Crystal Structure and Solid-State Behavior of a Diazonium Iodide: 3-Carboxy-2-naphthalenediazonium Iodide Hydrate

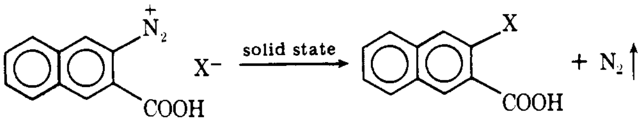
J. Z. Gougoutas

Contribution from the Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455.
Received April 2, 1979

Abstract: The photochemically and thermally unstable orthorhombic crystal structure of 3-carboxy-2-naphthalenediazonium iodide hydrate (**1a**, $C_{11}H_7N_2O_2I\cdot H_2O$; a = 15.42, b = 16.96, c = 9.59 Å; space group *Pbca*, Z = 8) has been examined at −50 °C (R = 0.12 for 303 observed reflections) and its solid-state behavior compared with that of the corresponding triclinic diazonium bromide hydrate, **1b**. The immediate environment of the essentially planar diazonium cation is similar in both structures: three halide ions, the carbonyl oxygen of a neighboring cation, and a water molecule are arranged about the $C^+N\equiv N$ group with the shortest halide-nitrogen distance involving the *outer* nitrogen (3.4 Å in **1a**, 3.27 Å in **1b**). Each halide is coordinated to two diazonium groups and hydrogen bonded to two waters. Each water is hydrogen bonded to two halides and the carboxyl group. Despite these similarities, **1a** and **1b** exhibit markedly different solid-state stabilities. TGA and DSC studies indicate that **1a** rapidly decomposes in the interval 30-60 °C with simultaneous loss of N_2 and H_2O, and is transformed to the corresponding iodo acid (83% isolated yield). By contrast, the more stable **1b** decomposes stepwise: loss of H_2O (65-100 °C), loss of N_2 (100-135 °C) (heating rate 2.5 °C/min). Solid-state decomposition mechanisms in **1a** involving either a displacement of $-N_2^+$ by iodide ion or a unimolecular ionization to give aryl cations seem unlikely in view of the above comparisons. Instead, an electron-transfer process in which iodide ion is oxidized to atomic iodine (possibly through a radical-chain mechanism) is proposed.

Introduction

In a recent study of the structure and solid-state chemistry of the ionic salt 3-carboxy-2-naphthalenediazonium bromide (**1b**),[1] we reported that replacement of the diazonium group by the indigenous bromide ion (**1** → **2**) occurs in good yield (>70%) in the crystalline matrix. The solid state thus may present a sheltered environment in which effectively only the counteranion is available for replacement of the diazonium group.



1 2

a, X = I c, X = I_3
b, X = Br d, X = BF_4

We report here the structure of the corresponding crystalline diazonium iodide, **1a**, and its facile solid-state conversion to the aryl iodide, **2a**.

Results

Although a few diazonium iodides and triodides have been isolated,[2] they have not been well characterized. No structural investigations have been reported for these unstable solids which sometimes precipitate during syntheses of aryl iodides upon the addition of iodide ion to acidic aqueous solutions of diazotized amines. Crystalline **1a**, which separates during the synthesis[3] of **2a**, together with variable amounts of a dark powder which contains some **2a**, **1c**,[4] and free iodine, can be obtained as single crystals for X-ray analysis through the addition of concentrated hydriodic acid to aqueous solutions of the purified crystalline diazonium bisulfate.[5] The iodide is not readily soluble in water and we have been unable to recrystallize it from other solvents. It can be partially purified by virtue of the fact that it is essentially insoluble in nonpolar solvents such as benzene and isoamyl acetate which dissolve most of the dark contaminants.

The elemental composition of bulk samples has not been analyzed; however, the unit cell volume and crystal density (Table I), measured from single crystals, are in good agreement with a hydrated diazonium iodide, and not triodide, crystal structure (experimental mol wt of the asymmetric unit 353; calcd for $C_{11}H_7N_2O_2I\cdot H_2O$, 344), and thermogravimetric results (vide infra) also are consistent with this formulation.

The highly unstable orange crystals of **1a** rapidly turn brown upon standing at room temperature. Their characteristic infrared absorption at 2250 cm^{-1} (RN_2^+) in Nujol mulls rapidly decreases during successive scans through the 3500-600-cm^{-1} region at room temperature. After ~0.5 h, the mulls exhibit essentially only the infrared absorption bands of the expected product, **2a**.

Thermogravimetric studies (Figure 1) indicate that the diazonium iodide is considerably less stable than the bromide **1b**. The latter hydrated structure decomposes[1] stepwise: (a) endothermic (+17 kcal/mol) loss of water of crystallization in the interval 65-100 °C resulting in the topotactic formation of an isolable intermediate anhydrous diazonium bromide crystal structure (β phase); (b) exothermic (−36 kcal/mol) decomposition with evolution of N_2 and formation of polycrystalline **2b** during further heating of the β phase to ~135 °C. The triclinic diazonium bisulfate monohydrate exhibits similar stability and stepwise decomposition.[6] By contrast, the decomposition of **1a** to **2a** (83% isolated yield[7]) with evolution of *both* N_2 and H_2O of crystallization is already complete by 65 °C under the same conditions (heating rate 2.5 °C/min). The smooth weight-loss curve indicative of the more or less simultaneous loss of N_2 and H_2O is consistent with differential scanning calorimetric studies of **1a** which show only a relatively smooth exotherm (30-65 °C). The total amount of heat evolved (−20 kcal/mol) from **1a** is essentially the sum of the stepwise endo- and exotherms observed for **1b**.[8]

Topotaxy has not been observed during the decomposition of **1a**; in these thermal studies, **2a** was formed as a partially amorphous, partially polycrystalline product.

While the overall packing in the orthorhombic structure of **1a** and the triclinic structure of **1b** are fundamentally different, the immediate environment of the diazonium group is quite similar in both structures (Figure 2): all 15 C, N, and O atoms of the cations are nearly coplanar, with the closest nonbonded intramolecular approach (2.5 Å) to the diazonium nitrogens occurring between the carbonyl oxygen O13 and the *inner* nitrogen, N14. The shortest *inter*molecular approach to a nitrogen (2.9 Å) involves the *outer* nitrogen N15 and a neigh-

0002-7863/79/1501-5672$01.00/0

Table I. Crystal Data

structure	*a*, Å	*b*, Å	*c*, Å	α, deg	β, deg	γ, deg	space group	*z*	ρ, g cm^{-3}
1a[a]	15.42 (1)	16.96 (1)	9.59 (1)	90	90	90	*Pbca*	8	1.87
1a[b]	15.36	16.90	9.60	90	90	90	*Pbca*	8	*c*
1b	7.532	9.892	9.182	65.2	94.4	76.8	*P*1̄	2	1.654

[a] At 22 °C. [b] At −50 °C. [c] Not measured.

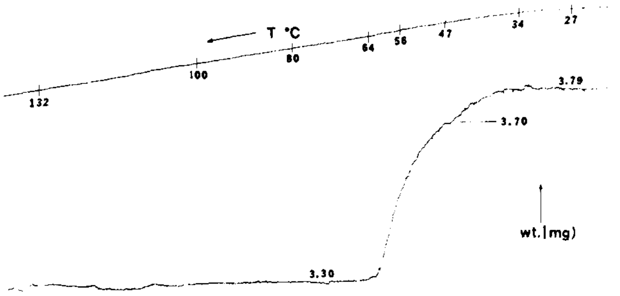


Figure 1. Thermogram of **1a** at a heating rate of 2.5 °C/min. Temperature (upper line) and weight curves were recorded simultaneously.

boring carbonyl oxygen, O13. In addition to these two oxygens, the diazonium group is coordinated to two halide ions. The shortest halide–nitrogen distance (3.4 Å in **1a**, 3.27 Å in **1b**) involves the *outer* nitrogen and is significantly shorter than the sum of the corresponding ionic and van der Waals radii. The other halide-(outer) nitrogen distance is 3.8 Å in **1a** (3.50 Å in **1b**).

Each halide ion is coordinated to two diazonium groups and hydrogen bonded to two water molecules (halide---OH_2 distances 3.4 and 3.6 Å in **1a**; 3.27 and 3.29 Å in **1b**). Further, the water molecules, O16, also are hydrogen bonded to the carboxyl groups, -COOH---OH_2, through an O12---O16 distance of 2.6 Å in **1a** (2.54 Å in **1b**) and lie directly above the C2–N14 bond at a distance of 3.3 Å (3.39 Å in **1b**) from C2 (the closest intermolecular approach to C2).

The two immediate environments of the diazonium groups in **1a** and **1b** essentially differ only through the interchange of (halide ion)$_a$ (see Figure 2) and the intermolecularly coordinated carbonyl O′13. The differences in halide–nitrogen distances in **1a** and **1b** are consistent with the ~0.2 Å difference in ionic radii of iodide and bromide.

The initial arrangement of halide and diazonium ions would be expected to influence the stability of the crystal structures if the loss of nitrogen occurred by a displacement mechanism involving attack by halide ion (presumably either (halide ion)$_b$ or (halide ion)$_c$) at C2. However, the contrast between the similar environments and different stabilities of the diazonium group in **1a** and **1b** argues against such a mechanism. This proximity of halide ions to the leaving group clearly does not lead to displacement of nitrogen in **1b**; dehydration and some solid-state packing reorganization to another diazonium structure (β phase) occurs instead. The stability of the diazonium group in the β phase of **1b** (~2 h at 95 °C) further argues against an alternative unimolecular mechanism involving the irreversible loss of molecular nitrogen and the formation of aryl cations during the comparatively rapid decomposition of **1a** at 30–60 °C. It is probable that the difference in stability of the diazonium group in the similar environments of **1a** and **1b** reflects the greater ease of oxidation of iodide ions to iodine atoms (vis-à-vis bromide to bromine) through the transfer of an electron to the diazonium cation.

Once initiated (for example, by I_a^-) such an electron-transfer process could be propagated in a chain mechanism involving other iodide ions (for example, I_b^-; see Figure 3).

Table II. Fractional Atomic Coordinates for **1a**

atom	*x*	*y*	*z*
I$^-$	0.2143(6)	0.1687(5)	0.229(1)
C1	−0.031(9)	0.108(5)	−0.681(9)
C2	−0.04(1)	0.137(5)	−0.56(1)
C3	−0.061(8)	0.109(6)	−0.42(1)
C4	−0.099(8)	0.036(6)	−0.46(1)
C5	−0.162(9)	−0.054(7)	−0.65(1)
C6	−0.170(7)	−0.083(6)	−0.77(2)
C7	−0.119(9)	−0.056(8)	−0.91(1)
C8	−0.068(9)	0.018(6)	−0.86(1)
C9	−0.071(6)	0.045(5)	−0.74(2)
C10	−0.118(8)	0.004(8)	−0.59(1)
C11	−0.072(7)	0.146(5)	−0.31(1)
O12	−0.119(6)	0.111(4)	−0.211(9)
O13	−0.017(5)	0.200(3)	−0.277(8)
N14	0.022(8)	0.212(6)	−0.53(1)
N15	0.063(6)	0.270(5)	−0.51(1)
O16	0.158(6)	0.708(4)	0.51(1)

This difference in the chemistry of **1a** and **1b** may be further amplified through the different modes of hydrogen bonding which in both structures link each halide ion to two waters, and each water to two halide ions. In **1b**, two bromides and two waters are joined *cyclically*, about inversion centers, into *discrete* hydrogen-bonded groups, whereas, in **1a**, the hydrogen bonds link glide and translationally related atoms into *chains* of alternating iodide ions and water molecules which extend along the entire length of the crystal in the *c* direction (see Figure 4). Vacancy defects due to the absence of water or the prior removal of a halide ion (through conversion to aromatic halide) would be expected to facilitate the generation of new vacancy (chain) defects through successive losses of iodide ions and water along the interrupted chain of hydrogen bonds.[10] A smaller effect on the packing arrangement and reactivity of neighboring ions would be expected for the more localized (point) defects which would arise from similar vacancies in **1b**.

It is of interest that a different *monoclinic* crystal structure of **1a** is formed when aqueous solutions of the diazonium bisulfate are combined with aqueous neutral solutions of KI. Preliminary evidence suggests that the new form is isostructural with the corresponding tetrafluoroborate, **1d**. The latter salts have long been recognized as relatively stable derivatives of diazonium ions which, through (solid state) decomposition with evolution of N_2 and BF_3, serve as practical laboratory precursors of aryl fluorides (Schiemann reaction[11]). The virtually identical ionic radii of BF_4^- and I^- (2.16 Å[9]) suggest that in general the corresponding diazonium salts may be crystallographically isostructural. That being the case, structural results from studies of the stable tetrafluoroborate crystal may be used as a basis for interpreting the solid-state chemistry of the more elusive diazonium iodide structure.

Experimental Section

Preparation of 1a. The recrystallized diazonium bisulfate[5] (213 mg) was dissolved in 10 mL of water at room temperature and cooled to

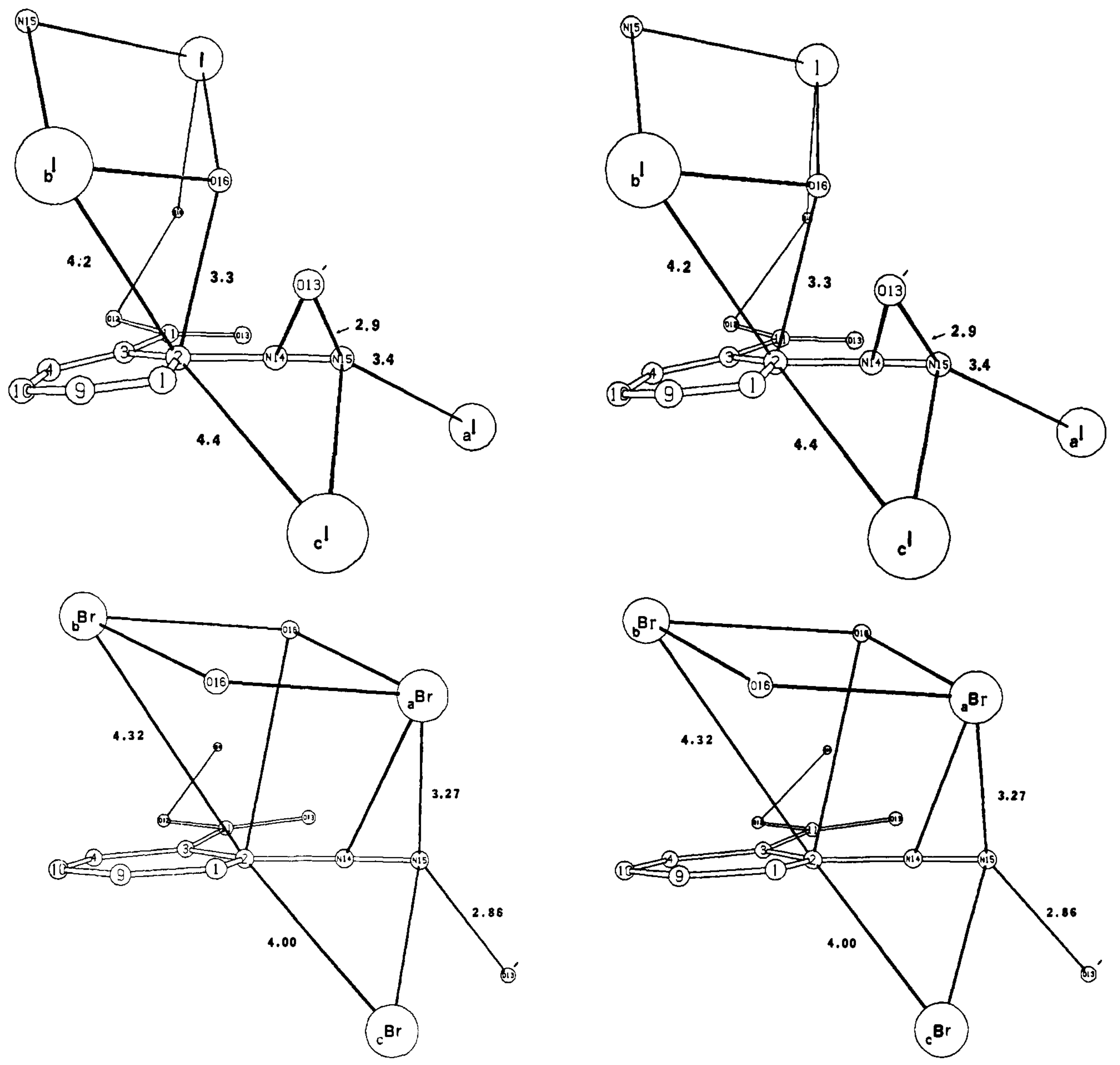


Figure 2. Stereodrawings presenting a comparison of the immediate environments of the diazonium groups in the crystal structures of **1a** (top) and **1b**. The oxygen of the water molecules is O16; the full numbering scheme is shown in Figure 4. The unsubstituted aromatic ring fused to C9 and C10 is not shown. The structures are aligned with the planes of N15, C2, C11 (the carboxyl carbon) parallel, and with collinear C2-N15 vectors. Distances are given in angstroms; see text for unspecified distances.

5 °C. Aqueous 55% HI (3.5 mL) previously cooled to −5 °C was added all at once to the yellow solution of the bisulfate. Crystals of **1a** formed within a few minutes. After further cooling at 5 °C for ~0.5 h, the crystals were filtered off and washed with ice-water, cold benzene, isoamyl acetate, and again with benzene. The tiny, orange crystals (170 mg, 73%) turn red-brown within 1 h at room temperature: ν_{max} (cm^{-1}, Nujol) 3310 (m), 3200-2325 (m), 2260 (m), 1705 (s), 1616 (w), 1583 (w), 1330 (w), 1292 (s), 1236 (m), 1126 (m), 937 (w), 863 (w), 810 (w), 780 (m).

X-ray Studies. Crystal density (1.87 g cm^{-3}) was measured by flotation in CH_2I_2-CCl_4 mixtures at room temperature. Unit cell parameters (Table I) were determined diffractometrically at room temperature. The somewhat high calculated molecular weight of the asymmetric unit probably is due to partial decomposition of **1a** to **2a** (density 2.02 g cm^{-3} [12]).

The lifetime of single crystals (maximum dimension 0.08 mm) at room temperature in the X-ray beam (Mo Kα; λ = 0.7107 Å) is a couple of hours. The same crystal structure persists at least down to −50 °C where it appears to be stable in the absence of X-rays. Even at this temperature however, the crystals decompose in the X-ray beam during data acquisition. The X-ray decomposed specimens are dark red, essentially amorphous pseudomorphs which show only a few faint

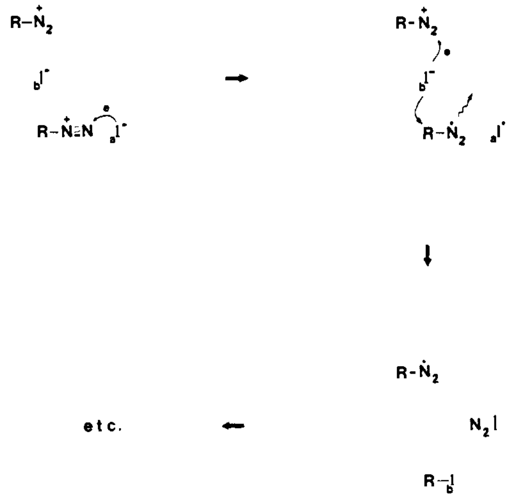


Figure 3. A possible electron transfer, free-radical chain mechanism for the decomposition of **1a**.

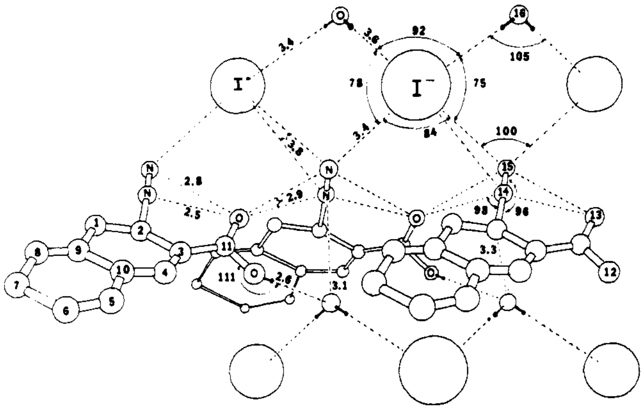


Figure 4. The packing of **1a** into chains composed of glide and translationally related aryl cations, iodide ions, and water molecules. The chains extend along *c* (the horizontal axis); the *a* axis is vertical.

powder diffraction rings at 2θ values consistent with the most intense reflections of **2a**.[12]

Weissenberg and precession photographs of freshly prepared crystals of **1a** are interpretable in terms of an orthorhombic structure, of space group *Pbca*, exhibiting a pseudohalving of the *a* axis (the longest crystal dimension). Crystal size and instability, together with the generally weak *h*-odd reflections, have limited the quantity and quality of intensity data from **1a**, and its structure is much less precisely defined than that of **1b**. Nine different crystals had to be used to obtain a data set at −50 °C, using a PAILRED diffractometer. The reflections from each crystal were corrected for exponential decay,[13] converted to F^2, and merged to a common scale. Although 1393 symmetry-independent reflections were measured, only 303 had net counts significantly above local background counts. Of these, 72 had an odd *h* index.

The structure was solved by Patterson and Fourier methods and refined, assuming isotropic thermal parameters for the light atoms (anisotropic I^-), by least-squares methods. The quantity minimized was $\Sigma\omega(|F_o|^2 - |F_c|^2)^2$ with $\omega = \sigma^{-2}$. Errors, σ, were assigned according to σ = 10% I for $I > 350$ and $\sigma = 35$ for $I \leq 350$. The refinements converged to $R = \Sigma||F_o| - |F_c||/\Sigma F_o = 0.12$ ($R = 0.10$ for *h* even and $R = 0.20$ for the weak *h*-odd reflections).

Scattering factors were taken from the International Tables for X-ray Crystallography.[14] The atomic coordinates are given in Table II.

TGA and DSC 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).

The 12.9% observed weight loss from **1a** in the interval 27–70 °C (Figure 1) is in good agreement with the 13.4% weight loss expected for loss of both N_2 and H_2O.

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 (4 pages). Ordering information is given on any current masthead page.

References and Notes

(1) J. Z. Gougoutas and J. Johnson, *J. Am. Chem. Soc.*, **100**, 5816 (1978).
(2) J. G. Carey and I. T. Millar, *Chem. Ind. (London)*, 97 (1960).
(3) H. Goldstein and E. Cornamusary, *Helv. Chim. Acta*, **14**, 200 (1931).
(4) Two different crystalline forms of the dark triiodide are obtained when the diazonium bisulfate is combined with aqueous solutions of potassium triiodide. Their structures and solid-state behavior are currently under investigation.
(5) J. Z. Gougoutas, *Cryst. Struct. Commun.*, **7**, 183 (1978). In the preparation of the crystalline bisulfate, the solution of the amino acid in aqueous Na_2CO_3–$NaNO_2$ is added dropwise to the aqueous sulfuric acid, rather than vice versa, as previously reported.[1]
(6) Topotactic loss of water in the temperature interval 60–100 °C to give a new anhydrous diazonium salt which decomposes with loss of nitrogen at 127 °C.
(7) As even small (<5 mg) samples of freshly prepared **1a** sometimes detonated during the TGA measurements, it should be regarded as a hazardous material. The yield was determined through controlled decomposition of ~6 mg of **1a**; **2a** was isolated from the decomposed crystals by sublimation at ~170 °C at atmospheric pressure.
(8) The lattice enthalpies of diazonium iodides and bromides are estimated to differ by ~5 kcal mol^{-1} at 25 °C; opposing this factor is the ~9 kcal mol^{-1} difference in the standard enthalpies of formation of aromatic iodides and bromides.[9]
(9) H. F. Halliwell and S. C. Nyburg, *J. Chem. Soc.*, 4603 (1960).
(10) No preferred direction of decomposition relative to crystal morphology has been observed.
(11) G. Balz and G. Schiemann, *Ber.*, **60**, 1186 (1927).
(12) J. Z. Gougoutas and B. K. Toeplitz, *Cryst. Struct. Commun.*, **6**, 331 (1977).
(13) Intensities were adjusted by an exponential curve fitted to the ~25% observed decay in the intensities of two check reflections. This method of correction is based on the assumption that all reflections decay at the same rate. Our unpublished studies of various topotactic transformations indicate that this often is not the case. Decay corrections in those cases are further complicated by the possibility that reflections from the developing product phase may coincide with reflections from the initial parent structure.
(14) C. H. MacGillavry and G. D. Riech, Ed., "International Tables for X-ray Crystallography", Kynoch Press, Birmingham, England.