

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

J. Zanos Gougoutas* and J. Johnson

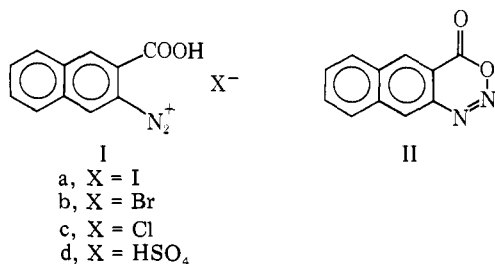
Contribution from the Department of Chemistry, University of Minnesota,
Minneapolis, Minnesota 55455. Received February 7, 1978

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 [$(\text{C}_6\text{H}_5\text{N}_2^+\text{Cl}^-)^2$ and its acetic acid solvate,³ $(\text{C}_6\text{H}_5\text{N}_2^+\text{Br}_3^-)$,⁴ the zwitterionic sulfonates ($p\text{-O}_3\text{SC}_6\text{H}_4\text{N}_2^+$),⁵ and the hydrate of 2-diazonium-4-phenol-sulfonate⁶], $(\text{C}_6\text{H}_5\text{N}_2^+\text{Cu}_2\text{Br}_3^-)$,⁷ ($o\text{-CH}_3\text{OC}_6\text{H}_4\text{N}_2^+\text{FeCl}_4^-$),⁸ $((p\text{-(CH}_3)_2\text{NC}_6\text{H}_4\text{N}_2^+)_2\text{ZnCl}_4^{2-})$,⁹ $(p\text{-N}_2^+\text{C}_6\text{H}_4\text{N}_2^+\text{ZnCl}_4^{2-})$.^{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.



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 $\text{C1–C2–N14–N15} = 0.7^\circ$ 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-

Table I. Crystal Data

structure	<i>a</i> , Å	<i>b</i> , Å	<i>c</i> , Å	α , deg	β , deg	γ , deg	ρ	<i>Z</i>	space group	<i>V</i> , Å ³	$\nu(\text{C}=\text{O})$, cm ⁻¹	$\nu(\text{N}=\text{N})$, cm ⁻¹
Ia	15.36	16.90	9.60	90	90	90	1.870	8	<i>Pbca</i>	2509	1705	2260
Ib	7.532 (3)	9.892 (5)	9.182 (4)	65.2 (1)	94.4 (1)	76.8 (1)	1.654	2	<i>P</i> $\bar{1}$	593.2	1693	2255
Ib β	10.3	6.8	8.3	90	102	90		2	?	570	1720	2268
Ic	7.340	9.986	9.035	65.16	93.27	76.85	1.45	2	<i>P</i> $\bar{1}$	576.4	1690	2255
Id	7.032	10.425	10.225	73.05	101.38	72.34	1.611	2	<i>P</i> $\bar{1}$	648.8	1695	2255
Ie ^a	6.753	10.497	8.620	73.6	120.1	85.3		2	<i>P</i> $\bar{1}$	488.4	1630, ¹⁷ 1648	2280

^a Ie is the zwitterion: naphthalene-2-diazonium-3-carboxylate, crystallized from water-acetone.

zation leading to II, is consistent with the presence of a strong interaction between the carbonyl oxygen O13 and the inner nitrogen N14 (N-O distance = 2.57 Å; angles O13--N14--N15 = 104°, O13--N14--C2 = 85°). The strong intermolecular interaction between O13 and the outer nitrogen N15 (vide infra) may also contribute to this distortion. A similar though less pronounced bending away from the carboxyl was found in Id.

Molecular Packing. The water molecule is involved in all of the three intermolecular hydrogen bonds present in this crystal structure; however, it does not interact significantly with the diazonium group. Rather diffuse peaks consistent with hydrogen atoms of the water were evident in a difference map; each of these hydrogens is hydrogen bonded to a different bromide ion such that two water molecules and two bromide ions are joined by four hydrogen bonds about an inversion center with O16---Br distances of 3.27 and 3.29 Å (Figure 1).

The C-O bond lengths and bond angles of the carboxyl group suggest that O13 is the carbonyl oxygen; in support of this assignment, the difference map contained a peak consistent with a hydrogen atom between O12 of the carboxyl and the water molecule. The O16--O12 distance of this H bond is 2.54 Å and the C11--O12--O16 angle is 116°. The angles of H bonding about the water are O12---O16---Br = 125°, O12--O16--Br' = 130°, Br--O16--Br' = 102°, while angle O16--Br--O16' = 78°. Although the water lies directly beneath the diazonium group, essentially on the perpendicular bisector of the C2--N14 bond which is normal to the naphthalene plane, the shortest distances between O16 and the organic ion, O16--C2 = 3.39, and O16--N14 = 3.40 Å, suggest no abnormal feature. It is of interest that no other atom intermolecularly approaches closer to C2 than O16.

In addition to the H-bond interactions with two water molecules, each bromide ion approaches the diazonium nitrogens of two inversion-related cations, with resultant Br--N distances in the range 3.27–3.58 Å. It is of interest that the shortest Br--N interaction, which is significantly shorter than the sum of ionic and van der Waals radii for Br⁻ and N, involves the outer nitrogen, N15, as was found to be the case in benzenediazonium tribromide (shortest Br--N distance = 3.31 Å).^{4,15} The Br--N vectors are approximately perpendicular to the diazonium group: angles Br--N15--N14 = 92°, Br'--N15--N14 = 85°, Br'--N14--N15 = 77°, and Br'--N14--C2 = 96°. The closest approach of bromine to C2 is 4.00 Å.

The closest intermolecular distance of all, 2.86 Å, occurs between the carbonyl oxygen of an inversion-related cation and the outer nitrogen. The angles for this surprisingly short interaction are O13--N15--N14 = 115° and N15--O13--C11 = 117°. Although the coordinating oxygen O13 is not in plane P1 of the diazonium group, it is clearly anti to C2, with respect to the bent diazonium group (torsional angle C2--N14--N15--O13 = 135°), such that a further shortening of this O13--N15 distance through a hypothetical intermolecular

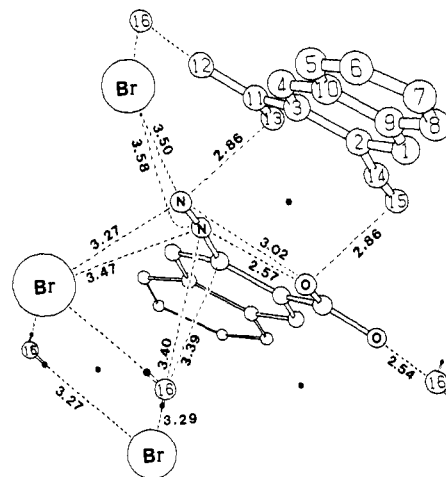


Figure 1. The solid-state environment of the diazonium group in the crystal structure of Ib, viewed approximately down the *b* axis. The *a* axis is directed toward the top of the drawing. The numbered molecule (top right) is related to the other by inversion through the point (1, 1/2, 1/2). The aromatic hydrogens have been omitted.

solid-state coupling reaction could be imagined to result in a covalent anti diazocarboxylate structure.¹⁶

The plane of the naphthalene rings is roughly parallel to (3 $\bar{1}$ 1) and perpendicular to (011). The hydrogen bonds join the molecules pairwise across inversion centers (1/2, 1/2, 1), while the short intermolecular N15---O13 interactions across inversion centers (1, 1/2, 1/2) extend these pairs into infinite sheets of molecules parallel to (1 $\bar{1}$ 1) ($d(1\bar{1}1) = 3.616$ Å). ($F(1\bar{1}1)$ is the largest structure factor of Ib). The shortest Br'---N interaction occurs between these sheets (Figure 2).

Solid-State Behavior of Ib. Crystals of Ib do not decompose appreciably when exposed to X-rays (or UV light -2537 Å) for several weeks under ambient laboratory conditions of temperature and humidity—the conditions chosen for the structure analysis—and samples stored at 10 °C for about 1 year still give rise to sharp diffraction patterns. When examined by differential scanning calorimetry at a heating rate of 2.5 °C/min, crystals of Ib exhibit a broad endotherm commencing at ~65 °C (total heat absorbed = 17 kcal/mol (heat of vaporization of H₂O at 100 °C \approx 10 kcal/mol)), becoming exothermic in the temperature interval 110–137 °C (total heat released = 36 kcal/mol), and a broad endotherm (200–218 °C) corresponding to the melting of 3-bromo-2-naphthoic acid (lit.¹⁸ 219–220 °C). Independent thermal gravimetric analysis of Ib (Figure 3) at the same heating rate correlates well with the calorimetric results; the (endothermic) weight loss commences at ~66 °C and levels off somewhat at 98 °C, at which temperature slightly more weight (7%) has been lost than expected (6%) for dehydration. Further (exothermic) weight loss occurs during heating to ~135 °C, with maximum gas evolu-

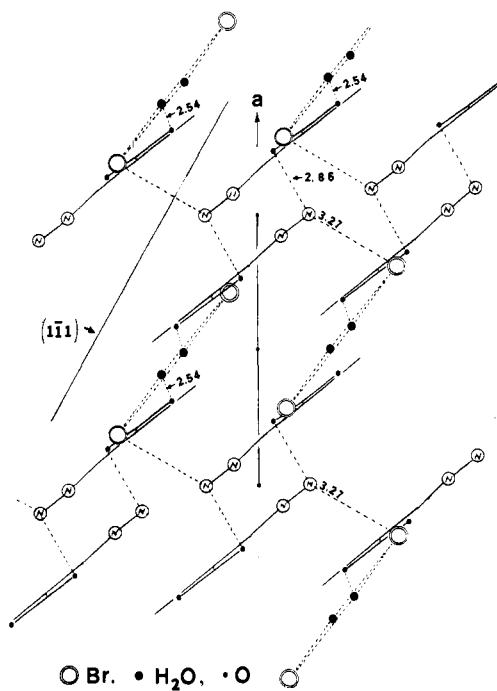


Figure 2. A schematic representation of the packing of Ib into sheets which are parallel to $(1\bar{1}1)$ and perpendicular to (011) (see also Figure 4). The hydrogen bonds between Br^- and H_2O and between H_2O and $\text{O}12$ (2.54 Å) as well as the $\text{O}13\text{--N}15$ intermolecular interactions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

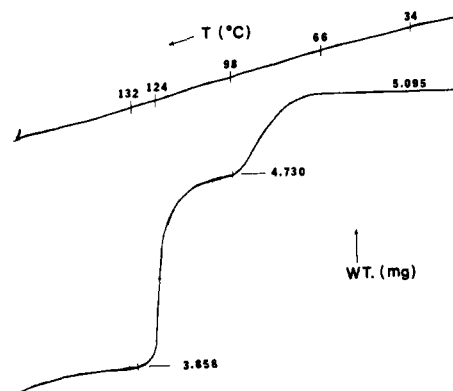


Figure 3. Thermal gravimetric analysis of Ib at a heating rate of $2.5^\circ\text{C}/\text{min}$. Temperature (upper line) and weight curves were recorded simultaneously.

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 $a = 10.3\text{ Å}$, $b = 6.8\text{ Å}$, $c = 8.3\text{ Å}$, $\alpha = 90^\circ$, $\beta = 102^\circ$, $\gamma = 90^\circ$ and a calculated unit cell volume (570 Å^3) smaller than the initial volume (593 Å^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 ($d(\bar{1}\bar{1}\bar{1}) = 4.4\text{ Å}$) 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

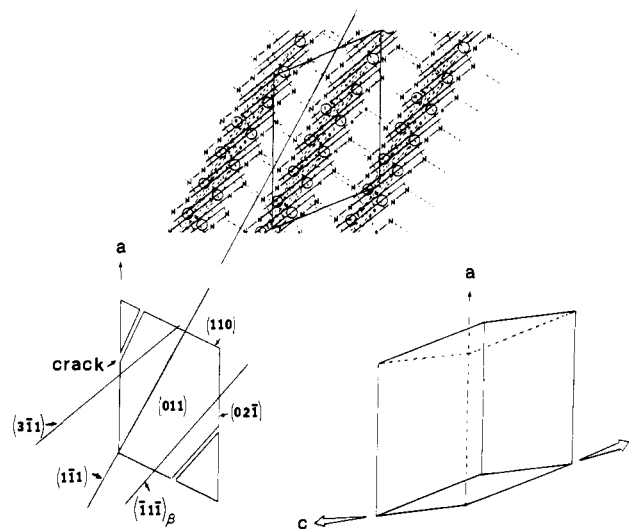


Figure 4. The plane of the drawing is parallel to (011). (Lower right): the unit cell of Ib. (Lower left): The traces of several planes and idealized crack boundaries which are nearly perpendicular to (011) are shown relative to a typical crystal of Ib. (Top): The arrangement of the (111) sheets (see 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–C11	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*ol*)_{Ib β} photographs of heated samples of Ib.

The structure analysis of Ib was performed on 1274 ("observed" with *I* > 3 σ) 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 -2 θ 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.

Acknowledgment. This research was funded through a grant from the Graduate School of the University of Minnesota.

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.

References and Notes

- G. Balz and G. Schiemann, *Ber.*, **60**, 1186 (1927).
- C. Romming, *Acta Chem. Scand.*, **17**, 1444 (1963).
- C. Romming and T. Tjornhom, *Acta Chem. Scand.*, **22**, 2934 (1968).
- O. Andersen and C. Romming, *Acta Chem. Scand.*, **16**, 1882 (1962).
- C. Romming, *Acta Chem. Scand.*, **26**, 523 (1972).
- B. Greenberg and Y. Okaya, *Acta Crystallogr., Sect. B*, **25**, 2101 (1969).
- C. Romming and K. Waerstad, *Chem. Commun.*, **14**, 299 (1965).
- T. N. Polynova, N. G. Bokli, and M. A. Porai-Koshits, *Zh. Strukt. Khim.*, **6**, 841 (1965).
- Ya. M. Nesterova and M. A. Porai-Koshits, *Zh. Strukt. Khim.*, **12**, 108 (1971).
- A. Mostad and C. Romming, *Acta Chem. Scand.*, **22**, 1259 (1968).
- 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}
- Carey and Millar have reported the isolation of solid *o*-toluenediazonium iodide: J. G. Carey and I. T. Millar, *Chem. Ind. (London)*, 97 (1960).
- J. Z. Gougoutas, *Cryst. Struct. Commun.*, **7**, 183 (1978).
- 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 (ν_{\max} 1630 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.
- C. F. Wilcox and S. S. Talwar, *J. Chem. Soc.*, 2162 (1970).
- J. Kenner, W. H. Ritchie, and R. L. Wain, *J. Chem. Soc.*, 1526 (1937).
- A small amount of the dark residue, remaining after the sublimation of the bromo acid, sublimes upon further heating to 350°C . On the basis of its UV spectrum, it is possible that this impure yellow sublimate contains some dibenzo[*b,h*]biphenylene (reported²⁰ to sublime at 340 – 345°C at atmospheric pressure).
- R. F. Curtis and G. Viswanath, *J. Chem. Soc.*, 1670 (1959).
- The lb/β phase has been found to persist at room temperature for periods up to 30 h, then suddenly to revert to lbα. Further studies of the effects of temperature and relative humidity on the transformations $\alpha \rightleftharpoons \beta$ are underway.
- C. W. Burnham, *Am. Mineral.*, **51**, 159 (1966).
- C. H. MacGillivray and G. D. Riech, Eds., "International Tables for X-ray Crystallography", Vol. III, Kynoch Press, Birmingham, England, 1962.

Ozonation of Nucleophiles. 10. Ethers¹

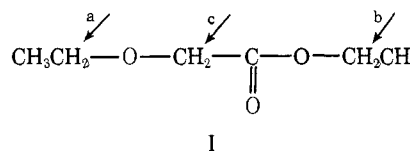
Philip S. Bailey* and Duane A. Lerdal

Contribution from the Department of Chemistry, The University of Texas at Austin, Austin, Texas 78712. Received March 6, 1978

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