕ) for 2-Methyl-2,3,3-trinitrobutane

Bond length	(l/Å)	Bond angle	(ϕ/°)
C(1)–C(2)	1.543 (5)	C(1)–C(2)–C(3)	112.9 (3)
C(2)–C(11)	1.481 (6)	C(3)–C(2)–C(11)	111.5 (3)
C(3)–C(4)	1.538 (5)	C(3)–C(2)–N(1)	108.5 (2)
C(3)–N(3)	1.530 (5)	C(2)–C(3)–C(4)	112.1 (3)
C(2)–C(3)	1.555 (4)	C(4)–C(3)–N(2)	108.2 (3)
C(2)–N(1)	1.554 (5)	C(4)–C(3)–N(3)	107.8 (3)
C(3)–N(2)	1.549 (4)	C(1)–C(2)–C(11)	110.6 (3)
		C(1)–C(2)–N(1)	103.3 (2)
		C(11)–C(2)–N(1)	109.6 (3)
		C(2)–C(3)–N(2)	110.2 (3)
		C(2)–C(3)–N(3)	114.6 (3)
		N(2)–C(3)–N(3)	103.4 (3)

cal tetranitroethanediide ion, the O(2)···O(4) distance is 2.57 Å;11) the corresponding distances in compound **I** are 2.957 and 3.000 Å for O(22)···O(31) and O(22)···O(11) respectively. Least-squares planes through the CNO_2 groups show that all the NO_2 groups are approximately planar with the nitrogen atoms deviating by at most 0.027 Å from the planes. The average N–O distance is 1.21 Å. The average O–N–O and O–N–C angles are 125 and 117° respectively.

The bond lengths and angles at the two central tetrasubstituted carbon atoms require some comments. After least-squares refinements, the molecule showed a central C–C bond length of 1.555(4) Å. In the X-ray study of 2,3-dimethyl-2,3-dinitrobutane,10) the central C–C bond length was found to be 1.574 Å. This shortening of the central C–C bond may be attributed to the decrease in steric crowding when one of the methyl groups is replaced by an NO_2 group. Of the C–C–C bond angles, the largest at both ends of the molecule is that involving atoms C(1), C(2), and C(3) (112.9(3)°). This widening is presumably due to the steric congestion between the methyl and synclinal NO_2 group. The N–C–C bond angle of this NO_2 group is 114.6(3)°. The remaining N–C–C angles have values which are less than the tetrahedral value.

Crystal Structure of 2-Methyl-2,3,3-trinitropentane (II). Single crystals formed as colorless prisms were obtained upon recrystallization from methanol. Crystallization proved extremely difficult because the crystals obtained were often soft and poorly formed. As a consequence, the extent of the data was limited and the precision of the structure reduced.

Molecules of **II** have no crystallographic symmetry as can be seen from the projected view down the central C(2)–C(3) bond (Fig. 1). Figure 4 shows the structure of **II**. Important bond lengths and bond angles are given in Table 8.14) The NO_2 groups are again found to be planar with an average N–O distance of 1.21 Å, O–N–O angle of 124° and O–N–C angle of 118°. The central C–C bond length, 1.567(9) Å, is marginally longer in this structure than in **I**. This is consistent with the increased steric crowding expected on increase of the chain length. Bond angles also show evidence of this stress. While the C(3)–C(4)–C(5) bond angle (115.9(7)°) is larger than the mean value of 114(1)° in hexane as obtained from X-ray crystal studies,19) there is a slight reduction in the C(2)–C(3)–C(4) bond angle of 112.9(6)°. This may be attributed to the need for the ethyl group to maintain appropriate distances from the neighboring groups. The resulting structure also shows that the ethyl group is nearly coplanar with the central C–C bond, the C(2)–C(3)–C(4)–C(5) torsion angle being 168.6(6)°.

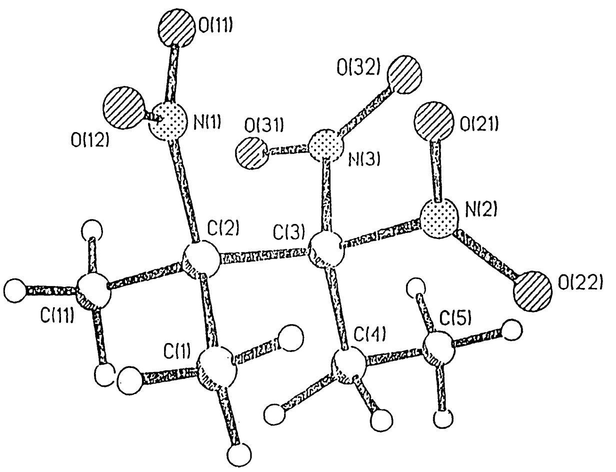


Fig. 4. Perspective view of **II** with atomic numbering.

Table 8. Selected Bond Lengths (l) and Bond Angles (ϕ) for 2-Methyl-2,3,3-trinitropentane

Bond length	(l/Å)	Bond angle	(ϕ/°)
C(1)–C(2)	1.537 (9)	C(1)–C(2)–C(3)	108.8 (5)
C(2)–C(11)	1.507 (10)	C(3)–C(2)–C(11)	114.4 (6)
C(3)–C(4)	1.524 (13)	C(3)–C(2)–N(1)	109.4 (5)
C(3)–N(3)	1.542 (8)	C(2)–C(3)–C(4)	112.9 (6)
C(2)–C(3)	1.567 (9)	C(4)–C(3)–N(2)	111.5 (6)
C(2)–N(1)	1.556 (9)	C(4)–C(3)–N(3)	106.4 (7)
C(3)–N(2)	1.525 (11)	C(3)–C(4)–C(5)	115.9 (7)
C(4)–C(5)	1.533 (16)	C(1)–C(2)–C(11)	111.6 (6)
		C(1)–C(2)–N(1)	107.9 (5)
		C(11)–C(2)–N(1)	104.6 (6)
		C(2)–C(3)–N(2)	107.6 (6)
		C(2)–C(3)–N(3)	113.9 (6)
		N(2)–C(3)–N(3)	104.2 (6)

The molecule as a whole adopts a *gauche* conformation with N(1)–C(2)–C(3)–N(2) and N(1)–C(2)–C(3)–N(3) torsion angles of 64.5(6) and −50.5(7)° respectively. As in **I**, structural analysis also shows that all the NO_2 groups in **II** do not adopt a nearly perpendicular conformation with respect to the central C–C bond, the torsion angles C(3)–C(2)–N(1)–O(11), C(2)–C(3)–N(3)–O(31), and C(2)–C(3)–N(2)–O(21) being 48.8(8), −60.9(11), and −51.8(8)° respectively. However, the observed structure shows that in this molecule, the replacement of a methyl group by a bulkier ethyl group causes one of the geminal NO_2 groups to twist by about 20° from the N–C(2)–C(3) plane. This conformation appears to be inherently more stable despite the expectation that the oxygen atoms on the geminal NO_2 groups would tend to avoid each other to the maximum extent. In this conformation, the nonbonded interatomic distances C(5)···O(22) and O(21)···O(32) are 3.010 and 2.775 Å compared with 3.284 and 2.957 Å for C(5)···O(32) and O(22)···O(31) respectively.

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References

1) B. G. Tan, L. H. L. Chia, and H. H. Huang, *J. Chem. Soc., Perkin Trans. 2*, **1984**, 1407.

2) S. Y. Lee, N. W. Tan, and H. H. Huang, *J. Mol.*

Struct., **192**, 117 (1989).

3) J. Schmidt, *Ber.*, **35**, 3733 (1902).

4) A. J. Miller, Ph. D. Thesis, Purdue University, 1943.

5) K. E. Calderbank, R. J. W. Le Fevre, and G. L. D. Ritchie, *J Chem. Soc. B*, **1968**, 503.

6) H. H. Huang and E. P. A. Sullivan, *Aust. J. Chem.*, **21**, 1721 (1968).

7) a) R. J. W. Le Fevre, "Dipole Moments," 3rd ed, Methuen, London (1953), Chap. 2; b) R. J. W. Le Fevre, *Adv. Phys. Org. Chem.*, **3**, 1 (1965).

8) M. J. S. Dewar, E. G. Zoebisch, E. F. Healey, and J. J. P. Stewart, *QCPE Bull.*, **6**, 24 (1986).

9) M. J. S. Dewar, E. G. Zoebisch, E. F. Healey, and J. J. P. Stewart, *J. Am. Chem. Soc.*, **107**, 3902 (1985).

10) Y. Kai, P. Knochel, S. Kwiatkowski, J. D. Dunitz, J. F. M. Oth, D. Seebach, and H. O. Kalinowski, *Helv. Chim. Acta*, **65**, 137 (1982).

11) M. Dyke and R. L. Sass, *J. Phy. Chem.*, **72**, 266 (1968).

12) W. Klyne and V. Prelog, *Experientia*, **16**, 521 (1960).

13) Siemens Analytical X-Ray Instruments Inc., SHELXTL PLUS Release 3.4 (1989).

14) Some additional bond lengths and angles, the torsion angles, the positional and thermal parameters of hydrogen atoms, the anisotropic thermal parameters, and F_o-F_c tables are deposited as Document No. 8986 at the Office of the Editor of Bull. Chem. Soc. Jpn.

15) J. E. Lennard-Jones and H. H. M. Pike, *Trans. Faraday Soc.*, **30**, 830 (1934).

16) B. G. Tan, L. H. L. Chia, and H. H. Huang, *J. Chem. Soc., Perkin Trans. 2*, **1986**, 31.

17) B. G. Tan, L. H. L. Chia, and H. H. Huang, *J. Chem. Soc., Perkin Trans. 2*, **1986**, 2025.

18) A. L. McClellan, "Tables of Experimental Dipole Moments," Freeman, San Francisco (1963).

19) N. Norman and H. Mathisen, *Acta Chem. Scand.*, **15**, 1755 (1961).