# Structure of the Bromination Product of 2-Ethyl-1,4-benzothiazin-3(4*H*)-one

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2-Ethyl-1,4-benzothiazin-3(4*H*)-one and bromine react smoothly to give Z-2-(1-bromoethylidine)-2(*H*)-1,4-benzothiazin-3(4*H*)-one, which results from a complex bromination-oxidation sequence. The structure of this product was determined by an X-ray study.

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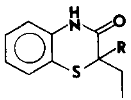
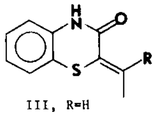
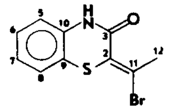
As part of a program involving new heterocycles, we reacted 2-ethyl-1,4-benzothiazin-3(4*H*)-one (I) (1) with an equivalent of bromine. Elemental and spectral analyses of the product showed it not to be the simple monobromide II, but rather a bromination-oxidation product of molecular formula $C_{10}H_8BrNOS$. As we could not distinguish spectrally among structures IV-VI, any of which might be obtainable from bromination of the presumed oxidized intermediate III, an X-ray study was undertaken on this substance.



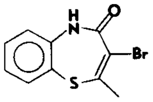
I, R=H
II, R=Br



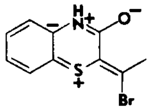
III, R=H
IV, R=Br



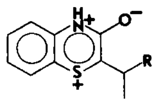
V



VI



VII



VIII, R=H
IX, R=Br

Though the small size of the largest crystal obtained precluded determination of the atomic parameters with the definition usually available in X-ray studies, the structure was readily solved and refined to R = 0.093. The final atomic coordinates are given in Table I, and the structure is depicted in Figure 1. The compound is clearly V or its hydroxyimine tautomer; the standard deviations in the bond lengths and angles (Figure 2) are too large to distinguish between them. The N-C(3) bond is shorter and the C(3)-O bond is longer than are the corresponding bonds in other *cis*-amides (N-CO 1.34-1.38 Å and NC=O 1.20-1.23 Å in isatin (2) and a cyanuric acid complex (3)); this would seem to favor the hydroxyimine tautomer, but contribution from the dipole-stabilized resonance form VII could cause the same bond length changes for tautomer V.

The benzene, amide and alkene groupings in V are each essentially planar, with angles of 9° between benzene and amide and 22° between amide and alkene. The two molecules in a unit cell are held together by two hydrogen bonds across a center of symmetry (Figure 1); the N-O distance in each hydrogen bond is 2.92(4) Å.

The small temperature factor for C(12) and the long C(11)-C(12) bond suggest that the crystal may have contained a small amount of stereoisomer IV. While we think this is the case, efforts to clearly demonstrate it have failed. A difference map failed to show a peak at the expected location for the minor bromine, and when a partial bromine was put in at this location, it consistently refined to meaningless positions. The multiplier of the major bromine did drop to 0.94 on refinement.

The reaction which produces V may proceed by the sequence I → II → VIII → III → IX → V, or perhaps without II if the initial carbon radical is oxidized directly by bromine to VIII. In any case, the first step is rate-limiting, as no intermediate is observed; with bromine as the limiting reagent, virtually the only organic substances present after reaction are V and unreacted starting material I. The rapidity of the steps leading to VIII and IX is presumably related to the formation of the second aromatic ring.

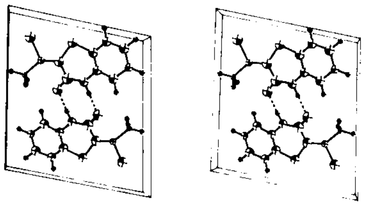


Figure 1. Stereoscopic view of a unit cell, *a* axis projection, *c* axis vertical, with 50% probability thermal spheres for non-hydrogens, smaller spheres for hydrogens, and dashed lines for hydrogen bonds.

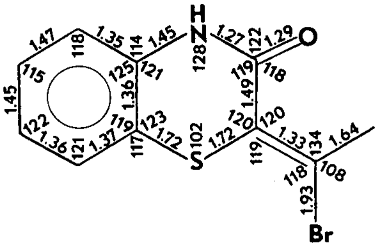


Figure 2. Bond lengths (Å) and angles (°); estimated standard deviations are 0.03-0.05 Å and 2°.

Table I

Final Positional (× $10^{-3}$) Parameters With Estimated Standard Deviations in Parentheses

| | x | y | z |
|---|---|---|---|
| Br | −6(1) | 847.8(4) | 167.7(4) |
| S | −35(2) | 557(1) | 148(1) |
| O | 516(6) | 645(2) | 444(2) |
| N | 199(6) | 466(3) | 367(2) |
| C(2) | 141(7) | 644(3) | 277(3) |
| C(3) | 298(9) | 580(3) | 367(3) |
| C(5) | −128(7) | 270(4) | 316(3) |
| C(6) | −346(8) | 174(3) | 234(3) |
| C(7) | −461(7) | 213(3) | 129(2) |
| C(8) | −369(8) | 330(3) | 107(2) |
| C(9) | −156(7) | 415(3) | 185(2) |
| C(10) | −43(7) | 382(3) | 285(3) |
| C(11) | 156(6) | 770(3) | 293(3) |
| C(12) | 308(7) | 882(2) | 400(2) |
| HN | 315 | 426 | 431 |
| HC(5) | −51 | 248 | 395 |
| HC(6) | −414 | 86 | 251 |
| HC(7) | −605 | 142 | 64 |
| HC(8) | −457 | 349 | 30 |
| H(1)C(12) | 327 | 975 | 395 |
| H(2)C(12) | 535 | 861 | 425 |
| H(3)C(12) | 163 | 872 | 461 |

## EXPERIMENTAL

*Z*-2-(1-Bromoethylidine)-2(*H*)-1,4-benzothiazin-3(4*H*)-one (V).

Compound I (19.3 g, 0.10 mole) (1) was dissolved in a minimum of chloroform, and to the stirred, chilled (ice bath) solution was added dropwise a solution of bromine (16 g, 0.10 mole) in chloroform (20 ml). After 20 minutes, the solvent was removed *in vacuo* and the resulting buff solid recrystallized from ethanol to give V (11.9 g, 88% based on bromine) as pale buffy-yellow needles, mp 178-179° (dec, uncorrected); ir: 3300-2700, 1660, 1585, 1565 (shoulder), 1495, 1470, 1360, 840, 730 $cm^{-1}$; $^1H$ nmr (deuteriochloroform): $\delta$ 2.98 (s, 3H), 6.75-7.32 (m, 4H), 9.50 (bs, 1H, exchanged by deuterium oxide).

*Anal.* Calcd. for $C_{10}H_8BrNOS$: C, 44.46; H, 2.99; N, 5.19; Br, 29.58. Found: C, 44.15; H, 3.03; N, 5.22; Br, 29.73.

X-Ray Analysis of V.

The unit cell constants ($a$ = 4.078(7), $b$ = 10.81(2), $c$ = 12.01(3) Å; $\alpha$ = 99.9(2), $\beta$ = 96.2(2), $\gamma$ = 94.5(1)°) and space group $P\bar{1}$ were consistent with 2 molecules per unit cell (calculated density 1.74 Mg $m^{-3}$). Small crystal size (0.05 × 0.05 × 0.3 mm) limited the number of observable intensities. Thus, of 2112 reflections with $2\theta < 50°$ measured diffractometrically (Mo K$\alpha$, $\lambda$0.71069 Å) using the $\theta$-$2\theta$ variable scan rate technique, only the 600 with $I > 2\sigma(I)$ were considered observed.

The structure was solved with Multan (5) with the first *E* map revealing all the nonhydrogen atoms. Refinement with isotropic temperature factors gave R = 0.146 without hydrogens and 0.138 with hydrogens added in calculated positions. Further refinements with anisotropic temperature factors for the nonhydrogens reduced R to its final value of 0.093. Refinements were based on $F_o$, the quantity minimized being $\Sigma w(F_o - F_c)^2$. The weighting scheme was based on counter statistics with p = 0.03 (6). Scattering factors were taken from the literature (7).

Acknowledgement.

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