ACTA CHEMICA SCANDINAVICA 17 (1963) 2419–2422

Crystal Structure of an Unstable Monoclinic Form of Dinitrogen Tetroxide

P. GROTH

Universitetets Kjemiske Institutt, Oslo 3, Norway

When liquid dinitrogen tetroxide is cooled in a capillary tube an unstable, monolinic form of the solid may be obtained. It proved possible to take X-ray diagrams of this new modification and to determine its crystal structure. The space group is $P2_1/c$ and two molecules are present in the unit cell with lattice parameters $a = 5.93$ Å, $b = 4.77$ Å, $c = 6.56$ Å, $\beta = 117.2°$. The parameters of the (planar) molecule correspond satisfactorily to those previously found for the free molecule [2] and from X-ray investigations of the 1:1 molecular compound dinitrogen tetroxide, 1,4-dioxan [3] but differ significantly from those reported for the cubic modification.[1]

The interatomic distances and angles in the N_2O_4 molecule reported for the solid oxide [1] are in only poor agreement with those determined from electron diffraction measurements in the gas.[2] In a recently published X-ray crystallographic investigation of the addition compound N_2O_4-1,4-dioxane [3] an N—N distance and an N—O—N angle were obtained which correspond closely to the electron diffraction results (see Table 2).

When starting a reinvestigation of the crystal structure of N_2O_4, the liquid oxide enclosed in a capillary tube was cooled down. Examining the crystals obtained under the polarizing microscope a non-cubic modification was observed. This turned out to be unstable with respect to the cubic form.

This new crystalline form of N_2O_4 belongs to the monoclinic system and the unit cell containing two molecules has the following parameters:

$a = 5.93$ Å, $b = 4.77$ Å, $c = 6.56$ Å, $\beta = 117.2°$.

The space group is $P2_1/c$.

Fairly good intensity data could be collected from precession diagrams precessing about [201]. Because of the instability of the crystals only a few (not integrated) Weissenberg diagrams could be obtained, however. The rotation axes were [010] and [001].

The best resolved electron density map should be expected in the projection along the shortest axis, $b = 4.77$ Å. The correct interpretation of the

$h0l$-Patterson function could not easily be found, however. The c-axis is halved in this projection and therefore the number of atoms $N_{h0l} = 6$. Since we have

$$\sigma = \sqrt{\langle U^2_{h0l} \rangle} \approx 1/\sqrt{N_{h0l}} = 0.41$$

an attack by direct methods appeared promising.

The structure factors were statistically put on an absolute scale and the temperature factor together with the unitary structure factors were calculated.

Applying the Harker-Kasper inequalities

$$(U_H \pm U_{H'})^2 \leqq (1 \pm U_{H+H'}) \ (1 \pm U_{H-H'})$$

together with a statistical use of Sayres sign relationship

$$s_H = s_{H'} \cdot s_{H+H'}$$

about 70 % of the structure factor signs could be expressed in terms of one unknown sign, $s(10\bar{1})$.

The two sets of signs corresponding to $s(10\bar{1}) = +$ and $s(10\bar{1}) = -$led to two widely different Fourier maps one of which was almost identical with the final map reproduced in Fig. 1.

The R-value arrived at using least squares refinement was 12.9 % and only two of the structure factor signs originally determined, $s(10\bar{3})$ and $s(104)$, turned out to be wrong.

A sharpened Patterson map was worked out for the $hk0$-projection. The known x-parameters, a model and a few Bragg-Lipson charts were used in finding the correct interpretation. Fourier methods and finally least squares refinement led to an R-value of 14.6 %.

The projection along [201] could now be refined directly by least squares method, the R-value arrived at was 7.0 %.

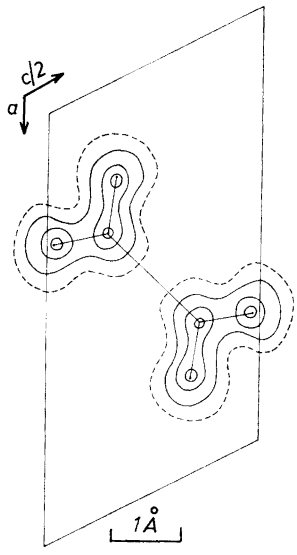

Fig. 1. Electron density map for the $h0l$-projection of N_2O_4.

Table 1. Final atomic coordinates for N_2O_4.

	x	*y*	*z*
O_1	0.280	−0.197	0.137
O_2	0.196	0.187	−0.080
N	0.158	−0.003	0.024

Table 2. Distances and angles in the N_2O_4-molecule.

	N_2O_4-1,4-dioxane [3]	Free molecule [2]	Solid N_2O_4 (cubic) [1]	Solid N_2O_4 (monoclinic)
Distance N—O	1.18 Å	1.180 Å	1.17 ± 0.03 Å	1.21 Å
» N—N	1.75 »	1.750 »	1.64 ± 0.03 Å	1.75 »
Angle O—N—O	135°	133.9°	126° ± 1°	135°

The final atomic parameters (Table 1) led to the N—N distance, the O—N—O angle and the mean value of the two N—O distances listed in Table 2. The mean value of the two N—N—O angles is 112.5°, thus confirming the planarity of the molecule. Fig. 2 shows the Fourier projection along [001], and the calculated structure factors (F_c) together with the observed values (F_o) may be found in Table 3.

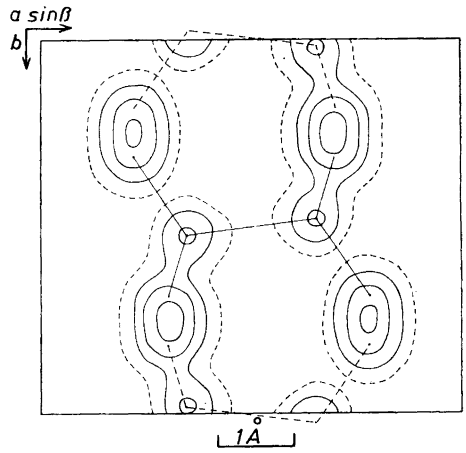

Fig. 2. Electron density map for the *hk*0-projection of N_2O_4.

Table 3. Observed and calculated structure factors for N_2O_4.

*hk*0-projection

h k 0	F_o	F_c
0 2 0	−14.4	−14.0
0 4 0	6.6	7.6
0 6 0	4.2	5.9
1 0 0	−18.0	−19.1
1 1 0	− 2.4	− 2.1
1 2 0	− 7.7	− 6.4
1 3 0	1.2	1.7
1 4 0	− 4.6	− 3.9
1 5 0	1.0	0.4
1 6 0	− 1.0	− 0.5
2 0 0	−37.7	−39.5
2 1 0	−19.4	−17.1
2 2 0	15.5	14.6
2 3 0	2.9	3.7
2 4 0	− 1.7	− 3.1
2 5 0	1.8	2.0
3 0 0	16.2	14.4
3 1 0	4.7	4.0
3 2 0	6.6	4.7
3 5 0	0.7	0.2
4 0 0	3.8	1.0
4 1 0	10.4	10.9
4 2 0	− 8.1	− 8.7
4 3 0	− 1.4	− 3.0
4 4 0	− 2.0	− 1.2
5 0 0	− 1.5	− 0.6
5 1 0	− 2.1	− 3.0
5 2 0	0.6	0.7
5 3 0	1.7	2.1
5 4 0	− 0.6	− 0.3
6 0 0	2.1	2.5
6 1 0	− 3.5	− 4.1
6 2 0	2.6	1.9

*h*0*l*-projection

h 0 *l*	F_o	F_c
0 0 2	−28.8	−27.0
0 0 4	− 7.0	− 7.0
1 0 −4	− 8.2	− 6.2
1 0 −2	−25.6	−24.6
1 0 0	18.0	17.8
1 0 2	− 7.2	− 6.0
1 0 4	13.0	12.2
2 0 −8	3.0	2.8
2 0 −6	− 8.0	− 6.2
2 0 −4	13.8	11.6
2 0 −2	29.6	28.2
2 0 0	−38.2	−45.0
2 0 2	− 2.2	− 2.2
2 0 4	4.0	6.6
3 0 −6	− 9.8	− 9.8
3 0 −2	30.4	28.4
3 0 0	−19.6	−17.0
3 0 2	10.6	9.8
3 0 4	−11.0	−10.0
4 0 −8	− 5.4	− 4.2
4 0 −6	10.4	8.4
4 0 −4	−11.8	− 9.4
4 0 −2	−11.8	− 9.6
4 0 0	7.0	3.6
4 0 2	12.0	13.2
4 0 4	− 5.6	− 6.8
5 0 −8	− 4.8	− 6.4
5 0 −6	14.0	14.0
5 0 −2	−13.0	−11.2
6 0 0	2.8	5.0
7 0 −6	− 7.4	− 9.8
7 0 −2	2.2	2.0

Projection along [201]

h k *l*	F_o	F_c
0 2 0	−12.1	−12.0
0 4 0	6.9	7.4
0 6 0	4.6	5.5
1 0 −2	22.5	23.8
1 1 −2	−17.1	−16.2
1 2 −2	6.8	5.9
1 3 −2	3.8	3.6
1 4 −2	6.4	5.3
1 5 −2	1.6	1.5
1 6 −2	1.6	1.3
2 0 −4	9.6	9.5
2 1 −4	10.2	10.0
2 2 −4	− 3.0	− 2.7
2 3 −4	− 2.1	− 2.0
3 0 −6	7.4	6.9
3 1 −6	− 1.8	− 2.7
3 2 −6	− 8.0	− 7.8
3 4 −6	− 1.3	− 1.1
4 0 −8	− 3.9	− 4.2
4 1 −8	− 1.4	− 1.4
4 2 −8	− 2.1	− 1.6

REFERENCES

1. Broadley, J. S. and Robertson, J. M. *Nature* **164** (1949) 915.
2. Smith, D. W. and Hedberg, K. *J. Chem. Phys.* **25** (1956) 1282.
3. Groth, P. and Hassel, O. *Proc. Chem. Soc.* **1962** 379.

Received June 18, 1963.