

Structure and Solid-State Chemistry of 3-Carboxy-2-naphthalenediazonium Bromide

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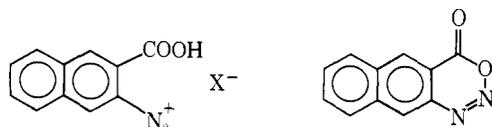
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Abstract: 3-Carboxy-2-naphthalenediazonium bromide (Ib) crystallizes as a relatively stable triclinic monohydrate ($a = 7.532 \text{ \AA}$, $b = 9.892 \text{ \AA}$, $c = 9.182 \text{ \AA}$, $\alpha = 65.23^\circ$, $\beta = 94.4^\circ$, $\gamma = 76.80^\circ$, $P\bar{1}$, $Z = 2$). Its crystal structure at 23°C has been determined through analysis of 1274 single-crystal X-ray intensities ($R = 0.06$). Thermal gravimetric and calorimetric analyses demonstrate that the water of crystallization is lost in the interval $65\text{--}100^\circ \text{C}$ (total heat absorbed = 17 kcal/mol) prior to the exothermic loss of N_2 in the interval $100\text{--}135^\circ \text{C}$ (total heat released = 36 kcal/mol) which results in the formation of 3-bromo-2-naphthoic acid (70% yield). Two intermediate phases (Ib α and Ib β) are formed topotactically at ~ 65 and $\sim 90^\circ \text{C}$. The latter phase, which reverts to Ib α upon cooling, shows infrared absorption ($2268, 1721 \text{ cm}^{-1}$) consistent with an anhydrous structure which has retained the diazonium and carboxyl groups. It decomposes to polycrystalline bromo acid within a couple of hours at 95°C . The crystal structure of the parent Ib consists of aromatic diazonium ion, hydrogen bonded through the carboxyl group to water, which in turn is hydrogen bonded to bromide ion. Close approaches to the cation involve the outer nitrogen with (a) bromide ion (3.27 \AA) and (b) the carbonyl oxygen of a neighboring molecule (2.86 \AA). The closest intramolecular interaction with the diazonium group involves the inner nitrogen and the proximate ortho carbonyl oxygen (2.57 \AA). The outer nitrogen is displaced away from this oxygen resulting in an appreciably distorted C-N-N bond angle (171°).

Introduction

Except for the thermal decomposition of solid diazonium fluoroborates (Schiemann reaction¹), little is known of the solid-state reactions of aromatic diazonium salts. These explosive solids are rarely isolated during synthesis; nevertheless, several crystal structure determinations have been reported for diazonium salts containing anions of low nucleophilic power [(C₆H₅N₂⁺Cl⁻)₂ and its acetic acid solvate,³ (C₆H₅N₂⁺Br₃⁻),⁴ the zwitterionic sulfonates (*p*-O₃SC₆H₄N₂⁺),⁵ and the hydrate of 2-diazonium-4-phenol-sulfonate⁶), (C₆H₅N₂⁺Cu₂Br₃⁻),⁷ (*o*-CH₃OC₆H₄N₂⁺·FeCl₄⁻),⁸ ((*p*-(CH₃)₂NC₆H₄N₂⁺)₂ZnCl₄²⁻),⁹ (*p*-N₂⁺C₆H₄N₂⁺ZnCl₄²⁻)¹⁰].¹¹

We have undertaken a study of the structure and behavior of diazonium salts containing nucleophilic anions, and in some cases, solvent molecules which could be expected to replace or couple with the labile diazonium group during reactions in the crystalline state. We chose to study salts derived from 3-amino-2-naphthoic acid after isolating the corresponding crystalline diazonium iodide, Ia.¹² Orthorhombic single crystals of this unstable material evolve nitrogen at room temperature and are transformed into polycrystalline 3-iodo-2-naphthoic acid. A full account of the structure and behavior of Ia will be published in a separate report. The triclinic diazonium bromide, Ib, and chloride, Ic, are crystallographically isostructural (Table I) and, as in the case of the corresponding bisulfate,¹³ Id, crystallize as monohydrates, the structures of which are described in this report.



- I
a, X = I
b, X = Br
c, X = Cl
d, X = HSO₄

In terms of molecular structure, diazonium ions having ortho carboxyl groups are of particular interest with regard to intramolecular nonbonded interactions between the ortho substituents, and their relationship to the possible formation of the covalent heterocyclic diazo structure, II.

DSC, TGA, and X-ray diffraction studies at elevated temperatures demonstrate that the triclinic hydrated structure Ib loses water topotactically above 65°C and is transformed to an intermediate phase, α , which, in turn, topotactically is transformed at $\sim 90^\circ \text{C}$ to another single crystal phase, β . Thermal decomposition of the β phase ($T \sim 100^\circ \text{C}$) is accompanied by the evolution of nitrogen and the formation of 3-bromo-2-naphthoic acid (70% isolated yield). Although the other products have not yet been characterized, little if any of the naphthol 3-hydroxy-2-naphthoic acid appears to be formed.

Results

The intramolecular bond distances and angles (Table III) of the naphthalenediazonium ion are identical within experimental error with the corresponding values found in the similar triclinic crystal structure of Id.¹³ The increase in the internal ring angle at C2, as well as the C-N and N-N distances, are in reasonable agreement with values found in other X-ray determinations.²⁻¹⁰ However, unlike the other structures which do not have ortho carboxyl groups, the C-N-N angle deviates significantly from linearity ($171 \pm 1^\circ$ in Ib, $174.6 \pm 0.8^\circ$ in Id).

The entire cation is approximately flat (Figure 1). The nature of the bending of the diazonium group and other deviations from planarity are best described by three least-squares planes: P1 (atoms C1, C2, C3, N14, N15; av dev from plane = 0.0004 \AA), P2 (atoms C2, C3, C4, C11; av dev from plane = 0.005 \AA), and P3 (atoms C3, C11, O12, O13; av dev from plane = 0.003 \AA). The dihedral angle of 6° between P1 and P2 suggests a twisting about the C2-C3 bond so as to displace the diazonium nitrogens and the carboxyl group to opposite sides of the naphthalene plane, while the 1° dihedral angle between P2 and P3 indicates virtually no rotation of the carboxyl group about the C3-C11 bond. The corresponding angles in Id were found to be 5 and 2° , respectively. The carbonyl oxygen O13 is proximate to the diazonium group.

The near planarity of the five atoms of P1 together with the torsional angle C1-C2-N14-N15 = 0.7° indicates that the 9° distortion from linearity of the diazonium group represents a bending displacement in P1 of the outer nitrogen N15 away from the *o*-carboxyl group.¹⁴ This bending, which is contrary to the geometric changes necessary for intramolecular cycli-

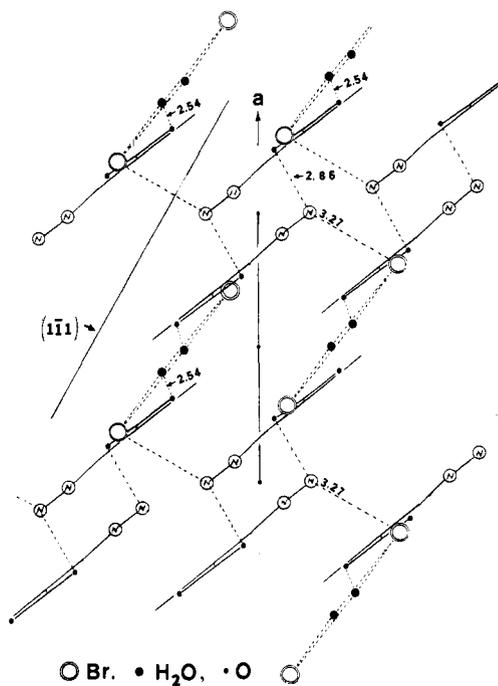


Figure 2. A schematic representation of the packing of Ib into sheets which are parallel to $(1\bar{1}\bar{1})$ and perpendicular to (011) (see also Figure 4). The hydrogen bonds between Br^- and H_2O and between H_2O and $\text{O}12$ (2.54 Å) as well as the $\text{O}13\text{--N}15$ intermolecular interactions (2.86 Å) occur within these sheets. The closest Br^- -- $\text{N}15$ interactions (3.27 Å) occur between the sheets. The naphthalene plane is nearly perpendicular to (011) , the plane of the drawing.

tion at $\sim 124^\circ\text{C}$. More than the theoretical weight change (18% observed instead of the 9% further reduction of the original weight expected for loss of N_2) occurs during this second weight loss, and it is clear that, to some extent in the intermediate anhydrous crystal, other chemical reactions resulting in other volatile products compete with the Sandmeyer-type replacement of the diazonium group by bromine. No doubt some of the excess weight loss is due to the observed sublimation of small amounts of the rather volatile bromo acid, a process which results in further gradual weight loss during heating to higher temperatures.

The infrared spectrum of crystals of Ib heated to $\sim 140^\circ\text{C}$ verifies the loss of the diazonium group and the formation of the bromo acid as the principal product. The latter is conveniently isolated in a relatively pure form by slow sublimation at atmospheric pressure through further heating of decomposed Ib at $\sim 170^\circ\text{C}$. In a typical run, 70% of the theoretical yield of bromo acid (identified by IR and X-ray diffraction studies) was obtained in this manner.¹⁹

X-ray studies of Ib at elevated temperatures reveal the occurrence of *two* topotactic phase transformations during the endothermic loss of water in the interval $65\text{--}100^\circ\text{C}$. The first occurs at $\sim 65^\circ\text{C}$ where most crystals of Ib crack and become opaque. Cracking usually occurs along several divergent boundaries which are approximately perpendicular to the flat (011) crystal face. The resulting phase ($\text{Ib}\alpha$) is formed as an extensive mosaic which gives rise to relatively broad reflections which have not yet been indexed.

Since our primary goal in the study of Ib is to determine the structure of the solid-state environment in which the bromo acid is formed, it is fortunate that the relatively poorly defined α phase transforms topotactically at $\sim 90^\circ\text{C}$ to a more ordered single-crystal structure ($\text{Ib}\beta$). No further change of crystal shape is apparent during this second transformation. The IR spectrum of the β phase is devoid of the absorption attributable to water of crystallization ($\sim 3315\text{ cm}^{-1}$) but has absorptions

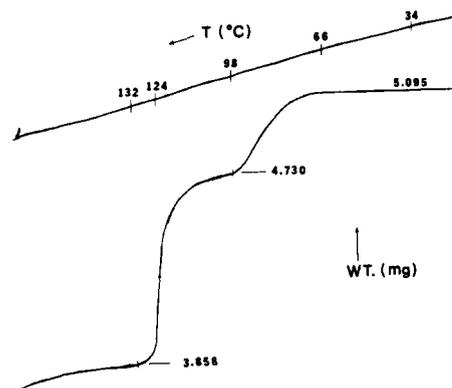


Figure 3. Thermal gravimetric analysis of Ib at a heating rate of $2.5^\circ\text{C}/\text{min}$. Temperature (upper line) and weight curves were recorded simultaneously.

consistent with the presence of diazonium and carboxyl groups. The appreciable changes in the latter group frequencies (28 cm^{-1} blue shift of the carbonyl absorption and appreciable changes in the $1200\text{--}1300\text{ cm}^{-1}$ region) probably are due to the disruption of the hydrogen bonding of the carboxyl group to water in Ib.

This interesting phase is only moderately stable. Its decomposition to *polycrystalline* bromo acid is complete within a couple of hours at $\sim 95^\circ\text{C}$. When allowed to cool to room temperature it eventually reverts²¹ to a single crystal phase (probably $\text{Ib}\alpha$) which can be reconverted to $\text{Ib}\beta$ through heating at $\sim 90^\circ\text{C}$. However, recycling, $\text{Ib}\beta \rightarrow \text{Ib}\alpha \rightarrow \text{Ib}\beta$, markedly diminishes the quality of the β phase; the best samples of $\text{Ib}\beta$ were obtained by placing Ib in an oven, preheated to 95°C , for 10 min.

The $\text{Ib}\beta$ phase has the apparent cell constants $a = 10.3\text{ \AA}$, $b = 6.8\text{ \AA}$, $c = 8.3\text{ \AA}$, $\alpha = 90^\circ$, $\beta = 102^\circ$, $\gamma = 90^\circ$ and a calculated unit cell volume (570 \AA^3) smaller than the initial volume (593 \AA^3 ; $Z = 2$) of its hydrated precursor, Ib. It follows from the experimentally derived topotactic matrix relating the unit cell vectors of $\text{Ib}\beta$ and Ib

$$\begin{pmatrix} \bar{a} \\ \bar{b} \\ \bar{c} \end{pmatrix}_{\text{Ib}\beta} = \begin{pmatrix} -0.36 & 1.15 & -0.23 \\ 0.91 & 0 & 0 \\ -0.11 & 0.07 & -0.94 \end{pmatrix} \begin{pmatrix} \bar{a} \\ \bar{b} \\ \bar{c} \end{pmatrix}_{\text{Ib}}$$

that the b axis of $\text{Ib}\beta$ is generated parallel to a of Ib, while the angles between the c axes of $\text{Ib}\beta$ and Ib, and between a of $\text{Ib}\beta$ and b of Ib, are 174 and 16° , respectively.

To date, the best crystals of $\text{Ib}\beta$ which we have been able to produce give rise to discrete single crystal reflections only out to relatively low values of 2θ . Of these, the $(\bar{1}\bar{1}\bar{1})$ reflection ($d(\bar{1}\bar{1}\bar{1}) = 4.4\text{ \AA}$) is considerably more intense than the others. It is of interest that the $(\bar{1}\bar{1}\bar{1})$ planes of $\text{Ib}\beta$ are aligned within 14° with the $(1\bar{1}\bar{1})$ planes which define the sheets of molecules of Ib, and both characterize the most frequently observed directions of crack boundaries which develop during the solid-state dehydration (Figure 4). These observations are qualitatively consistent with a dehydration process in which the sheet structure of Ib is retained in $\text{Ib}\beta$ while the packing within sheets is altered as a consequence of the disruption of the hydrogen bonds. Further studies of the topotactically aligned crystal structure of $\text{Ib}\beta$ hopefully will provide further insight into the solid-state mechanisms by which it is formed through dehydration and subsequently transformed into the bromo acid product.

In any case it is clear that the crystal matrix of diazonium salts provides a "sheltered" environment in which essentially only the counteranion is available for replacement of the diazonium group.

Table II. Fractional Atomic Coordinates

| atom | x | y | z |
|-------------------|------------|------------|-------------|
| Br ⁻ | 0.6922 (2) | 0.6870 (2) | -0.1205 (2) |
| C1 | 0.872 (1) | 0.242 (1) | 0.207 (1) |
| C2 | 0.854 (1) | 0.299 (1) | 0.319 (1) |
| C3 | 0.782 (1) | 0.236 (1) | 0.465 (1) |
| C4 | 0.742 (1) | 0.101 (1) | 0.497 (1) |
| C5 | 0.714 (1) | -0.108 (1) | 0.422 (1) |
| C6 | 0.723 (1) | -0.167 (1) | 0.313 (1) |
| C7 | 0.776 (2) | -0.090 (1) | 0.163 (1) |
| C8 | 0.830 (1) | 0.043 (1) | 0.130 (1) |
| C9 | 0.823 (1) | 0.105 (1) | 0.240 (1) |
| C10 | 0.758 (1) | 0.033 (1) | 0.389 (1) |
| C11 | 0.752 (1) | 0.319 (1) | 0.566 (1) |
| O12 | 0.685 (1) | 0.2490 (9) | 0.6941 (9) |
| O13 | 0.784 (1) | 0.443 (1) | 0.5276 (9) |
| N14 | 0.917 (1) | 0.436 (1) | 0.280 (1) |
| N15 | 0.969 (1) | 0.536 (1) | 0.235 (1) |
| O16 | 0.448 (1) | 0.5871 (9) | 0.1662 (9) |
| H1 ^a | 0.92 | 0.30 | 0.11 |
| H4 ^a | 0.70 | 0.05 | 0.60 |
| H5 ^a | 0.68 | -0.16 | 0.52 |
| H6 ^a | 0.69 | -0.26 | 0.34 |
| H7 ^a | 0.77 | -0.13 | 0.08 |
| H12 ^b | 0.66 | 0.30 | 0.78 |
| H16a ^b | 0.50 | 0.62 | 0.06 |
| H16b ^b | 0.44 | 0.50 | 0.16 |

^a Assigned coordinates; not refined. ^b Observed in difference map; not refined.

Experimental Section

Synthesis and Isolation of Id.¹³ 3-Amino-2-naphthoic acid (5.09 g from EtOH) was dissolved with warming in 19 mL of 1 M aqueous Na₂CO₃ solution. After cooling to room temperature, the solution was combined with a solution of 1.88 g of NaNO₂ in 32 mL of H₂O. A solution (41 mL) of 12 mL of concentrated H₂SO₄ in 50 mL of H₂O was added dropwise with stirring at room temperature over a period of 45 min. The diazonium bisulfate begins to crystallize after ~1/4 of the acid has been added. The suspension was stirred for an additional 15 min, then cooled at 10 °C for 3 h. Id was collected by filtration, washed with cold sulfuric acid of the above concentration, washed with cold 2-propanol, which removes a burgundy colored impurity, and air dried (7.18 g of thick, orange-yellow, triclinic prisms of the monohydrate; further cooling of the mother liquors gave an additional 0.22 g; yield, 87%): ν_{\max} (cm⁻¹, KBr) 3320 (s), 3120–2325 (m), 2255 (m), 1695 (s), 1612 (w), 1470 (m), 1414 (m), 1357 (m), 1322 (m), 1287 (s), 1217 (s), 1172 (s), 1122 (m), 887 (m), 862 (m), 808 (m), 779 (m), 754 (m).

Preparation of Ib. Id (210 mg) was dissolved in 3.5 mL of warm aqueous hydrobromic acid (48%), and the clear yellow solution cooled for several hours at 10 °C. The resulting yellow plates of Ib were isolated by filtration, washed successively with small amounts of cold water and benzene, and air dried: 160 mg (80% theory); ν_{\max} (cm⁻¹, KBr) 3314 (s), 3125–2325 (m), 2255 (m), 1693 (s), 1612 (w), 1466 (m), 1290 (s), 1196 (m), 1121 (m), 1010 (w), 938 (w), 890 (w), 865 (w), 804 (m), 775 (m), 760 (m).

Ib β . The IR spectrum of Ib β was determined from a sample of Ib which had been heated (98 °C) only until it had lost the theoretical weight of water (monitored by TGA). The sample was cooled to room temperature and its spectrum measured within 10 min after the weight loss: ν_{\max} (cm⁻¹, KBr) 3075–2325 (m), 2268 (m), 1720 (s), 1612 (w), 1464 (m), 1429 (w), 1400 (m), 1356 (m), 1238 (m), 1216 (m), 1198 (s), 1120 (m), 1012 (w), 922 (w), 798 (w), 770 (m), 736 (m).

DSC and TGA Measurements. A Perkin-Elmer Model DSC-1B differential scanning calorimeter was used for the calorimetric studies. Samples (~5 mg) were heated at atmospheric pressure in covered, but not sealed, aluminum pans. The total transition energies were estimated through comparisons with the 14.5 cal/g heat of fusion of pure tin. Curve areas were estimated with a planimeter.

For the TGA studies, samples were heated in open aluminum pans at atmospheric pressure, with continuous weight monitoring (Cahn electrobalance).

X-ray Diffraction Studies. Precession photography was used to

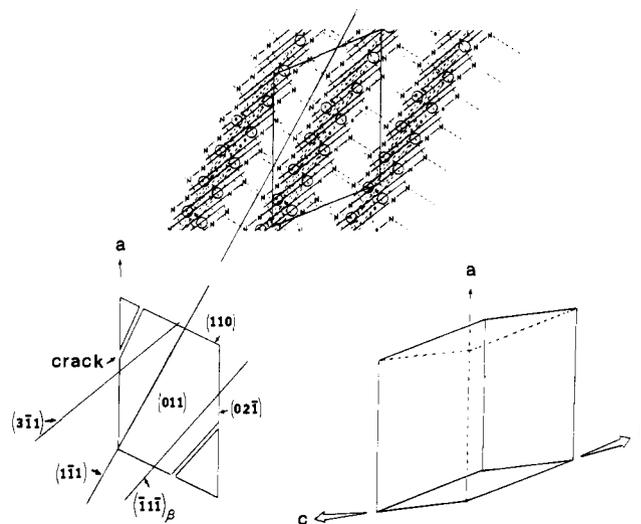


Figure 4. The plane of the drawing is parallel to (011). (Lower right): the unit cell of Ib. (Lower left): The traces of several planes and idealized crack boundaries which are nearly perpendicular to (011) are shown relative to a typical crystal of Ib. (Top): The arrangement of the (111) sheets (see also Figure 2) relative to the crystal morphology and unit cell of Ib.

Table III. Bond Distances and Angles

| Bond Distances (Å) | | | |
|--------------------------------|----------|-------------|----------|
| C1–C2 | 1.36 (2) | C8–C9 | 1.38 (2) |
| C2–C3 | 1.43 (1) | C9–C10 | 1.44 (1) |
| C3–C4 | 1.36 (2) | C9–C1 | 1.41 (2) |
| C4–C10 | 1.41 (2) | C2–N14 | 1.45 (2) |
| C10–C5 | 1.42 (2) | N14–N15 | 1.08 (2) |
| C5–C6 | 1.35 (2) | C3–C11 | 1.47 (2) |
| C6–C7 | 1.41 (2) | C11–O12 | 1.30 (1) |
| C7–C8 | 1.38 (2) | C11–O13 | 1.21 (2) |
| Bond Angles ^a (deg) | | | |
| C1–C2–C3 | 126 | C8–C9–C1 | 122 |
| C2–C3–C4 | 115 | C1–C9–C10 | 118 |
| C3–C4–C10 | 123 | C9–C1–C2 | 118 |
| C4–C10–C9 | 120 | C1–C2–N14 | 114 |
| C4–C10–C5 | 123 | C3–C2–N14 | 120 |
| C5–C10–C9 | 117 | C2–N14–N15 | 171 |
| C10–C5–C6 | 121 | C2–C3–C11 | 120 |
| C5–C6–C7 | 121 | C4–C3–C11 | 125 |
| C6–C7–C8 | 120 | C3–C11–O12 | 114 |
| C7–C8–C9 | 121 | C3–C11–O13 | 122 |
| C8–C9–C10 | 120 | O12–C11–O13 | 124 |

^a All errors are 1°.

determine the Miller indexes of the crystal faces of Ib and the crack boundaries which develop during its dehydration. Crystals of Ib are elongated along *a* with (011) parallel to the flat plate face; some crystals also have well-developed edges parallel to (110) and (021). The crack boundaries are approximately perpendicular to (011). Some of these boundaries are roughly parallel to the (111) sheets of associated molecules of Ib while others tend to develop more nearly parallel to (111) of Ib β . Nucleation of the product phases occurs primarily at the crystal edges and along the crack boundaries.

Weissenberg photography at elevated temperatures was used to study the transformations Ib \rightarrow Ib α \rightleftharpoons Ib β . Aligned single crystals were heated continuously by a stream of warm, dry nitrogen gas; the temperature was monitored by a thermocouple positioned within a few millimeters of the crystal. The topotactic matrix was derived from the cell constants of Ib β and Ib, and the angles between *a**, *c** of Ib β and *b**, *c** of Ib observed on (0*kl*)_{Ib} \rightarrow (*h*0*l*)_{Ib β} photographs of heated samples of Ib.

The structure analysis of Ib was performed on 1274 ("observed" with $I > 3\sigma$) intensities which had been measured diffractometrically (graphite-monochromatized Cu K α radiation: $\lambda K\alpha_1 = 1.5405$ Å, $K\alpha_2 = 1.5443$ Å) at 23 °C using the θ - 2θ variable scan rate technique.

Background counts, B_1 , B_2 , were measured for half the scan time at each end of the scan range. The sample ($0.20 \times 0.10 \times 0.05$ mm) was exposed to the atmosphere throughout data collection. The intensities ($2\theta_{\max} = 110^\circ$) were corrected for absorption²² ($\mu = 52.0 \text{ cm}^{-1}$) and converted to F^2 . No attempt was made to correct the data for the $\sim 7\%$ crystal decomposition evident in the decay of two check reflection intensities. Standard deviations were assigned according to $\sigma(I) = (C = B_1 + B_2)^{1/2}$ where C is the total integrated reflection count. The positions of all nonhydrogen atoms were obtained by Patterson and Fourier methods, and refined together with their anisotropic thermal parameters, by full-matrix least-squares methods in which the quantity minimized was $\sum w(|F_o|^2 - |F_c|^2)^2$ with $w = 1/\sigma^2$. Atomic scattering factors, including the anomalous components for bromine, were taken from the International Tables for X-ray Crystallography.²³ Further refinement of the nonhydrogen atoms, after introduction of the aromatic hydrogens at calculated positions, resulted in $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o| = 0.07$. At this stage, the hydrogen atoms bonded to oxygen were located in a difference map, and included, though not refined, in the final least-squares calculations. A final difference map showed no peaks above $0.7 \text{ e } \text{Å}^{-3}$; parameter shifts during the final cycle of refinement were approximately one-third of the estimated errors. The final R factors are $R_1 = 0.06$, $(\sum w(|F_o|^2 - |F_c|^2)^2 / \sum w F_o^4)^{1/2} = 0.14$. The final fractional atomic coordinates are given in Table II while Table III presents the calculated bond distances and angles.

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Supplementary Material Available: Tables of temperature factors, and the observed and calculated structure factors (13 pages). Ordering information is given on any current masthead page.

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- To increase further the stability of the salts, several of the structures were sealed in Pyrex capillary tubes, and examined at -10 to -25°C ; some instability to light and X-rays has been reported.^{3,10} The zwitterionic sulfonates were examined at ambient temperatures and apparently are quite stable.^{5,6}
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- Deviations from linearity of a similar magnitude have been observed in crystal structures of several covalent cyanides. See, for example, K. Emerson and D. Britton, *Acta Crystallogr.*, **17**, 1134 (1964).
- The shortest N-Br distance (3.65 Å) in $\text{C}_6\text{H}_5\text{N}_2^+\text{Cu}_2\text{Br}_3^-$ involves the inner nitrogen atom.⁷
- The possibility that this close approach reflects an electrostatic attraction between the diazonium cation and carboxylate anion (several short intermolecular distances, in the range 2.73-3.06 Å were observed between oxygen and nitrogen atoms in the zwitterionic structure of *p*-benzenediazonium sulfonate³) seems unlikely in view of the IR spectrum of lb and the observed geometry of atoms C11, O12, O13. The (unrefined) coordinates of the hydrogen, H12, between O12 and O16 lead to the calculated distances O12-H12 = 1.1 Å and O16-H12 = 1.5 Å. The alternative formulation of lb in which H12 is covalently bonded to the water would consist of $\text{H}_3\text{O}^+\text{Br}^-$ ions hydrogen bonded to the zwitterionic naphthalene-2-diazonium-3-carboxylate. The crystal structure of the zwitterion¹⁷ ($\nu_{\max} 1630 \text{ cm}^{-1}$) prepared from lb and Ag_2O is currently under investigation in this laboratory. lb and ld have the same infrared carbonyl absorption frequencies even though in ld no comparable interaction exists between the carbonyl oxygen and the diazonium group.
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Ozonation of Nucleophiles. 10. Ethers¹

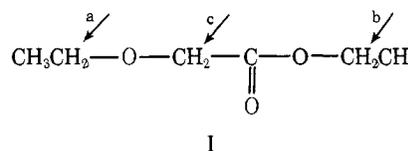
Philip S. Bailey* and Duane A. Lerdal

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Abstract: The ozonations of four ethers, ethyl isopropyl ether (VI), 4-oxa-2-heptanone (VII), 2-chloro-1-ethoxyethane (VIII), and ethyl ethoxyacetate (I), were studied in Freon 11 at 0 , -30 , and -78°C , using ozone in a nitrogen stream. The ozone attack on VI was largely at the tertiary hydrogen, presumably by 1,3-dipolar insertion. The attack on VII occurred principally at the more acidic methylene group, as expected of internal oxidation, while the other two ethers were attacked, near equally, by both routes. Mechanisms of reactions leading from the initial attack to products are discussed.

Diethyl ether appears to be the first organic substance ever ozonized, by Schönbein in 1855.² Other early studies with ethers were made by von Babo,³ Berthelot,⁴ Harries,⁵ and Fischer.⁶ More recently, the mechanism of ether ozonation has been investigated by Price and Tumulo⁷ and by Erickson, Hansen, and Harkins.⁸

Price and Tumulo⁷ showed that only carbon-hydrogen bonds α to the ether oxygen were attacked and that the less acidic these were, the faster the ozonation. For example, the tertiary hydrogen of propyl isopropyl ether was found to be, on a statistical basis, 1.7 times more reactive than an α secondary hydrogen. Likewise, for ethyl ethoxyacetate (I) the overall ozone attack was slow, but occurred at positions a, b,



and c, in the proportions 72:21:6.⁷ The ozonations were carried out at room temperature with ozone in an oxygen stream. The fact that a maximum of 1.18 mol of ether reacted per mol of ozone consumed indicated that ozone was the major oxidant and that very little autoxidation was involved. Price and Tumulo⁷ proposed an ozone insertion mechanism similar to the 1,3-dipolar insertion suggested by White and Bailey⁹ and