

## Incipient Nucleophilic Additions. IV. 1,5-Dinitro-3-methyl-3-azabicyclo[3,3,1]nonan-7-one

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$C_9H_{15}N_3O_5$ ,  $M=245.24$ . Two crystalline modifications were obtained. (A) Monoclinic,  $P2_1/c$ ,  $a=8.018$ ,  $b=20.247$ ,  $c=8.346$  Å,  $\beta=123.97^\circ$ ,  $Z=4$ ,  $D_x=1.434$  g cm $^{-3}$ . (B) Orthorhombic,  $Pccn$ ,  $a=18.877$ ,  $b=11.031$ ,  $c=10.707$  Å,  $Z=8$ ,  $D_x=1.446$  g cm $^{-3}$ . Both structures show high thermal motion (or disorder), especially of the nitro groups. The bicyclo[3,3,1]nonane skeleton has the usual chair-chair conformation with  $N \cdots C=O$  distance of 2.76 Å (A) and 2.69 Å (B).

## Introduction

The compound was synthesized by Dr C. Ganter

(ETH, Zürich) and recrystallized from  $CCl_4$  to yield two crystal forms (A) and (B). Details of data collection, structure analysis and refinement were much as in other papers of this series (Kaftory & Dunitz, 1975a): reflexions measured, 1973 (A), 1960 (B); above background, *i.e.*  $>1.5\sigma(I)$ , 1072 (A), 1308 (B); final

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Table 1. 1,5-Dinitro-3-methyl-3-azabicyclo[3,3,1]nonan-7-one: atomic coordinates ( $\times 10^4$ ) and vibrational tensor components ( $\times 10^3$ ) for non-hydrogen atoms (*e.s.d.*'s in parentheses)The  $U_{ij}$  values (Å $^2$ ) correspond to the temperature factor expression  $T = \exp[-2\pi^2(U_{11}h^2a^{*2} \dots + 2U_{12}hka^*b^* \dots)]$ 

## Form (A)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
O	554 (11)	2723 (3)	3596 (11)	125 (6)	44 (4)	112 (5)	1 (7)	94 (10)	-18 (7)
O(1)	6346 (16)	1927 (6)	3443 (21)	140 (9)	136 (10)	368 (18)	-21 (14)	200 (23)	11 (20)
O(2)	6618 (13)	935 (6)	4177 (18)	100 (7)	165 (10)	245 (13)	51 (14)	133 (16)	61 (18)
O(3)	-1138 (8)	611 (3)	-1184 (8)	64 (4)	64 (4)	43 (4)	-3 (7)	22 (7)	-11 (6)
O(4)	-2594 (9)	438 (4)	265 (10)	53 (4)	102 (6)	76 (5)	-27 (8)	32 (8)	-15 (8)
N	2290 (9)	1176 (3)	5373 (9)	49 (4)	45 (4)	50 (4)	0 (7)	35 (7)	1 (7)
N(1)	5749 (11)	1446 (5)	3745 (13)	39 (5)	101 (7)	89 (6)	-10 (10)	43 (9)	-1 (11)
N(2)	-1254 (10)	671 (3)	188 (10)	44 (4)	43 (4)	52 (5)	7 (7)	25 (7)	4 (7)
C(1)	3768 (11)	1483 (4)	3676 (12)	40 (5)	55 (5)	69 (6)	-11 (8)	40 (10)	-11 (9)
C(2)	3124 (13)	2194 (4)	3483 (13)	69 (6)	41 (5)	78 (6)	-19 (9)	55 (11)	-13 (9)
C(3)	983 (13)	2262 (4)	2967 (11)	78 (6)	45 (5)	42 (5)	-2 (9)	41 (10)	-1 (8)
C(4)	-526 (11)	1775 (4)	1620 (11)	47 (5)	43 (4)	51 (5)	12 (8)	32 (8)	13 (8)
C(5)	343 (10)	1078 (4)	1894 (10)	32 (4)	40 (5)	48 (5)	1 (7)	22 (8)	-1 (8)
C(6)	777 (11)	767 (4)	3761 (12)	46 (5)	45 (5)	63 (5)	8 (8)	38 (9)	17 (8)
C(7)	4186 (11)	1156 (4)	5513 (12)	36 (4)	59 (6)	49 (5)	-3 (8)	19 (8)	3 (9)
C(8)	2241 (11)	1080 (4)	1898 (10)	53 (5)	40 (5)	48 (5)	5 (8)	37 (8)	2 (8)
CM	2519 (14)	967 (5)	7156 (12)	83 (6)	61 (6)	60 (6)	7 (10)	51 (11)	12 (9)

## Form (B)

O	577 (2)	-1843 (4)	225 (4)	108 (3)	67 (3)	98 (3)	5 (5)	-66 (6)	-23 (5)
O(1)	1622 (3)	3047 (5)	1241 (7)	148 (5)	72 (3)	196 (7)	-40 (8)	3 (10)	21 (8)
O(2)	1627 (5)	2225 (7)	-447 (7)	423 (14)	172 (7)	114 (5)	-131 (15)	-24 (14)	86 (11)
O(3)	2032 (2)	-1134 (4)	4681 (4)	114 (4)	103 (4)	48 (2)	15 (6)	-20 (5)	18 (5)
O(4)	2765 (2)	-1143 (4)	3148 (4)	54 (2)	74 (3)	91 (3)	10 (5)	-28 (5)	-7 (5)
N	406 (2)	181 (4)	2576 (4)	34 (2)	60 (3)	46 (2)	3 (4)	6 (4)	-5 (5)
N(1)	1514 (4)	2205 (6)	614 (7)	119 (5)	76 (4)	93 (5)	-29 (8)	-31 (9)	42 (8)
N(2)	2181 (3)	-978 (4)	3594 (4)	70 (3)	40 (3)	58 (3)	8 (5)	-21 (6)	-1 (5)
C(1)	1277 (3)	1020 (4)	1225 (5)	51 (3)	40 (3)	51 (3)	-12 (5)	-5 (5)	16 (5)
C(2)	1093 (3)	118 (6)	217 (4)	56 (3)	80 (4)	31 (3)	12 (6)	-1 (5)	-1 (6)
C(3)	982 (3)	-1133 (5)	719 (5)	55 (3)	53 (3)	53 (3)	13 (6)	-10 (6)	-19 (6)
C(4)	1459 (3)	-1552 (4)	1765 (5)	53 (3)	43 (3)	54 (3)	9 (5)	-17 (6)	-10 (5)
C(5)	1590 (2)	-556 (4)	2713 (4)	35 (2)	39 (3)	41 (3)	2 (4)	-6 (5)	0 (5)
C(6)	930 (3)	-277 (5)	3453 (4)	74 (4)	54 (3)	38 (3)	1 (6)	1 (6)	2 (5)
C(7)	619 (3)	1306 (5)	2022 (5)	58 (3)	45 (3)	53 (3)	14 (5)	-11 (5)	-6 (6)
C(8)	1867 (3)	593 (4)	2050 (5)	48 (3)	44 (3)	49 (3)	-2 (5)	-10 (5)	5 (5)
CM	-303 (3)	274 (6)	3153 (6)	53 (4)	119 (5)	66 (4)	17 (7)	12 (7)	-9 (8)

$R$ ,\* 0.086 (*A*), 0.081 (*B*). Final atomic coordinates and temperature factors are listed in Tables 1 and 2.

### Discussion

Analysis of the vibrational ellipsoids in terms of rigid-body motion (Schomaker & Trueblood, 1968) gave poor agreement between observed and calculated  $U_{ij}$  values for both structures. A model in which the nitro groups were allowed to undergo torsional librations about the respective C–N bonds (Dunitz & White, 1973; Huber-Buser, 1974) led to much improved agreement for (*A*) but was still unsatisfactory for (*B*) (Table 3). It is difficult to imagine any kind of non-rigid motion involving planar nitro groups that could account, even qualitatively, for the large difference between the vibration ellipsoids of O(1) and O(2) in (*B*).

In neither form do the nitro group orientations conform to the approximate mirror-symmetry of the sub-

stituted bicyclo[3,3,1]nonane skeleton. One nitro group N(1) closely eclipses C(1)–C(2) in both forms, the torsion angles O(1)–N(1)–C(1)–C(2) being  $-8^\circ$  in (*A*) and  $-11^\circ$  in (*B*). The other nitro group is nearly perpendicular to C(5)–C(4) in (*A*) [torsion angle O(3)–N(2)–C(5)–C(4) =  $96^\circ$ ] but eclipses C(5)–C(6) in (*B*) with an O(3)–N(2)–C(5)–C(6) torsion angle of  $6^\circ$ . The molecules of (*A*) and (*B*) (depicted stereoscopically in Fig. 1) are thus conformational isomers; the potential for rotation of the nitro groups is very flat [barrier only 0.006 kcal mole $^{-1}$  in nitromethane (Tannenbaum, Myers & Gwinn, 1956)] and presumably one orientation or the other is slightly stabilized by packing forces.

The difference in the puckering of the two six-membered rings, already noted for a 3-oxabicyclo[3,3,1]nonan-7-one derivative (Kaftory & Dunitz, 1975*b*), is also observed for the 3-aza derivative. The ring containing the carbonyl group is less puckered than the one containing the N atom, as seen by comparing mean bond angles or torsion angles:

	$\langle\theta\rangle$ ( $^\circ$ )	$\langle\omega\rangle$ ( $^\circ$ )
Ring containing C=O	112.0 ( <i>A</i> ), 111.8 ( <i>B</i> )	50.8 ( <i>A</i> ), 51.8 ( <i>B</i> )
Ring containing N	108.3 ( <i>A</i> ), 108.7 ( <i>B</i> )	62.7 ( <i>A</i> ), 62.0 ( <i>B</i> )

\* Lists of structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31324 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. 1,5-Dinitro-3-methyl-3-azabicyclo[3,3,1]nonan-7-one: fractional coordinates ( $\times 10^3$ ) and isotropic temperature factors for hydrogen atoms

	Form ( <i>A</i> )				Form ( <i>B</i> )			
	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> ( $\text{\AA}^2$ )	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> ( $\text{\AA}^2$ )
HC(2,1)	402 (12)	246 (4)	466 (12)	4.8 (2.2)	62 (3)	42 (5)	27 (6)	3.6 (1.6)
HC(2,2)	324 (12)	243 (4)	237 (12)	6.1 (2.3)	148 (3)	12 (5)	-40 (5)	4.7 (1.5)
HC(4,1)	-165 (12)	178 (4)	158 (12)	5.2 (2.2)	115 (3)	-229 (5)	218 (5)	3.9 (1.5)
HC(4,2)	-93 (12)	190 (4)	49 (12)	3.1 (2.2)	191 (3)	-195 (5)	143 (5)	5.7 (1.5)
HC(6,1)	202 (12)	133 (4)	78 (12)	1.9 (2.2)	107 (3)	40 (5)	411 (6)	7.6 (1.6)
HC(6,2)	265 (12)	65 (4)	196 (12)	3.7 (2.2)	73 (3)	-96 (5)	390 (5)	5.5 (1.6)
HC(7,1)	133 (12)	29 (4)	404 (12)	2.9 (2.3)	17 (3)	168 (5)	149 (5)	7.1 (1.5)
HC(7,2)	-35 (12)	72 (4)	367 (12)	6.7 (2.2)	80 (3)	203 (5)	264 (6)	3.1 (1.5)
HC(8,1)	524 (12)	144 (4)	669 (12)	3.2 (2.2)	234 (3)	41 (5)	156 (5)	3.9 (1.5)
HC(8,2)	465 (12)	72 (4)	556 (12)	3.3 (2.2)	198 (3)	118 (5)	264 (5)	5.3 (1.5)
HM(1)	119 (13)	104 (4)	687 (12)	5.3 (2.1)	-43 (3)	-61 (5)	359 (5)	5.1 (1.6)
HM(2)	344 (12)	124 (4)	804 (12)	4.6 (2.2)	-59 (3)	50 (5)	250 (6)	6.5 (1.5)
HM(3)	291 (12)	51 (5)	742 (12)	3.6 (2.2)	-33 (3)	86 (5)	385 (5)	6.2 (1.6)

Table 3. Summary of results of thermal motion analysis for the two crystal forms of 1,5-dinitro-3-methyl-3-azabicyclo[3,3,1]nonan-7-one

	( <i>A</i> )	( <i>B</i> )
$\langle\sigma^2(U_{ij})\rangle$	0.008 $\text{\AA}^2$	0.005 $\text{\AA}^2$
Rigid-body model $\langle\Delta^2(U_{ij})\rangle^{1/2}$	0.019 $\text{\AA}^2$	0.026 $\text{\AA}^2$
Non-rigid-body model $\langle\Delta^2(U_{ij})\rangle^{1/2}$	0.009 $\text{\AA}^2$	0.019 $\text{\AA}^2$
Eigenvalues of translation tensor ( $\text{\AA}^2$ )	0.049 0.034 0.026	0.172 0.051 0.029
Eigenvalues of libration tensor (rad $^2$ )	0.0085 0.0052 0.0008	0.0175 0.0092 -0.0033*
Mean-square libration amplitudes of nitro groups (rad $^2$ )	0.193 (11) (N1) 0.023 (11) (N2)	0.101 (27) (N1) 0.028 (16) (N2)

\* Note the negative eigenvalue, not significantly different from zero and set to zero for subsequent calculations.

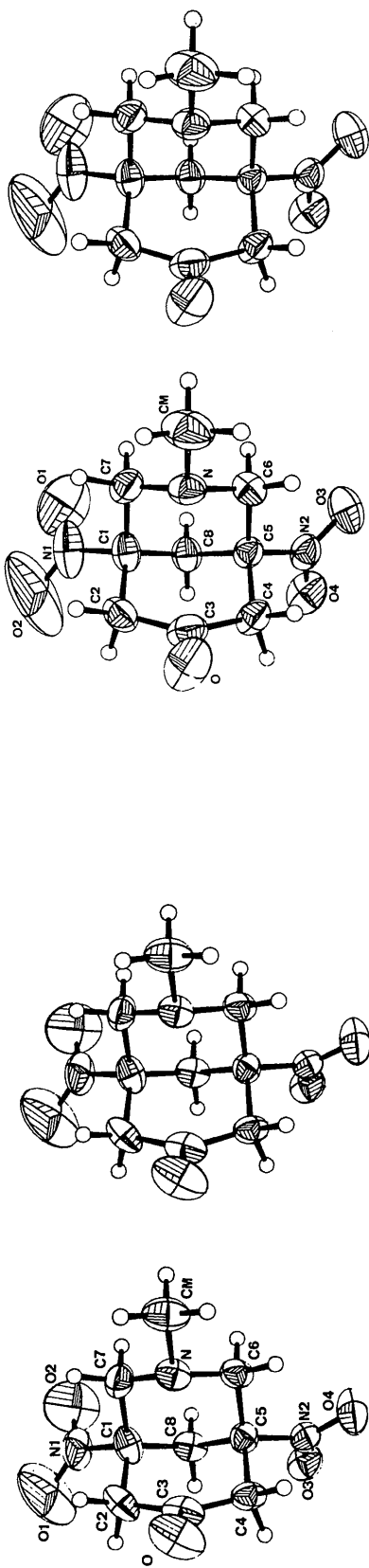


Fig. 1. 1,5-Dinitro-3-methyl-3-azabicyclo[3.3.1]nonan-7-one: stereoscopic view of molecule, showing vibration ellipsoids at the 50% probability level (Johnson, 1965). Left, form (A); right, form (B).

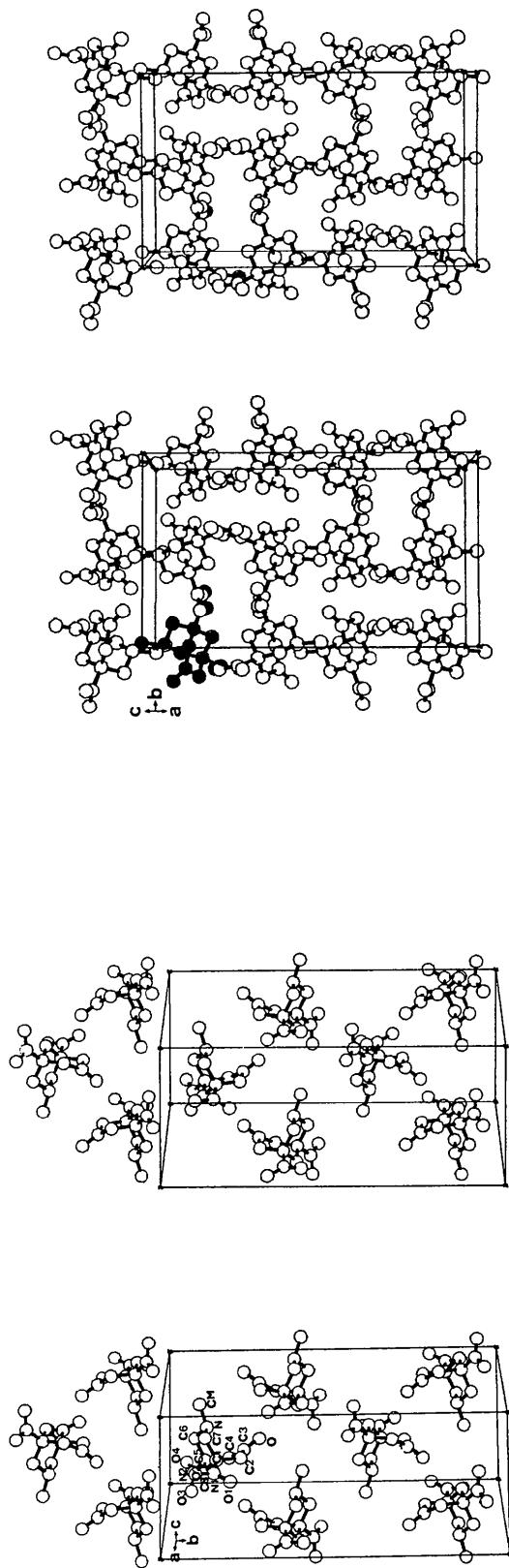


Fig. 2. Stereoscopic view of crystal structures of 1,5-dinitro-3-methyl-3-azabicyclo[3.3.1]nonan-7-one. Left, form (A); right, form (B).

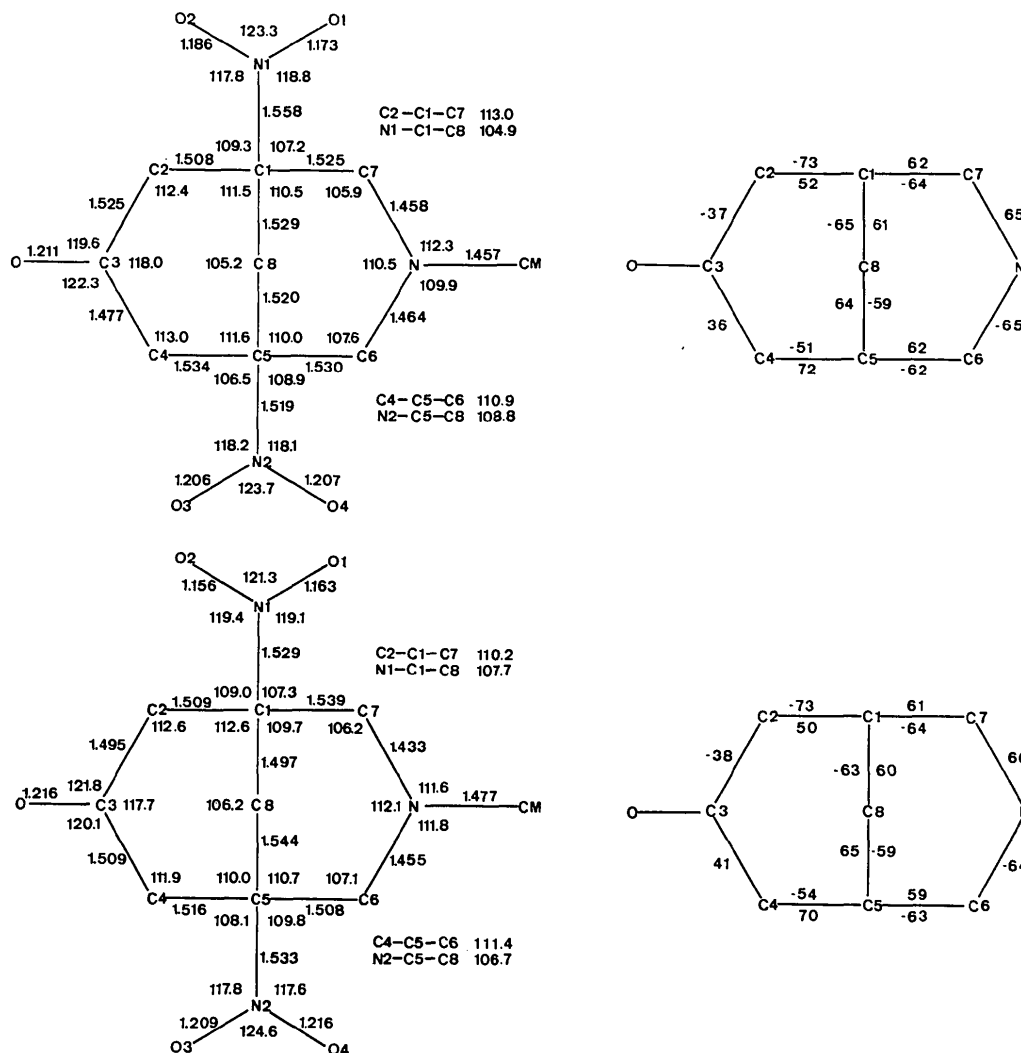


Fig. 3. 1,5-Dinitro-3-methyl-3-azabicyclo[3,3,1]nonan-7-one: left, bond distances and angles; right, torsion angles in the rings. Top, form (A); bottom, form (B).

The  $N \cdots C=O$  distances are 2.76 (A), 2.69 Å (B) and the deviations of the carbonyl C from the plane of its three neighbours are 0.023 (A), 0.054 Å (B), in both cases towards the nucleophile N. It would seem that the nucleophilic addition process has proceeded a little further along the reaction coordinate in (B) than in (A), but it should be kept in mind that the molecular parameters (Fig. 3) in both molecules are not very well determined, mainly on account of the large thermal motion in both crystals. The dimensions cited for the nitro groups are particularly untrustworthy, but even in the rest of the molecule pairs of chemically equivalent bonds and angles appear to differ appreciably [by up to 0.05 Å and 4° in (A), and up to 0.03 Å and 3° in (B)].

The packing arrangements in (A) and (B) are quite different; they are illustrated in Fig. 2.

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