

Oxatrane Is a Parent Compound of a New Atrane Family: Crystal and Molecular Structure of Triethanolamine *N*-Oxide

Academician M. G. Voronkov^{a†}, E. A. Zel'bst^b, A. D. Vasil'ev^{c,d}, M. S. Molokeevev^{c,d}, and G. A. Kuznetsova^a

Received March 27, 2014

DOI: 10.1134/S0012500814090031

Tertiary amine *N*-oxides of general formula $\bar{\text{O}}-\overset{+}{\text{N}}\text{R}_3$ (previously $\text{O}=\text{NR}_3$ or $\text{O} \rightarrow \text{NR}_3$) continue to attract interest of synthetic, theoretical, and applied chemists. They are already used in cosmetics, as bio-medical agents, and as oxidants in a number of organic reactions (catalytic epoxidation and dihydroxylation of alkenes, catalytic oxidation of alcohols, etc.) [1, 2]. The most general method of their synthesis is the oxidation of tertiary amines with hydrogen peroxide, peroxy acids, dioxiranes, and oxazapyridines [1].

Triethanolamine *N*-oxide (TEA) formulated as $\bar{\text{O}}-\overset{+}{\text{N}}(\text{CH}_2\text{CH}_2\text{OH})_3$ and obtained by the oxidation of triethanolamine with hydrogen peroxide [3] is also attributed to trialkylamine *N*-oxides. The authors [3] obviously did not know that TEA and its salts $\text{X}[\text{NH}(\text{CH}_2\text{CH}_2\text{OH})_3]^+$ are protatranes [4] that have *endo* structure in contrast to trialkylamines and trialkylammonium salts. In compounds of atrane series, the nitrogen atom is shifted inside from the plane of its bonded carbon atoms and is surrounded by three $\text{CH}_2\text{CH}_2\text{OH}$ groups [4–6]. According to quantum chemical calculations and X-ray diffraction studies, TEA has *endo* conformation, which is the most stable one irrespective of protonation of the nitrogen atom and crystal packing [7]. Such a structure of TEA molecules and protatranes is explained by through-space intramolecular inductive interaction of nitrogen and oxygen atoms [5, 8].

[†] Deceased.

^a Favorskii Institute of Chemistry, Siberian Branch, Russian Academy of Sciences, ul. Favorskogo 1, Irkutsk, 664033 Russia

^b East Siberian State Academy of Education, Nizhnyaya Naberezhnaya 6, Irkutsk, 664011 Russia

^c Kirenskii Institute of Physics, Russian Academy of Sciences, Krasnoyarsk, 660036 Russia

^d Siberian Federal University, pr. Svobodnyi 79, Krasnoyarsk, 660036 Russia
e-mail: zelbst@rambler.ru

A particular interest in tertiary amine *N*-oxides has increased in recent years. Triethanolamine *N*-oxide, which was considered to have structure $\text{O}=\text{N}(\text{CH}_2\text{CH}_2\text{OH})_3$ [3], was ascribed to them by analogy, but its molecular structure was not established. Therefore, we determined the structure by X-ray diffraction, presuming that the oxide oxygen atom in this molecule is bound to the nitrogen atom and surrounded by three $\text{CH}_2\text{CH}_2\text{OH}$ groups like hydrogen atom in protatranes [4]. The obtained data proved to be unexpected and, nonetheless, allowed us to name TEA *N*-oxide as oxatrane (OA) by analogy with protatranes, Fig. 1.

The structure of an OA complex with TEA (OATEA) has been reported recently [9]. The *N*-oxide oxygen atom in this compound occupies the *exo* position with respect to the $\text{CH}_2\text{CH}_2\text{OH}$ groups and is involved in hydrogen bonds with the hydroxyl hydrogen atoms of the ligand, TEA.

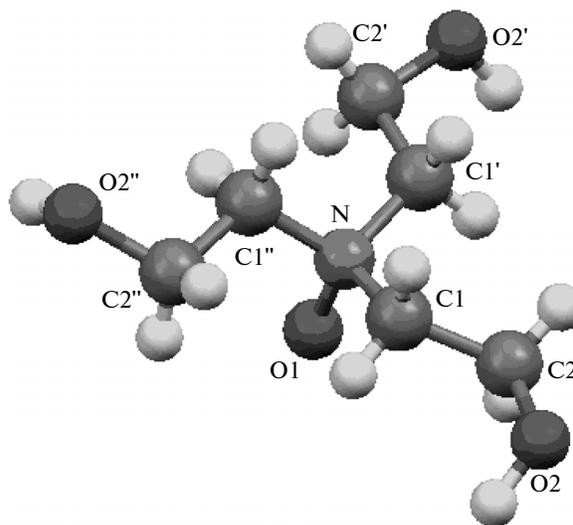


Fig. 1. Oxatrane molecule.

Experimental details and refinement parameters for the oxatrane structure

| | |
|-------------------------------------|--|
| Chemical formula | C ₆ H ₁₅ NO ₄ |
| Temperature, K | 300(2) |
| Space group, <i>Z</i> | <i>P</i> $\bar{3}$, 2 |
| <i>a</i> , <i>b</i> , <i>c</i> , Å | 8.24015(11), 8.24015(11), 6.75661(10) |
| α , β , γ , deg | 90, 90, 120 |
| <i>V</i> , Å ³ | 397.31(1) |
| <i>d</i> , g/cm ³ | 1.3808 |
| μ , mm ⁻¹ | 0.976 |
| $2\theta_{\max}$, deg | 140 |
| Step, deg | 0.0160352 |
| Number of profile points | 8419 |
| Number of reflections | 507 |
| Number of refined parameters | 16 |
| <i>R</i> _{wp} , % | 6.159 |
| <i>R</i> _{exp} , % | 1.806 |
| <i>R</i> _p , % | 4.843 |
| <i>R</i> _B , % | 0.71 |

We obtained triethanolamine *N*-oxide by the reaction of TEA with hydrogen peroxide. Yield 90%, mp 104–105°C.

Molecular formula C₆H₁₅NO₄.

For C₆H₁₅NO₄ anal. calcd. (%): C, 43.63, H 9.15, N 8.48.

Found (%): C, 43.38; H, 9.12; N, 8.76.

After recrystallization from acetonitrile, transparent single crystals of OA are not hygroscopic and have well-defined shiny facets.

X-ray diffraction study of OA was performed on a Bruker AXS D8-ADVANCE diffractometer, CuK α radiation, VANTEC linear detector. Variable counting time (VCT) and variable step scanning (VSS) procedures were used in the experiment [10–12]. The exposure time increased with 2θ angle, which resulted in considerable improvement of X-ray diffraction patterns. As a rule, 5–8 experimental points should fall on a full width at half maximum (FWHM); however, peaks were considerably broadened with increasing 2θ angle; therefore, the step was increased in high-angle regions to decrease the experiment time [13].

A structure model was found by molecule modeling in direct space with phase annealing [14]. Oxatrane crystals have trigonal symmetry. The non-hydrogen atoms were refined in the isotropic approximation by the Rietveld method. Hydroxyl hydrogen atoms were placed in positions most probable for O–H \cdots O hydrogen bond, and the other hydrogen atoms were placed in geometrically calculated positions. The table shows experimental data and refining parameters for oxatrane structure. Structural data for this compound were deposited with the Cambridge Crystallographic Data Centre: CCDC 984100 (www.ccdc.cam.ac.uk/data_request/cif).

Each oxatrane molecule lies on a 3-fold symmetry axis passing along the N–O1 bond (Fig. 1). The oxide oxygen atom O1 is bound via hydrogen bonds to the O2 hydroxyl atoms of the three nearest identical molecules: O1 \cdots O2 = 2.738(6) Å, O1 \cdots H–O2 angle is 178.33(1)° (close to linear) (Fig. 2). These values are

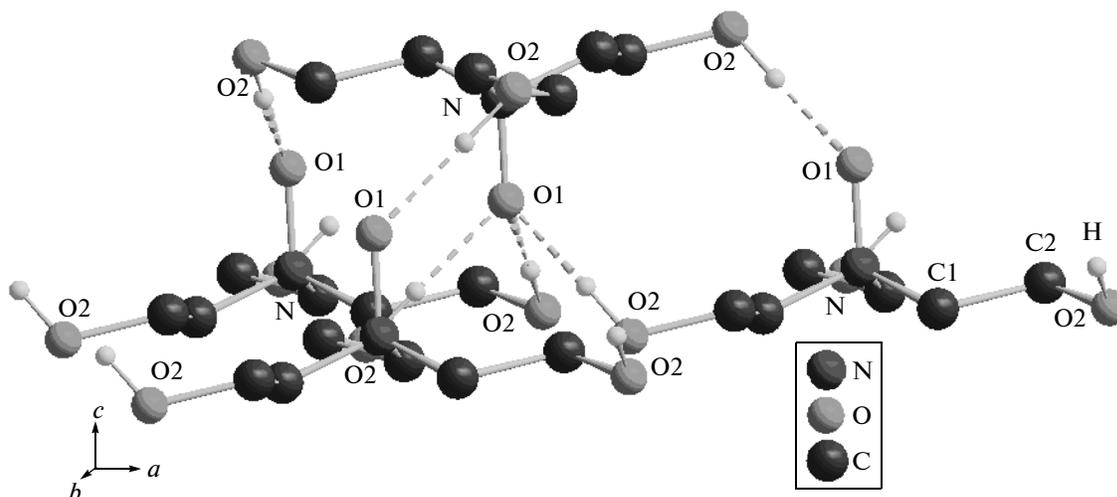


Fig. 2. Hydrogen bonds O1 \cdots H–O2 in oxatrane (hydrogen atoms in CH₂ are omitted).

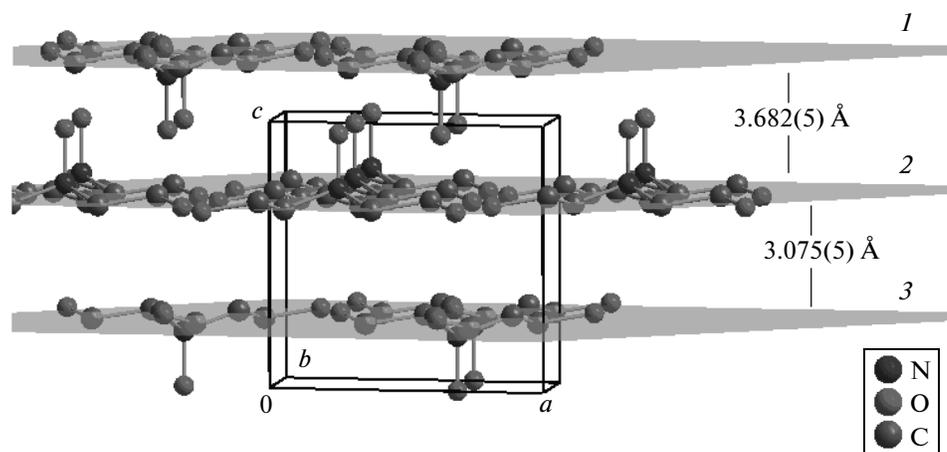


Fig. 3. Layer-by-layer packing of oxatrane molecules in crystal (hydrogen atoms are omitted for clarity).

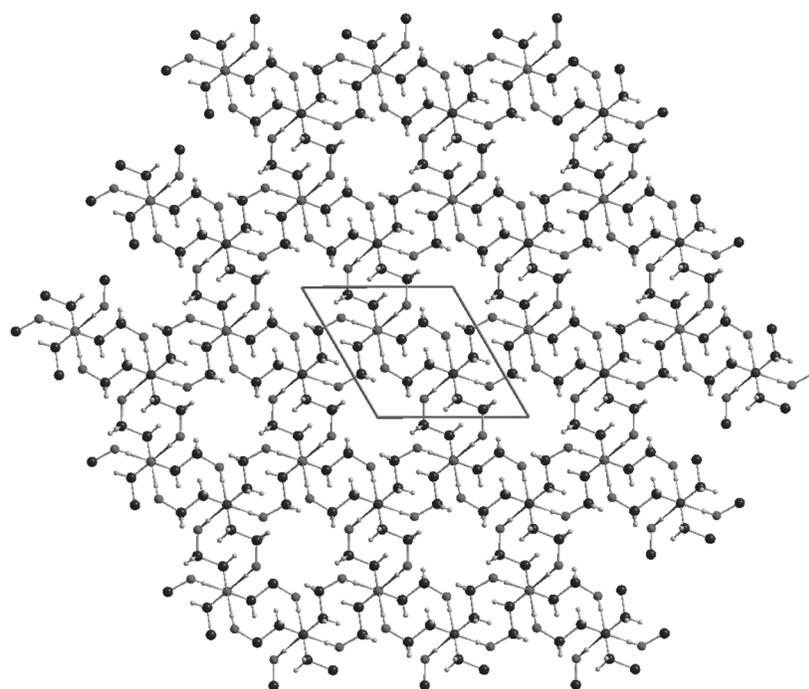


Fig. 4. The packing of oxatrane molecules in crystal in projection on the *ab* plane.

close to the values of hydrogen bonds in the OATEA complex [9], 2.705(7) Å, and in the TEA dimer, O1...O2 – 2.696(7) Å [15].

Because of strong intermolecular hydrogen bonds O1...H-O2', the O2 atoms are turned from the center of the molecule (N–O1 bonds) and are located at the same level with the C1 atoms, i.e., in the same plane with them (Fig. 1). The C1C1'C1'' and O2O2'O2''' planes are only 0.02 Å apart from each other. The N...O2 intramolecular distance (3.779(6) Å) is much longer than this distance in TEA (2.991(5) Å). Each of the three hydrogen bonds O2–H...O1 connects the

“internal” O1 oxygen atoms with O2H hydroxy groups of the nearest molecules. At the same time, three hydroxy groups of each oxatrane molecule are connected by hydrogen bonds with the O1 oxygen atoms of the three nearest molecules. Due to strong intermolecular interaction and the trigonal symmetry of crystal space, the molecules form layers parallel to the *ab* face of the unit cell in contrast to OATEA complex [9], where molecule packing is compared with a cap, and the TEA itself [15] producing dimers owing to hydrogen bonds of the nearest molecules.

These layers are hydrogen bonded in pairs, whereas there are only van der Waals bonds between the pairs (Fig. 3). The distances between the layers in the pairs (layers 1 and 2) and between the couples of layers (layers 2 and 3) are shown in Fig. 3.

The packing of oxatrane molecules in crystal and conformations of the molecules display considerable features unusual to protatrane crystals, which retain *endo* configuration with 2-hydroxyethyl groups turned to the same direction, so that the molecules resemble a “lampshade” or “lantern” of approximate C_3 symmetry enclosing hydrogen atom or the lone pair of electrons of the nitrogen atom [5].

The projection of the unit cell onto the *ab* plane along the *c* axis displays “columns” of small diameter unfilled with atoms (Fig. 4).

Judging from interatomic distances, the ionicity of N–O bond in the oxatrane molecule (1.387(5) Å) is lower than in the OATEA complex (1.423(6) Å) [9] and corresponds to the ionicity in trimethylamine *N*-oxide (CH₃)₃N–O (1.388(5) Å) and triethylamine *N*-oxide (CH₂CH₃)₃N–O (1.396(6) Å). This allows us to describe the N–O bond as ionic $\bar{O}-\overset{+}{N}$.

The N–C bond distances in oxatrane molecule are the same as in the OATEA complex (1.49(1) Å), C–C bonds are also close to each other (1.52(1)–1.53(1) Å, like in silatranes), while C–O interatomic distances (1.453(8) and 1.425(6) Å in OA and OATEA, respectively) differ by 0.02 Å. The CNC, NCC, and CCO bond angles are common for the NCH₂CH₂OH chain.

ACKNOWLEDGMENTS

This work was supported by the Council for Grants of the President of the Russian Federation for Support

of Leading Scientific Schools (grant no. NSh-3649.2014.3).

REFERENCES

1. Limnios, D. and Kokotos, C.J., *Eur. J. Chem.*, 2014, vol. 20, pp. 559–563.
2. Albin, A., *Synthesis*, no. 3, pp. 263–277.
3. Colladon, M., Scarso, A., and Strukul, G., *Green Chem.*, 2008, vol. 10, pp. 793–798.
4. Voronkov, M.G. and Baryshok, V.P., *Vestn. Ross. Akad. Nauk*, 2010, vol. 80, no. 11, pp. 985–992.
5. Shklover, V.E., Gridunova, G.V., Struchkov, Yu.T., and Voronkov, M.G., *Dokl. Akad. Nauk SSSR*, 1983, vol. 269, no. 2, pp. 387–390.
6. Pestunovich, V.A., Kirpichenko, S.V., and Voronkov, M.G., in: *The Chemistry of Organic Silicon Compounds*, New York: Wiley, 1998, vol. 2, part 2, pp. 1447–1537.
7. Parkanyi, L., Hensel, P., and Nyulaszi, L., *J. Mol. Struct.*, 1996, vol. 377, pp. 27–33.
8. Voronkov, M.G., Zel'bst, E.A., and Belyaeva, V.V., *Dokl. Chem.*, 2014, vol. 455, parts 1–2, pp. 49–52.
9. Kemmit, T., Gainsford, G.J., and Steel, P.J., *Acta Crystallogr., Sect. E*, 2002, vol. 58, p. o851.
10. Madsen, I.C. and Hill, R.J., *Adv. X-ray Anal.*, 1992, no. 35, p. 39.
11. Madsen, I.C. and Hill, R.J., *J. Appl. Crystallogr.*, 1994, no. 27, p. 385.
12. David, W.I.F., in: *Accuracy in Powder Diffraction: Optimization of Data Collection Strategies. Abstr. P2.6*, NIST Spec. Publ., Gaithersburg, 1992, no. 846, p. 210.
13. Bruker, Diffrac-Plus, Basic XRD Wizard, Bruker, AXS, Karlsruhe, 2002/2007.
14. Bruker, TOPAS V4: General Profile and Structure Analysis Software for Powder Diffraction Data, User's Manual, Bruker, AXS, Karlsruhe, 2008.
15. Mootz, D., Brodalla, D., and Wiebcke, M., *Acta Crystallogr., Sect. C*, 1989, vol. 45, pp. 754–757.

Translated by I. Kudryavtsev