Synthesis and Characterisation of Ionic Ozonides with Bisquaternary Ammonium Counterions☆

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The bisquaternary ammonium ozonides $Me_3N^+(CH_2)_n{}^+NMe_3(O_3^-)_2$ with $n = 3, 4, 6$ (**1**, **2**, **3**), $Me_3N^+(CH_2)_3{}^+NMe_3(O_3^-)_2 \cdot 3\ NH_3$ (**1a**), $Me_3N^+(p\text{-}Ph)^+NMe_3(O_3^-)_2$ (**4**) and $Me_3N^+(p\text{-}Ph)^+NMe_3(O_3^-)_2 \cdot NH_3$ (**4a**) were obtained in quantitative yields by cation exchange starting from CsO_3. The compounds **1a** and **3** have been studied by single crystal X-ray analysis. The influence of C−H···O and N−H···O hydrogen bonds on the bond length and the bond angle of the ozonide anion is discussed; earlier results are included. The difference between the two bond lengths within the O_3^- ion [137.4(3) pm and 129.5(3) pm] in **1a** is unexpectedly large. Thermal stabilities determined by DTA/TG methods range from 24−83 °C.

Few attempts have been undertaken to synthesize ionic ozonides with divalent counterions. The reaction of a solution of ozone in Freon 12 with strontium and barium peroxides results in red products contaminated by superoxide and peroxide[1-4]. Recently, we have succeeded in preparing stable solutions of strontium and barium ozonide in liquid ammonia; however, no solid products could be isolated[5]. This is probably due to oxidation of ammonia by the ozonide anion upon removal of the solvent[6].

The ozonides of the alkali metals Cs, Rb and K are accessible in gram-amounts and have been well characterized[7]. The intermolecular distances between the ozonide anions decrease from CsO_3 to KO_3. The magnetic properties of the paramagnetic 19 electron ozonide anion in these compounds indicate antiferromagnetic ordering with increasing Neel temperature. This suggests an increase of intermolecular interactions at decreasing O−O contacts. Thus, smaller cations like Na^+ and Li^+ should lead to an even stronger interaction. However, while concentrated solutions of NaO_3 and LiO_3 in liquid ammonia may be easily prepared by cation exchange, the solid binary compounds cannot be recovered, because the ozonides of the ammine complexes decompose immediately upon precipitation[6]. Thus, bisquaternary ammonium cations with varying chain lengths may offer a more feasible approach to the variation of the distance between the ozonide anions.

The "intrinsic" geometry of the ozonide anion still seems to be uncertain (cf. Table 1). Until now eleven single crystal structures of ionic ozonides have been reported[5,6,8,9,10,11]. Five of them contain the ozonide anion in a more or less disordered state and will not be discussed here[5,6,8,11]. With respect to O−O bond lengths and bond angles the ozonide anions in the remaining six compounds can be classified into two groups: the ozonides of the heavy alkali metals with an average bond length of 134 pm and an average bond angle of 114°, and the quaternary tetraorganylammonium ozonides with an average bond length of 129 pm and an average bond angle of 119°. One of the explanations offered for this phenomenon was based on C−H···O hydrogen interactions that would remove electron density from the antibonding HOMO in O_3^-[11].

Thus, the main objectives of our attempts to synthesize and characterize ozonides of bisquaternary ammonium cations are (i) tuning the $O_3^- - O_3^-$ separation in the solid and (ii) gaining additional experimental data in order to settle the discrepancies concerning the geometry of the ozonide anion.

Table 1. Average bond lengths [pm] and angles [°] of the ozonide anion in the compounds **1a**, **3** and **5**−**10**

	Ozonide	Distances[a]	Angles
5	KO_3 [9]	135.7(5)	114.6(13)
6	RbO_3 [9]	134.1(5)	113.4(8)
7	β–CsO_3 [10]	133.3(9)	114.6(6)
8	$(Me_3PhN)O_3$ [8]	131.5(2)	117.0(2)
9	$(Et_3BzN)O_3$ [8]	129.0(5)	116.4(7)
10	$(Me_4N)O_3$ [11]	128.8(3)	119.6(4)
3	$[(Me_3N(CH_2)_6NMe_3)](O_3)_2$	132.4(2)	115.8(1)
1a	$[(Me_3N(CH_2)_3NMe_3)](O_3)_2 \cdot 3NH_3$	130.8(4),133.4(3)	117.9(2),114.7(2)

[a] Average O–O distance.

Cation exchange reactions in liquid ammonia are a generally applicable route to the synthesis of ionic ozonides[8]. Applying this technique we have been able to prepare the new ozonides **1**−**4**, **1a** and **4a**.

ozonide	spacer, $R = Me_3N^+$
1	$R\text{-}(CH_2)_3\text{-}R$
1a	$R\text{-}(CH_2)_3\text{-}R \cdot 3NH_3$
2	$R\text{-}(CH_2)_4\text{-}R$
3	$R\text{-}(CH_2)_6\text{-}R$
4	R-Ph-R
4a	$R\text{-Ph-}R \cdot NH_3$

Allowing the loaded ion exchange resin to react immediately with dissolve CsO_3 resulted in pure, microcrystalline products in the case

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of **2**, **3** and **4a**. They had to be separated mechanically from the solid exchange resin. In order to obtain larger crystals, the exchange reaction took place under diffusion control at −40 °C. In the case of **1a**, which showed better solubility than **2**, **3** and **4a**, the product could be isolated from the resin by repeated extraction with liquid ammonia. Compound **1a** tends to rapidly evolve ammonia at about −30 °C, which leads to microcrystalline powders of **1**. Compound **4a** tends to evolve ammonia slowly at −26 °C or at 10^{-3} mbar and −78 °C leaving microcrystalline powders of **4**. All compounds are highly sensitive towards air and moisture, and are thermally unstable at room temperature. ***Compound 1 explodes spontaneously.***

Figures **1** and **2** show parts of the crystal structures of **3** and **1a** (cf. Table 2)[12]. The thin lines mark C−H···O and N−H···O hydrogen bonds with the lengths of C···O and N···O bonds, respectively, less than 340 pm, this distance being the upper limit generally accepted for hydrogen bonds.

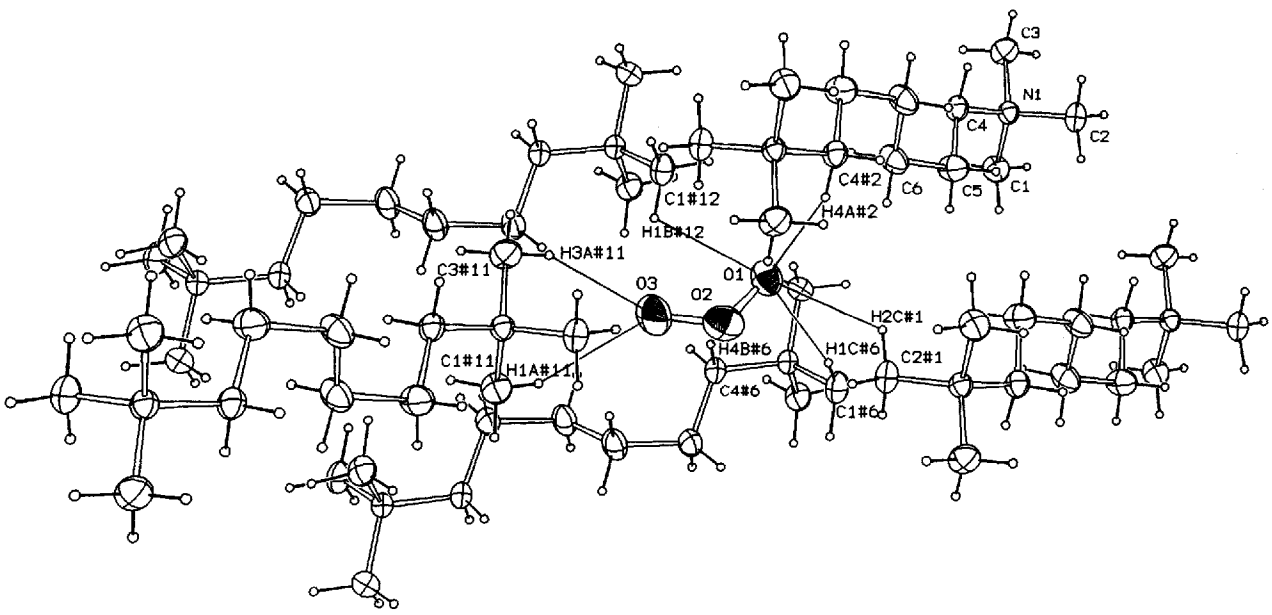
According to DTA/TG **1**, **2**, **3**, and **4** decompose within the temperature range from 24 °C (**1**) to 83.1 °C (**3**).

The results presented show that ionic ozonides with divalent quaternary ammonium counter ions can be easily prepared using the ion exchange route. While no progress could be made, so far, towards our goal of realising shorter intermolecular distances between ozonide anions, the rather accurate crystal data obtained on **1a** and **3** improve the basis for the discussion of the geometry of the ozonide anion. Theoretical studies are in agreement with spectroscopic data[13]. However, the calculated bond length of 136 pm[14] differ significantly from the range of bond lengths (128 to 134 pm) determined experimentally. The discrepancy is most pronounced in the case of tetraorganylammonium ozonides. In principle, this is also true for the new ozonides with bisquaternay ammonium counterions. The main structural difference between tetraorganylammonium ozonides and alkali metal ozonides is the presence of hydrogen bonds in the former. Thus, the tentative explanation of the significant shortening of the bond length and the widening of the angle (which are correlated in agreement with the predictions derived from a Walsh type diagram) being a consequence of hydrogen bonds accepted by oxygen is gaining additional support. There are several C−H···O hydrogen bonds shorter than 340 pm and with angles from 174 to 112° that lie within the limits generally accepted for C−H···O hydrogen bonds. C−H···O hydrogen bonds are believed to be active for C···O distances up to 340 pm[15] and C−H···O angles down to 90° for intramolecular and 110° for intermolecular hydrogen bonds[16]. Mean values for intermolecular N−H···O distances and angles are 290 pm and 160°[17]; the upper limit seems to be at 340 pm and 104°[18]. Our results confirm the existence of C−H···O hydrogen bonds in **3** and the existence of N−H···O hydrogen bonds together with C−H···O hydrogen bonds in **1a**.

In the structure of **3** there are seven C−H···O hydrogen bonds per unit cell. O(1) is involved in five hydrogen bonds, O(3) in two (Figure 1). Their influence on the bond length and angle of the ozonide anion is obviously not as strong as in **10**, but cannot be ignored, as is indicated by the average O−O distance of 132 pm.

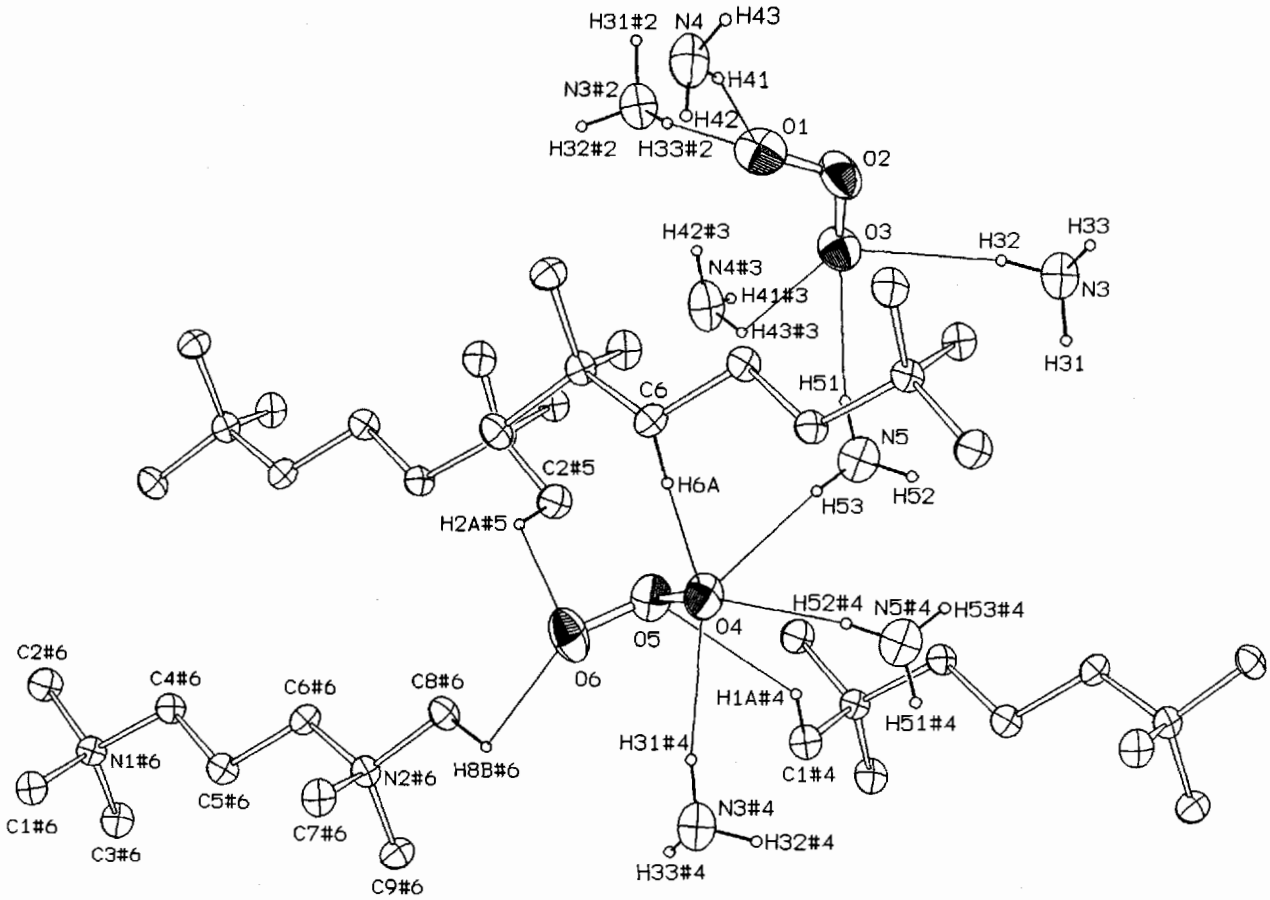
The structure of **1a** contains two crystallographically different ozonide anions. In the case of the ozonide anion O(1)−O(2)−O(3), there are five N−H···O hydrogen bonds (Figure 2). The average O−O bond length of 131 pm and the bond angle (118°) compare well with those of the quaternary ammonium ozonides investigated so far (cf. Table 1). The second ozonide anion O(4)−O(5)−O(6) participates in seven hydrogen bonds. Three of them are N−H···O hydrogen bonds and involve O(4), which is also an acceptor of a C−H···O hydrogen bond. From the three remaining C−H···O hydrogen bonds, one involves O(5) and two involves O(6). This asymmetric environment leads to an extremely large intramolecular difference between the two

Figure 1. ORTEP plot of the cationic coordination sphere of O_3^- in **3** in the range of 340 pm (50% probability ellipsoids)[a]



[a] Selected bond lengths [pm] and bond angles [°]: O(1)−O(2) 132.8(2), O(2)−O(3) 131.9(2), O(1)−O(2)−O(3) 115.8(1), O(1)−H(2C)#1 268(2), O(1)−C(2)#1 333.3(2), O(1)−H(2C)#1−C(2)#1 126(1), O(1)−H(4A)#2 232(2), O(1)−C(4)#2 324.0(2), O(1)−H(4A)#2−C(4)#2 160(1), O(1)−H(4B)#6 257(2), O(1)−C(4)#6 342.5(2), O(1)−H(4B)#6−C(4)#6 150(1), O(1)−H(1C)#6 246(2), O(1)−C(1)#6 335.3(2), O(1)−H(1C)#6−C(1)#6 157(2), O(1)−H(1B)#12 283(2), O(1)−C(1)#12 333.0(2), O(1)−H(1B)#12−C(1)#12 112(1), O(3)−H(3A)#11 245(2), O(3)−C(3)#11 334.1(2), O(3)−H(3A)#11−C(3)#11 152(1), O(3)−H(1A)#11 254(2), O(3)−C(1)#11 339.3(2), O(3)−H(1A)#11−C(1)#11 149(1). Symmetry operators used to generate equivalent atoms: #1 = −x, −y, −z + 1; #2 = −x + 1, −y, −z + 1; #6 = x, −y + 0.5, z + 0.5; #11 = x + 1, y, z + 1; #12 = x + 1, −y + 0.5, z + 0.5.

Figure 2. ORTEP plot of the cationic and solvent coordination sphere of O_3^- in **1a** in the range of 340 pm (50% probability ellipsoids)[a]



[a] Selected bond lengths [pm] and bond angles [°]: O(1)–O(2) 130.6(4), O(2)–O(3) 130.9(4), O(1)–O(2)–O(3) 117.9(2), O(4)–O(5) 137.4(3), O(5)–O(6) 129.5(3), O(4)–O(5)–O(6) 114.7(2), O(1)–H(41)#1 221(5), O(1)–N(4)#1 304.2(4), O(1)–H(41)#1–N(4)#1 165(4), O(1)–H(33)#2 238(5), O(1)–N(3)#2 319.2(5), O(1)–H(33)#2–N(3)#2 172(4), O(3)–H(43)#3 272(5), O(3)–N(4)#3 323.1(4), O(3)–H(43)#3–N(4)#3 123(4), O(3)–H(32)#1 235(5), O(3)–N(3)#1 320.4(5), O(3)–H(32)#1–N(3)#1 163(4), O(3)–H(51)#1 220(5), O(3)–N(5)#1 308.5(5), O(3)–H(51)#1–N(5)#1 168(4), O(4)–H(53)#1 238(5), O(4)–N(5)#1 324.2(5), O(4)–H(53)#1–N(5)#1 174(4), O(4)–H(52)#4 218(5), O(4)–N(5)#4 308.9(5), O(4)–H(52)#4–N(5)#4 167(3), O(4)–H(31)#4 233(5), O(4)–N(3)#4 327.7(5), O(4)–H(31)#4–N(3)#4 171(3), O(4)–H(6A)#1 226.9(4), O(4)–C(6)#1 323.2(4), O(4)–H(6A)#1–C(6)#1 163.8(1), O(5)–H(1A)#4 262(2), O(5)–C(1)#4 335.5(4), O(5)–H(1A)#4–C(1)#4 132(1), O(6)–H(2A)#5 265.7(9), O(6)–C(2)#5 337.2(4), O(6)–H(2A)#5–C(2)#5 130.1(8), O(6)–H(8B)#6 278.4(6), O(6)–C(8)#6 328.0(4), O(6)–H(8B)#6–C(8)#6 112.0(5). Symmetry operators used to generate equivalent atoms: #1 = x, y, z; #2 = x − 0.5, −y + 0.5, z − 0.5; #3 = x + 0.5, −y + 0.5, z − 0.5; #4 = −x + 1, −y, −z; #5 = x, y, z − 1; #6 = −x, −y, −z − 1.

bond lengths within the ozonide anion. One distance [O(5)–O(6): 130 pm] fits into the group of quaternary ammonium ozonides, the other [O(4)–O(5): 137 pm] is longer than the longest one observed in the group of alkali metal ozonides.

The interpretation of the crystal structures of both **1a** and **3** leads to the conclusion that the ozonide anion is very sensitive to its environment in the solid state. Hydrogen bonds apparently lead to a shortening of the bond lengths in the ozonide anion, which is in agreement with earlier findings[11].

Experimental

All experiments have been carried out in closed all-glass systems, which were dried in vacuo. Air and moisture were excluded, the products were handled under dried argon using standard Schlenk techniques and cooled during handling with liquid nitrogen or ethanol/dry ice. – IR: KBr-pellets, preparation of samples in a glove box. Spectrometer Bruker IFS 113v. Identification through comparison with halide spectra measured under the same conditions. – DTA/TG: Netzsch STA 429. Samples were inserted into the cooled oven (0–8 °C) in sealed glass tubes and opened under streaming argon. Heating rate was 5K/min. – Elemental analyses: Mikroanalytisches Institut Pascher, Remagen. – Crystal structure analysis: Crystals of **1a** were taken out of liquid ammonia, transferred into a inert oil mixture 3:1 Perfluoropolyether RS 3000 (Riedel-de Haën)/Perfluoropolyether 216 (Riedel-de Haën) and picked up by a Lindemann glass capillary. The inert oil mixture was cooled by a cold stream of dry nitrogen to −40 °C. Crystals of **3** were mechanically separated from the ionic exchange resin and wedged into Lindemann glass capillaries. Measurements were carried out with cooling (−160 °C in case of **1a** and −70 °C in case of **3**) on a four circle diffractometer CAD 4, Enraf Nonius, λ = 71.069 pm, graphite monochromator. The structures were solved by direct methods[19]; in the case of **3** hydrogen atoms bound to carbon were localised in the difference fourier map and refined with isotropic atomic displacement parameters[20]. In the case of **1a** hydrogen atoms were geometrically inserted and refined using a riding model.

Table 2. Crystallographic data for **1a** and **3**

	1	**3**
Formula	$C_9H_{24}N_2O_6 \cdot 3NH_3$	$C_{12}H_{30}N_2O_6$
Molecular mass [g/mol]	307.39	298.38
a [pm]	814.0(2)	552.5(1)
b [pm]	2102.0(9)	1210.7(1)
c [pm]	986.2(6)	1213.9(2)
ß [°]	96.01(4)	100.03(1)
Z	4	2
$d_{calcd.}$ [g/cm^{-3}]	1.217	1.239
Crystal system	monoclinic	monoclinic
Space group	P 2_1/n	P 2_1/c
V [$\cdot 10^6$ pm^3]	1678(1)	799.6(2)
µ [cm^{-1}]	0.99	0.98
Crystal size [mm^3]	0.3x0.5x1	0.8x0.9x1
T [K]	112	203
Reciprocal space	0–h, 0–k, –l–l	–h–0, –k–0, –l–l
2 Θ max [°]	44	54
Scan method	ω/θ	ω/θ
Total no.of reflections	2312	2041
No. of unique reflections	2067	1733
R_{int}	0.0414	0.0184
No. of observed reflections [$F_o > 4\sigma F_o$]	1714	1439
No. of refined parameters	216	152
GooF (F^2)	1.281	1.197
R1(observed)	0.0531	0.0420
wR2(for all)	0.1716	0.1208
Residual electron Density [e$\cdot 10^6$ • Å^{-3}]	max 0.26/min –0.26	max 0.25/min –0.19

Hydrogen atoms bound to nitrogen were identified in the difference fourier map and refined with equal isotropic atomic displacement parameters. – Materials: CsO_3 was prepared as reported previously[10]. Ammonia (Bayer AG) was made anhydrous by distilling it first from sodium, then from potassium, and was stored as a potassium-ammonia solution at −78 °C. Amberlyst 15 (Fluka) was used as ion exchange resin. 1,3-Bis(trimethylammonium)propane diiodide, 1,4-bis(trimethylammonium)butane diiodide and 1,6-bis-(trimethylammonium)hexane diiodide were prepared according to general methods[21] using iodomethane (Merck) and 1,3-bis(dimethylamino)propane (Lancaster), 1,4-bis(dimethylamino)butane (Fluka), 1,6-bis(dimethylamino)hexane (Lancaster). 1,4-Bis(trimethylammonium)benzene diiodide was prepared as reported previously[22] using dimethylsulfate (Merck) and 1,4-diaminobenzene (Merck).

General Procedure: Compound **1a** was prepared according to the procedure given in the litcrature[8], but stored under liquid ammonia at −78 °C. ***Caution:*** Evaporation of ammonia and attempts to transfer the product for further investigations led in four of five cases to ***severe spontaneous explosions***. Compounds **2**–**4** were prepared using an U-shaped vessel containing a glass sieve (porosity 3). 1 g of the ionic exchange resin loaded with the particular diiodide ammonium salt was placed into one side and about $8 \cdot 10^{-4}$ mol CsO_3 (about 145 mg CsO_3) was placed into the other side of vessel under cooling (ethanol/dry ice). Ammonia was condensed into both sides until the glass sieve was completely covered. The reaction mixture was stored at −40 °C for seven days to react by slow diffusion. After the reaction was completed, ammonia was slowly evaporated at −60 °C leaving a mixture of red crystalline products **2**–**4** and ion exchange resin. The resin was separated mechanically in vacuo while cooling with liquid nitrogen. The products were sealed in glass ampoules under argon and stored at −30 °C. Storage over several months without significant decomposition was possible. In case of the compounds **1a** and **4a** no analysis except of the crystal structures could be carried out due to the loss of ammonia. All analytical data are related to the ammonia free compounds **1** and **4**.

1,3-Bis(trimethylammonium)propane diozonide · 3 NH_3 (**1a**): 98%, plate-shaped dark red crystals.

1,3-Bis(trimethylammonium)propane diozonide (**1**): 98%, dark red powder. – DTA/TG: sharp, exothermic decomposition at 24.0 °C under loss of weight.

1,4-Bis(trimethylammonium)butane diozonide (**2**): 90%, small bright red needles. – DTA/TG: sharp, exothermic decomposition at 61.2 °C under loss of weight. – IR: I = 790 cm^{-1} [$\nu_{as}(O_3^-)$], 585 cm^{-1} [$\delta(O_3^-)$]. $C_{10}H_{26}N_2O_6$ (270.33): calcd. C 44.43, H 9.69, N 10.36; found C 43.51, H 9.01, N 12.7.

1,6-Bis(trimethylammonium)hexane diozonide (**3**): 97%, column-shaped, deep dark red crystals. – DTA/TG: sharp, exothermic decomposition at 83.1 °C under loss of weight. – IR: I = 793 cm^{-1} [$\nu_{as}(O_3^-)$], 588 cm^{-1} [$\delta(O_3^-)$]. $C_{12}H_{30}N_2O_6$ (298.38): calcd. C 48.31, H 10.13, N 9.39; found C 47.69, H 9.55, N 8.72.

1,4-Bis(trimethylammonium)benzene diozonide · NH_3 (**4a**): 95%, orange-red plates.

1,4-Bis(trimethylammonium)benzene diozonide (**4**): 95%, orange-red powder. – DTA/TG: sharp, exothermic decomposition at 49.0 °C under loss of weight. – IR: I = 790 cm^{-1} [$\nu_{as}(O_3^-)$], 588 cm^{-1} [$\delta(O_3^-$]. $C_{12}H_{22}N_2O_6 \cdot NH_3$ (307.35): calcd. C 46.90, H 8.20, N 13.67; found C 50.10, H 8.35, N 14.10.

☆ Dedicated to Professor *Max Herberhold* on the occasion of his 60th birthday.

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