

Short Communications

The Structure of *O*-[3-Phenyl-5-(1,2,3,4-oxatriazolio)] Oxide at -165°C

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In a recent study¹ the structure of the *meso*-ionic compound *N*-[3-phenyl-5-(1,2,3,4-oxatriazolio)phenylamide] was investigated by X-ray diffraction methods. The results obtained for the central five-membered ring showed the same structural features as those found for the isoelectronic syndones² (*i.e.* a planar ring with bond distances indicating a conjugated system, except for a relatively long intra-ring C—O length (1.40–1.42 Å), and an exocyclic “pure” double bond). *meso*-Ionic structures have recently attracted considerable interest because of their marked pharmacological activity associated with certain members of this group of organic compounds.^{3,4} In order to study this *meso*-ionic oxatriazolio system further and to complement the earlier results, a structure investigation of the title compound was undertaken.

The compound^{5,6} was recrystallized from ethanol. The space group was determined as $P2_1/c$ by film methods, and it was found that there are eight molecules in the unit cell, *i.e.*

two molecules in the asymmetric unit (in the following denoted A and B, respectively). A computer controlled Syntex-P1 diffractometer with graphite-monochromatized $\text{MoK}\alpha$ radiation and equipped with an Enraf-Nonius liquid nitrogen cooling device, modified by H. Hope, was utilized for preliminary experiments and for the measurement of diffraction intensities. A crystal of approximate dimensions $0.2 \times 0.1 \times 0.05$ mm was used. Unit cell parameters were determined by a least-squares treatment of the angular coordinates of thirty symmetry-independent reflections with 2θ -values between 17 and 37° . The temperature at the crystal site was -165°C . The crystal data are: *O*-[3-phenyl-5-(1,2,3,4-oxatriazolio)]oxide, $\text{C}_7\text{H}_5\text{N}_3\text{O}_3$, $M=163.1$ amu, space group $P2_1/c$, $a=15.160(3)$ Å, $b=5.030(1)$ Å, $c=19.769(7)$ Å, $\beta=111.49(2)^{\circ}$, $V=1402.8$ Å³, $Z=8$, $D_{\text{calc}}=1.544$ g/cm³, $F(000)=672$.

Three-dimensional intensity data were recorded using the ω - 2θ scanning mode with scan speed variable from 2 to 8°min^{-1} , depending on the peak intensity of the reflection. Background counting time was equal to $0.7 \times$ (scan time). Reflections with 2θ -values larger than 40° , which had integrated counts of less than 7 cps, determined in a 2 s scan over the reflection were not measured. The variations in the intensities of three standard reflections which were remeasured after every hundred reflections, were random and less than three times their standard deviations. Accordingly no corrections were applied for these varia-

Table 1. Fractional atomic coordinates and thermal parameters with estimated standard deviations for non-hydrogen atoms. The temperature factor is given by $\exp[-2\pi^2(u_{11} \times (a^*h)^2 + u_{22}(b^*k)^2 + u_{33}(c^*l)^2 + u_{12}(a^*b^*hk) + u_{13}(a^*c^*hl) + u_{23}(b^*c^*kl)]$.

Atom	x	y	z	u_{11}	u_{22}	u_{33}	u_{12}	u_{13}	u_{23}
O1A	.7787(3)	.3908(18)	.1614(2)	.0287(27)	.0361(34)	.0263(25)	.0076(26)	.0057(22)	-.0016(27)
N2A	.7493(3)	.5089(12)	.1849(2)	.0284(31)	.0313(39)	.0222(28)	.0093(32)	.0057(26)	.0011(36)
N3A	.6583(3)	.6276(11)	.1354(2)	.0165(29)	.0263(34)	.0198(27)	.0010(30)	.0046(24)	-.0020(31)
N4A	.6336(3)	.4639(12)	.0782(2)	.0295(34)	.0290(30)	.0193(28)	.0003(31)	.0008(26)	-.0022(29)
C5A	.7106(5)	.3043(15)	.0930(3)	.0291(42)	.0241(45)	.0290(41)	.0021(39)	.0130(36)	.0040(38)
O6A	.7279(3)	.1185(18)	.0618(2)	.0404(31)	.0380(31)	.0406(29)	.0076(29)	.0262(25)	-.0008(29)
C7A	.5944(4)	.8321(13)	.1421(3)	.0189(34)	.0189(41)	.0187(33)	.0003(33)	.0058(29)	.0005(33)
C8A	.6217(4)	.9922(14)	.2054(3)	.0201(34)	.0423(44)	.0150(31)	.0047(34)	.0073(28)	.0009(34)
C9A	.6619(4)	1.1751(14)	.2189(3)	.0357(43)	.0272(44)	.0204(33)	.0005(30)	.0134(33)	.0004(36)
C10A	.4749(4)	1.2168(15)	.1555(3)	.0301(42)	.0251(43)	.0321(38)	.0006(30)	.0174(34)	.0007(36)
C11A	.4466(4)	1.0594(14)	.0923(3)	.0285(39)	.0239(43)	.0228(33)	.0004(35)	.0072(30)	.0011(34)
C12A	.5892(4)	.8617(14)	.0800(3)	.0263(38)	.0210(40)	.0230(33)	.0003(36)	.0106(31)	.0011(36)
O1B	.7255(3)	.0959(11)	.4011(2)	.0266(28)	.0438(38)	.0471(33)	.0067(30)	.0081(25)	-.0019(33)
N2B	.7782(3)	-.0353(13)	.4631(3)	.0282(36)	.0364(45)	.0589(44)	.0123(35)	.0100(34)	-.0017(38)
N3B	.8521(3)	.1136(12)	.4992(2)	.0252(31)	.0249(36)	.0295(31)	.0001(32)	.0159(26)	-.0008(32)
N4B	.8677(3)	.3351(12)	.4558(2)	.0217(32)	.0363(41)	.0216(30)	.0004(32)	.0005(26)	.0003(32)
C5B	.7762(5)	.3277(17)	.3958(4)	.0336(46)	.0346(55)	.0337(42)	.0063(44)	.0145(39)	-.0010(43)
O6B	.7433(3)	.4839(12)	.3453(2)	.0429(33)	.0630(44)	.0259(26)	.0136(32)	.0051(25)	.0004(31)
C7B	.9261(5)	.0371(14)	.5585(3)	.0346(41)	.0239(41)	.0265(36)	.0049(30)	.0166(32)	-.0003(36)
C8B	.9119(5)	-.1848(16)	.5055(4)	.0634(50)	.0298(50)	.0514(52)	.0074(47)	.0428(47)	.0003(46)
C9B	.9827(7)	-.2444(18)	.6511(4)	.1000(70)	.0377(54)	.0442(54)	.0128(60)	.0577(57)	.0009(47)
C10B	1.0649(6)	-.0990(19)	.6065(3)	.0748(66)	.0520(65)	.0236(40)	.0277(60)	.0230(45)	.0007(47)
C11B	1.0775(5)	.6483(3)	.6483(3)	.0467(50)	.0451(58)	.0231(38)	.0130(48)	.0122(37)	-.0006(44)
C12B	1.0068(4)	.1853(14)	.5823(3)	.0270(38)	.0389(46)	.0222(34)	.0101(38)	.0100(31)	.0003(37)

tions. The estimated standard deviations were taken as the square root of the total counts with a 2% addition of the net intensity for experimental uncertainties. Of the 2279 reflections measured ($2\theta_{\max} = 60^\circ$), 1422 had intensities larger than twice their standard deviations. These were regarded as "observed" reflections and used in the refinements. The intensities were corrected for Lorentz and polarization effects. The computer program used, as well as programs subsequently employed, is part of a local assembly of computer programs for CYBER-74 and is described in Ref. 7. The atomic scattering factors used were those of Doyle and Turner⁸ for carbon, nitrogen and oxygen, and of Stewart *et al.*⁹ for hydrogen.

The phase problem was solved by the MULTAN program package.¹⁰ The structure model was refined to a conventional R of 0.15. At this point the hydrogen atoms were placed in calculated positions and given a common isotropic temperature factor of 2.5 \AA^2 . Anisotropic thermal parameters for all nonhydrogen atoms were introduced. Indications of disorder (*i.e.* large anisotropic thermal parameters, *small* spurious peaks in a Fourier synthesis) were found for both phenyl rings. Full-matrix least-squares refinement of all positional and anisotropic thermal parameters for the nonhydrogen atoms converged to a conventional R of 0.074 and a weighted R_w of 0.072. Final parameters for nonhydrogen atoms are listed in Table 1, and calculated positional parameters used for hydrogen atoms are given in Table 2. A list of observed and calculated structure factors is available from the author upon request. (Also available from Department of Chemistry, University of Oslo, Norway). Standard deviations in molecular parameters were calculated from the correlation matrix ignoring standard deviations in cell parameters.

Mean bond lengths and bond angles are listed in Fig. 1, where the numbering of the

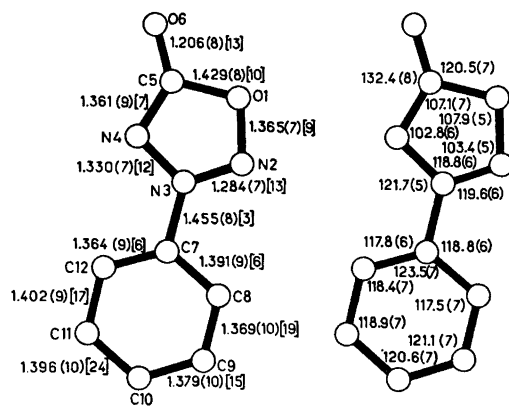


Fig. 1. Mean bond lengths (\AA) and bond angles ($^\circ$) with estimated standard deviations. The numbers in brackets are the differences ($\times 10^3$) in the results obtained for the two molecules.

atoms is indicated. Deviations from least-squares planes through the five and six-membered rings, respectively, are given in Table 3. The rings are planar and the dihedral angles N2-N3-C7-C8 and N2-N3-C7-C12 are, respectively, $-4.6(9)$ and $176.9^\circ(6)$ for molecule A, and $-4.7(9)$ and $174.3^\circ(6)$ for molecule B. The molecular dimensions obtained for the five-membered rings confirm the results found for *N*-[3-phenyl-1,2,3,4-oxatriazolol)]phe-

Table 3. Deviations ($\text{\AA} \times 10^3$) from least-squares planes. Those for atoms used to define the plane are given in italicized figures. The first two columns are results for molecule A, the next two for molecule B.

Table 2. Calculated fractional coordinates used for hydrogen atoms.

Atom	<i>x</i>	<i>y</i>	<i>z</i>
C8HA	0.685	0.949	0.246
C9HA	0.580	1.293	0.255
C10HA	0.430	1.357	0.161
C11HA	0.384	1.092	0.052
C12HA	0.491	0.742	0.041
C8HB	0.853	-0.307	0.575
C9HB	0.947	-0.384	0.694
C10HB	1.118	-0.159	0.732
C11HB	1.137	0.231	0.670
C12HB	1.016	0.342	0.552

	Plane A1	Plane A2	Plane B1	Plane B2
O1	-4	29	-4	4
N2	6	82	-2	64
N3	-5	12	7	-31
N4	1	-63	-9	-173
C5	3	-53	9	-128
O6	-19	-126	-7	219
C7	-27	10	6	-11
C8	-134	-11	-105	12
C9	-139	3	-143	-11
C10	-72	6	-15	7
C11	2	-7	106	-4
C12	28	-1	134	6

Angle between planes A1 and A2: 3.7°
 Angle between planes B1 and B2: 5.9°

nylamid,¹ and again indicate the relationship between these *meso*-ionic systems and the isoelectronic sydnonones.

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The Gas Phase Electron Diffraction Pattern of Beryllium Borohydride

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Despite extensive investigations by a variety of techniques¹⁻⁹ there remain some puzzling aspects to the structure of gaseous beryllium borohydride. These are perhaps most clearly brought out by the electron diffraction experiments¹⁻⁴ from which at least two types of intensity curves have been obtained. A possible, but we feel unlikely, explanation for this difference is gross impurities in the solid sample used in one of the studies. A second possibility is that two or more species of gaseous molecule can be obtained from solid BeB_2H_6 in amounts depending on the state of the sample. This explanation gains plausibility from the fact that BeB_2H_6 is known to exist as polymeric chains in the crystal.¹⁰ Indeed one type of diffraction pattern is known to have been obtained from freshly sublimed material kept at liquid N_2 temperature until just before the experiments were performed,³ another from an aged sample.⁴ Moreover, the infrared and Raman spectra of gaseous and matrix isolated BeB_2H_6 have been interpreted as evidence for the presence of two forms of monomeric BeB_2H_6 in equilibrium in the gas phase.⁷

We have carried out experiments designed to test the hypothesis described above. These involve solid samples of different histories and an all-glass nozzle-inlet system to eliminate the possibility of sample decomposition by contact with metal.

The BeB_2H_6 had been prepared by Dr. T. H. Cook at the University of Wyoming from B_2H_6 and $\text{Be}(\text{CH}_3)_2$. All the material used came from the same preparation and had been carefully purified by sublimation.

An all-glass inlet system was designed for Balzers Eldigraph KD-G2 which permitted the reservoir containing the solid sample to be kept outside the diffraction chamber. The diffraction patterns were recorded with a nozzle-to-plate distance of 327.3 mm and an electron wavelength of 0.0585 Å. Sufficient vapor pressure was obtained by submerging the reservoir in an oil bath maintained at 55 °C. In order to prevent condensation in the inlet system and particularly at the glass nozzle tip the latter was heated to 60–70 °C.

First the scattering pattern was recorded with a sample of BeB_2H_6 consisting of large clear colorless crystals. Then crystalline BeB_2H_6 was distilled into a liquid N_2 cooled cold finger and kept in liquid N_2 until 2 or 3 min before the diffraction pattern was recorded. Then