

## 12. Structure, Synthesis, and Properties of Some Persubstituted 1,2-Dinitroethanes. In Quest of Nitrocyclopropyl-Anion Derivatives

by Yasushi Kai<sup>1)</sup>, Paul Knochel<sup>2)</sup>, Stefan Kwiatkowski<sup>3)</sup>, Jack D. Dunitz<sup>4)</sup>, Jean F. M. Oth and Dieter Seebach<sup>4)</sup>

Laboratorium für Organische Chemie der Eidgenössischen Technischen Hochschule, ETH-Zentrum, Universitätstrasse 16, CH-8092 Zürich

and Hans-Otto Kalinowski

Institut für Organische Chemie der Justus-Liebig-Universität, Heinrich-Buff-Ring 58, D-6300 Giessen

(20. XI. 81)

---

### Summary

Attempts to deprotonate nitrocyclopropane led to solutions which showed strong ESR. signals (*Fig. 1*) and from which 1-nitro-1'-nitroso-bicyclopropyl (**3**) and 1,1'-dinitro-bicyclopropyl (**2**) were isolated. The activation energy for rotation about the central C,C-bond of **2** is estimated to be about 12 kcal/mol (<sup>1</sup>H-NMR. spectra in *Fig. 2*). In contrast, the open-chain analogue 2,3-dimethyl-2,3-dinitrobutane (**1**) shows a methyl singlet down to -70° C. Low-temperature X-ray analyses of **1**, **2**, **3**, and also of 1,1'-dinitro-bicyclobutyl (**4**) show that all four molecules have *gauche*-conformations but reveal striking structural differences between the open-chain and the cyclic derivatives (*Fig. 4–6*): the central C,C-bond is long in **1** (1.575 Å), short in **2** (1.479 Å); the C,N-bonds are long in **1** (1.549 Å), short in **2** (1.488 Å); the orientation of the nitro groups is bisected in **2** and perpendicular in **1**. The crystal structure of the nitro-nitroso compound **3** is isomorphous with that of the dinitro compound **2** and thus disordered (*Fig. 15–16*). The effect of the nitro group as  $\pi$ -electron acceptor on the molecular conformations and bond lengths is discussed. From analysis of the anisotropic vibrational parameters of **2** the root-mean-square librational amplitude of the nitro groups about their C,N-bonds is estimated to be about 5.8° at 95 K, corresponding to a rotational barrier of about 9 kcal/mol, *i. e.* the same order of magnitude as the NMR. estimate of about 12 kcal/mol for C,C-rotation.

---

In this paper we describe the synthesis of some persubstituted 1,2-dinitroethanes and discuss their physical properties, basing the discussion mainly on results of low-temperature crystal-structure analyses of the derivatives **1–4** with open-chain and small-ring C-skeletons.

---

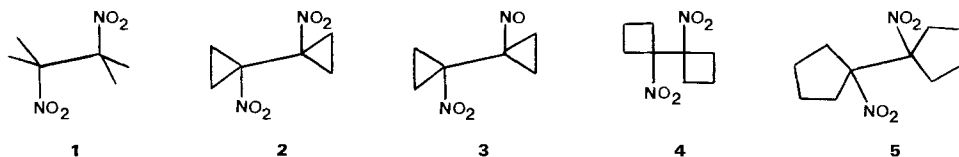
<sup>1)</sup> On leave from Osaka University (Japan), 1978/79.

<sup>2)</sup> Part of the projected Dissertation of P. K., ETH-Zürich.

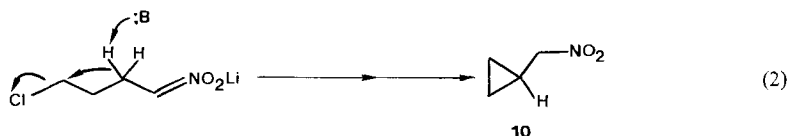
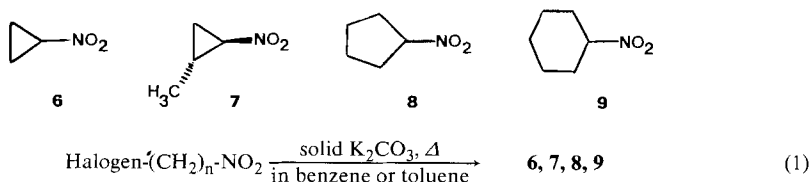
<sup>3)</sup> On leave from the Polytechnical University, Warsaw (Poland), 1978/79.

<sup>4)</sup> Authors to whom correspondence should be addressed.

Like so many other research projects, this study started along a different track and forked off, following some unexpected observations. In connection with our studies on the use of metallated aliphatic nitro compounds in organic synthesis [1] we wished to determine the crystal structure of the lithium salt of 2-*aci*-nitropropane; attempts to recrystallize this compound from aqueous solution gave crystals of a different compound, the X-ray analysis of which showed it to be the dimer **1**, evidently formed by air oxidation<sup>5</sup>). Another unexpected observation that stimulated our interest was the spontaneous dimerization to **2** and **3** that occurred whenever we tried to generate 1-lithio-1-nitrocyclopropane (or the lithium salt of the corresponding *aci*-nitroalkane) and to combine it with electrophiles. Finally, **5** was one of the products of oxidation of the lithium salt or silyl ester [1b] [2] of *aci*-nitrocyclopentane with lead tetraacetate<sup>6</sup>).



**1. Preparation of the nitrocycloalkanes.** – These compounds have all been described before. The most general method of preparing them is the bromination of cycloalkanone oximes with subsequent reductive debromination [5] (*Eqn. 6 in Section 3*). The nitrocyclopropanes are not available by this route and are made by  $\gamma$ -elimination from 1-halo-3-nitropropanes [6]. We could improve the yield of this process by using potassium carbonate as a base under heterogeneous conditions (*Eqn. 1*, up to 53% of **6**, over 70% of **7**); application to the five- and six-membered ring was, however, unsatisfactory (27% of **8**, 20% of **9**). A surprising result was the formation of (nitromethyl)cyclopropane (**10**) from 4-*aci*-nitro-1-chlorobutane (see *Eqn. 2*), a conversion that could be optimized to 40% yield by using lithium diisopropyl amide (LDA) as a base. This makes the interesting nitro compound **10** amply accessible for synthetic purposes<sup>7</sup>). Mechanistically, the elimination leading to **10** is reminiscent of the  $\alpha,\beta$ -double deprotonation of certain nitroethanes [7].



<sup>5</sup>) It turns out that **1** is actually available commercially from *Aldrich*.

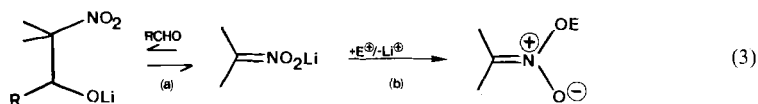
<sup>6</sup>) Compound **5** [3] and the six-membered ring analogue [3] [4] have been described before.

<sup>7</sup>) Previously, the compound **10** was obtained from cyclopropanecarbonitrile in a yield of 6% over several steps [8].

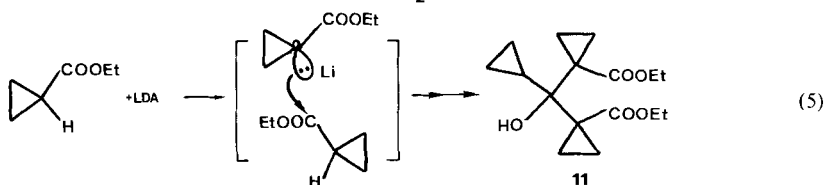
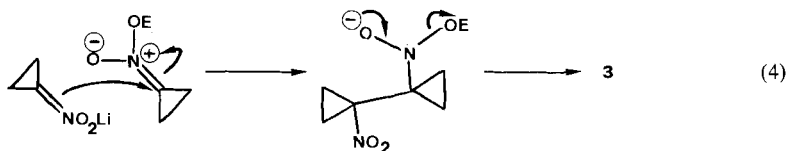
## 2. Formation of the bicyclic propyls 2 and 3. The elusive nitrocyclopropyl anion. –

When we treated nitrocyclopropane at temperatures between  $-80$  and  $-110^\circ$  with bases such as butyllithium, LDA, or potassium hexamethyldisilazane in tetrahydrofuran (THF), we obtained yellow to red solutions which were thought to contain the lithium salt of *aci*-nitrocyclopropane. Workup after any amount of time, rise of temperature, or addition of any electrophile with or without oxidizing properties always led to the isolation of mixtures of the colourless dinitro-compound 2 (m. p.  $128^\circ$ , up to 60%) and of the deep-blue nitro-nitroso compound 3 (m. p.  $64^\circ$ , up to 45%). Although we added a large variety of possible reaction partners: water ( $\text{H}_2\text{O}$ ,  $\text{D}_2\text{O}$ ), acetic acid, carbon dioxide, methyl iodide, benzyl bromide and chloride, *p*-nitrobenzyl chloride, benzaldehyde,  $\omega$ -nitrostyrene, *p*-benzoquinone, iodine, we failed to isolate or identify any compound besides the dimerization products 2 and 3<sup>8)</sup>. Thus, nitrocyclopropane cannot be used in C,C-bond-forming synthetic steps, under the conditions employed here.

What should have been expected? Quantitatively generated salts of *aci*-nitroalkanes do not react with aldehydes or ketones under aprotic conditions, *i. e.* the equilibrium (a) in Equation 3 lies on the right [9]; with other electrophiles, such as chlorosilane, they give *aci*-nitro derivatives [1] [2], see (b) in Equation 3. On the other hand, the anion generated by deprotonating nitrocyclopropane is expected to be much more reactive than those from other nitroalkanes; with a  $\text{p}K_a$  of 27 on the Bordwell-scale [10], nitrocyclopropane is about 10 orders of magnitude less acidic than its open-chain analogue 2-nitropropane [11]. As indicated in Equation 4, the lithium salt of *aci*-nitrocyclopropane might be so reactive that it adds the also highly reactive<sup>9)</sup> products derived from it by attack of an electrophile at oxygen, eventually giving the nitro-nitroso compound 3 (Mechanism A). We have observed this kind of behaviour when we tried to generate the enolate of ethyl cyclopropane-carboxylate (see Eqn. 5): only the product 11 of self-addition could be isolated (see *Exper. Part*).



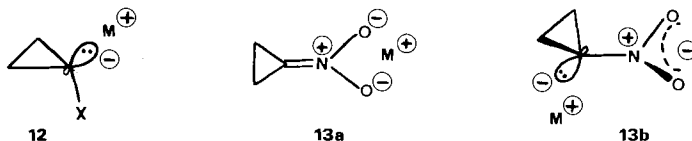
Mechanism A



<sup>8)</sup> In air, the nitro-nitroso derivative 3 is rapidly oxidized to the dinitro compound 2.

<sup>9)</sup> The strain energy of methylenecyclopropane and of cyclopropane is 41 and 27 kcal/mol, respectively, and cyclopropanone can hardly be isolated [12].

The strongly decreased acidity of nitrocyclopropane is a consequence of the well documented resistance of centers in three-membered rings towards becoming planar<sup>9)10)</sup>. Thus, organometallic derivatives<sup>10)</sup> of substituted cyclopropanes **12** exhibit chemical properties and stereochemical features different from those of open-chain analogues. Accordingly, the nitronate derived from **6** might be expected not to have a planar structure **13a** but to be the bent species **13b**, stabilized more by polar than by conjugative effects.

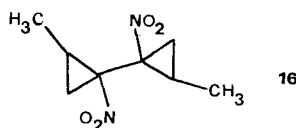
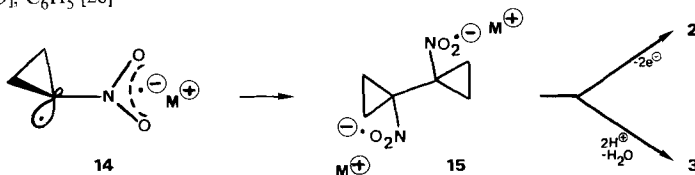


X = Halogen [16]

CN [17], NC [18]

COOR [19], C<sub>6</sub>H<sub>5</sub> [20]

Mechanism B

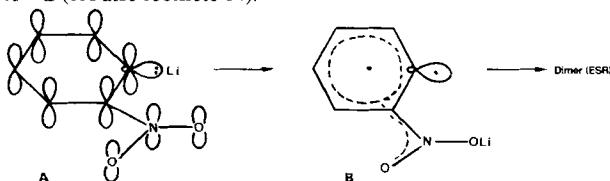


The tendency of **13** to give dimeric products **2** and **3** could also be a consequence of the unsurpassed ability of the NO<sub>2</sub>-group to act as one-electron acceptor<sup>11)</sup>. If one-electron transfer were accompanied by 90° rotation about the C,NO<sub>2</sub>-bond (**13** → **14**) a perpendicular combination **14** of a cyclopropyl radical [15] and a nitro radical anion results<sup>12)</sup>. The dimerization product **15** of this diradical **14** might be

<sup>10)</sup> Non-carbanionoid species also show this effect. In the recently determined structure of a *N*-nitroaziridine the aziridine N-atom is distinctly pyramidal, as judged from Figure 1 of [13a], cf. the high inversion barrier in aziridines [13b] and the chemistry of cyclopropyl cations [14]; in contrast, cyclopropyl radicals invert rapidly [15]. Compare also the reluctance of cyclopropane and cyclobutane derivatives to undergo S<sub>N</sub>2-substitutions [16].

<sup>11)</sup> «The nitro group is the best one-electron acceptor in organic chemistry» (*N. Kornblum*, statement in a lecture delivered in Zürich, 5th June 1978; cf. [3b]).

<sup>12)</sup> Compare the radical formation [21] by the formally forbidden «90°-jump» of an electron from the σ-plane into the perpendicular π-system of *ortho*-lithio-nitrobenzene, occurring at temperatures above -100°, **A** → **B** (see also footnote 14).



present in the solution<sup>13</sup>), and addition of electrophiles/oxidants would then give the observed products **2** and **3** (*Mechanism B*). According to *Mechanism A*, dimer formation occurs only *after* addition of electrophile (oxidant), whereas *Mechanism B* implies at least an equilibrium concentration of the diradical dianion derivative. In order to test the second possibility, we transferred a solution, after mixing the nitrocyclopropane and LDA components, into an ESR. tube, diluted to 0.05M, and measured the ESR. spectrum as quickly as possible between  $-80^{\circ}$  and  $+20^{\circ}$ . *Figure 1* shows the intense signal<sup>14</sup>) observed. It must arise from more than one radical species, some of which are stable for several hours at room temperature.

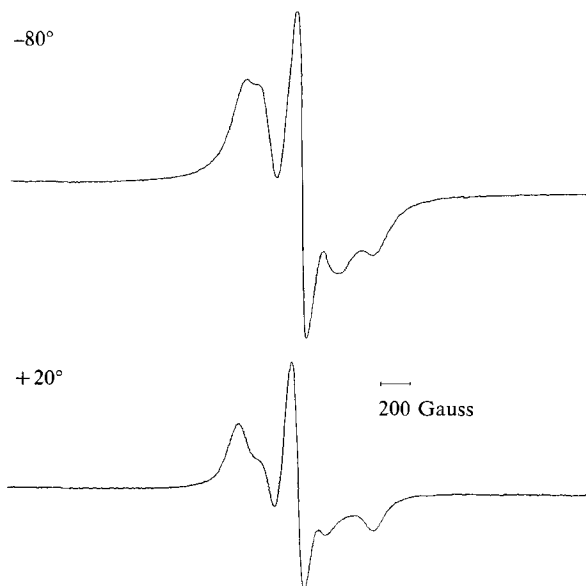
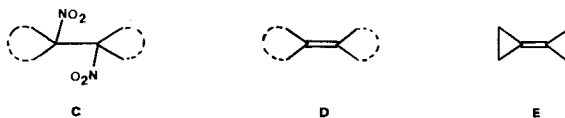


Figure 1. ESR. spectra of solutions obtained from nitrocyclopropane (**6**) and LDA (see also *Exper. Part*)

The existence of long-lived paramagnetic species in the solution is in accord with *Mechanism B*, although it does not disprove *Mechanism A*.

Deprotonation of 2-methyl-1-nitrocyclopropane (**7**) with LDA also furnishes a deep red solution at  $-78^{\circ}$ , from which again no monomeric derivative could be retrieved; addition of *p*-benzoquinone produced the corresponding dinitro-bicyclopropyl compound **16** in 72% yield.

<sup>13</sup>) Such species are probably involved in the reductive elimination [3] leading from persubstituted *vic.*-dinitroethanes to olefins (**C**  $\rightarrow$  **D**) with  $\text{Na}_2\text{S}$  (+ polysulfides), an indiscriminate donor of electrons. – Bicyclopropylidene is not formed in the present case (**15**†E +  $2\text{NO}_2^{\cdot -}$ ) for strain reasons [12]<sup>9</sup>).



<sup>14</sup>) Solutions of lithiated *N*-nitrosamines also give rise to intense ESR. signals, but at the same time, these reagents are highly nucleophilic in C,C-bond-forming processes [22].

**3. Variable temperature  $^1\text{H}$ -NMR. spectra of the dinitroethane derivatives 1, 2, 4, and 5.** – The  $^1\text{H}$ -NMR.-spectrum of the dinitro-bicyclopropyl **2** consists of an  $AA'BB'$  set of signals, see Figure 2 (top). On each cyclopropyl, the two H-atoms *cis* to  $\text{NO}_2$  are thus equivalent and so are the two *trans* to  $\text{NO}_2$  (or *cis* to the other ring), indicating a preferred or averaged conformation **17** of  $C_{2h}$ -symmetry with antiperiplanar  $\text{NO}_2$ -groups (or the less likely *syn*-periplanar  $C_{2v}$ -arrangement). From spectra obtained with NMR. spectrometers of different frequencies, we noticed that there must be a change of the spectrum of **2** slightly below room temperature. This was confirmed by low-temperature spectroscopy: at 100 MHz and  $-5^\circ$ , the coupling pattern of Figure 2 (top) had totally disappeared; the slow-exchange spectrum is shown at the bottom of Figure 2, the coalescence spectrum in the middle of Figure 2. The preferred conformation of **2** has thus four types of H-atoms as in **18** ( $C_2$ -symmetry); the activation enthalpy  $\Delta G^\ddagger$  is estimated to be about 12.5 kcal/mol. In contrast, the  $^1\text{H}$ -NMR. spectrum of the open-chain analogue **1** shows a sharp singlet down to  $-100^\circ\text{C}$ . Likewise, the bicyclobutyl derivative **4**, prepared as indicated in Equation 6, and the bicyclopentyl derivative **5** show spectra, Figure 3, which do not change on cooling to  $-80^\circ$ . These derivatives must either have a different minimum-energy conformation or the barriers to rotation around the central bonds must be much lower than in the bicyclopropyl derivative **2**. Before discussing possible reasons for these differences, we describe results of low-temperature crystal-structure analyses of the open-chain compound and of the small-ring derivatives **2**, **3** and **4**.

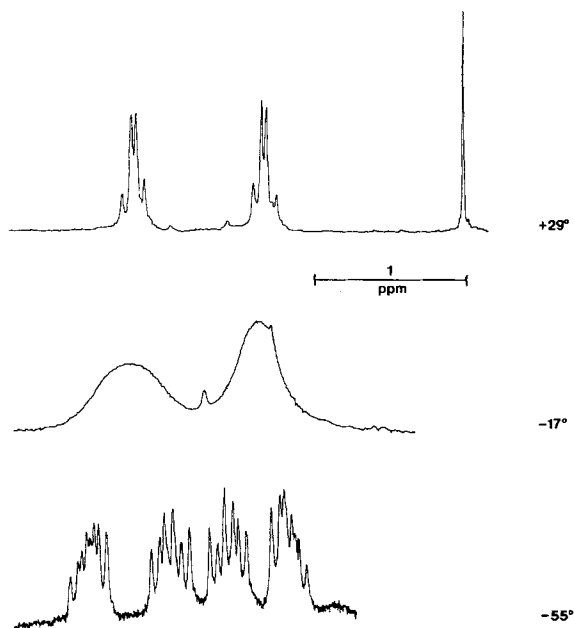


Fig. 2. Temperature-dependent  $^1\text{H}$ -NMR. spectra of 1,1'-dinitrobicyclopropyl (**2**) at 100 MHz (Varian XL100 spectrometer) in  $\text{CD}_2\text{Cl}_2$  (Deuterium lock; internal standard tetramethylsilane. From a separation of  $\Delta\nu=45$  Hz in the slow-exchange spectrum (no further changes are observed when decreasing the temperature to  $-70^\circ$ ) and a coalescence temperature of  $-17^\circ$  (256K) we calculate a  $\Delta G^\ddagger$  of 51 kJ/mol (12.5 kcal/mol) for the activation enthalpy)

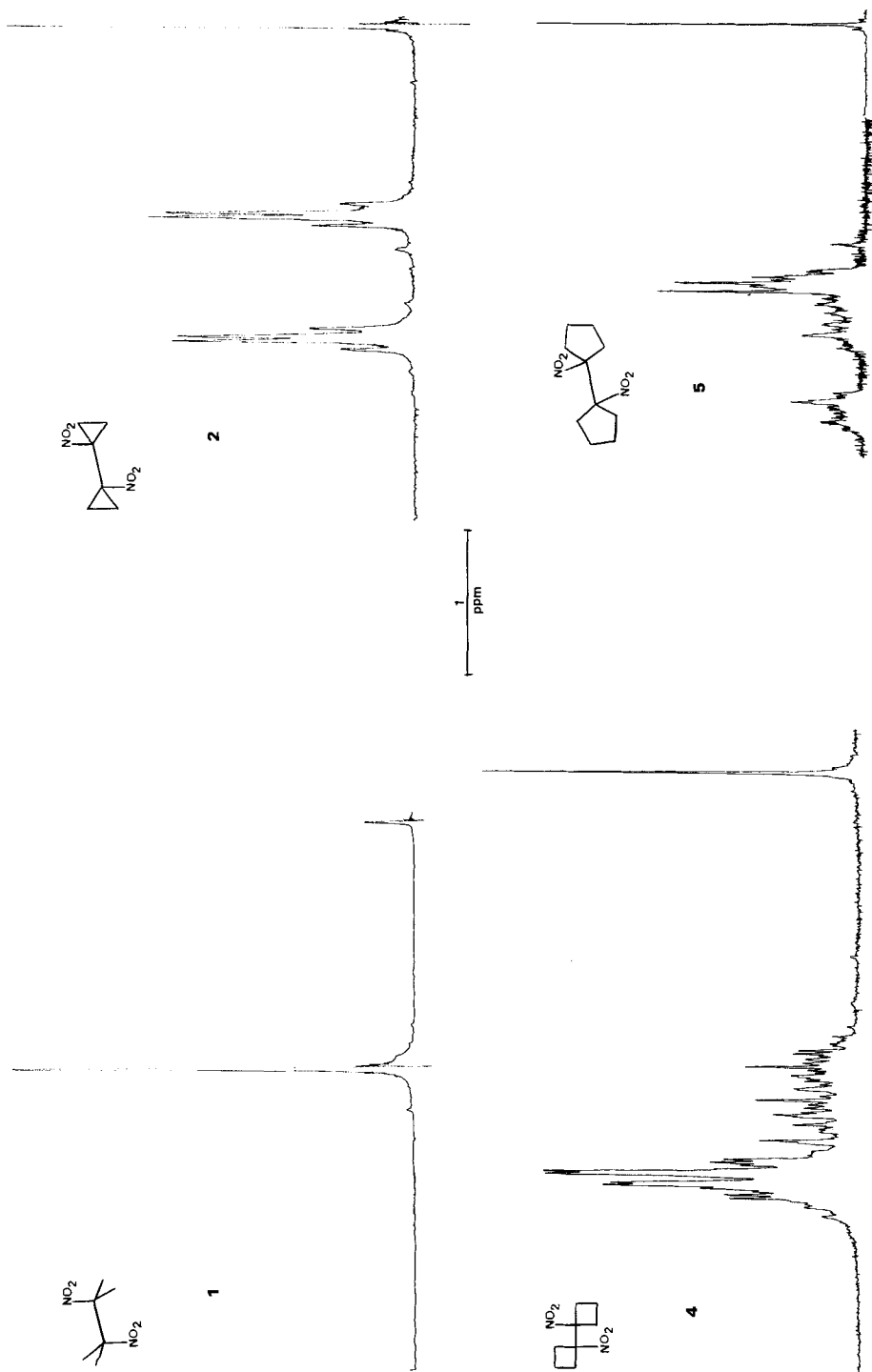
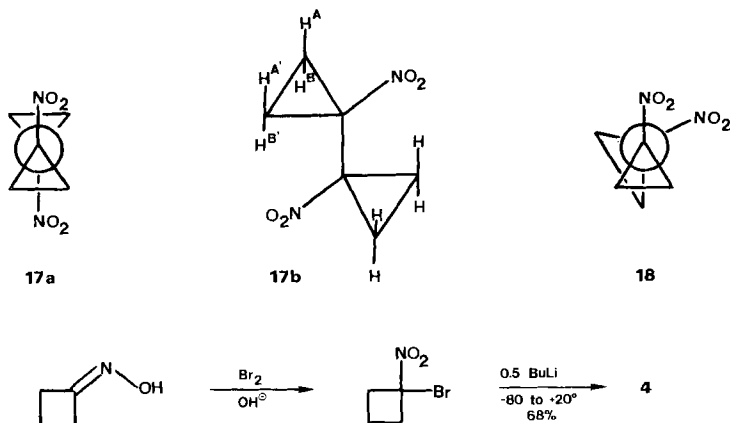


Fig. 3.  $^1\text{H}$ -NMR-spectra of the persubstituted dinitroethanes **1**, **2**, **4**, and **5** at 100 MHz (Solvent  $\text{CD}_2\text{Cl}_2$ , temperature  $+30^\circ\text{C}$ . With the exception of the spectrum of **2** (see Fig. 2), these spectra do not change upon cooling to at least  $-70^\circ$ )



**4. Discussion of crystal structure results.** – Crystallographic data for compounds 1–4 are given in Table 1 together with some experimental details.

Table 1. *Crystallographic data* (standard deviations in brackets) *and experimental details* (N(M) is the number of independent reflexions measured, N(S) the number significantly ( $3\sigma$ ) above background,  $p$  is the exponent in the modified weighting system used [32] and  $R$  is the final agreement index)

Crystal	1 C <sub>6</sub> H <sub>12</sub> N <sub>2</sub> O <sub>4</sub>		2 C <sub>6</sub> H <sub>8</sub> N <sub>2</sub> O <sub>4</sub>	3 C <sub>6</sub> H <sub>8</sub> N <sub>2</sub> O <sub>3</sub>	4 C <sub>8</sub> H <sub>12</sub> N <sub>2</sub> O <sub>4</sub>
Temperature	RT	95K	95K	95K	173K
<i>a</i> (Å)	6.371(2)	6.300(5)	10.855(3)	10.382(3)	11.385(3)
<i>b</i> (Å)	6.535(2)	6.380(3)	6.129(3)	6.186(2)	13.624(3)
<i>c</i> (Å)	12.353(4)	11.851(9)	11.328(4)	11.584(3)	12.421(3)
<i>α</i> (deg)	103.31(4)	100.73(6)	90	90	90
<i>β</i> (deg)	79.31(4)	81.00(6)	97.52(3)	99.11(3)	90
<i>γ</i> (deg)	119.84(3)	118.72(5)	90	90	90
<i>V</i> (Å <sup>3</sup> )	432.6	409.2	747.2	734.6	1926.6
<i>Z</i>		2	4	4	8
Space group		<i>P</i> $\bar{1}$	<i>C</i> 2/ <i>c</i>	<i>C</i> 2/ <i>c</i>	<i>Pbca</i>
Mol-weight		176.2	172.1	156.1	200.2
<i>D<sub>x</sub></i> (gcm <sup>−3</sup> )	1.352	1.429	1.529	1.411	1.380
<i>θ</i> <sub>max</sub> (Mo <i>Kα</i> )	25°	30°	35°	30°	27°
N(M)	1522	2360	1642	1068	2084
N(S)	739	1997	1104	661	1105
<i>p</i>	5	5	5	3.5	5
<i>R</i>	0.031	0.035	0.035	0.061	0.035

Intensity measurements were made with a CAD-4 ENRAF-NONIUS diffractometer equipped with graphite monochromator (MoK $\alpha$ , radiation,  $\lambda = 0.71069 \text{ \AA}$ ) and cooling device. Other details of the individual analyses are mentioned below in case that any special comment seems required. Atomic coordinates and vibrational parameters are listed in Tables 2–5. The structure of the nitro-nitroso compound 3 is disordered and therefore much less accurately determined than the other three. Bond lengths and angles for the three dinitro molecules 1, 2 and 4 are shown in Figures 4, 5 and 6, where librational corrections to the bond lengths are also indicated. A more detailed discussion of the thermal motion of the molecules in these crystal structures is postponed to Section 4.5. Before we discuss the structures individually we outline very briefly the main similarities and differences among them.



All four molecules occur in the *gauche*-conformation with N–C–C–N torsion angles in the range 50–70°, as can clearly be seen from the *Newman* projections shown in *Figure 7*. Apart from this common feature, the tetramethyl derivative **1** and the bicyclopropyl derivative **2** show marked differences that portray vividly the far-reaching influence of the change from open-chain to small-ring compound: *a*) the central C,C-bond is 0.1 Å longer in **1** (1.575 Å) than in **2** (1.479 Å); *b*) likewise, the C,N-bonds are markedly longer in **1** (~1.550 Å) than in **2** (1.488 Å); *c*) the NO<sub>2</sub>-groups rotate by 90° on going from **1** (perpendicular conformation) to **2** (bisecting conformation). The bicyclobutyl derivative **4** shows intermediate behaviour with respect to all three differences.

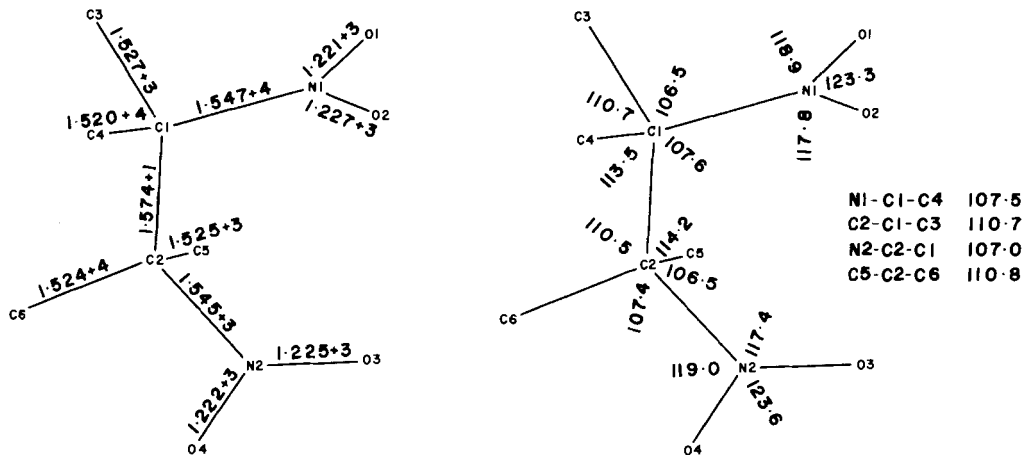


Fig. 4. Bond distances and angles in **1** with libration corrections indicated (estimated standard deviations are less than 0.002 Å and 0.1°. Distances and angles involving H-atoms are not shown; average values are: C–H, 0.97(2) Å; HCH, 108.0(17)°; HCC, 110.9(13)°)

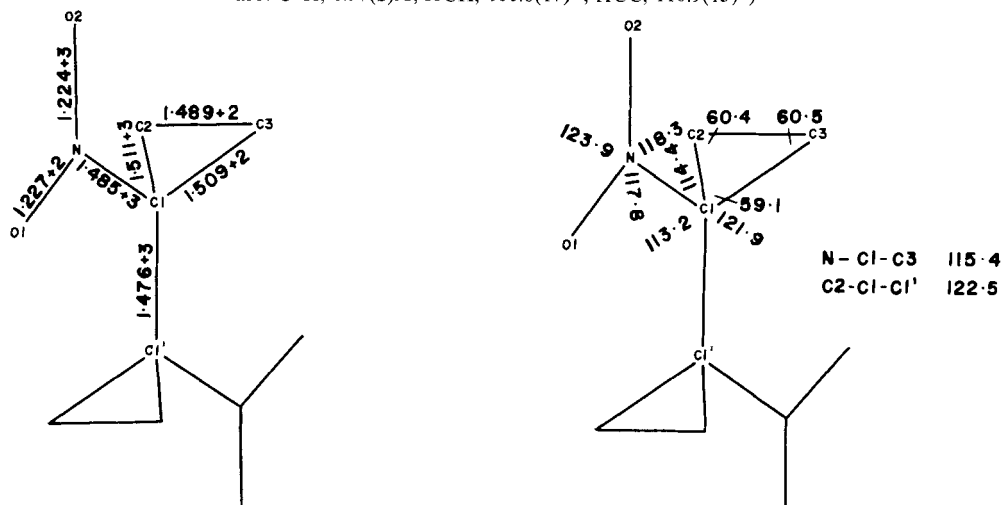


Fig. 5. Bond distances and angles in **2** with libration corrections indicated (estimated standard deviations are less than 0.002 Å and 0.1°. Distances and angles involving H-atoms are not shown; average values are: C–H, 0.96(2) Å; HCH, 116.6(17)°; H–C–C, 116.9(12)°)

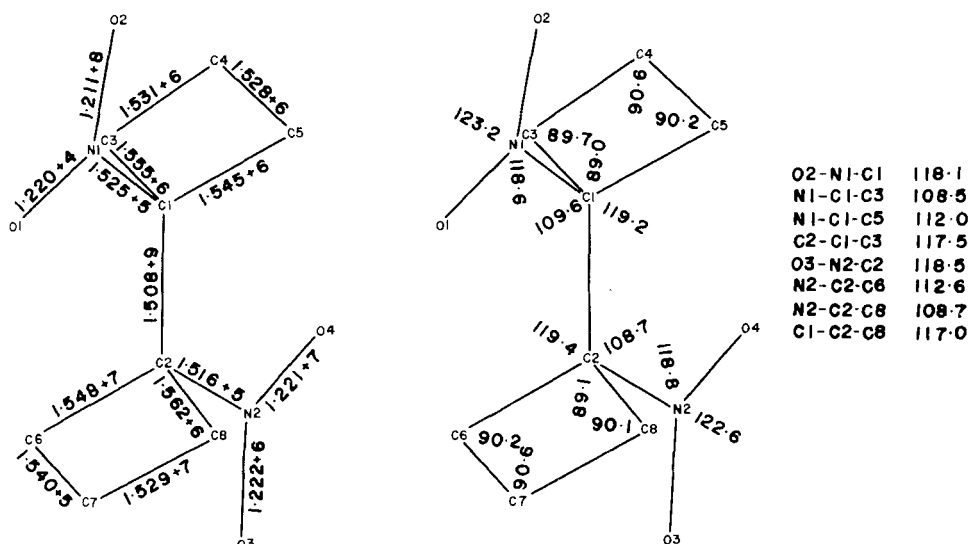


Fig. 6. Bond distances and angles in **4** with libration corrections indicated (estimated standard deviations are about 0.003 Å and 0.2°). Distances and angles involving H-atoms are not shown; average values are: C-H, 0.97(3)°; HCH, 111.1(26)°; HCC, 113.5(18)°)

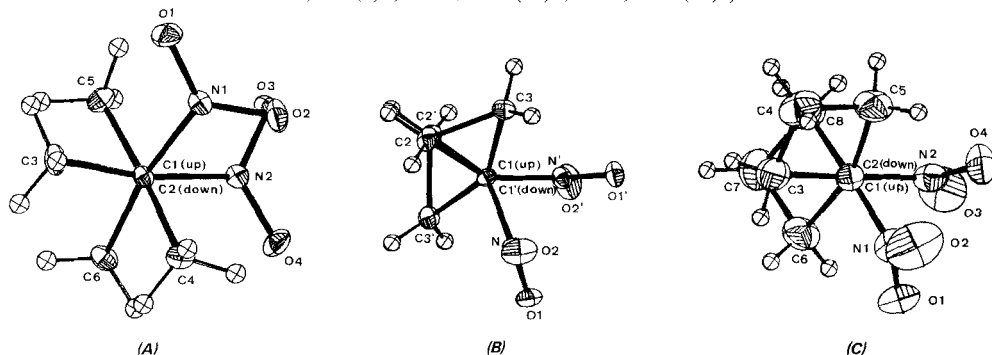


Fig. 7. Newman projections of **1** (A), **2** (B) and **4** (C) down the central C,C-bonds (vibrational ellipsoids are drawn for C-, N- and O-atoms at the 50% probability level [40], H-atoms are indicated by circles of radius 0.1 Å)

**4.1. Crystal structure of 2,3-dimethyl-2,3-dinitrobutane (1).** – Crystals were obtained by slow evaporation of an aqueous solution of the lithium salt of 2-*aci*-nitropropane and were first assumed to be the crystalline salt; however, preliminary X-ray examination showed a large discrepancy between the measured density of 1.351 g·cm<sup>-3</sup> and the calculated density of 1.459 g·cm<sup>-3</sup> for four molecules of C<sub>3</sub>H<sub>6</sub>LiNO<sub>2</sub> in the unit cell (or 1.282 g·cm<sup>-3</sup> for two molecules of C<sub>3</sub>H<sub>6</sub>LiNO<sub>2</sub>·4H<sub>2</sub>O). The identity of the crystals was established directly by X-ray analysis based on intensity measurements made at room temperature. A first attempt with MULTAN77 [23] yielded an uninterpretable E-map, but a second attempt based on a different starting-set gave an E-map in which the heavy-atom skeleton of **1** was clearly recognizable. After least-squares refinement (final *R*=0.031) the molecule showed

unusually long C,N-bonds (1.550–1.553 Å) and also a longish central C,C-bond (1.564 Å). We were doubtful about the reliability of these results, especially in view of the large atomic vibrational parameters and because the standard reflexions had suffered a 40% decrease in integrated intensity during data collection.

In order to define the structural parameters with higher accuracy, a new, more extensive set of data was collected with the crystal held at  $-178^{\circ}\text{C}$ . No significant variations in the intensity of the standard reflexions were observed for this data set. After least-squares refinement (final  $R=0.035$ ) the mean-square vibrational amplitudes were less than a third of their values at room temperature and the e.s.d.'s in bond lengths were less than  $0.002\text{ Å}$ . With C,N-bond lengths of  $1.551$  and  $1.548\text{ Å}$ , and a central C,C-bond length of  $1.575\text{ Å}$  the low-temperature analysis confirms both of the apparently anomalous features of the room-temperature study that led us to undertake the new measurements. Atomic positions and vibrational parameters are listed in Table 2. A stereo-view of the molecule is shown in Figure 8.

Table 2. Fractional coordinates and vibrational parameters for **1** (95K data) in units of  $10^{-5}$  and  $10^{-4}\text{ Å}^2$  respectively ( $10^{-3}$  and  $10^{-3}\text{ Å}^2$  for H-atoms)

	x	y	z	U <sub>11</sub>	U <sub>22</sub>	U <sub>33</sub>	U <sub>12</sub>	U <sub>13</sub>	U <sub>23</sub>
O1	58185 (14)	116476 (12)	32953 (7)	259(3)	115(3)	237(3)	84(3)	-47(3)	-4(2)
O2	67395 (12)	97793 (14)	27889 (7)	158(3)	231(3)	234(3)	92(3)	-76(2)	-32(3)
O3	71196 (12)	86874 (13)	12768 (7)	128(3)	167(3)	298(4)	24(3)	43(3)	-13(3)
O4	56271 (14)	49820 (14)	14847 (7)	238(3)	221(4)	279(4)	164(3)	39(3)	38(3)
N1	58281 (13)	98816 (13)	34375 (6)	135(3)	132(3)	97(3)	61(2)	-13(2)	-22(2)
N2	54229 (12)	67323 (14)	14708 (6)	126(3)	154(3)	97(3)	67(3)	-3(2)	-18(2)
C1	27547 (13)	73568 (14)	31682 (7)	189(3)	186(3)	95(3)	46(2)	-8(2)	-2(2)
C2	29814 (13)	66883 (14)	18191 (7)	93(3)	127(3)	98(3)	47(3)	-3(2)	-3(2)
C3	5582 (15)	77822 (17)	35493 (8)	145(3)	217(4)	141(3)	187(3)	16(3)	3(3)
C4	27647 (17)	55747 (16)	38488 (7)	231(4)	152(4)	121(3)	98(3)	-3(3)	27(3)
C5	27289 (16)	82851 (17)	11184 (7)	283(4)	218(4)	111(3)	116(3)	-12(3)	33(3)
C6	18823 (15)	48884 (16)	15853 (8)	148(3)	147(4)	151(4)	19(3)	-21(3)	-34(3)

	x	y	z	U
H31	-88 (3)	638 (4)	337 (2)	29(4)
H32	54 (3)	833 (3)	439 (2)	24(4)
H33	62 (3)	905 (3)	318 (2)	26(4)
H41	124 (3)	488 (4)	381 (2)	32(4)
H42	481 (3)	509 (3)	357 (2)	28(4)
H43	388 (3)	631 (3)	465 (2)	26(4)
H51	111 (3)	888 (3)	115 (2)	23(4)
H52	389 (3)	786 (3)	38 (2)	22(4)
H53	388 (3)	1088 (3)	133 (2)	23(4)
H61	-55 (3)	387 (3)	178 (2)	31(4)
H62	116 (3)	282 (3)	187 (2)	24(4)
H63	112 (3)	361 (4)	66 (2)	32(4)

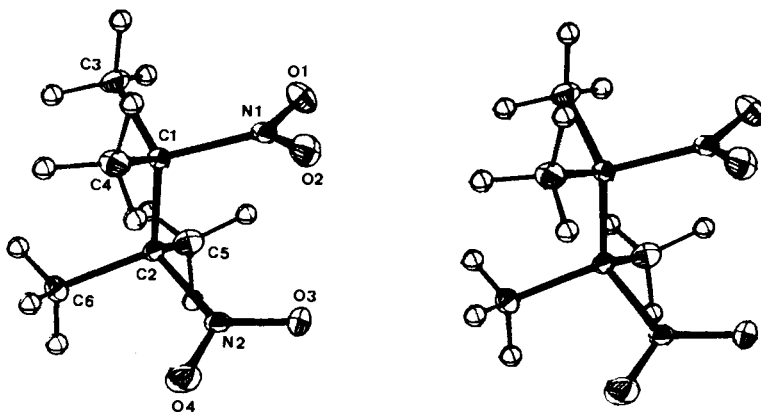


Fig. 8. Stereo-view of molecule **1** drawn by ORTEP[40] with vibrational ellipsoids for C-, N- and O-atoms drawn at the 50% probability level, H-atoms indicated by spheres of radius  $0.1\text{ Å}$

Although the molecule has no crystallographic symmetry, it shows approximate twofold rotational symmetry, as may be seen from the projected view down the central bond C(1),C(2) (Fig. 7A). The N–C–C–N torsion angle is  $52.5^\circ$  and both NO<sub>2</sub>-groups adopt a nearly perpendicular conformation with respect to the central bond, the torsion angles C(1)–C(2)–N(2)–O(3) and C(2)–C(1)–N(1)–O(2) being  $-86^\circ$  and  $-99^\circ$  respectively. This difference in the torsion angles goes together with a corresponding difference in the nonbonded distances between the NO<sub>2</sub>-groups. 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 in Figure 7A) exactly halfway between them.

The bond angles (Fig. 4) at the two, central, tetra-substituted C-atoms require comment. At both atoms the three N–C–C bond angles are  $2-3^\circ$  less than the tetrahedral angle, while the three C–C–C bond angles are greater. Of the C–C–C angles the largest at both ends of the molecule are those between the central C, C-bond and the C,CH<sub>3</sub>-bond that is synclinal to the opposite NO<sub>2</sub>-substituent. This widening is presumably due to steric congestion. Apart from this factor, the long C, N-bond lengths and the general pattern of bond-angle deformations are consistent with predictions based on *Bent's Rule* [24] concerning the effect of electron-withdrawing substituents on hybridization. Alternatively, one can think of the deformation in terms of a slight movement along a reaction path leading to heterolytic fission of the C, N-bond to leave a trisubstituted carbonium ion. Analogous deformations of inorganic tetrahedral anions, such as SO<sub>4</sub><sup>2-</sup>, etc., have been interpreted in this way [25].

A stereo-view of the crystal packing is shown in Figure 9. There are no specially short intermolecular contacts.

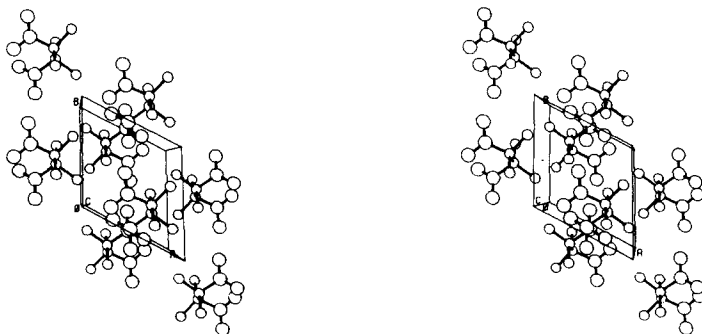


Fig. 9. Stereo-view of crystal structure of **1** drawn by PLUTO [41]

**4.2. Crystal structure of 1,1'-dinitro-bicyclopentyl (2).** This structure analysis actually followed that of the isomorphous nitro-nitroso compound (**3**, see Section 4.4.) and did not present any special difficulties; for details see Table 1 and for final atomic parameters see Table 3. Bond distances and angles are shown in Figure 5. Both the central C, C-bond and the C, N-bonds are markedly shorter than in **1**; the C, C-bond is 1.479(2) Å, roughly the same as in bicyclopentyl, 1.487 Å [26], and the C, N-bond is 1.488(2) Å, exactly the same as in nitrocyclopentane [27].

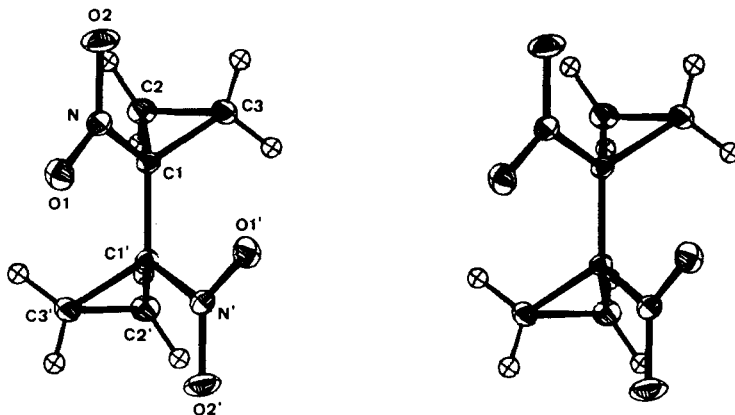
Table 3. Fractional coordinates and vibrational parameters for **2** (units as in Table 2)

	x	y	z	U <sub>11</sub>	U <sub>22</sub>	U <sub>33</sub>	U <sub>12</sub>	U <sub>13</sub>	U <sub>23</sub>
O1	37856 (8)	61328 (15)	27667 (7)	217(3)	183(3)	185(3)	54(3)	50(3)	-34(3)
O2	29032 (8)	51283 (19)	18018 (8)	218(3)	355(5)	212(4)	123(4)	-76(3)	-5(4)
N	36488 (7)	49119 (16)	19028 (7)	134(3)	164(4)	150(3)	33(3)	15(2)	6(3)
C1	45475 (8)	38772 (15)	19538 (8)	113(3)	112(3)	115(3)	7(3)	5(2)	-8(3)
C2	48239 (10)	9981 (16)	13712 (9)	195(4)	159(4)	171(4)	-49(3)	3(3)	-35(3)
C3	48966 (9)	23476 (17)	7691 (9)	176(4)	178(4)	121(3)	7(3)	20(3)	-19(3)

	x	y	z	U
H21	432 (2)	-38 (3)	174 (2)	21(4)
H22	317 (2)	185 (4)	187 (2)	27(5)
H31	575 (2)	187 (3)	79 (2)	16(4)
H32	455 (2)	314 (3)	9 (2)	25(4)

The molecule has a crystallographic twofold rotation axis, as can be seen from the stereo-view shown in Figure 10. The Newman projection down the central bond is shown in Figure 7B. The NO<sub>2</sub>-groups adopt the bisected conformation with respect to the cyclopropyl rings, as in nitrocyclopropane itself [27], and the N–C–C–N torsion angle is 69°, about 17° greater than in the tetramethyl derivative **1**. In this *gauche*, doubly bisected conformation the O(1) . . . O(1') contact distance between the NO<sub>2</sub>-groups is 2.95 Å, almost the same as the O(2) . . . O(3) distance in **1** (2.93 Å), and the larger N–C–C–N torsion angle in **2** may be required to help to achieve this; the O(1) . . . N' distance is 2.94 Å, halfway between the two corresponding values in **1**. The other O-atom, O(2) makes close contacts with the methylene groups of the cyclopropane ring (2.79 and 2.82 Å to the C-atoms, 2.50 and 2.52 Å to the H-atoms). Judging from the near equality of the C–N–O bond angles (both 118.0 ± 0.3°) the repulsion between O(2) and the methylene groups is just about balanced by that between the two O(1)-atoms across the twofold axis.

Fig. 10. Stereo-view of molecule **2** (details as in Fig. 8).

Bicyclopropyl itself has the *trans*-conformation, at least in the crystal [26], and so does *anti,cis,cis*-2,2',2''-dibromo-bicyclopropyl [28]. With NO<sub>2</sub>-groups in the bisected conformation, the *trans*-arrangement of the cyclopropane rings would lead to non-bonded distances of 2.0 Å or less between nitro O-atoms and methylene H-atoms across the molecule. These short distances could be alleviated by rotating the NO<sub>2</sub>-groups into the perpendicular conformation, where they are found in **1**, or by rotating about the central C<sub>1</sub>C<sub>1'</sub>-bond. The observed structure shows that the second alternative, which preserves the bisected conformation of the NO<sub>2</sub>-groups, is ener-

getically more favourable. The preference of  $\pi$ -acceptor substituents for the bisected conformation is well known and follows from the MO model of *Hoffmann & Davidson* [29] in which one of the degenerate pair of HOMO's of the cyclopropane ring interacts with the LUMO of a  $\pi$ -acceptor substituent (*Fig. 11*). Maximum overlap of these orbitals is attained in the bisected conformation. The observed shortening of the distal C,C-bond of the cyclopropane ring by 0.021(2)Å compared with the proximal bonds can also be attributed to this interaction [30]. Similar deformations have been observed in other cyclopropane derivatives with  $\pi$ -acceptors [31]. Our example is by no means one of the largest observed deformations, but it is probably the most accurately determined. If this MO. argument is pressed a little further, it would imply that in molecule **1** the HOMO of the tetramethylethane fragment must be localized largely on the central C,C-bond, which is indeed the longest and presumably the weakest of the C,C-bonds. The implications for the bicyclobutyl case are left to the following section.

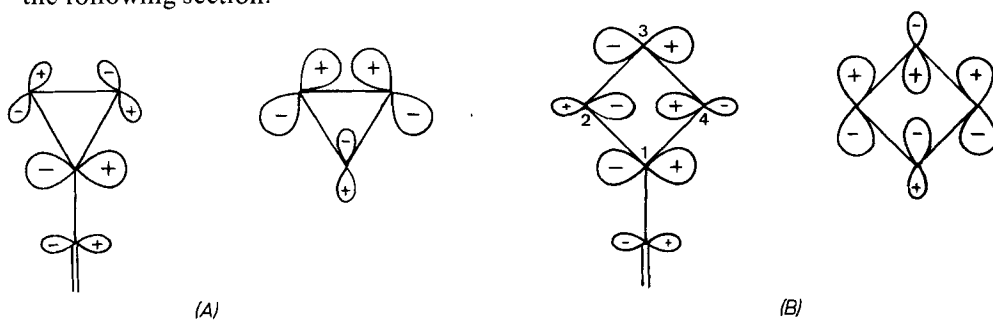


Fig. 11. Schematic view of overlap of a  $\pi$ -acceptor orbital LUMO with the symmetry-adapted degenerate pair of HOMO's of cyclopropane (A) and cyclobutane (B)

The crystal packing is illustrated in *Figure 12*. There are no specially short intermolecular contacts.

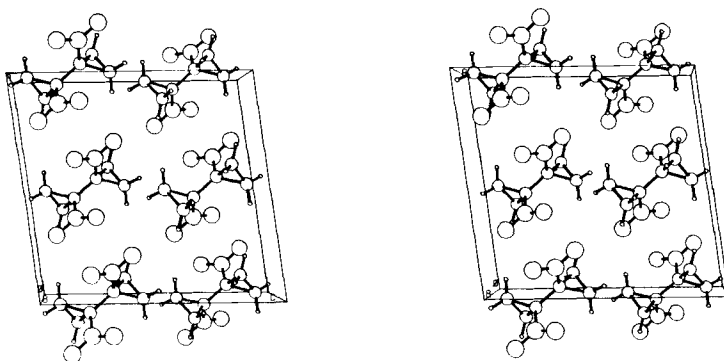


Fig. 12. Stereo-view of crystal structure of **2** drawn by PLUTO [41]

**4.3. Crystal structure of 1,1'-dinitro-bicyclobutyl (4).** The main experimental problem here concerned the thermal stability of the crystals, which sublime at room temperature and shatter on cooling between  $-110^{\circ}$  and  $-140^{\circ}\text{C}$ , possibly because of a phase transition. This is why the diffractometer measurements on **4** were made with

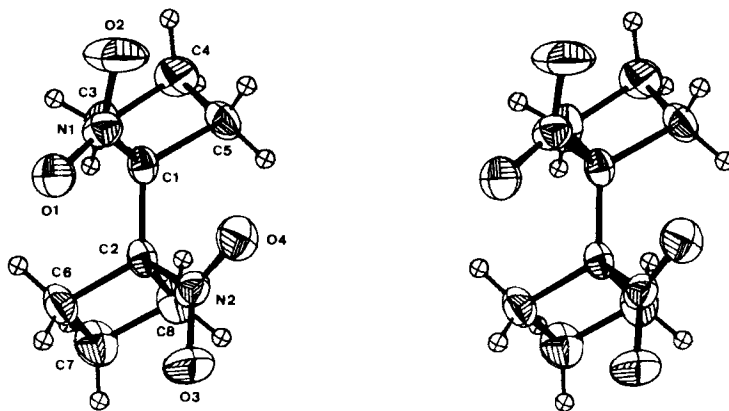
the crystal held at  $-100^{\circ}\text{C}$  instead of about  $-180^{\circ}\text{C}$ , as for the other crystals (see *Table 1*). Apart from that, the analysis did not present any special difficulties. However, the higher temperature of measurement manifests itself in the larger vibrational amplitudes of the atoms, as well as in the somewhat lower accuracy. Final atomic parameters are in *Table 4*. Although the molecule has no crystallographic symmetry, it has an approximate twofold rotation axis, as can be seen from the stereo-view (*Figure 13*).

*Table 4. Fractional coordinates and vibrational parameters for 4 in units of  $10^{-4}$  and  $10^{-4}\text{\AA}^2$  respectively ( $10^{-3}$  and  $10^{-3}\text{\AA}^2$  for H-atoms)*

	x	y	z	U <sub>11</sub>	U <sub>22</sub>	U <sub>33</sub>	U <sub>12</sub>	U <sub>13</sub>	U <sub>23</sub>
O 1	2373 (2)	2239 (1)	3253 (1)	465(11)	493(12)	397(9)	22(8)	-159(9)	-77(9)
O 2	2308 (2)	539 (1)	2753 (2)	971(17)	433(11)	343(15)	323(11)	-246(14)	-72(12)
O 3	-406 (2)	3334 (1)	3299 (2)	559(12)	515(11)	747(13)	143(9)	91(11)	-192(11)
O 4	-227 (2)	1769 (1)	3256 (1)	436(12)	466(12)	416(12)	-54(8)	131(9)	41(9)
N 1	2037 (2)	1394 (1)	2646 (2)	390(12)	379(11)	363(11)	50(12)	-2(13)	-46(9)
N 2	-16 (2)	250 (2)	2971 (2)	202(9)	392(11)	359(10)	22(13)	-37(8)	-62(9)
C 1	1291 (2)	1630 (2)	1677 (2)	314(11)	355(11)	255(12)	-33(9)	4(10)	-35(12)
C 2	723 (2)	2661 (2)	1898 (2)	339(11)	316(12)	232(14)	-77(9)	-65(9)	29(9)
C 3	2354 (3)	1501 (2)	644 (2)	333(14)	714(19)	326(13)	-94(15)	72(13)	-140(13)
C 4	1357 (3)	664 (2)	326 (2)	567(19)	525(17)	421(14)	26(14)	-63(15)	-192(14)
C 5	525 (3)	813 (2)	1275 (2)	468(15)	335(13)	474(14)	-132(13)	-33(14)	-113(12)
C 6	1484 (3)	3632 (2)	1869 (2)	440(15)	338(12)	542(13)	-114(12)	-68(15)	61(13)
C 7	726 (3)	4819 (2)	953 (3)	653(22)	467(17)	592(19)	-64(16)	-77(18)	231(15)
C 8	-49 (3)	3133 (2)	972 (3)	494(17)	511(16)	443(16)	-76(15)	-134(14)	153(14)

	x	y	z	U
H 31	211 (3)	152 (2)	73 (2)	53(9)
H 32	193 (3)	216 (2)	16 (3)	53(11)
H 41	182 (3)	6 (2)	38 (3)	70(13)
H 42	132 (3)	69 (2)	-33 (2)	61(9)
H 51	47 (2)	28 (2)	176 (2)	62(9)
H 52	-28 (2)	104 (2)	135 (2)	58(8)
H 61	227 (3)	344 (2)	165 (2)	53(9)
H 62	151 (3)	395 (2)	255 (3)	69(9)
H 71	121 (3)	487 (2)	31 (3)	61(11)
H 72	32 (4)	463 (2)	129 (3)	111(16)
H 81	-35 (3)	323 (2)	119 (2)	55(11)
H 82	9 (3)	269 (2)	37 (3)	69(13)



*Fig. 13. Stereo-view of molecule 4 (details as in Fig. 8)*

Bond distances and angles are shown in *Figure 6*. Both the central C,C- and the C,N-bond lengths are intermediate between those observed in the 2,3-dimethylbutane derivative **1** and the bicyclopentyl derivative **2**. This intermediate behaviour is also shown in the conformation of the  $\text{NO}_2$ -groups relative to the ring system; they are again in the bisected position, but not as exactly as in **2**. Whereas the two C-C-N-O(2) torsion angles in **2** differ only by  $9^{\circ}$  in magnitude ( $-37^{\circ}$  and  $29^{\circ}$ ), the corre-

sponding angles in **4** differ much more ( $-70^\circ$  and  $27^\circ$  for one group,  $-62^\circ$  and  $35^\circ$  for the other). Nevertheless, as *Figures 7C* and *13* show, the description as bisected is still approximately valid. The N–C–C–N torsion angle is  $59^\circ$ , smaller than in **2** ( $69^\circ$ ), but the O(1) . . O(4) distance, between, the inward-pointing O-atoms, is not shorter than in **2** but even slightly longer ( $2.98\text{\AA}$ ), largely because of the greater rotational freedom of the  $\text{NO}_2$ -groups. On the other hand, the O . . N distances are the shortest in the series (O(1) . . N(2),  $2.85\text{\AA}$ ; O(4) . . N(1),  $2.74\text{\AA}$ ). Both cyclobutane rings are approximately planar, the torsion angles being  $5.4^\circ$  for the ring including C(1) and  $0.9^\circ$  for the ring including C(2).

*Hoffmann & Davidson* [29] have given arguments for  $\pi$ -acceptor substituents on a cyclobutane ring to retain the bisected conformation although with a less decided preference (smaller rotational barrier) than for cyclopropane. These authors did not, however, discuss the bond-length and bond-angle changes that might occur on such substitution. From the MO picture given in *Figure 11*, and using arguments analogous to those used for the three-membered ring case [30] one would expect: *a*) a slight, uniform change in length of all four C,C-bonds; *b*) a decrease in the non-bonded C(2) . . C(4) cross-ring distance, and a corresponding increase in the C(1) . . C(3) distance; or equivalently, a decrease in the bond angles at the C-atoms 1 and 3, and a widening of the angles at the C-atoms 2 and 4. What is actually observed in both cyclobutane rings is a decrease in bond angle at atom 1 ( $89.0$  and  $89.1^\circ$ ) combined with a widening at the opposite atom 3 ( $90.6^\circ$  twice), with practically no change in the angles at the C-atoms 2 and 4. These bond-angle changes are equivalent to a slight increase in the length of the vicinal bonds ( $1.545$ ,  $1.555$ ,  $1.548$ ,  $1.562\text{\AA}$ ) compared with the distal ones ( $1.528$ ,  $1.531$ ,  $1.529$ ,  $1.540\text{\AA}$ , all uncorrected and all with e.s.d.'s of about  $0.005\text{\AA}$ ). Straightforward application of the MO model does not seem to be as successful for the cyclobutane ring as for the cyclopropane one.

The crystal packing is shown in *Figure 14*.

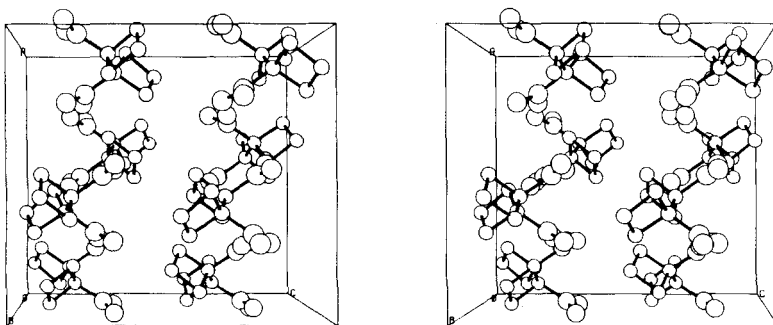


Fig. 14. Stereo-view of crystal structure of **4** drawn by PLUTO [41]

**4.4. Crystal structure of 1-nitro-1'-nitroso-bicyclopentyl(3).** The deep-blue crystals are isomorphous with the dinitro compound **2**. With space group  $C2/c$ ,  $Z=4$ , the crystallographic symmetry rules would require the molecule to have either a centre of inversion or a twofold rotation axis, both of which are incompatible with the chemical constitution; obviously the crystal structure is disordered. Nevertheless, it



could be solved without difficulty in space group  $C2/c$  using MULTAN77 [23]. The molecule adopts at random one of two possible orientations related by a twofold rotation axis of the space group. Thus the averaged molecule can be described in terms of an asymmetric unit consisting of a cyclopropyl ring plus half-weight  $\text{NO}_2^-$  and  $\text{NO}$ -groups. In fact, the half-weight peak for the nitroso-O atom overlaps strongly with that for one of the nitro-O atoms, and there is a similar overlap between the peaks for the two N-atoms. When each of these pairs of overlapping peaks was treated as a single scattering centre, least-squares analysis with anisotropic temperature factors refined to  $R=0.068$ , with all H-atoms located from a difference map and included in the refinement.

The resulting structure is shown in *Figure 15*, from which the vibrational ellipsoids of the two composite atoms N and O(1) appear to be abnormally large in some directions. The calculated mean-square vibrational amplitudes are about  $0.05\text{\AA}^2$  for

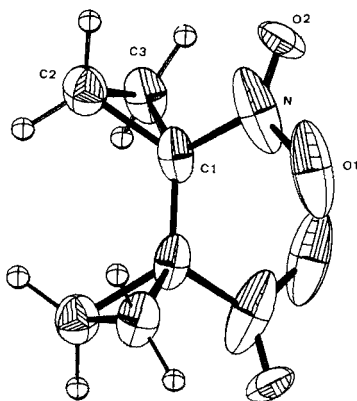


Fig. 15. Structure of disordered nitro-nitroso molecule **3** showing vibrational ellipsoids derived by least-squares refinement with single scattering centres for N and O(1) (Other details as in Fig. 8)

the C-atoms and for the half-weight atom O(2); for the composite atoms they range up to about  $0.10\text{\AA}^2$  for N and  $0.13\text{\AA}^2$  for O(1), not excessive compared with results of many room-temperature analyses but large enough to offer the possibility of resolving each of these composite atoms into its components. For each, two half-weight atoms were located roughly along the major axis of the vibrational ellipsoid at a separation of about  $0.5\text{\AA}$ . The positions and isotropic vibrational parameters of the four half-weight atoms were then allowed to vary in a full-matrix least-squares refinement, leading to the results shown in *Table 5* (final  $R$  was 0.061). In the final structure the distances between the two pairs of half-weight atoms are  $0.602\text{\AA}$  for N(11)–N(12) and  $0.649\text{\AA}$  for O(11)–O(12). The positions of these half-weight atoms are still strongly correlated with each other and must be regarded as particularly uncertain; the quoted e.s.d.'s for these atoms are not very meaningful because they do not include the covariance. Besides, the positions of the other atoms are also affected by the disorder, as shown by their mean-square vibrational amplitudes (*Table 5*) which are 2–3 times larger than those of the isomorphous **2** at the same temperature.

	x	y	z	U or U <sub>11</sub>	U <sub>22</sub>	U <sub>33</sub>	U <sub>12</sub>	U <sub>13</sub>	U <sub>23</sub>
U11	3376 ( 4)	5922 ( 6)	2373 ( 4)	306 ( 9)					
U12	3028 ( 3)	6132 ( 5)	2819 ( 3)	272 ( 7)					
U13	3146 ( 4)	6242 ( 7)	993 ( 3)	485 (24)	512 (21)	261 (16)	222 (10)	14 (15)	81 (15)
U11	3357 ( 5)	4572 ( 8)	1572 ( 5)	369 (10)					
U12	3769 ( 4)	4948 ( 6)	1941 ( 3)	225 ( 7)					
U13	4550 ( 3)	3016 ( 3)	1941 ( 2)	526 (14)	242 (10)	427 (12)	64 ( 9)	386 (10)	68 ( 6)
U2	4037 ( 3)	959 ( 4)	1322 ( 3)	521 (16)	365 (12)	415 (13)	-11 (11)	166 (12)	33 (10)
U3	4962 ( 3)	2292 ( 4)	885 ( 2)	594 (16)	348 (12)	442 (13)	82 (12)	293 (11)	43 (10)
	x	y	z	U					
H21	430 ( 3)	-35 ( 6)	171 ( 3)	44 ( 8)					
H22	317 ( 5)	186 ( 7)	95 ( 4)	72 (12)					
H31	589 ( 4)	189 ( 5)	69 ( 3)	46 ( 8)					
H32	461 ( 3)	317 ( 6)	8 ( 3)	53 ( 9)					

The figure displays two ORTEP diagrams of the independent molecules in the asymmetric unit of compound 1. The left diagram shows the first molecule with bond lengths (Å) and angles (°) labeled. The right diagram shows the second molecule with bond lengths (Å) and angles (°) labeled. Both structures are shown in a perspective view with thermal ellipsoids at the 50% probability level.

**Left Molecule (Molecule 1):**

- Bond lengths (Å): O2—C2 1.246, C2—C3 1.479, C2—N12 1.247, C1—C2 1.444, C1—C3 1.524, C1—C1' 1.473, C1'—C2' 1.573, C1'—N11' 1.246.
- Angles (°): O2—C2—C3 91.1, O2—C2—N12 124.7, C2—C3—C1 152.4, C2—C1—C3 144.4, C2—C1—C1' 147.3, C1—C2—C3 91.1, C1—C2—N12 124.7, C1—C1'—C2' 157.3, C1'—C2'—C3' 152.4, C1'—C1—C3 144.4, C1'—C1—C1' 147.3, C1'—C1—N11' 124.6.

**Right Molecule (Molecule 2):**

- Bond lengths (Å): O2—C2 1.246, C2—C3 1.479, C2—N12 1.247, C1—C2 1.444, C1—C3 1.524, C1—C1' 1.473, C1'—C2' 1.573, C1'—N11' 1.246.
- Angles (°): O2—C2—C3 91.1, O2—C2—N12 124.6, C2—C3—C1 152.4, C2—C1—C3 144.4, C2—C1—C1' 147.3, C1—C2—C3 91.1, C1—C2—N12 124.6, C1—C1'—C2' 157.3, C1'—C2'—C3' 152.4, C1'—C1—C3 144.4, C1'—C1—C1' 147.3, C1'—C1—N11' 124.6.

$$\Delta_{A,B} = z_{A,B}^2 - z_{B,A}^2 \sim 0$$

where  $z_{A,B}^2$  is the mean-square vibrational amplitude of atom A in the direction of the interatomic vector A,B etc. This condition holds best for the C-skeletons and worst for the vectors involving the O-atoms of the NO<sub>2</sub>-groups. For example,  $\langle \Delta^2 \rangle^{1/2} = 6 \cdot 10^{-4} \text{Å}^2$  for the 15 C,C vectors in **1**, while  $\Delta$ 's involving the O-atoms range up to about  $100 \cdot 10^{-4} \text{Å}^2$ .

It is therefore not surprising that analysis of the observed  $U_{ij}$  values in terms of rigid-body vibrations [34] does not give very good agreement (*Table 6*). The agreement is considerably improved by allowing for torsional vibration of the NO<sub>2</sub>-groups about their respective C,N-bonds. The main remaining discrepancies seem to have a systematic character; in all three analyses the experimental vibrational tensor of each N-atom is slightly (about  $20 \cdot 10^{-4} \text{Å}^2$  for **1** and **2**) too large in the plane of its NO<sub>2</sub>-group, as revealed by the uniformly positive values of  $\Delta_{A,B}$  for bonds emanating from the N-atoms. One explanation could be that least-squares refinement tends to compensate for an electron-density deficit at the N-atom by an artificial increase in the temperature factor of this atom. Thus, this systematic feature could be an indication of a residual positive charge at the N-atoms, due to the polarity of the N,O-bonds. A similar effect has been noted for the temperature factor of Li-atoms in polar C,Li-bonds [36].

The r.m.s. librational amplitudes obtained for the torsional motion about the N,C-bonds by the non-rigid-body thermal motion analysis [37] are shown in *Table 6*. The values obtained for **4** are larger than for **1** and **2**, in keeping with the higher temperature of measurement. The temperature dependence can be allowed for in rough approximation if we assume that the motions in question are adequately described as classical harmonic oscillators with *Boltzmann* distribution of energy. The mean-square amplitude is then given by  $\langle \varphi^2 \rangle = RT/k$  where  $k$  is the quadratic force constant. For **4** we obtain an average value of  $11.5 \text{ kcal mol}^{-1} \text{rad}^{-2}$  for the two independent NO<sub>2</sub>-groups, and for **2** we obtain the distinctly higher value of  $18.7 \text{ kcal mol}^{-1} \text{rad}^{-2}$ , in keeping with the expected stronger preference for the bisected position in **2** compared with **4** [29].

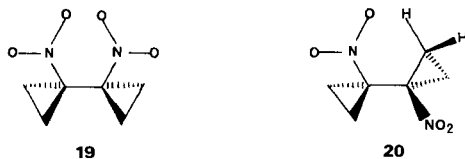
Table 6. Results of thermal-motion analyses; (A) rigid-body analysis, (B) allowing for libration of NO<sub>2</sub>-groups about their C,N-bonds (for each analysis, the principal values of the molecular libration and translation tensors **T** and **L** are given, together with the r.m.s. libration amplitude  $\langle \varphi^2 \rangle^{1/2}$  for the internal motion and some measures of agreement,  $R = [\Sigma(\Delta U_{ij})^2 / \Sigma(U_{ij})^2]^{1/2}$  and  $\langle (\Delta U_{ij})^2 \rangle^{1/2}$ )

	1 (95K)		2 (95K)		4 (173K)	
	A	B	A	B	A	B
L <sub>1</sub> (deg <sup>2</sup> )	13.70	13.37	11.08	8.80	26.7	23.3
L <sub>2</sub>	7.10	3.24	8.56	7.08	16.1	15.1
L <sub>3</sub>	4.69	2.39	4.93	1.84	15.0	2.2
T <sub>1</sub> (Å <sup>2</sup> · 10 <sup>-4</sup> )	120	126	106	109	312	316
T <sub>2</sub>	98	104	106	108	279	293
T <sub>3</sub>	90	84	100	103	212	230
$\langle \varphi^2 \rangle^{1/2}$ (deg)	—	5.9(4)	—	5.8(4)	—	10.3(9)
		7.0(3)				9.6(9)
R(U <sub>ij</sub> )	0.173	0.096	0.113	0.082	0.156	0.120
$\langle (\Delta U)^2 \rangle^{1/2}$ (Å <sup>2</sup> · 10 <sup>-4</sup> )	19	11	13	9	48	37

In fact, if we are prepared to make two further assumptions we can even derive a value for the energy barriers to the internal rotations in question. The first assumption is that the derived force constant is truly for the internal molecular motion, *i. e.* that the effect of the crystal environment is negligible. The second assumption is that the potential energy for rotation of the NO<sub>2</sub>-group about its C–N axis is a simple cosine function  $E = V(1 - \cos 2\phi)/2$ , with energy barrier  $V$ . The quadratic force constant is then  $k = (\partial^2 E)/(\partial \phi^2) = 2V$ , leading to a barrier of about 9 kcal mol<sup>-1</sup> for rotation of the NO<sub>2</sub>-groups in **2**. This can only be a rough estimate but it is much larger than the reported barrier height of  $3.3 \pm 1.5$  kcal mol<sup>-1</sup> for rotation of the NO<sub>2</sub>-group in nitrocyclopropane [27]. On the other hand it is the same order of magnitude as the value of about 12.5 kcal mol<sup>-1</sup> for the activation energy of the process that makes the two *cis*- or *trans*-protons of each cyclopropane ring equivalent in pairs (see Section 3). Perhaps the approximations may not be so bad after all<sup>15)</sup>.

**5. Possible transition states for topomerization of 1,2-dinitroethanes.** – Unless 1,1'-dinitro-bicyclopropyl (**2**) has an equilibrium conformation with C<sub>2v</sub> or C<sub>2h</sub>-symmetry (see **17a**), the four AB pairs of geminal protons are not all equivalent. In an equilibrium conformation with C<sub>2</sub>-symmetry, as observed in the crystal structure, there are two pairs of homotopic H-atoms *cis* and two pairs *trans* to a NO<sub>2</sub>-group. The <sup>1</sup>H-NMR.-spectrum observed at –55° (Fig. 2) is consistent with this type of structure. Figure 2 also shows that, on warming, the four *cis* H-atoms become equivalent on the NMR. time-scale, and so do the four *trans* ones, the activation energy being about 12 kcal mol<sup>-1</sup>.

Rotation about the central C,C-bond of **2**, the internal motion which is required for this equivalence, is probably coupled to rotation about the C,N-bonds. For otherwise, if the NO<sub>2</sub>-groups were to maintain the bisected conformation in which they are observed in the crystal, an intolerably short O...O contact would be produced at N–C–C–N torsion angle 0° (see **19**) or else a pair of intolerably short O...H contacts at N–C–C–N torsion angles of about ±150° (see **20** for one of such a pair). These short contacts can be alleviated by drastic bond-angle deformations or by rotation of the NO<sub>2</sub>-groups. The barrier to rotation about the C,N-bonds in **2** is not known, but the analysis of the vibrational ellipsoids in the crystal structure (see Section 4.5) suggests it may be of the same order of magnitude as the NMR. activation energy itself.



The question as to whether or not the C–C rotation is coupled to the rotation of the NO<sub>2</sub>-groups is amenable to experimental investigation involving <sup>17</sup>O-labelling on the NO<sub>2</sub>-groups of **2**. From temperature-dependent <sup>17</sup>O-NMR. measurements it should be possible to estimate the activation energy for rotation about the C,NO<sub>2</sub>-bond. If this rotation is also the rate-determining step for rotation about the central

<sup>15)</sup> Similar arguments have been used to derive rotation barriers of methyl [38] and ammonium groups [39] in crystals from librational amplitudes based on neutron-diffraction data.

C,C-bond, the two rates should be the same. Experiments in this direction are under way in our laboratories.

We expect the activation energy for the open chain compound **1** to be lower than that of **2** because the NO<sub>2</sub>-groups adopt the perpendicular conformation, which does not lead to very short contacts either in the synplanar or antiplanar arrangements. For the bicyclobutyl **4** and the bicyclopentyl derivative **5** the activation energies should be intermediate.

### Experimental Part

**1. General remarks.** – For spectrometers, apparatuses, techniques, and reagents used, see our previous papers [1] [2] [7] [9]. The dihaloalkanes were all supplied by *Chemische Fabrik Kalk* (Germany), nitrocyclopentane (**8**) was purchased from *Fluka AG*, 2,3-dimethyl-2,3-dinitrobutane (**1**) from *Aldrich Chemical Company*.

**2. Preparation of  $\omega$ -halonitroalkanes.** – The *1-halo-3-nitroalkanes* were prepared by modification of a known procedure [6] from the corresponding dihalides and NaNO<sub>2</sub> in dimethylsulfoxide (DMSO). The yields can be greatly improved if the reaction is quenched with water earlier than recommended [6].

*Preparation of 1-chloro-3-nitropropane.* A vigorously stirred solution of 280 g of 1-bromo-3-chloropropane (175 ml, 1.77 mol) in 700 ml DMSO was kept at 16° by cooling with ice while 106 g (1.53 mol) of dried (2 h, 130°) NaNO<sub>2</sub> was added in 10 portions within 20 min. The temperature of the mixture rose suddenly to 30° (ca. 10 min after completion of the salt addition, often accompanied by precipitation). At this moment, 1 l of water was poured into the reaction mixture. Transfer to a separatory funnel containing another l of water and workup as described [6] gave 137 g of unreacted 1,3-dihalide and 73 g (40%) of 1-chloro-3-nitropropane, b.p. 78–83°/17 Torr.

In a similar way, the following 1-halo-3-nitroalkanes (>95% pure) were obtained in the yields (y.) and with the recoveries of dihalides (r.) as stated: *1-chloro-2-methyl-3-nitropropane* from 1-bromo-3-chloro-2-methylpropane (y. 21%, r. 55%), b.p. 84–85°/14 Torr. – *1-Chloro-4-nitrobutane* was obtained according to ref. [42]. – *1-Bromo-4-nitrobutane* from 1,4-dibromobutane (y. 27%), b.p. 59–60°/0.015 Torr. – *1-Bromo-5-nitropentane* from 1,5-dibromopentane (y. 27%, r. 33%), b.p. 73–74°/0.02 Torr. – *1-Bromo-6-nitrohexane* from 1,6-dibromohexane (y. 27%, r. 30%), b.p. 102–104°/0.25 Torr.

*1-Iodo-3-nitropropane* (88–95%) and *1-iodo-2-methyl-3-nitropropane* (84%) were obtained from above chloro-derivatives by a *Finkelstein* reaction in acetone, following the procedure in ref. [6].

**3. Cyclizations of  $\omega$ -halonitroalkanes with potassium carbonate in benzene or toluene.** – *Preparation of nitrocyclopropane (6).* A vigorously stirred mixture of 96 g (0.45 mol) of 1-iodo-3-nitropropane, 112 g (0.8 mol) of K<sub>2</sub>CO<sub>3</sub> (dried by keeping at 130° for 4 h), and 400 ml benzene was refluxed for 2.75 h. Filtering, washing the filter-cake three times with 50 ml benzene, carefully removing the benzene down to a volume of 70 ml through a 20 cm *Vigreux* column, and distilling furnished 18.4 g (53%) of **6**, b.p. 32–35°/11 Torr., pure by GC, IR. and <sup>1</sup>H-NMR. (cf. [43]).

*Preparation of trans-1-methyl-2-nitrocyclopropane (7).* A mixture of 45.2 g of 1-iodo-2-methyl-3-nitropropane (0.20 mol), 40 g K<sub>2</sub>CO<sub>3</sub>, and 250 ml benzene was stirred and refluxed for 20 h. After addition of 200 ml water the organic layer was dried (MgSO<sub>4</sub>) and distilled through a column as above. Yield of **7**: 15.5 g (72%), b.p. 44°/12 Torr. – <sup>1</sup>H-NMR. (CCl<sub>4</sub>): 3.92 (d, *t*, *J* = 7 and 3.5, 1H, CHNO<sub>2</sub>); 2.1–1.6 (m, 2H, CH<sub>2</sub> and H–C(3) *cis* to NO<sub>2</sub>); 1.20 (d, *J* = 6, 3H, CH<sub>3</sub>); 0.97 (m, 1H, H–C(3) *trans* to NO<sub>2</sub>). For other physical data see [11d].

*Preparation of nitrocyclopentane (8) and nitrocyclohexane (9).* They were obtained from the corresponding bromonitroalkanes in only low yields of 28 and 20%, respectively, following the K<sub>2</sub>CO<sub>3</sub>-procedure described for the preparation of **6** and **7**. The physical data of **8** and **9** resembled those given in the literature [5].

*Preparation of (nitromethyl)cyclopropane (10) from 1-chloro-4-nitrobutane and LDA.* A solution of LDA was prepared in the usual way from 30 mmol each of diisopropylamine and butyllithium (1.6M in hexane) in a mixture of 70 ml THF and 10 ml hexamethylphosphoric acid triamide (HMPT). 1-Chloro-4-nitrobutane (2.06 g, 15 mmol) was added at –78° within 5 min (orange colour). Stirring and cooling at

–78° were continued overnight. A large amount of precipitate was formed, and the reaction quenched by addition of 5 ml HOAc. The solvents were removed at reduced pressure in a rotatory evaporator (20°/20 mm), the residue was triturated with 200 ml pentane. The pentane solution was washed with 7 × 50 ml water, dried over Na<sub>2</sub>SO<sub>4</sub> and distilled under normal pressure. The residual liquid distilled at 53–63°/12 Torr. Yield of **10**: 0.62 g (41%, purity by GC.: 99%). – IR. (film): 3095, 3008, 2960, 2940, 2910, 1550s, 1432, 1397s, 1368s, 1310, 1240, 1200, 1160, 1105, 1060, 1030s, 1010, 940, 895, 840s, 810, 725, 705, 622. – <sup>1</sup>H-NMR. (CCl<sub>4</sub>): 4.20 (*d*, *J* = 7.5, 2H, CH<sub>2</sub>NO<sub>2</sub>); 1.7–1.2 (*m*, 1H, CH–CH<sub>2</sub>NO<sub>2</sub>); 0.85–0.60 (*m*, 2H); 0.50–0.20 (*m*, 2H).

**Preparation of ethyl 1-[(cyclopropyl-(1-ethoxycarbonylcyclopropyl)hydroxy)methyl]cyclopropanecarboxylate (11).** To a LDA solution (from 50 mmol of diisopropylamine, 50 mmol of butyllithium in 70 ml THF) was added dropwise at –78° a solution of 5.707 g (50 mmol) ethyl cyclopropanecarboxylate. The reaction mixture was poured into water after 1/2 h. at –78° and extracted with CH<sub>2</sub>Cl<sub>2</sub>. The crude product isolated after washing the organic phase with water, drying over MgSO<sub>4</sub>, and evaporating the solvent was distilled under reduced pressure (110°/0.1 Torr.) to give **11** as colourless, analytically and gas-chromatographically pure, sole product. – IR. (CCl<sub>4</sub>): 3560, 3455, 3090, 2980, 2940, 2900, 2870, 1710, 1550, 1320, 1150, 1040, 960, 900, 800–730, 600. – <sup>1</sup>H-NMR. (CDCl<sub>3</sub>): 0.25 (*m*, 2H); 0.45 (*m*, 2H); 0.70–1.5 (*m*, 16H); 4.12 (*qa*, 4H, 2CH<sub>2</sub>O). – <sup>13</sup>C-NMR. (CDCl<sub>3</sub>): 0.78 (*t*); 10.11 (*t*); 11.29 (*t*); 13.96 (*qa*); 14.19 (*d*); 32.66 (*t*); 60.45 (*t*); 69.72 (*s*, C OH); 174.16 (*s*, C=O). – MS. (72 eV): 296 (1), 268 (1), 251 (10), 223 (4), 209 (8), 195 (5), 184 (12), 183 (100), 159 (9), 137 (62), 113 (9), 69 (56), 41 (16). – Mol.-weight (osmom. in CH<sub>2</sub>Cl<sub>2</sub>): Calc. 296.35 Found 299.47.

C<sub>16</sub>H<sub>24</sub>O<sub>5</sub> Calc. C 64.84 H 8.16% Found C 64.67 H 8.08%

**4. Deprotonation and dimerization of 6 and 7 to give the bicyclopropyl derivatives, 2, 3 and 16.** – *Deprotonation of nitrocyclopropane.* To a solution of LDA in THF, prepared from 5 ml (36 mmol) diisopropylamine and 20 ml of a 1.5M BuLi in hexane (30 mmol) in 100 ml of THF (–78° to –30°, 30 min), 2.64 g (30 mmol) of neat nitrocyclopropane were added within 10 min. A deep red solution resulted.

When this solution was quenched with water or D<sub>2</sub>O, it turned blue, and work-up yielded mixtures of the dinitro and nitro-nitroso compounds **2** and **3**. When transferred to an ESR. tube, the red solution showed the radical spectrum of *Figure 1* (see also below). The highest yields of the blue nitro-nitroso compound **3** were obtained with water (**2/3** ca. 1:1), CO<sub>2</sub>(1:2), C<sub>6</sub>H<sub>5</sub>COCl(1:2), while electrophiles capable of undergoing one-electron transfer (e. g. I<sub>2</sub>, *p*-NO<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>Cl (→ diarylethane), quinone) gave mainly the dinitro compound **2**.

**Preparation of 1,1'-dinitrobicyclopropyl (2).** The above red solution from 30 mmol of nitrocyclopropane was treated with 1.62 g (15 mmol) of *p*-benzoquinone, a solution of which in 20 ml THF was added within 15 min at –78°. The first drop of the oxidant turned the solution blue. The mixture was left overnight, quenched with 6 ml of acetic acid at –30°, freed from solvents in a rotatory evaporator, and triturated with 450 ml of CH<sub>2</sub>Cl<sub>2</sub>. The solution was washed five times with 100 ml each of water, dried (MgSO<sub>4</sub>) and concentrated to give 2.30 g (87%) of crystalline **2**. Recrystallization from ethanol and sublimation (80°/0.05 mm) yielded 1.56 g (59%) of **2**, m.p. 127.7–127.9°. – IR. (CCl<sub>4</sub>): 3022, 2922, 2900, 2850, 1550s, 1440, 1407, 1358s, 1350s, 1152, 1076, 1041, 885, 865, 644. – <sup>1</sup>H-NMR. (CDCl<sub>3</sub>): 2.15 (*d* × *d*, 4H); 1.24 (*d* × *d*, 4H); see *Figures 2* and *3*. – <sup>13</sup>C-NMR. (CDCl<sub>3</sub>): 88.98 (*s*, C–NO<sub>2</sub>); 19.26 (*t*, CH<sub>2</sub>). – Mol.-weight (osmom. in CH<sub>2</sub>Cl<sub>2</sub>): Calc. 172.14 Found 172.

C<sub>6</sub>H<sub>8</sub>N<sub>2</sub>O<sub>4</sub> (172.14) Calc. C 41.86 H 4.68 N 16.28% Found C 41.72 H 4.62 N 16.06%

**Preparation of 1-nitro-1'-nitroso-bicyclopropyl (3).** To a red solution (from 2.8 ml of diisopropylamine, 15 mmol of BuLi, 15 mmol **6**, in 40 ml THF) was added dropwise at –78° 2.02 g (15 mmol) benzoylchloride (within 15 min). A violet solution resulted. After warming up overnight, the solution was blue and salts had deposited. After removal of the solvents in a rotatory evaporator, 40 ml of 10% aq. acetic was added, followed by three extractions with 100 ml each of ether. The combined, deep green solution was washed with aq. NaHCO<sub>3</sub>-solution (3 × 40 ml), dried over MgSO<sub>4</sub>, and evaporated to give a blue oil. Chromatography on 50 g SiO<sub>2</sub> (Merck 60–230–400 mesh) with CCl<sub>4</sub>/CHCl<sub>3</sub> 1:1 furnished 0.55 g (43%) of blue **3**, m.p. 63.8–64.8 (from ethanol) and 0.21 g of the slower-moving, colourless **2**. The deep blue nitroso compound **3** is readily oxidized to the colourless dinitro-derivative **2** (see subsequent procedure). At normal temperature, **3** shows the following NMR.-spectra. <sup>1</sup>H-NMR. (CDCl<sub>3</sub> + CCl<sub>4</sub>): two AA'BB' systems which look like four first-order *d* × *d*, *J* ≈ 9 and 6, at 2.75, 2.00, 1.60 and 0.90. – <sup>13</sup>C-NMR. (CDCl<sub>3</sub>): 65.25s, 62.60s, 20.58t, 16.88t.

**Oxidation of the nitro-nitroso-compound 3 to the dinitro-derivative 2 with periodate.** To a solution of 0.92 g (ca. 5 mmol) of a (2/3)-mixture in 10 ml THF was added 1.07 g (4.7 mmol) of periodic acid. After stirring overnight, the blue solution had turned colourless, and the THF was evaporated off. The residue was treated with 10 ml of a thiosulfate solution and 20 ml  $\text{CH}_2\text{Cl}_2$ . The combined organic layers were washed with water, dried over  $\text{MgSO}_4$ , and concentrated. Yield of **2** after one recrystallization from ethanol: 0.59 g (64%).

**ESR-Measurement.** Part of a solution prepared from 0.67 g (6 mmol) of diisopropylamine, 6.0 mmole of BuLi (1.6M hexane), 0.522 g (6 mmol) of **6** in 20 ml of THF under Ar was transferred through a vacuum system directly into an ESR. tube cooled with liquid  $\text{N}_2$ . THF was added, so that a ca. 0.05 molar solution of the deprotonated nitrocyclopropane resulted. The ESR. spectrum was first recorded at  $-80^\circ$ , then at higher temperatures, with a Varian E. 12 spectrometer.

**Preparation of 1,1'-dinitro-2,2'-dimethylbicyclopropyl (16).** As described above for the non-methylated derivative, 1.52 g (15 mmol) of **7** were added to an equimolar amount of LDA in 50 ml THF at  $-78^\circ$  to give a red solution to which 0.81 g (7.5 mmol) benzoquinone (in 20 ml THF) were added, causing a colour change to dark blue. After 1 h at  $-78^\circ$ , the solvents were removed, 100 ml  $\text{H}_2\text{O}$  were added to the residue, followed by three extractions with ether (250 ml total). The combined organic layers were washed with 50 ml each of 10% HCl-solution and of water, dried over  $\text{MgSO}_4$ , and concentrated to give 1.08 g (72%) of colourless crystals. M.p. after recrystallization from benzene/hexane 1:1  $70-74.2^\circ$ . Column chromatography (30 g  $\text{SiO}_2$ ,  $\text{CHCl}_3/\text{CCl}_4$  1:1) provides crystals of **16** of m.p.  $72.0-76.5^\circ$ . –  $^1\text{H-NMR}$ . ( $\text{CDCl}_3$ ): 2.15 ( $d \times d$ , 1H); 1.9–1.5 ( $m$ , 1H); 1.5–1.2 ( $m$ , 4H).

**4. The persubstituted dinitroethanes 4 and 5.** – **Preparation of 1,1'-dinitrobicyclobutyl (4).** 1-Bromo-1-nitrocyclobutane was prepared as described in reference [5], see Eqn. 5. – IR. (film): 3105, 2965, 2890, 1550s, 1425, 1360s, 1250, 1215, 1125, 1065, 855, 825, 735, 710, 610. –  $^1\text{H-NMR}$ . ( $\text{CCl}_4$ ): three very complex  $m$ , centered at 3.2, 2.85, and 2.1 (1:1:1). – The dimerization of 1-bromo-1-nitrocyclobutane (3.6 g, 20 mmol) was achieved in the following way: A solution in 50 ml THF was stirred in a  $-100^\circ$  bath and combined with 10 mmol of BuLi (pentane solution, addition time 15 min, vigorous stirring). After 4 h at  $-78^\circ$  and 3 h at  $+20^\circ$  a colourless precipitate had separated. The solvents were removed in a rotatory evaporator, the residue treated with 50 ml  $\text{H}_2\text{O}$  and extracted four times with a total of 200 ml pentane. Washing with water, drying over  $\text{Na}_2\text{SO}_4$  and removing the solvent gave a solid mass which was chromatographed (30 g  $\text{SiO}_2$ , Merck 60, 70–230 mesh, toluene as eluant): 0.52 g of starting material ( $R_f$  0.58,  $\text{SiO}_2$ , TLC., toluene) and 0.98 g (68%) **4** ( $R_f$  0.37). An analytical sample was obtained by recrystallization (ether/pentane) and subsequent sublimation ( $60^\circ/10$  Torr.), m. p.  $72.7-73.1^\circ$ . – IR. ( $\text{CCl}_4$ ): 3005, 2962, 2880, 1547s, 1450, 1360s, 1260, 1252, 1125, 1100, 1070, 872, 860s, 822s, 780, 730, 710  $\text{cm}^{-1}$ . –  $^1\text{H-NMR}$ . ( $\text{CCl}_4$ ): 3.7–1.7 very complex  $m$  (cf. Fig. 3). –  $^{13}\text{C-NMR}$ . ( $\text{CDCl}_3$ ): 91.4 ( $s$ , 2C); 30.0 ( $t$ , 4C); 14.8 ( $t$ , 2C). – Mol.-weight (osmom.,  $\text{CH}_2\text{Cl}_2$ ): Calc. 200.19 Found 200.03.

$\text{C}_8\text{H}_{12}\text{N}_2\text{O}_4$  (200.19) Calc. C 47.99 H 6.04 N 13.99% Found C 47.91 H 6.06 N 13.99%

**Preparation of 1,1'-dinitrobicyclopentyl (5).** A solution of lithium methoxide was prepared by adding 11 mmol of BuLi (1.5M in hexane) to 20 ml of dry  $\text{CH}_3\text{OH}$  at  $0^\circ$ . Nitrocyclopentane (**8**, 1.19 g, 10 mmol) was injected to furnish a slightly yellow solution of the lithium nitronate which was combined in small portions with 4.8 g (10.8 mmol) of solid  $\text{Pb}(\text{OAc})_4$  (Fluka). Towards the end of addition, the solution turned green, after 15 min at  $0^\circ$  and 30 min at  $25^\circ$  the reaction mixture was poured into 150 ml  $\text{EtOEt}/\text{H}_2\text{O}$  2:1 giving a blue organic and an orange inorganic layer. The ether solution was washed twice each with 50 ml aq.  $\text{NaHCO}_3$ - and sat.  $\text{NaCl}$ -solution and dried over  $\text{Na}_2\text{SO}_4$ . The crude product (1.3 g) obtained after evaporation of the solvents was mixed with pentane which caused colourless crystals to deposit, 200 mg of **5** (17%), m.p.  $80.8-81.3^\circ$  (from pentane/ether). Since this product has only been briefly mentioned in the literature [3], we have fully characterized it. – IR. ( $\text{CCl}_4$ ): 2970s, 2880s, 1550 very  $s$ , 1470, 1455s, 1435s, 1355s, 1335, 1190, 1045, 850. –  $^1\text{H-NMR}$ . ( $\text{CDCl}_3$ ): 2.8–2.5 ( $m$ , 4H); 2.2–1.4 ( $m$ , 12H), see also Figure 3. – Mol.-weight (osmom. in  $\text{CH}_2\text{Cl}_2$ ) Calc. 228.24 Found 223.

$\text{C}_{10}\text{H}_{16}\text{N}_2\text{O}_4$  (228.24) Calc. C 52.62 H 7.07 N 12.27% Found C 52.49 H 7.11 N 12.26%

## REFERENCES

- [1] a) Review: *D. Seebach, E. W. Colvin, F. Lehr & T. Weller*, *Chimia* 33, 1 (1979).  
b) *E. W. Colvin, A. K. Beck, B. Bastani, D. Seebach, Y. Kai & J. D. Dunitz*, *Helv. Chim. Acta* 63, 697 (1980).
- [2] *E. W. Colvin, A. K. Beck & D. Seebach*, *Helv. Chim. Acta* 64, 2264 (1981); *E. W. Colvin, A. D. Robertson, D. Seebach & A. K. Beck*, *J. Chem. Soc., Chem. Commun.* 1981 952.
- [3] a) *N. Kornblum, S. D. Boyd, H. W. Pinnick & R. G. Smith*, *J. Am. Chem. Soc.* 93, 4316 (1971).  
b) Review: *N. Kornblum*, *Angew. Chem.* 87, 797 (1975); *Angew. Chem. Int. Ed.* 14, 734 (1972).
- [4] *A. H. Pagano & H. Shechter*, *J. Org. Chem.* 35, 295 (1970).
- [5] *D. C. Iffland, G. X. Criner, M. Koral, F. J. Lotspeich, Z. B. Papanastassiou & S. M. White*, *J. Am. Chem. Soc.* 75, 4044 (1953); *D. C. Iffland & G. X. Criner*, *ibid.* 75, 4047 (1953).
- [6] *G. M. Lampman, D. A. Horne & G. D. Hager*, *J. Chem. Engin. Data* 14, 396 (1969).
- [7] *R. Henning, F. Lehr & D. Seebach*, *Helv. Chim. Acta* 59, 2213 (1976); *D. Seebach, R. Henning, F. Lehr & J. Gonnermann*, *Tetrahedron Lett.* 1977 1161; *D. Seebach, R. Henning & J. Gonnermann*, *Chem. Ber.* 112, 234 (1979); *D. Seebach, R. Henning & T. Mukhopadhyay*, *Chem. Ber.*, in press.
- [8] *F. G. Bordwell & J. E. Bartness*, *J. Org. Chem.* 43, 3101 (1978).
- [9] *D. Seebach & F. Lehr*, *Helv. Chim. Acta* 62, 2239 (1979).
- [10] Review: *F. G. Bordwell*, *Pure Appl. Chem.* 49, 963 (1977).
- [11] a) *P. W. K. Flanagan, H. W. Amburn, H. W. Stone, J. G. Traynham & H. Shechter*, *J. Am. Chem. Soc.* 91, 2797 (1969); b) *W. T. van Wijnen, H. Steinberg & T. J. de Boer*, *Tetrahedron*, 28, 5423 (1972); c) *F. G. Bordwell, N. R. Vanier, W. S. Matthews, J. B. Hendrickson & P. L. Skipper*, *J. Am. Chem. Soc.* 97, 7160 (1975); d) *F. G. Bordwell, J. E. Bartmess & J. A. Hautala*, *J. Org. Chem.* 43, 3113 (1978).
- [12] *A. Greenberg & J. F. Liebman*, 'Strained Organic Molecules', Academic Press, New York, San Francisco, London 1978 and references therein; *D. Wendisch*, 'Methoden der Organischen Chemie (Houben-Weyl), Carbocyclische Dreiring-Verbindungen', Georg Thieme Verlag, Stuttgart 1971.
- [13] a) *M. J. Haire & R. L. Harlow*, *J. Org. Chem.* 45, 2264 (1980). b) *D. Felix & A. Eschenmoser*, *Angew. Chem.* 80, 197 (1968); *Angew. Chem. Int. Ed.* 7, 224 (1968).
- [14] *C. H. Depuy*, *Acc. Chem. Res.* 1, 33 (1968); *R. B. Woodward & R. Hoffmann*, *Angew. Chem.* 81, 797 (1969); *Angew. Chem. Int. Ed.* 8, 781 (1969).
- [15] *L. J. Altman & T. R. Erdman*, *Tetrahedron Lett.* 1970, 4891.
- [16] *D. Seebach, R. Dammann, H. J. Lindner & B. Kitschke*, *Helv. Chim. Acta* 62, 1143 (1979); *H. J. Lindner, B. Kitschke, M. Liesner & D. Seebach*, *Helv. Chim. Acta* 60, 1151 (1977), and references cited therein.
- [17] *M. P. Periasamy & H. M. Walborsky*, *J. Am. Chem. Soc.* 99, 2631 (1977); *H. M. Walborsky & M. P. Periasamy*, *J. Am. Chem. Soc.* 96, 3711 (1974); *G. Boche, K. Buckl, D. Martens, D. R. Schneider & H.-U. Wagner*, *Chem. Ber.* 112, 2961 (1979).
- [18] *H. M. Walborsky & M. P. Periasamy*, *J. Am. Chem. Soc.* 96, 3711 (1974); *U. Schöllkopf, K.-W. Henneke, K. Madawinata & R. Harms*, *Justus Liebigs Ann. Chem.* 40 (1977).
- [19] *P. L. Creger*, Abstracts, 11th ACS Midwest Meeting, Carbondale, Ill., Oct. 30–31, 1975; *C. Ainsworth & Y. N. Kuo*, *J. Organomet. Chem.* 46, 73 (1972); *J. Wemple*, *Tetrahedron Lett.* 1975 3255; *P. Knochel & D. Seebach*, *Nouv. J. Chim.* 5, 75 (1981).
- [20] *M. Schlosser & P. Schneider*, *Helv. Chim. Acta* 63, 2404 (1980).
- [21] *P. Buck, R. Gleiter & G. Köbrich*, *Chem. Ber.* 103, 1431 (1970).
- [22] *D. Seebach & D. Enders*, *Angew. Chem.* 87, 1 (1975); *Angew. Chem. Int. Ed.* 14, 15 (1975); *D. Seebach, R. Dach, D. Enders, B. Renger, M. Jansen & G. Brachtel*, *Helv. Chim. Acta* 61, 1622 (1978).
- [23] *P. Main, L. Lessinger, M. M. Woolfson, G. Germain & J. P. Leclercq*, MULTAN 77. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data. Universities of York, England, and Louvain, Belgium 1977.
- [24] *H. A. Bent*, *Chem. Rev.* 60, 276 (1960).
- [25] *P. Murray-Rust, H. B. Bürgi & J. D. Dunitz*, *J. Am. Chem. Soc.* 97, 921 (1975).
- [26] *J. Eraker & C. Rømming*, *Acta Chem. Scand.* 21, 2721 (1967); see also *W. Luttke, A. de Meijere, H. Wolff, H. Ludwig & H. W. Schrötter*, *Angew. Chem.* 78, 141 (1966); *O. Bastiansen & A. de Meijere*, *ibid.* 142.
- [27] *A. R. Mochel, C. O. Britt & J. E. Boggs*, *J. Chem. Phys.* 58, 3221 (1953).
- [28] *C. Schrumpf & P. Süss*, *Chem. Ber.* 105, 3041 (1972).
- [29] *R. Hoffmann & R. B. Davidson*, *J. Am. Chem. Soc.* 93, 5699 (1971).



- [30] *R. Hoffmann*, *Tetrahedron Letters*, 1970, 2907.
- [31] *F. H. Allen*, *Acta Crystallogr. B36*, 81 (1980); *R. Usha & K. Venkatesan*, *ibid.* 335.
- [32] *J. D. Dunitz & P. Seiler*, *Acta Crystallogr. B29*, 598 (1973).
- [33] *K. N. Trueblood, R. E. Rosenfield & J. D. Dunitz*, *Acta Crystallogr. A34*, 828 (1978).
- [34] *V. Schomaker & K. N. Trueblood*, *Acta Crystallogr. B24*, 63 (1968).
- [35] *F. L. Hirshfeld*, *Acta Crystallogr. A32*, 239 (1976).
- [36] *R. Amstutz & J. D. Dunitz*, unpublished results.
- [37] *J. D. Dunitz & D. N. J. White*, *Acta Crystallogr. A29*, 93 (1973).
- [38] *E. O. Schlemper, W. C. Hamilton & S. J. La Placa*, *J. Chem. Phys.* 54, 3990 (1971).
- [39] *T. F. Koetzle, M. S. Lehmann, J. J. Verbist & W. C. Hamilton*, *Acta Crystallogr. B28*, 3207 (1972).
- [40] Program ORTEP. *C. K. Johnson*, Oak Ridge National Laboratory Report ORNL-3794 (1965).
- [41] Program PLUTO, Cambridge Crystallographic Data Centre, University Chemical Laboratory, Cambridge, England.
- [42] *H. Takayama, S. Yoneda, H. Kitano & K. Fukui*, *Kogyo Kagaku Zasshi* 64, 1153 (1961).
- [43] *K. B. Wiberg, D. E. Barth & P. H. Schertler*, *J. Org. Chem.* 38, 378 (1973).