a vinyl hydrogen (5.10 ppm), and hydroxyls (3410 cm^{-1}) in which three are secondary (3.66, 4.08, 4.32 ppm). On acetylation, G-VII gave the diacetate (XIII), mp 183—184°, which still has a secondary hydroxyl (4.54 ppm) besides two secondary O-acetyls (1722, 1712, 1250 cm^{-1}, 2.08, 2.09, 4.75, ~4.90 ppm). The NMR spectrum of the diacetate (XIII) is similar to that of G-III 3,6-diacetate (XIV), however, the signal at 1.29 ppm for the two tertiary methyls on the hydroxyl-bearing carbons (C-10 and C-16) in the latter is replaced by signals at 4.91 and 5.07 ppm for a vinylidene and those at 1.75 and 5.10 ppm for a vinyl methyl and a vinyl hydrogen, respectively, in the former. From the combined evidence, it is suggested that G-VII may probably be represented by formula IV. Then G-VII was treated with acetone and copper sulfate to furnish G-VII acetonide, mp 145—146°, which was found to be identical with the previous acetonide (XI). It follows that G-VII is shown as IV.

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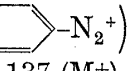
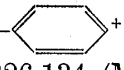
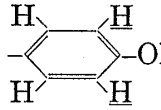
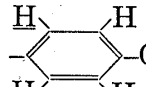
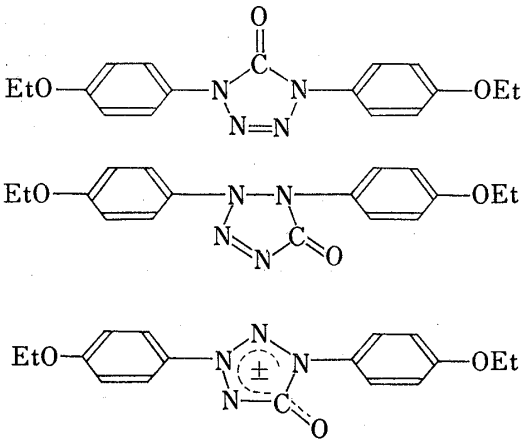
Isolation and Structural Analysis of a Fluorescent Compound produced by the Reaction of Dulcin with Sodium Nitrite

The present authors have reported a new fluorometric determination of dulcin using sodium nitrite.[1] This communication deals with the isolation and structural analysis of a fluorescent compound obtained in this reaction.

According to the conditions for this determination, dulcin was treated with sodium nitrite in the presence of hydrochloric acid at room temperature. The reaction mixture was made alkaline with sodium hydroxide, and extracted with chloroform. The extract was chromatographed on a silica gel column. From the fluorescent fraction, colorless leaflets (from a mixture of ethanol and chroroform, 5:2), mp 183—184°, were obtained.

Fluorescence spectra $\lambda_{max}^{CHCl_3}$ mμ: excitation, 354; emission, 446. *Anal.* Calcd. for $C_{17}H_{18}O_3N_4$: C, 62.57; H, 5.52; N, 17.17. Found: C, 62.68; H, 5.42; N, 17.17. Mass Spectrum *m/e*: 326 (M^+), 149 (EtO-  -N_2^+), 121 (EtO-  $^+$). Mirimass Spectrum *m/e*: *Anal.* Calcd. for $C_{17}H_{18}O_3N_4$: 326.137 (M^+). Found: 326.134 (M^+). UV $\lambda_{max}^{CHCl_3}$ mμ (log ε): 287 (4.01), 296 (3.99), 348 (4.25). IR cm^{-1} (KBr): $\nu_{C=O}$ 1680. NMR $\delta_{ppm}^{CDCl_3}$: 1.46 (6H, triplet, J=6.75 cps, $-OH_2C\underline{H}_3\times2$), 4.13 (4H, quartet, J=6.75 cps, $-OC\underline{H}_2CH_3\times2$), 7.03 (4H, doublet, J=9.15 cps,  -OEt×2), 8.02, 8.06 (each 2 H, doublet, J=9.15 cps,  -OEt×2).

1) S. Uchiyama, T. Kondo, and I. Kawashiro, *Yakugaku Zasshi*, **89**, 828 (1969).



Reduction of this compound with zinc and hydrochloric acid yielded *p*-phenetidine and *p*-phenetylurea.

These results suggest that the strutural formula should be one of the following three (I, II, III).

Since this fluorescent compound was also obtainable from *p*-phenetidine, the coresponding 2-bromoethoxy derivative (IV, $C_{17}H_{16}O_3N_4Br_2$) was similarly synthesized from 4-(2-bromothoxy) aniline for X-ray analysis.

Recrystallization of IV from ethyl acetate solution yielded very thin flaky crystals flattened on (100) plane. The crystal belongs to the orthorhombic system with lattice constants, $a=33.0$, $b=4.68$, $c=12.5$ Å. The space group was determined to be $Pna2_1$ from the systematic absences. The density measured by flotation method was 1.732 $g\cdot cm^{-3}$ which agrees well with the value 1.738 $g\cdot cm^{-3}$, calculated by assuming four molecules in the unit cell. Since the crystals were quite thin and their faces were not completely flat, it proved to be very difficult to collect the three dimensional data from the equi-inclination Weissenberg photographs. The present analysis was therefore carried out only in two-dimensions using *h0l* intensity data. The *b*-axis projection of the structure was solved by utilizing the heavy atom method and refined by successive use of difference Fourier syntheses. The *R* value at the present stage is 0.17 for 111 observed structure factors.

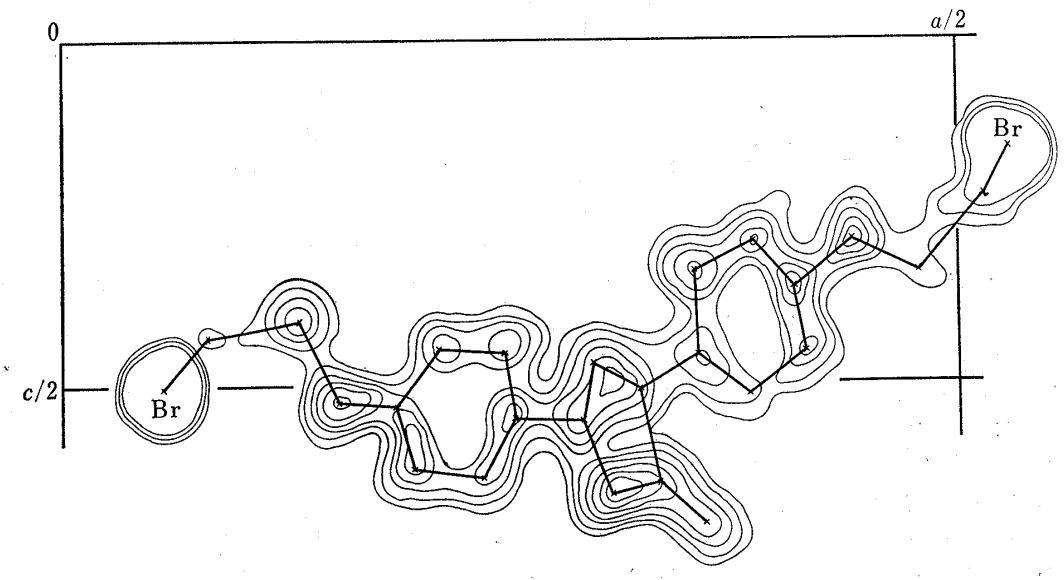


Fig. 1. *b*-Axias Projection of the Electron Density Distribution Function of IV

Contours are drawn at intervals of le./Å² starting at. 2e. 1/Å².
Those for bromine are not shown.

Fig. 1 shows *b*-axis projection of the electron density distribution function. The result of the X-ray analysis coincided with the structure III among those described above.

Consequently, the structure of this fluorescent compound was concluded to be III. The details will be reported in future.

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Syntheses of Ten-membered Ring Amine Derivatives and 1-Azabicyclo-[4,4,1]undecane from 3,4,6,7,8,9-Hexahydro-2*H*-quinolizine

It is known that the enamine reacted with trichloroacetic acid producing β,β,β-trichloro-alkylamine, which, on treatment with ethanol, gave N,N-disubstituted α-chloro amide.[1,2] Its application has led us to develop syntheses of ten-membered ring amines and 1-azabicyclo-[4,4,1]undecane (XVIII) from $\Delta^{1,10}$-hexahydro-quinolizine (II).

Reaction of the enamine[3] (II) obtained by mercuric acetate oxidation of octahydro-quinolizine (I), with trichloroacetic acid in benzene afforded in 15% yield a chloro lactam (III), mp 92—92.5°. *Anal.* Calcd. for $C_{10}H_{16}ONCl$: C, 59.55; H, 8.00; N, 6.94. Found: C, 59.58; H, 7.91; N, 7.27. IR ν_{max}^{Nujol} cm^{-1}: 1665 (–CO–N<), but not the expected trichloro compound (IV). Hydrolysis of the lactam (III) in dilute hydrochloric acid gave an amino acid hydrochloride (V), mp >300°. *Anal.* Calcd. for $C_{10}H_{19}O_2NCl_2$: C, 46.88; H, 7.48; N, 5.47.

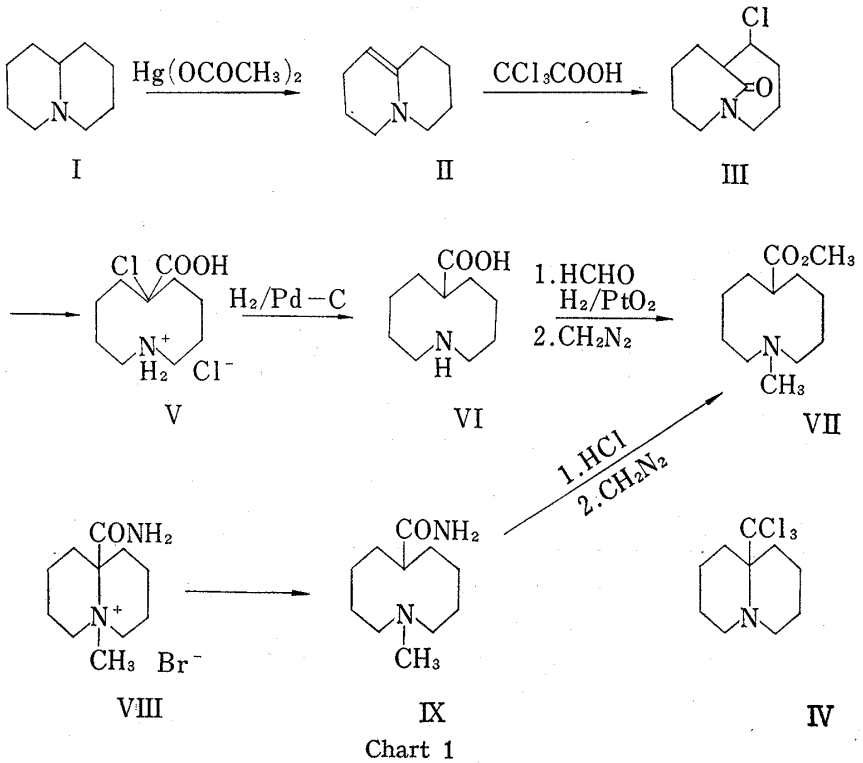

Chart 1

1) A. Łukasiewicz and J. Lesnka, *Tetrahedron*, **24**, 7 (1968).
2) A. Łukasiewicz, *Tetrahedron*, **24**, 513 (1968).
3) N.J. Leonard and A.S. Hay, *J. Am. Chem. Soc.*, **78**, 1984 (1956).