CRYSTAL AND MOLECULAR STRUCTURE OF TWO MODIFICATIONS OF BIS-(2,2,2-TRINITROETHYL)NITRAMINE

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The structures of the two modifications of bis-(2,2,2-trinitroethyl)nitramine have been studied. The crystals of modification A are orthorhombic, a = 22.995, b = 9.506, c = 6.147 Å, d_{calc} = 1.929 g/cm^3, space group $Pn2_1a$, four molecules in the unit cell. The crystals of modification B are monoclinic, a = 18.124, b = 10.362, c = 6.162 Å, γ = 118.65°, d_{calc} = 1.967 g/cm^3, space group $P2_1/a$, four molecules in the unit cell. The structures were determined from the intensities, recorded on a DAR-UM diffractometer, and refined by the method of least squares as far as R = 0.055 and R = 0.058 for 572 and 1988 reflections respectively. The intramolecular and intermolecular contacts in both modifications have been examined. On going from modification A to modification B there is slight loosening of the molecule, leading to a decrease in the intermolecular contacts. The molecules in modification B are less strained and more closely packed, leading to a slight increase in the density of the crystal.

According to published data [1], the density of bis-(2,2,2-trinitroethyl)nitramine (I) is 1.96 g/cm^3. The density of the crystals of the structural analog of compound I, bis-(2-fluoro-2,2-dinitroethyl)nitramine (II), according to our structural study, is 1.933 g/cm^3 [2]. The high value of the density of the crystals of compound I and the difference between their density and that of the crystals of compound II, in the light of the ideas which we are developing regarding the factors determining the density of molecular crystals [2], made it necessary to carry out an x-ray structural study of compound I.

EXPERIMENTAL

The colorless crystals of compound I in the form of transparent parallelepipeds (mp 95-95.5°) were obtained by condensing ammonium acetate with 2,2,2-trinitroethanol followed by N-nitration of the resulting bis-(2,2,2-trinitroethyl)amine [3]. The cell parameters were refined on a DRON-1 diffractometer with a single-

TABLE 1. Coordinates of the Atoms in the Structure of Modification A (× 10^4)

Atom	x	y	z	Atom	x	y	z
C(1)	743(4)	517(11)	6956(17)	O(2)	546(3)	391(8)	2722(13)
C(2)	813(3)	2119(12)	7339(12)	O(3)	1549(4)	3690(9)	8192(16)
C(3)	1716(4)	—696(11)	6121(18)	O(4)	1552(3)	1636(8)	9783(12)
C(4)	1724(4)	—2306(10)	—6442(18)	O(5)	1230(3)	2781(7)	4073(12)
N(1)	1158(4)	—79(9)	5456(14)	O(6)	415(3)	3755(9)	4873(14)
N(2)	994(3)	—226(9)	3288(13)	O(7)	—161(3)	2128(10)	8193(18)
N(3)	821(3)	2954(9)	5195(13)	O(8)	392(4)	3507(12)	9951(14)
N(4)	302(4)	2641(10)	8612(16)	O(9)	1518(4)	—4116(9)	3999(15)
N(5)	1360(4)	2513(8)	8536(16)	O(10)	2248(4)	—2789(10)	3339(15)
N(6)	1837(4)	—3141(11)	4374(16)	O(11)	1258(3)	—3448(8)	9325(14)
N(7)	1191(3)	—2906(9)	7580(1)	O(12)	736(3)	—2688(10)	6602(16)
N(8)	2259(4)	—2681(12)	7832(15)	O(13)	2423(3)	—3891(9)	7736(13)
O(1)	1316(3)	—920(7)	2151(13)	O(14)	2437(4)	—1762(9)	9043(14)

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TABLE 2. Coordinates of the Atoms in the Structure of Modification B ($\times 10^4$)

Atom	x	y	z	Atom	x	y	z
C(1)	1698(1)	6623(2)	3663(5)	O(2)	1626(1)	6279(2)	7872(3)
C(2)	1274(1)	7382(2)	3387(4)	O(3)	382(1)	7316(3)	5825(4)
C(3)	3077(1)	8120(2)	4232(5)	O(4)	1542(1)	8520(2)	6600(4)
C(4)	3628(1)	7622(2)	3760(5)	O(5)	2152(1)	8712(2)	876(4)
N(1)	2346(1)	7210(2)	5030(4)	O(6)	1498(2)	9458(2)	2484(5)
N(2)	2257(1)	6932(2)	7212(4)	O(7)	441(1)	7049(3)	574(4)
N(3)	1693(1)	8649(2)	2150(4)	O(8)	237(2)	5442(2)	2653(5)
N(4)	581(1)	6549(2)	2066(4)	O(9)	4283(1)	8239(3)	6953(4)
N(5)	1034(1)	7760(2)	5468(4)	O(10)	3829(1)	6232(2)	6035(4)
N(6)	3945(1)	7326(2)	5776(4)	O(11)	3770(2)	6381(2)	1064(4)
N(7)	3343(1)	6429(2)	2320(4)	O(12)	2715(1)	5621(2)	2623(5)
N(8)	4288(7)	8699(2)	2534(4)	O(13)	4140(1)	9353(2)	1349(5)
O(1)	2817(1)	7366(2)	8292(3)	O(14)	4879(1)	8772(3)	2843(6)

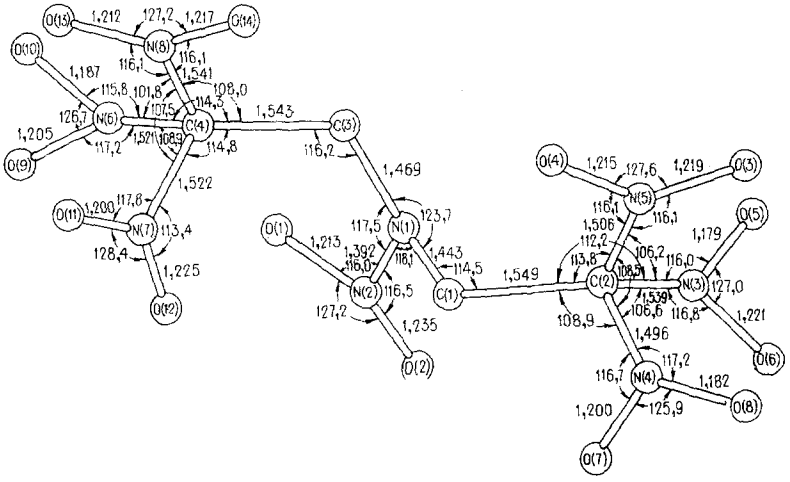

Fig. 1. Bond lengths and valence angles in the molecule of compound IA.

crystal attachment: $C_4H_4N_8O_{12}$, M = 388.1, a = 22.995(20), b = 9.506(8), c = 6.147(4) Å, V = 1343.7 Å^3, d_{meas} = 1.92, d_{calc} = 1.929 g/cm^3, Z = 4, space group $Pn2_1a$.

The intensities of 572 nonzero reflections ($0.04 \leq \sin\theta/\lambda \leq 0.63$) with $I > 2\sigma$ were measured on a DAR-UM automatic diffractometer using CuK_α radiation; no allowance was made for absorption (μ = 18 cm^{-1}). The structure was determined by the direct method using the program "Rentgen-75" under automatic conditions. The refinement by the method of least squares in the block-diagonal anisotropic approximation using a weighting scheme gave finally R = 0.055. The coordinates of the atoms are given in Table 1.* The difference in the values of the density obtained by us and given in [1] lie beyond the limits of error of the determination in both studies. This led to the suggestion of the existence of a second crystallographic modification of compound I having a density of 1.96 g/cm^3. In fact, crystals of the second modification could be obtained by crystallizing compound I from solution in carbon tetrachloride. The method used to study this modification (IB) was the same as that for the less dense form (IA).

The principal crystallographic data for compound IB are: a = 18.124(10), b = 10.362(7), c = 6.162(2) Å, γ = 118.65(3)° V = 1318.88 Å^3, d_{meas} = 1.96, d_{calc} = 1.967 g/cm^3, Z = 4, space group $P2_1/a$, 1998 nonzero independent reflections, R = 0.058. The coordinates of the atoms are given in Table 2.*

DISCUSSION OF THE STRUCTURES

The molecules of compound I in the crystals of the modifications A and B have very similar conformations. Figures 1 and 2 give the geometry of the molecule with the bond lengths and valence angles in the crystals of the two modifications. Tables 3 and 4 give the characteristics of the mean-square planes drawn through

*The tables of temperature factors for compounds IA and IB can be obtained from the authors.

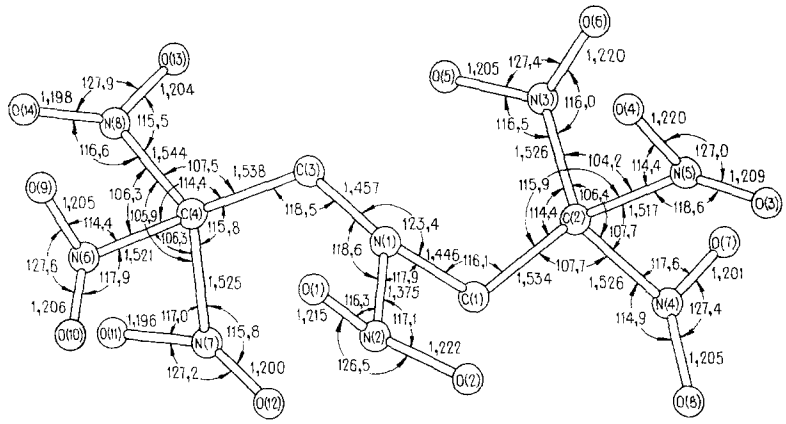

Fig. 2. Bond lengths and valence angles in the molecule of compound IB.

TABLE 3. Mean-square Planes of the Fragments of the Molecule of Modification A

Plane	Atoms	Equation of the plane	Deviations of the atoms from the plane, Å
I	C(1)N(1)C(3)N(2) O(1)O(2)	$10,5x+8,27y+1,12z=0,065$	−0,105, 0,056, 0,063, 0,012, −0,114, 0,087
II	C(2)N(4)O(7)O(8)	$3,0x+6,89y-4,14z=5,17$	0,002, −0,010, 0,004, 0,003
III	C(2)N(5)O(3)O(4)	$12,4x+3,70y+4,58z=8,93$	−0,004, 0,016, −0,006, −0,006
IV	C(2)N(3)O(5)O(6)	$-11,0x+7,13y+2,78z=1,12$	−0,010, 0,041, −0,016, −0,014
V	C(4)N(6)O(9)O(10)	$13,54x+5,93y-3,15z=5,55$	0,007, −0.027, 0,010, 0,010
VI	C(4)N(8)O(13)O(14)	$14,0x-2,76y+4,53z=4,50$	−0,004, 0,018 −0,006, −0,007
VII	C(4)N(7)O(11)O(12)	$3,04x+8,37y+2,78z=3,64$	−0,0003, 0,0001, −0,0005, −0,0006

Angles between the planes, deg

II/III=81	V/VI =78
II/IV=80	V/VII=67
III/IV=68	VI/VII=81

TABLE 4. Mean-square Planes of the Fragments of the Molecule of Modification B

Density	Atoms	Equation of the plane	Deviations of the atoms from the plane, Å
I	O(1)O(2)N(2)N(1) C(3)C(1)	$-12,079x+11,534y+1,039z=6,022$	0,067, −0,074, 0,003, 0,017, −0,066, 0,054
II	O(7)O(8)N(4)C(2)	$-15,479x+6,848y+3,774z=4,362$	0,001, 0,001, −0,003, 0,001
III	O(4)O(3)N(5)C(2)	$-8,840x+10,379y-2,939z=5,542$	−0,002, −0,002, 0,006, −0,002
IV	O(5)O(6)N(3)C(2)	$11,805x+0,670y+4.491z=3,525$	0,007, 0,007, −0,019, 0,005
V	C(4)N(6)O(9)O(10)	$17,341x-2,517y-3,072z=3,218$	0,001, −0,004, 0,002, 0,001
VI	O(13)O(14)N(8)C(4)	$-3,503x+7,517y+4,65z=6,211$	0,002, 0,002, −0,006, 0,002
VII	O(11)O(12)N(7)C(4)	$-11,909x+7,845y-4,234z=0,070$	0,004, 0,004, −0,011, 0,003

Angles between the planes, deg

II/III=77	V/VI =68
II/IV=84	V/VII=87
III/IV=73	VI/VII=82

TABLE 5. Intramolecular and Intermolecular Contacts for the Oxygen Atoms in the Structure of Modification A

Atom	Intramolecular distances for the oxygen atoms of the "right-hand" part of the molecule						
	O(8)	O(7)	O(3)	O(4)	O(5)	O(6)	O(2)
C*	2,29	2,30	2,32	2,32	2,31	2,36	2,64
C	3,48	2,69	3,62	2,76	3,01	3,42	3,34
C(N)	3,13	3,53	3,31	3,18	2,85	3,31	3,56
N	2,57	3,02	2,59	3,51	2,77	2,54	2,24
N	3,13	4,06	3,05	3,11	2,95	3,35	2,94
O	2,12	2,12	2,18	2,18	2,15	2,15	2,19
O	2,88	2,88	2,77	3,21	2,89	2,88	2,89
O	3,21	4,09	2,88	3,25	2,77	3,13	3,47
N						3,47	
Average for the atoms	2,85	3,09	2,84	2,94	2,71	2,96	2,91
Average for the "right-hand" part	2,90						

Atom	Intermolecular distances for the oxygen atoms of the "right-hand" part of the molecule						
	O(8)	O(7)	O(3)	O(4)	O(5)	O(6)	O(2)
N(C)	3,41	3,29	3,36	3,07	3,43	3,34	3,36
N(O)	3,26	3,00	2,89	2,95	2,95	3,03	3,25
O	3,03	3,25	3,32	2,88	3,26	3,08	3,27
O	3,25	3,27	3,10	2,95	3,02	3,29	3,16
O	3,43	3,23	3,07	3,02	3,10	3,11	3,08
Average for the atoms	3,28	3,21	3,15	2,97	3,15	3,17	3,22
Average for the "right-hand" part	3,16						

Atom	Intramolecular distances for the oxygen atoms of the "left-hand" part of the molecule						
	O(9)	O(10)	O(11)	O(12)	O(13)	O(14)	O(1)
C*	2,33	2,30	2,34	2,30	2,34	2,35	2,62
C	3,11	2,90	3,44	3,05	2,99	2,65	3,48
C(N)	3,39	3,66	3,15	2,96	3,58	3,84	3,09
N	2,59	2,76	2,58	2,75	2,57	3,19	2,21
N	3,21	3,57	3,33	2,91	3,11	3,44	2,79
O	2,14	2,14	2,18	2,18	2,18	2,18	2,19
O	3,28	2,88	2,88	2,76	2,88	3,15	2,88
O	2,76	2,93	3,39	3,16	2,93	3,66	3,28
N				3,48			
Average for the atoms	2,85	2,89	2,91	2,84	2,82	3,05	2,81
Average for the "left-hand" part	2,88						

Atom	Intermolecular distances for the oxygen atoms of the "left-hand" part of the molecule						
	O(9)	O(10)	O(11)	O(12)	O(13)	O(14)	O(1)
N(C)	3,30	3,22	3,39	3,54	3,35	2,85	2,88
N(O)	3,32	2,95	3,00	3,23	3,07	3,48	2,97
O	3,02	2,85	2,89	3,47	3,01	3,10	3,25
O	3,29	3,39	2,97	3,11	3,58	3,48	3,40
O	3,00	3,10	3,00	3,49	3,50	3,31	3,31
Average for the atoms	3,18	3,10	3,05	3,37	3,30	3,24	3,16
Average for the "left-hand" part	3,20						

*Only the type of atoms in contact is given in the column; each type includes several numbers, which are not given, to avoid increasing the size of the tables.

TABLE 6. Intramolecular and Intermolecular Contacts for the Oxygen Atoms in the Structure of Modification B

Atom	Intramolecular distances for the oxygen atoms of the "right-hand" part of the molecule						
	O(3)	O(4)	O(5)	O(6)	O(7)	O(8)	O(2)
O*	2.17	2.17	2.17	2.17	2.16	2.16	2.18
O	3.22	2.84	3.12	2.79	3.26	4.10	2.84
N	3.29	2.91	3.11	3.04	3.21	3.54	2.22
N	2.59	2.76	3.48	2.55	2.55	2.98	2.97
C(O)	2.35	2.31	2.77	2.88	2.34	2.72	2.62
C	3.46	3.01	3.25	3.64	3.45	2.31	3.28
C(N, O)	2.86	2.92	2.33	2.33	2.88	4.09	3.53
O	3.26	2.77	3.11	3.22	3.12	2.86	3.57
O		3.57					
Average for the atoms	2.90	2.81	2.92	2.83	2.87	3.09	2.90
Average for the "right-hand" part	2.90						

Atom	Intermolecular distances for the oxygen atoms of the "right-hand" part of the molecule						
	O(3)	O(4)	O(5)	O(6)	O(7)	O(8)	O(2)
N(O)	3.30	3.43	3.16	3.35	2.97	3.43	3.05
O	2.95	2.88	3.01	3.25	3.23	3.40	3.25
O	3.02	3.23	3.14	3.32	2.95	3.02	3.14
O	3.25	3.12	2.88	3.34	3.26	3.07	3.29
O	3.18	3.42	3.12	3.05	3.15	3.26	3.14
Average for the atoms	3.14	3.21	3.06	3.26	3.11	3.24	3.17
Average for the "right-hand" part	3.17						

Atom	Intramolecular distances for the oxygen atoms of the "left-hand" part of the molecule						
	O(9)	O(10)	O(11)	O(12)	O(13)	O(14)	O(1)
O *	2,16	2,16	2,24	2,14	2,16	2,16	2,18
O	2,81	3,28	3,07	2,94	3,76	2,75	2,81
N	3,54	2,55	3,07	3,06	3,09	3,07	2,20
N	3,70	3,37	2,58	2,77	3,52	2,34	2,82
C(O)	2,95	3,36	3,59	2,93	3,22	2,87	2,62
C	2,30	2,34	2,33	2,85	2,65	2,59	3,19
C(N, O)	2,77	2,94	2,83	2,31	2,33	3,52	3,51
O	2,75	3,07	3,22	3,53	3,81	3,36	3,28
O		3,45					
Average for the atoms	2,87	2,95	2,86	2,82	3,07	2,83	2,83
Average for the "left-hand" part	2,89						

Atom	Intermolecular distances for the oxygen atoms of the "left-hand" part of the molecule						
	O(9)	O(10)	O(11)	O(12)	O(13)	O(14)	O(1)
N(O)	3,41	3,25	3,18	3,05	3,34	2,95	3,12
O	3,04	3,18	3,22	3,32	3,22	3,10	3,01
O	3,29	3,09	3,18	3,18	3,09	3,37	3,22
O	3,15	3,30	3,11	3,13	3,30	3,05	3,22
O	3,11	3,10	3,05	3,04	3,37	3,29	3,18
Average for the atoms	3,20	3,18	3,15	3,14	3,26	3,15	3,15
Average for the "left-hand" part	3,17						

*See footnote to Table 5.

the atoms of the fragments of the molecules in the modifications A and B respectively. In the molecules of the two modifications, the two trinitroethyl groups are oriented in different ways relative to the C(1)–C(2) and C(3)–C(4) bonds and have the form of right-hand and left-hand propellers.

The marked similarity in the structures of the molecules in the two modifications does not reflect the observed significant difference in their densities. In this connection, we examined the intramolecular and intermolecular contacts in the two modifications. Since the molecules are unsymmetrical, the calculation was carried out separately for each trinitroethyl group. For the oxygen atoms, responsible for the intermolecular contacts of each half of the molecule, the eight shortest intramolecular contacts were obtained. The averaging was carried out first for each oxygen atom, and then with respect to the intramolecular contacts of all the oxygen atoms of each half of the molecule. An analogous calculation was carried out for the intermolecular contacts of the same oxygen atoms: Here, the five shortest intermolecular contacts were taken for each oxygen atom. The results of the calculation for the molecules of the modifications A and B are given in Tables 5 and 6 respectively. It can be seen that in the molecules of both modifications, the right-hand and left-hand parts are not equivalent as far as the steric strain is concerned. The right-hand parts of the molecules in both modifications are less strained, and their intermolecular contacts are shorter than those for the left-hand parts of the molecules. The numerical differences for the intermolecular contacts in relation to the intramolecular contacts in the right-hand and left-hand parts of the molecules are not so great as for the two conformers of compound II [2].

If we consider the intramolecular and intermolecular contacts for the entire molecule as a whole, then on going from modification A to modification B the molecules become slightly looser (2.889 and 2.896 Å respectively), leading to a slight decrease in the intermolecular contacts averaged with respect to the two halves of the molecule (3.182 and 3.173 Å for A and B respectively). Thus the molecules of compound I in the modification B are less strained and more closely packed, leading to a slight increase in the density of the crystal.

Thus as in the crystals examined earlier, the distribution of the intramolecular contacts in general is determined by the total energy of the molecule.

LITERATURE CITED

1. O. H. Johnson, U.S. Patent 3389026, June 18, 1968.
2. L. O. Atovmyan, R. G. Gafurov, N. I. Golovina, and L. T. Eremenko, Dokl. Akad. Nauk SSSR, 241, 1080 (1978).
3. H. E. Ungnade and Z. W. Kissinger, J. Org. Chem., 30, 354 (1965).