**Toluenesulfonate** (VIIIb).—A solution of tosylate VIIIb (37.6 mg.) in 20 ml. of ~ 99% formic acid was heated under a reflux for 2 hr. and then concentrated *in vacuo*. The product was extracted with benzene which was washed with sodium bicarbonate solution and with water. The spectra of the dry residue (27.6 mg.), of its first mother liquor and of the crude diacetate described below showed no tosylate bands nor any of the three bands reported above for *trans*-$\Delta^{17}$-5α-pregnen-3β-ol acetate. Recrystallization from methanol–acetone and from acetone gave 3.0 mg. of rods with m.p. 216–219° and $\lambda_{max}$ 8.06 and 9.74 μ (acetate)[32] and 8.50 μ (formate).[26] The spectrum differed from that of the crude reaction product in having weaker formate and stronger acetate absorption. An aliquot of the crude product was hydrolyzed to yield material of which all but a very small amount traveled as a single spot with the same $R_F$ as 5α-pregnane-3β,20β-diol. Non-identity was shown by comparison of the spectra of the diacetates.

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# Benzfuroxans. The Crystal and Molecular Structure of 5-Chlorobenzfurazan 1-Oxide and 5-Bromobenzfurazan 1-Oxide[1]

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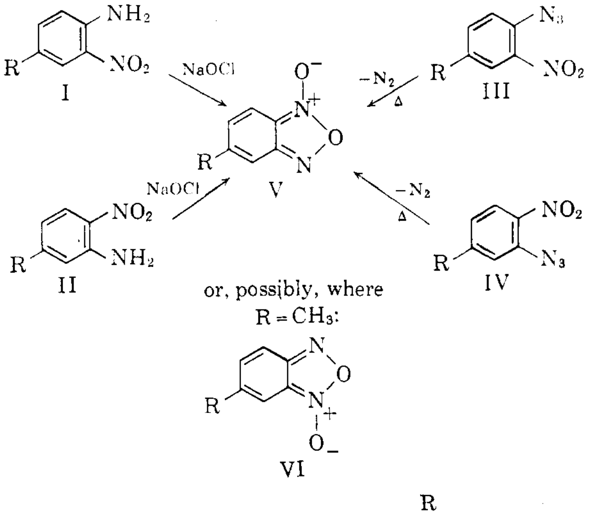
From a complete X-ray crystallographic study, 5-chlorobenzfuroxan is shown to have the 5-chlorobenzfurazan 1-oxide structure (Va), in which the chlorine substituent is *para* to the N-oxide nitrogen atom. The crystal structure of 5-bromobenzfuroxan is isomorphous, and the molecular structure is assumed to be analogous, that is 5-bromobenzfurazan 1-oxide (Vb).

In all cases of unsymmetrically substituted isomeric pairs of *o*-nitroanilines, including the nitrochloroanilines[2] Ia and IIa, the nitrotoluidines[2] Ic and IIc, and the nitronaphthylamines[3] VII and VIII, which have been subjected to alkaline sodium hypochlorite oxidation, only a single benzfuroxan product has been isolated. Similarly, with all the isomeric pairs of *o*-nitrophenylazides, the nitrobromophenylazides[4] IIIb and IVb and the nitrotolylazides[4] IIIc and IVc, and the nitronaphthylazides[5] IX and X, which have been subjected to thermal decomposition, only a single benzfuroxan product has been isolated. If the *o*-nitrogen atoms were to become incorporated in an unsymmetrical benzfuroxan (such as V–VI and XI–XII), analogous to the aliphatic furoxans,[6] as has been proposed,[7] then two isomeric products (V and VI, or XI and XII) might have been anticipated. Formation of a single product was rationalized[7,8] by assuming a relatively rapid interconversion in solution or in the liquid phase of the less stable isomer into the more stable isomer, proceeding through a single *o*-dinitrosobenzene intermediate (such as XIII). An alternative explanation has been advanced in which the product is itself considered to be a symmetrical resonance hybrid *o*-dinitrosobenzene (XIII↔XIV↔XV), a Ψ-*o*-dinitrosobenzene derivative,[9] and ultraviolet spectral evidence was cited in support of this view.[10]



| | R |
|---|---|
| Ia, IIa, Va, VIa | Cl |
| Ib, IIIb, IVb, Vb, VIb | Br |
| Ic, IIc, IIIc, IVc, Vc, VIc | $CH_3$ |

Since the chemical approach to the structure of the benzfuroxans gives an ambiguous answer, resort to a purely physical approach appeared desirable. While our work was in progress, it was reported from proton resonance data that benzfurazan 1-oxide (V. R = H)[11–13] and 4,7-dibromo-

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[1] Preliminary communication: D. Britton and W. E. Noland, *Chem. Ind.* (London), 563 (1962).

[2] A. G. Green and F. M. Rowe, *J. Chem. Soc.*, **103**, 897 (1913).

[3] A. G. Green and F. M. Rowe, *ibid.*, **111**, 612 (1917).

[4] M. O. Forster and M. F. Barker, *ibid.*, **103**, 1918 (1913).

[5] M. O. Forster and H. E. Fierz, *ibid.*, **91**, 1942 (1907).

[6] J. V. R. Kaufman and J. P. Picard, *Chem. Rev.*, **59**, 429 (1959).

[7] D. L. Hammick, W. A. M. Edwardes, and E. R. Steiner, *J. Chem. Soc.*, 3308 (1931).

[8] For an extensive list of pertinent references, see F. B. Mallory, K. E. Schueller, and C. S. Wood, *J. Org. Chem.*, **26**, 3312 (1961).

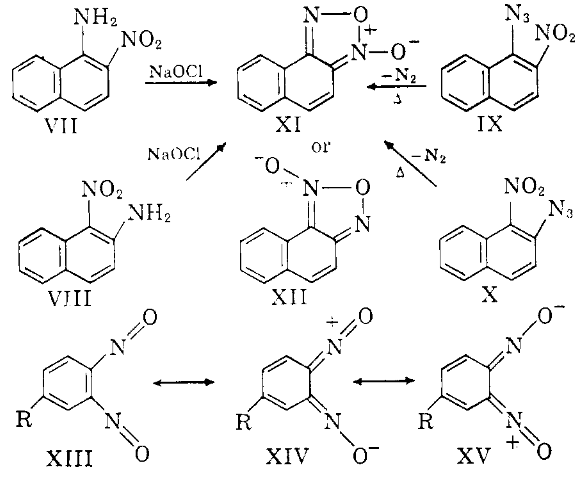
[9] J. H. Boyer, R. F. Reinisch, M. J. Danzig, G. A. Stoner, and F. Sahhar, *J. Am. Chem. Soc.*, **77**, 5688 (1955).

[10] J. H. Boyer, U. Toggweiler, and G. A. Stoner, *ibid.*, **79**, 1748 (1957).

[11] F. B. Mallory and C. S. Wood, *Proc. Nat. Acad. Sci. U.S.*, **47**, 697 (1961).

[12] (a) G. Englert, *Z. Naturforsch.*, **16b**, 413 (1961); (b) G. Englert, *Z. Anal. Chem.*, **181**, 447 (1961); (c) G. Englert, *Z. Elektrochem.*, **65**, 854 (1961).

[13] A. R. Katritzky, S. Øksne, and R. K. Harris, *Chem. Ind.* (London), 990 (1961).



benzfurazan 1-oxide[12a,c] have an unsymmetrical structure in solution at room temperature. At higher temperatures, however, the proton resonance patterns become symmetrical,[12,13] while the patterns of the 4,6(or 5,7?)-dinitro- and 5,6-dinitrobenzfurazan 1-oxides are symmetrical even at room temperature, possibly indicating rapid equilibration between the possible unsymmetrical isomers.[13] Proton and $^{17}O$ resonance spectra at different temperatures have been used to estimate the energy of activation for the unsymmetrical isomers of benzfurazan 1-oxide in chloroform solution (17.2 ± 1.5 kcal./mole)[14] and of 4,7-dibromobenzfurazan 1-oxide in methylene chloride solution (6 ± 2 kcal./mole).[12a,c] Recently, X-ray crystallographic data has been presented,[15] which favors the unsymmetrical benzfurazan 1-oxide structure (V, R = H) for benzfuroxan.

In the present X-ray crystallographic study benzfuroxans were chosen for examination which contain a single substituent so placed that the position of an unsymmetrical oxygen atom can be determined with respect to the substituent. 5-Chlorobenzfuroxan was prepared by alkaline sodium hypochlorite oxidation of 4-chloro-2-nitroaniline, essentially as previously described.[2] 5-Bromobenzfuroxan, which had been prepared previously[4] only by thermal decomposition of 4-bromo-2-nitrophenylazide (IIIb) and 5-bromo-2-nitrophenylazide (IVb), was prepared more conveniently in the present work by alkaline sodium hypochlorite oxidation of 4-bromo-2-nitroaniline (Ib).

We now wish to report that a complete X-ray crystallographic study of 5-chlorobenzfuroxan shows that it has the 5-chlorobenzfurazan 1-oxide structure (Va), with the acyclic oxygen atom located on the nitrogen atom *para* to the chloro substituent. We have found that the crystals of 5-bromobenzfuroxan (Vb) are isomorphous with those of 5-chlorobenzfuroxan (Va), so that the molecular structures are assumed to be the same. Thus, in the solid state the 5-chloro- and 5-bromobenzfuroxans, like benzfuroxan itself,[15] have the unsymmetrical benzfurazan 1-oxide structure, and the halogen substituent is *para* to the N-oxide nitrogen atom. It will be of interest to determine whether the same relationship also holds with other substituents having different electronic effects, such as methyl (Vc or VIc) and nitro.

The proton resonance spectrum of 5-chlorobenzfurazan 1-oxide (Va) at room temperature in carbon tetrachloride solution with tetramethylsilane as an internal reference has a quartet of peaks at 2.97, 2.79, 2.64, and 2.50 $\tau$ ($\tau$ = 56.44 c.p.s., average deviation $\pm 0.03$ $\tau$), increasing regularly in peak height towards the lower $\tau$ values. The spectrum of the 5-bromo derivative (Vb), however, has two peaks, the larger at 2.68 $\tau$ having about twice the area of the smaller peak at 2.27 $\tau$. 5-Methylbenzfuroxan (Vc or VIc) has a methyl peak at 7.59 $\tau$, and a quartet of discernible ring peaks with the relative intensities and $\tau$ values ($\pm$0.03) $2.88 > 2.73 > 2.57 > 3.06$ $\tau$.

## Experimental

**Synthetic Data. 5-Chlorobenzfurazan 1-Oxide (Va)** (with Larry L. Schaleger, 1958).—The procedure is essentially that of Green and Rowe.[2] 4-Chloro-2-nitroaniline (Eastman Kodak Yellow Label, m.p. 118.5–119°, 50 g.) was dissolved in a solution of sodium hydroxide (10 g.) in methanol (1 l.), producing a moderately red color (in ethanol solution a much deeper, brilliant red color was produced). The solution was cooled in an ice bath and 5% aqueous sodium hypochlorite solution was added dropwise, with vigorous stirring, until the red color (which became brilliant red after addition of the first few drops) had completely disappeared. The fluffy yellow precipitate which formed was filtered with suction, washed with water, and recrystallized several times from ethanol, yielding yellow crystals, m.p. 46–48°; reported 95%,[16] m.p. 48°[2,16]; $\nu_{C=N}$ 1620s in $CCl_4$, 1619s in $CS_2$, ~1615s in KBr, 1625s and 1617s (doublet) cm.$^{-1}$ in Nujol.

It was necessary to carry out several recrystallizations in order to free the product completely from a red crystalline contaminant. When the oxidation with sodium hypochlorite was carried out in the absence of added alkali, the orange-red crystalline product was obtained in much greater relative amount. Recrystallization from methylene chloride–petroleum ether (b.p. 60–68°) yielded a sample, m.p. 249–252°. The compound is assumed to be 4,4′-dichloro-2,2′-dinitroazobenzene, reported m.p. 251° (from benzene),[17] the product of oxidation of 4-chloro-2-nitroaniline with phenyl iodosoacetate in acetic acid.

**4-Bromo-2-nitroacetanilide** (with Kent R. Rush, 1961).—The procedure of Frejka and Vymetal[18] for the nitration of 4-bromoacetanilide was modified as described below.

Concentrated nitric acid (*d* 1.42, 13.8 cc., 0.022 mole of nitric acid) was added dropwise with swirling to a solution of 4-bromoacetanilide (40.0 g., 0.187 mole) in concentrated sulfuric acid (300 cc.) cooled to 3°. The solution was then poured into ice water. The bright yellow crystalline pre-

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TABLE I

COMPARISON OF OBSERVED AND CALCULATED STRUCTURE FACTORS OF 5-CHLOROBENZFURAZAN 1-OXIDE

| h | k | l | 10Fo | 10Fc |
|---|---|---|---|---|
| 0 | 0 | 2 | 235 | 198– |
| 0 | 0 | 4 | 208 | 174– |
| 0 | 0 | 6 | 133 | 129– |
| 0 | 0 | 8 | 37 | 15– |
| 0 | 0 | 10 | 37 | 16 |
| 0 | 1 | 1 | 91 | 96– |
| 0 | 1 | 2 | 835 | 975– |
| 0 | 1 | 3 | 133 | 153 |
| 0 | 1 | 4 | 171 | 190– |
| 0 | 1 | 5 | 101 | 101 |
| 0 | 1 | 6* | 16 | 28 |
| 0 | 1 | 7 | 32 | 59– |
| 0 | 2 | 0 | 358 | 356– |
| 0 | 2 | 1* | 21 | 12– |
| 0 | 2 | 2 | 58 | 78– |
| 0 | 2 | 3 | 85 | 94 |
| 0 | 2 | 4 | 139 | 142 |
| 0 | 2 | 5 | 53 | 60– |
| 0 | 2 | 6 | 101 | 103 |
| 0 | 2 | 7* | 16 | 14 |
| 0 | 3 | 1 | 37 | 55 |
| 0 | 3 | 2 | 230 | 256 |
| 0 | 3 | 3 | 53 | 64 |
| 0 | 3 | 4 | 16 | 28 |
| 0 | 3 | 5* | 10 | 18– |
| 0 | 3 | 6 | 42 | 46– |
| 0 | 3 | 7* | 16 | 22 |
| 0 | 4 | 0 | 160 | 158 |
| 0 | 4 | 1 | 74 | 70– |
| 0 | 4 | 2 | 58 | 61 |
| 0 | 4 | 3 | 42 | 62– |
| 0 | 4 | 4 | 133 | 138– |
| 0 | 4 | 5* | 21 | 35 |
| 0 | 5 | 2 | 74 | 71– |
| 0 | 6 | 0 | 53 | 49– |
| 0 | 8 | 0 | 10 | 14 |
| 1 | 0 | 1 | 10 | 39 |
| 1 | 0 | 3 | 246 | 256 |
| 1 | 0 | 5* | 5 | 1– |
| 1 | 0 | 7 | 32 | 19 |
| 1 | 0 | 9 | 69 | 64 |
| 1 | 1 | 0 | 449 | 527 |
| 1 | 1 | 1 | 208 | 167 |
| 1 | 1 | 2 | 674 | 797– |
| 1 | 1 | 3 | 64 | 52 |
| 1 | 1 | 4 | 176 | 157 |
| 1 | 1 | 5 | 69 | 71 |
| 1 | 1 | 6* | 16 | 18 |
| 1 | 1 | 7 | 53 | 67 |
| 1 | 2 | 0 | 58 | 47 |
| 1 | 2 | 1 | 69 | 62 |
| 1 | 2 | 2 | 48 | 75– |
| 1 | 2 | 3 | 149 | 160 |
| 1 | 2 | 4 | 133 | 131 |
| 1 | 2 | 5 | 74 | 83 |
| 1 | 2 | 6* | 16 | 29– |
| 1 | 2 | 7 | 53 | 62– |
| 1 | 3 | 0 | 42 | 67– |
| 1 | 3 | 1 | 149 | 143 |
| 1 | 3 | 2* | 5 | 34 |
| 1 | 3 | 3 | 166 | 161 |
| 1 | 3 | 4 | 32 | 39– |
| 1 | 3 | 5 | 58 | 50– |
| 1 | 3 | 6 | 21 | 33 |
| 1 | 3 | 7 | 42 | 49– |
| 1 | 4 | 0 | 37 | 55 |
| 1 | 4 | 1* | 10 | 2 |
| 1 | 4 | 2* | 10 | 20 |
| 1 | 4 | 3* | 16 | 11– |
| 1 | 4 | 4* | 16 | 0 |
| 1 | 4 | 5 | 123 | 114– |
| 1 | 5 | 0 | 53 | 50– |
| 1 | 5 | 2* | 32 | 19 |
| 1 | 6 | 0 | 32 | 22 |
| 1 | 7 | 0* | 5 | 12 |
| 2 | 0 | 0 | 219 | 172 |
| 2 | 0 | 2 | 1231 | 1849– |
| 2 | 0 | 4 | 58 | 43 |
| 2 | 0 | 6 | 85 | 63 |
| 2 | 0 | 8 | 37 | 39 |
| 2 | 1 | 0 | 621 | 765– |
| 2 | 1 | 1 | 241 | 250 |
| 2 | 1 | 2 | 449 | 415– |
| 2 | 1 | 3 | 74 | 75– |
| 2 | 1 | 4 | 503 | 538 |
| 2 | 1 | 5 | 123 | 106– |
| 2 | 1 | 6 | 48 | 56 |
| 2 | 2 | 0 | 214 | 169– |
| 2 | 2 | 1 | 155 | 159– |
| 2 | 2 | 2 | 305 | 298 |
| 2 | 2 | 3 | 64 | 76– |
| 2 | 2 | 4 | 214 | 221 |
| 2 | 2 | 5 | 74 | 65– |
| 2 | 2 | 6 | 107 | 110– |
| 2 | 3 | 0 | 251 | 253 |
| 2 | 3 | 1 | 32 | 6 |
| 2 | 3 | 2* | 5 | 27 |
| 2 | 3 | 3 | 85 | 76– |
| 2 | 3 | 4 | 117 | 127– |
| 2 | 3 | 5* | 10 | 35– |
| 2 | 3 | 6 | 74 | 63– |
| 2 | 4 | 0 | 42 | 36– |
| 2 | 4 | 1 | 112 | 97– |
| 2 | 4 | 2 | 91 | 99– |
| 2 | 4 | 3* | 16 | 29 |
| 2 | 4 | 4 | 64 | 66– |
| 2 | 5 | 0 | 91 | 96– |
| 2 | 5 | 2* | 32 | 50– |
| 2 | 6 | 0 | 37 | 29– |
| 2 | 7 | 0* | 5 | 4 |
| 3 | 0 | 1 | 123 | 78– |
| 3 | 0 | 3 | 85 | 91– |
| 3 | 0 | 5* | 5 | 11– |
| 3 | 0 | 7 | 48 | 40 |
| 3 | 1 | 0 | 80 | 109 |
| 3 | 1 | 1 | 203 | 188– |
| 3 | 1 | 2 | 80 | 60 |
| 3 | 1 | 3 | 48 | 40 |
| 3 | 1 | 4 | 337 | 351 |
| 3 | 1 | 5* | 16 | 1– |
| 3 | 1 | 6 | 69 | 75– |
| 3 | 2 | 0 | 299 | 284 |
| 3 | 2 | 1 | 337 | 358 |
| 3 | 2 | 2 | 42 | 51– |
| 3 | 2 | 3 | 53 | 48– |
| 3 | 2 | 4 | 117 | 99 |
| 3 | 2 | 5* | 10 | 15– |
| 3 | 2 | 6 | 107 | 118– |
| 3 | 3 | 0 | 128 | 130– |
| 3 | 3 | 1 | 112 | 115– |
| 3 | 3 | 2 | 32 | 49 |
| 3 | 3 | 3 | 64 | 77– |
| 3 | 3 | 4* | 10 | 31– |
| 3 | 3 | 5 | 48 | 53– |
| 3 | 3 | 6 | 21 | 7– |
| 3 | 4 | 0 | 69 | 71– |
| 3 | 4 | 1 | 101 | 96– |
| 3 | 4 | 2* | 16 | 23– |
| 3 | 4 | 3 | 32 | 10– |
| 3 | 4 | 4 | 32 | 15 |
| 3 | 5 | 0* | 5 | 19– |
| 3 | 5 | 2 | 64 | 53 |
| 3 | 6 | 0 | 10 | 0 |
| 3 | 7 | 0 | 16 | 9– |
| 4 | 0 | 0 | 466 | 496– |
| 4 | 0 | 2 | 74 | 61– |
| 4 | 0 | 4 | 396 | 408 |
| 4 | 0 | 6 | 48 | 28 |
| 4 | 0 | 8 | 26 | 21– |
| 4 | 1 | 0 | 246 | 245 |
| 4 | 1 | 1 | 262 | 254– |
| 4 | 1 | 2 | 283 | 277 |
| 4 | 1 | 3 | 117 | 110– |
| 4 | 1 | 4 | 289 | 264 |
| 4 | 1 | 5* | 16 | 48 |
| 4 | 1 | 6 | 192 | 197– |
| 4 | 2 | 0 | 182 | 166 |
| 4 | 2 | 1 | 21 | 14– |
| 4 | 2 | 2 | 123 | 121 |
| 4 | 2 | 3 | 112 | 113 |
| 4 | 2 | 4 | 149 | 166– |
| 4 | 2 | 5 | 21 | 23 |
| 4 | 2 | 6 | 139 | 145– |
| 4 | 3 | 0 | 53 | 52– |
| 4 | 3 | 1 | 80 | 77– |
| 4 | 3 | 2 | 166 | 161– |
| 4 | 3 | 3 | 16 | 16– |
| 4 | 3 | 4 | 37 | 40– |
| 4 | 3 | 5 | 26 | 39 |
| 4 | 4 | 0 | 171 | 169– |
| 4 | 4 | 1 | 74 | 60– |
| 4 | 4 | 2* | 16 | 5 |
| 4 | 4 | 3 | 69 | 72 |
| 4 | 4 | 4 | 48 | 29 |
| 4 | 5 | 0* | 5 | 0 |
| 4 | 5 | 2 | 85 | 82 |
| 4 | 6 | 0 | 37 | 43 |
| 4 | 7 | 0 | 10 | 13– |
| 5 | 0 | 1 | 171 | 170– |
| 5 | 0 | 3 | 166 | 176 |
| 5 | 0 | 5 | 69 | 70 |
| 5 | 0 | 7 | 32 | 25– |
| 5 | 1 | 0* | 5 | 27– |
| 5 | 1 | 1 | 203 | 201 |
| 5 | 1 | 2* | 10 | 14– |
| 5 | 1 | 3 | 133 | 134 |
| 5 | 1 | 4 | 91 | 85– |
| 5 | 1 | 5 | 53 | 71– |
| 5 | 1 | 6 | 96 | 75– |
| 5 | 2 | 0 | 149 | 162– |
| 5 | 2 | 1 | 53 | 27 |
| 5 | 2 | 2 | 182 | 179– |
| 5 | 2 | 3 | 112 | 121– |
| 5 | 2 | 4* | 10 | 20 |
| 5 | 2 | 5* | 16 | 3– |
| 5 | 2 | 6 | 48 | 60– |
| 5 | 3 | 0 | 85 | 73– |
| 5 | 3 | 1 | 257 | 239– |
| 5 | 3 | 2 | 16 | 45 |
| 5 | 3 | 3* | 10 | 8 |
| 5 | 3 | 4* | 10 | 1– |
| 5 | 4 | 0 | 26 | 19– |
| 5 | 4 | 1 | 64 | 43– |
| 5 | 4 | 2 | 69 | 71 |
| 5 | 4 | 3 | 80 | 79 |
| 5 | 5 | 0 | 53 | 56 |
| 5 | 6 | 0 | 16 | 11– |
| 6 | 0 | 0 | 251 | 265– |
| 6 | 0 | 2 | 326 | 317 |
| 6 | 0 | 4 | 53 | 56 |
| 6 | 0 | 6 | 59 | 51– |
| 6 | 1 | 0 | 257 | 256 |
| 6 | 1 | 1 | 176 | 176 |
| 6 | 1 | 2 | 42 | 22 |
| 6 | 1 | 3 | 74 | 67 |
| 6 | 1 | 4 | 101 | 91– |
| 6 | 1 | 5* | 16 | 10 |
| 6 | 1 | 6 | 112 | 110– |
| 6 | 2 | 0 | 58 | 74– |
| 6 | 2 | 1 | 74 | 72– |
| 6 | 2 | 2 | 133 | 151– |
| 6 | 2 | 3* | 10 | 19– |
| 6 | 2 | 4 | 42 | 52– |
| 6 | 2 | 5 | 48 | 38– |
| 6 | 2 | 6 | 42 | 55 |
| 6 | 3 | 0 | 187 | 199– |
| 6 | 3 | 1 | 128 | 133– |
| 6 | 3 | 2 | 37 | 42 |
| 6 | 3 | 3 | 26 | 44 |
| 6 | 3 | 4 | 74 | 77 |
| 6 | 4 | 0 | 53 | 56 |
| 6 | 4 | 1* | 16 | 21 |
| 6 | 4 | 2 | 107 | 102 |
| 6 | 4 | 3 | 74 | 83 |
| 6 | 5 | 0 | 74 | 62 |
| 6 | 6 | 0 | 16 | 15– |
| 7 | 0 | 1 | 171 | 165 |
| 7 | 0 | 3* | 5 | 14– |
| 7 | 0 | 5 | 64 | 59– |
| 7 | 0 | 7 | 48 | 27– |
| 7 | 1 | 0 | 219 | 223– |
| 7 | 1 | 1* | 16 | 30– |
| 7 | 1 | 2 | 48 | 54 |
| 7 | 1 | 3 | 96 | 90– |
| 7 | 1 | 4* | 16 | 11– |
| 7 | 1 | 5 | 42 | 51– |
| 7 | 2 | 0* | 10 | 42– |
| 7 | 2 | 1 | 182 | 190– |
| 7 | 2 | 2 | 91 | 95 |
| 7 | 2 | 3 | 58 | 45– |
| 7 | 2 | 4 | 32 | 35 |
| 7 | 2 | 5 | 26 | 30 |
| 7 | 3 | 0 | 32 | 46 |
| 7 | 3 | 1* | 10 | 14– |
| 7 | 3 | 2 | 21 | 32 |
| 7 | 3 | 3 | 91 | 91 |
| 7 | 3 | 4 | 10 | 3– |
| 7 | 4 | 0* | 5 | 2 |
| 7 | 4 | 1* | 21 | 38 |
| 7 | 4 | 2* | 21 | 23 |
| 7 | 4 | 3 | 58 | 41 |
| 7 | 5 | 0* | 5 | 2 |
| 7 | 6 | 0 | 16 | 32– |
| 8 | 0 | 0 | 53 | 68 |
| 8 | 0 | 2 | 219 | 219 |
| 8 | 0 | 4 | 149 | 137– |
| 8 | 0 | 6 | 32 | 37– |
| 8 | 1 | 0* | 5 | 7 |
| 8 | 1 | 1 | 85 | 84– |
| 8 | 1 | 2 | 96 | 97– |
| 8 | 1 | 3 | 37 | 55– |
| 8 | 1 | 4 | 91 | 83– |
| 8 | 2 | 0 | 74 | 71– |
| 8 | 2 | 1 | 64 | 45– |
| 8 | 2 | 2 | 21 | 10– |
| 8 | 2 | 3* | 16 | 14 |
| 8 | 2 | 4 | 53 | 65 |
| 8 | 3 | 0 | 37 | 32– |
| 8 | 3 | 1* | 10 | 1– |
| 8 | 3 | 2 | 112 | 120 |
| 8 | 3 | 3 | 80 | 87 |
| 8 | 3 | 4 | 21 | 9– |
| 8 | 4 | 0 | 107 | 90 |
| 8 | 4 | 1 | 80 | 65 |
| 8 | 5 | 0 | 37 | 33– |
| 8 | 6 | 0 | 16 | 23– |
| 9 | 0 | 1 | 48 | 30– |
| 9 | 0 | 3* | 5 | 49– |
| 9 | 0 | 5* | 10 | 9 |
| 9 | 1 | 0 | 16 | 4 |
| 9 | 1 | 1 | 74 | 75– |
| 9 | 1 | 2 | 42 | 48 |
| 9 | 1 | 3* | 16 | 14– |
| 9 | 1 | 4* | 21 | 32– |
| 9 | 2 | 0* | 32 | 25– |
| 9 | 2 | 1 | 32 | 48– |
| 9 | 2 | 2 | 48 | 50 |
| 9 | 2 | 3 | 91 | 105 |
| 9 | 2 | 4 | 42 | 45– |
| 9 | 3 | 0 | 85 | 93 |
| 9 | 3 | 1 | 123 | 135 |
| 9 | 3 | 2* | 10 | 30– |
| 9 | 3 | 3* | 16 | 3 |
| 9 | 3 | 4* | 16 | 10– |
| 9 | 4 | 0 | 5 | 5– |
| 9 | 5 | 0* | 5 | 15– |
| 10 | 0 | 0 | 64 | 47– |
| 10 | 0 | 2 | 64 | 54– |
| 10 | 0 | 4 | 80 | 77– |
| 10 | 1 | 0 | 85 | 78– |
| 10 | 1 | 1 | 32 | 18– |
| 10 | 1 | 2* | 16 | 9 |
| 10 | 1 | 3 | 32 | 43 |
| 10 | 1 | 4 | 32 | 11 |
| 10 | 2 | 0 | 74 | 63 |
| 10 | 2 | 1 | 80 | 78 |
| 10 | 3 | 0 | 53 | 50 |
| 10 | 3 | 1 | 32 | 21 |
| 10 | 3 | 2* | 16 | 18 |
| 10 | 3 | 3* | 16 | 5 |
| 10 | 3 | 4 | 58 | 47– |
| 10 | 4 | 0 | 21 | 14 |
| 10 | 5 | 0 | 21 | 27– |
| 11 | 0 | 1 | 37 | 36– |
| 11 | 0 | 3* | 10 | 8– |
| 11 | 1 | 0* | 5 | 19– |
| 11 | 2 | 0 | 32 | 35 |
| 11 | 2 | 1 | 64 | 63 |
| 11 | 3 | 0 | 32 | 40 |
| 11 | 3 | 1 | 53 | 51 |
| 11 | 3 | 2 | 53 | 50– |
| 11 | 3 | 3 | 69 | 60– |
| 11 | 4 | 0 | 21 | 18– |
| 12 | 0 | 0 | 80 | 71– |
| 12 | 0 | 2 | 42 | 25 |
| 12 | 0 | 4 | 42 | 20 |
| 12 | 1 | 0 | 37 | 21 |
| 12 | 2 | 0* | 16 | 40 |
| 12 | 2 | 1 | 48 | 42 |
| 12 | 3 | 0* | 5 | 8 |
| 12 | 3 | 1 | 26 | 16 |
| 12 | 3 | 2 | 37 | 35– |
| 12 | 3 | 3 | 26 | 23– |
| 12 | 4 | 0 | 37 | 28– |
| 13 | 0 | 1* | 10 | 11– |
| 13 | 1 | 0 | 21 | 9– |
| 13 | 2 | 0* | 5 | 20 |
| 13 | 3 | 0 | 26 | 20– |
| 14 | 0 | 0* | 5 | 15– |
| 14 | 0 | 2 | 58 | 34 |
| 14 | 1 | 0 | 16 | 21 |
| 14 | 2 | 0 | 16 | 12– |
| 1– | 0 | 1 | 267 | 325– |
| 1– | 0 | 3 | 305 | 315– |
| 1– | 0 | 5 | 166 | 152– |
| 1– | 0 | 7 | 112 | 109– |
| 1– | 0 | 9 | 42 | 40 |
| 1– | 1 | 1 | 117 | 115– |
| 1– | 1 | 2 | 198 | 213– |
| 1– | 1 | 3 | 235 | 246– |
| 1– | 1 | 4 | 32 | 43– |
| 1– | 1 | 5 | 85 | 92– |
| 1– | 1 | 6 | 37 | 38 |
| 1– | 1 | 7 | 96 | 93 |
| 1– | 2 | 1 | 380 | 434– |
| 1– | 2 | 2 | 85 | 57 |
| 1– | 2 | 3 | 198 | 208– |
| 1– | 2 | 4 | 21 | 51 |
| 1– | 2 | 5 | 171 | 175 |
| 1– | 2 | 6* | 16 | 22 |
| 1– | 2 | 7* | 16 | 29 |
| 1– | 3 | 1 | 208 | 239– |
| 1– | 3 | 2 | 128 | 130 |
| 1– | 3 | 3 | 203 | 195 |
| 1– | 3 | 4 | 112 | 109– |
| 1– | 3 | 5* | 10 | 41 |
| 1– | 3 | 6* | 10 | 18– |
| 1– | 4 | 1 | 32 | 38 |
| 1– | 4 | 2 | 21 | 38– |
| 1– | 4 | 3 | 112 | 122 |
| 1– | 4 | 4 | 32 | 22– |
| 1– | 4 | 5 | 85 | 83– |
| 2– | 0 | 2 | 407 | 388 |
| 2– | 0 | 4 | 241 | 246 |
| 2– | 0 | 6 | 53 | 45 |
| 2– | 0 | 8 | 48 | 51– |
| 2– | 0 | 10* | 10 | 8– |
| 2– | 1 | 1 | 182 | 136 |
| 2– | 1 | 2 | 348 | 368 |
| 2– | 1 | 3 | 58 | 66– |
| 2– | 1 | 4 | 128 | 121– |
| 2– | 1 | 5 | 91 | 98 |
| 2– | 1 | 6* | 16 | 49– |
| 2– | 1 | 7* | 21 | 29– |
| 2– | 2 | 1 | 80 | 70– |
| 2– | 2 | 2 | 123 | 126– |
| 2– | 2 | 3 | 149 | 148 |
| 2– | 2 | 4 | 155 | 170– |
| 2– | 2 | 5 | 74 | 81– |
| 2– | 2 | 6 | 96 | 105 |
| 2– | 2 | 7 | 26 | 12– |
| 2– | 3 | 1 | 42 | 13 |
| 2– | 3 | 2* | 5 | 7– |
| 2– | 3 | 3 | 64 | 54– |
| 2– | 3 | 4 | 123 | 118 |
| 2– | 3 | 5* | 10 | 29– |
| 2– | 3 | 6 | 96 | 83 |
| 2– | 4 | 1* | 10 | 35 |
| 2– | 4 | 2 | 187 | 193 |
| 2– | 4 | 3* | 16 | 26– |
| 2– | 4 | 4 | 80 | 72 |
| 2– | 4 | 5* | 21 | 33 |
| 3– | 0 | 1 | 487 | 513 |
| 3– | 0 | 3 | 358 | 350 |
| 3– | 0 | 5 | 133 | 138 |
| 3– | 0 | 7 | 80 | 84– |
| 3– | 0 | 9 | 58 | 44– |
| 3– | 1 | 1 | 342 | 338 |
| 3– | 1 | 2* | 10 | 25 |
| 3– | 1 | 3 | 74 | 85 |
| 3– | 1 | 4 | 171 | 187– |
| 3– | 1 | 5 | 187 | 190– |
| 3– | 1 | 6 | 48 | 62 |
| 3– | 1 | 7 | 53 | 64– |
| 3– | 2 | 1 | 144 | 159 |
| 3– | 2 | 2 | 133 | 133– |
| 3– | 2 | 3 | 262 | 274– |
| 3– | 2 | 4* | 10 | 47– |
| 3– | 2 | 5 | 32 | 47– |
| 3– | 2 | 6 | 58 | 66 |
| 3– | 2 | 7 | 26 | 22 |
| 3– | 3 | 1 | 342 | 336– |
| 3– | 3 | 2 | 144 | 129 |
| 3– | 3 | 3 | 16 | 8 |
| 3– | 3 | 4 | 21 | 47 |
| 3– | 3 | 5 | 48 | 56 |
| 3– | 3 | 6* | 10 | 12 |
| 3– | 4 | 1* | 10 | 28– |
| 3– | 4 | 2* | 16 | 0 |
| 3– | 4 | 3 | 85 | 88 |
| 3– | 4 | 4 | 32 | 17– |
| 3– | 4 | 5 | 37 | 13 |
| 4– | 0 | 2 | 80 | 62– |
| 4– | 0 | 4 | 85 | 81– |
| 4– | 0 | 6 | 69 | 79 |
| 4– | 0 | 8* | 10 | 7 |
| 4– | 0 | 10 | 37 | 26– |
| 4– | 1 | 1 | 176 | 157– |
| 4– | 1 | 2 | 299 | 288 |
| 4– | 1 | 3 | 123 | 117– |
| 4– | 1 | 4* | 16 | 27 |
| 4– | 1 | 5* | 16 | 50 |
| 4– | 1 | 6* | 16 | 9– |
| 4– | 2 | 1 | 176 | 162– |
| 4– | 2 | 2 | 149 | 169 |
| 4– | 2 | 3 | 171 | 174 |
| 4– | 2 | 4 | 198 | 216– |
| 4– | 2 | 5 | 48 | 57 |
| 4– | 2 | 6 | 26 | 28– |
| 4– | 3 | 1 | 133 | 132 |
| 4– | 3 | 2 | 208 | 204– |
| 4– | 3 | 3 | 16 | 36 |
| 4– | 3 | 4 | 85 | 69– |
| 4– | 3 | 5* | 10 | 11 |
| 4– | 3 | 6 | 21 | 26 |
| 4– | 4 | 1* | 16 | 20 |
| 4– | 4 | 2 | 101 | 103– |
| 4– | 4 | 3 | 37 | 52– |
| 4– | 4 | 4 | 69 | 80 |
| 4– | 4 | 5* | 21 | 3– |
| 5– | 0 | 1 | 337 | 347– |
| 5– | 0 | 3 | 160 | 154– |
| 5– | 0 | 5 | 133 | 134 |
| 5– | 0 | 7 | 101 | 92 |
| 5– | 0 | 9 | 64 | 61– |
| 5– | 1 | 1 | 48 | 71– |
| 5– | 1 | 2 | 310 | 350 |
| 5– | 1 | 3 | 262 | 232 |
| 5– | 1 | 4 | 85 | 62– |
| 5– | 1 | 5 | 123 | 101 |
| 5– | 1 | 6* | 16 | 9– |
| 5– | 2 | 1 | 257 | 260 |
| 5– | 2 | 2 | 16 | 18 |
| 5– | 2 | 3 | 58 | 38 |
| 5– | 2 | 4 | 16 | 63– |
| 5– | 2 | 5 | 42 | 58– |
| 5– | 2 | 6* | 16 | 31 |
| 5– | 3 | 1 | 80 | 33– |
| 5– | 3 | 2 | 16 | 57– |
| 5– | 3 | 3 | 112 | 121– |
| 5– | 3 | 4 | 26 | 34 |
| 5– | 3 | 5* | 10 | 17– |
| 5– | 3 | 6* | 16 | 4– |
| 5– | 4 | 1 | 58 | 62– |
| 5– | 4 | 2 | 32 | 13 |
| 5– | 4 | 3 | 32 | 48– |
| 5– | 4 | 4 | 58 | 71 |
| 5– | 4 | 5 | 85 | 85 |
| 6– | 0 | 2 | 53 | 20 |
| 6– | 0 | 4 | 85 | 78– |
| 6– | 0 | 6* | 5 | 9 |
| 6– | 0 | 8 | 58 | 45 |
| 6– | 1 | 1 | 123 | 113 |
| 6– | 1 | 2 | 26 | 11 |

TABLE I (*Contineud*)

| *h* | *k* |  | 10Fo | 10Fc | *h* | *k* |  | 10Fo | 10Fc | *h* | *k* | *l* | 10Fo | 10Fc | *h* | *k* |  | 10Fo | 10Fc | *h* |  |  | 10Fo | 10Fc |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 6– | 1 | 3 | 48 | 77– | 7– | 0 | 3 | 139 | 128– | 8– | 0 | 2 | 85 | 64 | 9– | 0 | 5 | 101 | 95– | 10– | 2 | 4 | 80 | 35– |
| 6– | 1 | 4 | 37 | 52 | 7– | 0 | 5 | 133 | 108– | 8– | 0 | 4* | 10 | 58– | 9– | 1 | 1 | 42 | 31 | 10– | 3 | 1 | 16 | 3– |
| 6– | 1 | 5 | 37 | 66– | 7– | 0 | 7 | 96 | 92 | 8– | 0 | 6 | 64 | 45– | 9– | 1 | 2 | 32 | 1– | 10– | 3 | 2* | 16 | 11– |
| 6– | 1 | 6 | 74 | 80 | 7– | 1 | 1 | 160 | 164– | 8– | 1 | 1 | 37 | 50 | 9– | 1 | 3 | 107 | 119– |  |  |  |  |  |
| 6– | 2 | 1 | 133 | 147– | 7– | 1 | 2 | 26 | 14 | 8– | 1 | 2 | 80 | 87– | 9– | 2 | 1 | 96 | 113– | 11– | 0 | 1* | 10 | 5– |
| 6– | 2 | 2 | 192 | 194 | 7– | 1 | 3 | 96 | 87– | 8– | 1 | 3 | 85 | 90 | 9– | 2 | 2 | 32 | 46 | 11– | 0 | 3 | 48 | 65 |
| 6– | 2 | 3 | 123 | 127– | 7– | 1 | 4* | 16 | 18 | 8– | 1 | 4 | 107 | 95– | 9– | 2 | 3 | 48 | 41 | 11– | 0 | 5 | 48 | 3– |
| 6– | 2 | 4 | 69 | 75 | 7– | 1 | 5 | 96 | 108 | 8– | 1 | 5 | 58 | 62– | 9– | 2 | 4 | 26 | 33– | 11– | 1 | 1 | 96 | 82 |
| 6– | 2 | 5* | 16 | 33 | 7– | 2 | 1* | 10 | 20 | 8– | 2 | 1 | 133 | 133 | 9– | 2 | 5 | 26 | 6– | 11– | 2 | 1 | 26 | 38– |
| 6– | 2 | 6 | 32 | 48– | 7– | 2 | 2 | 21 | 14 | 8– | 2 | 2 | 96 | 99– | 9– | 3 | 1 | 42 | 56 | 11– | 2 | 2 | 26 | 32 |
| 6– | 3 | 1 | 16 | 19– | 7– | 2 | 3 | 91 | 110 | 8– | 2 | 3 | 42 | 67– | 9– | 3 | 2 | 64 | 62– | 11– | 2 | 3 | 26 | 1– |
| 6– | 3 | 2* | 10 | 3– | 7– | 2 | 4 | 32 | 40– | 8– | 2 | 4 | 91 | 83 | 9– | 3 | 3* | 16 | 5– | 11– | 3 | 1 | 32 | 6 |
| 6– | 3 | 3 | 21 | 31– | 7– | 2 | 5* | 16 | 14– | 8– | 2 | 5 | 85 | 37 | 9– | 3 | 4 | 37 | 26– | 11– | 3 | 2 | 64 | 29 |
| 6– | 3 | 4 | 26 | 32– | 7– | 2 | 6 | 26 | 21 | 8– | 2 | 6 | 74 | 37 |  |  |  |  |  |  |  |  |  |  |
| 6– | 3 | 5 | 42 | 48 | 7– | 3 | 1 | 155 | 175 | 8– | 3 | 1 | 10 | 10 | 10– | 0 | 2 | 64 | 91 | 12– | 0 | 2* | 10 | 9 |
| 6– | 3 | 6 | 58 | 42– | 7– | 3 | 2 | 80 | 93– | 8– | 3 | 2 | 53 | 43 | 10– | 0 | 4* | 10 | 18 | 12– | 2 | 1 | 26 | 23 |
| 6– | 4 | 1 | 69 | 71 | 7– | 3 | 3* | 10 | 19– | 8– | 3 | 3* | 10 | 27– | 10– | 1 | 1 | 53 | 54– | 12– | 2 | 2 | 48 | 23 |
| 6– | 4 | 2 | 123 | 106– | 7– | 3 | 4 | 42 | 47 | 8– | 3 | 4 | 58 | 38 | 10– | 1 | 2 | 85 | 65 | 12– | 2 | 3 | 53 | 14– |
| 6– | 4 | 3* | 21 | 9 | 7– | 4 | 1 | 32 | 52 |  |  |  |  |  | 10– | 2 | 1 | 69 | 69 |  |  |  |  |  |
|  |  |  |  |  | 7– | 4 | 2 | 53 | 49– | 9– | 0 | 1 | 91 | 73 | 10– | 2 | 2 | 64 | 75– | 13– | 0 | 1 | 16 | 32– |
| 7– | 0 | 1 | 123 | 118 | 7– | 4 | 3 | 74 | 102– | 9– | 0 | 3 | 85 | 61 | 10– | 2 | 3 | 85 | 41– | 13– | 0 | 3 | 48 | 4– |

* Unobserved reflection. Fo = half minimum observable value.

cipitate was washed with sodium bicarbonate solution and recrystallized from 95% ethanol, yielding yellow crystals (44.2 g., 0.171 mole, 91%), m.p. 103–104°; reported 80%, m.p. 103–104°,[18] 104°[19]; $\nu_{NH}$ 3330m, $\nu_{C=O}$ 1712s, $\nu_{NO_2}$ 1572s, 1337s cm.$^{-1}$ in Nujol.

**4-Bromo-2-nitroaniline** (with Kent R. Rush, 1961).—Hydrolysis of 4-bromo-2-nitroacetanilide with aqueous potassium hydroxide[19] or aqueous sulfuric acid (83% yield)[18] at room temperature has been described, but the details of desirable quantities of reactants have not previously been described.

**(A) From Hydrolysis with Dilute Sodium Hydroxide Solution.**—Aqueous 20% sodium hydroxide solution (200 cc.) was added to a solution of 4-bromo-2-nitroacetanilide (25.0 g., 0.097 mole) in ethanol (200 cc.). The solution was refluxed for 6 hr. and then cooled in an ice bath, producing an orange-brown precipitate (20.0 g., 0.092 mole, 95%), m.p. 104–109°.

When either orange-brown precipitate was dissolved in benzene and chromatographed on alumina, elution with benzene removed orange 4-bromo-2-nitroaniline, m.p. 111–112°; reported m.p. 110°,[19]; 112°[18]; $\nu_{NH}$ 3450m, 3320m in Nujol and halocarbon oil, $\nu_{NO_2}$ 1499s, 1339ms cm.$^{-1}$ in Nujol and halocarbon oil.

**5-Bromobenzfurazan 1-Oxide (Vb)** (with Kent R. Rush, 1961).—The procedure[2] for alkaline sodium hypochlorite oxidation of 4-chloro-2-nitroaniline was adapted to the preparation of this compound. Ice-cold aqueous sodium hypochlorite solution was added to an ice-cooled solution of 4-bromo-2-nitroaniline (14.35 g., 0.0661 mole) in ethanolic saturated potassium hydroxide solution (300 cc.) until the crimson color disappeared. The solution was allowed to evaporate overnight in an evaporating dish. The light brown precipitate was filtered off and then dissolved in 1:1 methanol–water solution (20 cc.). Evaporation and cooling produced yellow crystals (7.08 g., 0.0329 mole, 50%), m.p. 66–67°. The crystals were dissolved in petroleum ether (b.p. 60–68°) and chromatographed on alumina. Elution with petroleum ether and 4:1 mixtures with benzene removed nothing, but elution with 3:2 petroleum ether–benzene removed yellow crystals, m.p. 69°; reported m.p. 69°[4]; $\nu_{C=N}$ 1613s cm.$^{-1}$ in Nujol.

**5-Methylbenzfurazan 1-Oxide (Vc or VIc)** (with Albert W. Morgan, 1961).—Eastman Kodak White Label 4-methyl-2-nitroaniline in ethanolic potassium hydroxide solution was oxidized with hypochlorite solution to 5-methylbenzfurazan 1-oxide (55% yield), m.p. 91–94°, according to the general procedure of Green and Rowe.[20] Several recrystallizations from ethanol and ethanol–water yielded pale yellow crystals, m.p. 96–97°; reported 95%,[16] white needles 97°,[2,20] 98°[16]; $\nu_{C=N,\ C=C}$? 1618s, 1595s in $CCl_4$ and Nujol, 1618s, 1598s cm.$^{-1}$ in $CS_2$.

**X-Ray Data.**—The crystals of the chloro compound (Va, m.p. 46–48°) and the bromo compound (Vb, m.p. 69°) both sublimed readily in the X-ray beam. Mounting the crystals in sealed capillaries did not slow down appreciably the rate of sublimation out of the X-ray beam, and to keep the crystals intact it was necessary to fill the capillaries with water before sealing. The two compounds are monoclinic and isomorphous, with crystal data:

|  | $C_6H_3N_2O_2Cl$ | $C_6H_3N_2O_2Br$ |
|---|---|---|
| *a* | 12.47 ± 0.04 Å. | 12.62 ± 0.07 Å. |
| *b* | 7.06 ± 0.02 Å. | 7.29 ± 0.04 Å. |
| *c* | 8.01 ± 0.04 Å. | 7.98 ± 0.04 Å. |
| *β* | 92.4 ± 0.3° | 90.2 ± 0.4° |
| $D_{\text{Calcd.}}(Z = 4)$ | 1.607 ± 0.008 g./cc. | 1.942 ± 0.012 g./cc. |
| $D_{\text{Found}}$ | 1.610 ± 0.003 |  |

The systematic extinctions $h + l$ odd in $h0l$ and $k$ odd in $0k0$ fix the space group as $P2_1/n$. Weissenberg data were collected for $hk0$, $hk1$, $hk2$, and $hk3$ using Cu K$\alpha$ radiation, and for $h0l$, $h1l$, $h2l$, $h3l$, and $h4l$ using Mo K$\alpha$ radiation. The crystals used for the Cu photographs were about 0.6 × 0.6 × 1.2 mm., with the long direction along the $c$ axis. Approximate corrections were made for absorption assuming the crystals were cylindrical.[21] The crystals used for the Mo photographs were about 0.6 mm. in each direction and no absorption corrections were made. The crystals showed well developed 100, 110, 101, and $\bar{1}01$ faces.

Visual estimates, using the multiple film technique, were made of 491 independent reflections, and 112 more might have been visible on the pictures taken, before the high temperature factor led to all of the reflections being too faint to see. All of the calculations described below were made on the Univac Scientific 1103 computer[22] using programs and techniques that have been described previously.[23] The usual Lorentz and polarization corrections were made and the intensities were correlated on a relative scale by the use of reflections common to the two sets of data. The intensities were put on a rough absolute scale and the average temperature factor was found from a Wilson plot[24] of the $h0l$ data. The temperature factor was 7.3.

**Structure Determination.**—The 202 reflection was exceedingly strong, suggesting that the molecules were stacked roughly parallel to the 101 face. A three-dimensional

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(19) H. Hübner, *Ann.*, **209**, 355 (1881).

(20) A. G. Green and F. M. Rowe, *J. Chem. Soc.*, **101**, 2452 (1912).

(21) J. S. Kasper and K. Lonsdale, "International Tables for X-Ray Crystallography," Vol. 2, Kynoch Press, Birmingham, England, 1959, p. 295.

(22) We wish to thank the Numerical Analysis Center of the University of Minnesota for making the computer time available and for help.

(23) M. G. Rossman, R. A. Jacobson, F. L. Hirshfeld, and W. N. Lipscomb, *Acta Cryst.*, **12**, 530 (1959).

(24) H. Lipson and W. Cochran, "The Determination of Crystal Structures," G. Bell and Sons, Ltd., London, England, 1957, pp. 62, 138.

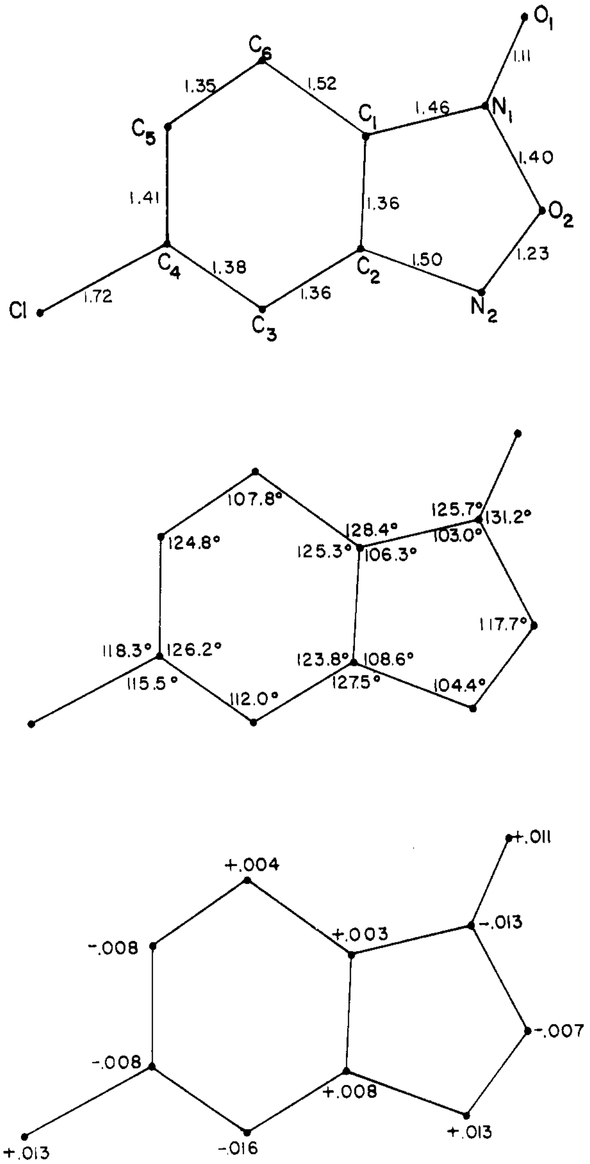

Fig. 1.—Chlorobenzfurazan 1-oxide. a. Names of the atoms and bond lengths in Å. b. Bond angles. c. Deviations (in Å.) from the mean plane of the molecule.

Patterson map showed prominent peaks around $^1/_4$, $^1/_2$, $^1/_4$ and $^1/_2$, 0, $^1/_2$, and lesser peaks at $^1/_2$, 0, 0; $^3/_4$, $^1/_2$, $^1/_4$; and 0, 0, $^1/_2$. The peaks were very broad and the map showed very little detail. The two intense peaks were taken to indicate that the chlorine atoms were located near $^1/_8$, $^1/_4$, $^1/_8$; $^3/_8$, $^3/_4$, $^3/_8$; etc. A graphical Patterson superposition using the minimum function yielded little new information; the molecules were parallel to 101 and the only peaks other than the chlorine were a set of very broad peaks at $-^1/_8$, $^3/_4$, $^3/_8$; $^5/_8$, $^1/_4$, $^1/_8$; etc.

Next, a Fourier map was prepared, using all the data, with the signs determined only by the chlorine atoms. The chlorine locations determined from the Patterson map put the chlorine atoms on the glide plane, and, therefore, would have led to a false mirror plane in the Fourier map. In order to avoid partially this difficulty the chlorine atoms were displaced by $y/b = 0.01$ from the glide plane. Knowing the final answer, the entire molecule can be seen in this map, but at the time only some peaks near the final nitrogen and oxygen positions appeared significant. On the basis of these peaks an attempt was made to put in the entire molecule except for the external oxygen atom, and a second Fourier map was prepared from this guess. It was a mistake to try to put the entire molecule in, and in this map and in several more that followed, which will not be described in detail, less information was obtained than might have been because too many atoms were guessed in the input structure. The rough position of the benzene ring appeared fairly early, but the nitrogen and oxygen positions varied considerably, sometimes appearing to be near $C_1$ and $C_2$ (see Fig. 1), and sometimes near $C_1$ and $C_6$. Eventually a structure, which appeared reasonable, was found in which

$$R = \Sigma||kF_o| - |F_c||/\Sigma|kF_o| = 0.46,$$

$$\text{and } r = \Sigma w_0^4(|kF_o|^2 - |F_c|^2)^2/\Sigma w_0^4|kF_o|^4 = 0.41.^{25}$$

After some least squares refinement indicated this was probably the correct structure, one further Fourier map was prepared in which the chlorine atom and the benzene ring were used to calculate the phases and no assumptions were made about the nitrogen and oxygen atoms. In the resulting map the carbon atoms had peak heights 3.4–5.4 $e$ Å.$^{-3}$, there were four peaks in approximately the expected positions for the nitrogen and oxygen atoms which had peak heights 1.7–2.8 $e$ Å.$^{-3}$, and there were only three other peaks, all of height 1.7 e Å.$^{-3}$, none of which were near the benzene ring. This was taken to indicate that the trial structure was correct.

**Refinement of the Structure.**—Starting at the point mentioned above where $R = 0.46$, $r = 0.41$, six cycles of least squares refinement reduced these values to $R = 0.29$, $r = 0.15$. At this point another Fourier map was prepared, the positional parameters were shifted slightly on the basis of this map, the value of $F_w$[25] was changed from 28, which had been used in the early calculations, to 14, which was approximately four times the minimum observed value of $F$, and further refinement was carried out. The changes led to the increased values, $R = 0.31$, $r = 0.55$, the very large change in r being due primarily to the change in $F_w$. After six cycles of refinement $R = 0.25$, $r = 0.22$. At this point anisotropic temperature factors were introduced, and after twelve more cycles refinement appeared to have ceased with $R = 0.154$, $r = 0.063$. This refinement was made using all the data, including the unobserved reflections, which were given half the minimum observable value of $F$. The observed and calculated structure factors are given in Table I. If the unobserved reflections were omitted, $R = 0.136$ and $r = 0.056$. Three cycles of refinement with the unobserved reflections omitted did not change these values and did not shift the atom positions enough to change any of the bond lengths by more than 0.01 Å. The results of this last calculation are used in the tables and the discussion of the structure which follow. If the anisotropic temperature factors were converted to averaged isotropic temperature factors, and only the observed reflections used, $R = 0.226$, $r = 0.195$.[26]

The final positional parameters are shown in Table II. The uncertainties are standard deviations estimated from the diagonal approximation inverse matrix. These positions

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[25] The weighting factor, $w_0$, was 1 for $|kF_o| \leqslant F_w$ and $F_w/|kF_o|$ for $|kF_o| > F_w$. Usually, $F_w = 14$ was used in the calculations.

[26] Primarily for our own education a Fourier map was prepared from the data with the isotropic temperature factors (only 15 of the weakest reflections had different signs in the anisotropic list), and this was compared with difference Fourier maps from both the isotropic and anisotropic lists. (The 202 reflection was omitted from the difference Fouriers.) The peak heights on the Fourier were: Cl − 14.2 $e$ Å.$^{-3}$; C, N, O − 2.9–4.7 $e$ Å.$^{-3}$. On the isotropic difference Fourier all peaks and valleys were under 1.0 $e$ Å.$^{-3}$ with the extrema very near to atom positions and indicative of anisotropic thermal motion. On the anisotropic difference Fourier the highest peaks and valleys are about 0.5 $e$ Å.$^{-3}$, and they correlate more poorly with the atom positions. There were no particular indications of the hydrogen atoms although all would be located in regions of positive electron density on the map.

TABLE II

FINAL PARAMETERS

| Atom | $x/a$ | $y/b$ | $z/c$ | $\bar{B}$[a] |
|---|---|---|---|---|
| Cl | 0.3751 ± 0.0003 | 0.7592 ± 0.0007 | 0.3961 ± 0.0004 | 9.3 ± 0.2 |
| $O_1$ | .643 ± .001 | .060 ± .002 | .047 ± .002 | 13.8 ± .7 |
| $O_2$ | .729 ± .001 | .347 ± .002 | .061 ± .001 | 10.7 ± .5 |
| $N_1$ | .647 ± .001 | .213 ± .002 | .079 ± .001 | 9.9 ± .6 |
| $N_2$ | .715 ± .001 | .508 ± .002 | .114 ± .001 | 10.6 ± .6 |
| $C_1$ | .565 ± .001 | .322 ± .002 | .162 ± .001 | 7.5 ± .6 |
| $C_2$ | .604 ± .001 | .500 ± .002 | .183 ± .001 | 7.9 ± .6 |
| $C_3$ | .549 ± .001 | .645 ± .002 | .252 ± .001 | 6.5 ± .5 |
| $C_4$ | .450 ± .001 | .588 ± .002 | .302 ± .001 | 5.7 ± .5 |
| $C_5$ | .406 ± .001 | .404 ± .002 | .284 ± .001 | 6.3 ± .5 |
| $C_6$ | .456 ± .001 | .255 ± .002 | .215 ± .001 | 8.1 ± .6 |

[a] This is an averaged value calculated from the anisotropic temperature factor parameters. See ref. 23.

lead to the bond lengths and angles given in Fig. 1. The standard deviations in the bond lengths, as estimated from the standard deviations in the positional parameters by the usual formulas for the propagation of errors, were about 0.03 Å. for all the bonds. Also shown in Fig. 1 are the deviations of the various atoms from a least squares plane through the molecule. All of the atoms were given equal weight in drawing the plane. As can be seen from the figure there is a suggestion that the molecule is puckered slightly, but none of the deviations of the individual atoms from the mean plane is as large as the standard deviation in the position of the molecule.

The final refinement, as indicated above, was made using anisotropic temperature factors for all of the atoms. It does not seem worthwhile to give a complete list of the least squares parameters and the derived values of the magnitudes and directions of the principal axes of the ellipsoid of vibration for each atom.[27] The results generally were that the minimum vibration of an atom occurred in a direction perpendicular to the plane of the molecule and that the largest vibrations occurred in the plane of the molecule in a direction perpendicular to the direction from the center of the molecule to the atom in question. The latter vibration was largest for the chlorine, nitrogen and oxygen atoms, and the motion may be looked upon as a rotational oscillation in the plane of the molecule.

The shortest intermolecular distances are 3.20 Å. between $O_1$ and $N_2$ on adjacent molecules and 3.28 Å. between $N_1$ and $N_2$. All of the other intermolecular distances are 3.40 Å. or greater. These distances are reasonable for van der Waal's interactions; there are no unusual features in the packing.

The experimental bond lengths in the molecule are somewhat surprising, and it is difficult to decide what meaningful conclusions can be drawn from them. The calculated standard deviations in the bond lengths suggest that $C_1$—$C_6$ is significantly longer than the rest of the C—C bonds, including $C_2$—$C_3$. The two C—N bonds look like single bonds, the $N_1$—$O_1$ bond is shorter than a normal double bond, and the $N_2$—$O_2$ bond is shorter than a normal single bond. All of these features are difficult to rationalize with any reasonable resonance structures. A more likely explanation is that the data are poor, being collected only 15–25° below the melting point, with no careful control of the temperature. In addition, the anisotropic thermal motion was considerable, and to assume that this motion is properly described by an ellipsoid is a poor approximation for a molecule of this shape.[28] Changing the ellipsoidal anisotropic thermal motion to isotropic thermal motion in the refinement changed the bond lengths by 0.01–0.06 Å. and increased the estimated standard deviations by about 50%.

In summary, the molecular structure has been determined to be 5-chlorobenzfurazan 1-oxide, but the bond lengths are sufficiently uncertain that little can be said about the details of the bonding.

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(27) These parameters were calculated according to the method described by M. G. Rossman and W. N. Lipscomb, *Tetrahedron*, **4**, 291 (1958). There is a small mistake in their description; the formulas given refer to the orthogonal axes $a^*$, $b$, and $c$, and not to $a$, $b$, and $c^*$.

(28) In the extreme cases (using the usual approximation that $B = 8\pi^2\overline{u^2}$) the mean thermal motion was about 0.5 Å. With this very large motion systematic errors of 0.05–0.01 Å. seem possible.