red-brown solids possessing a waxy appearance. The residue was suspended in acetone and filtered, the solids were then further leached of impurities with hexane (100 ml), and absolute EtOH (500 ml) was added to the boiling suspension. Cooling and filtration gave 56.7 g of buff-colored solids, mp 152–155°.

Recrystallization was effected by suspending the solid in isopropyl ether (600 ml), heating the suspension to boiling, and adding benzene dropwise to the hot solution until solution was complete. When this was cooled, 28.5 g of off-white crystals were obtained, mp 153–154.5°, representing a 14% yield; however, no attempts were made to optimize the yield.

Anal. Calcd for $C_{39}H_{73}N_3O_2$: C, 76.04; H, 11.94; N, 6.83; mol wt, 616. Found: C, 76.13; H, 12.06; N, 6.72; mol wt could not be determined because of insolubility in the available solvents.

N,N'-Dinorbornyl-2-norbornylaminomalonamide (13).—A 1-l. Monel beaker with a polyethylene cover containing apertures for an addition funnel and thermometer and provided with a magnetic stirrer was charged with 80 ml (4.0 mol) of HF and 25 ml (17.2 g, 0.64 mol) of HCN and cooled in an ice bath to 0°. Norbornene (47.0 g, 0.50 mol) was added by means of a spatula over a period of 37 min. Five hours later, 150 ml of water was added followed by 100 ml of CH_2Cl_2. The CH_2Cl_2 layer was shaken with dilute NaOH until neutral, and removal of the solvent left 60.0 g of a viscous amber liquid. A portion of the material was triturated with 85% acetone to give **13** which, when recrystallized from *n*-hexane and ethanol, melted at 180.5–182°. A total of 7.1 g of product was obtained.

Anal. Calcd for $C_{24}H_{37}N_3O_2$: C, 72.14; H, 9.33; N, 10.52; mol wt, 399.6. Found: C, 71.94; H, 9.32; N, 10.23; mol wt, 419.

The infrared and nmr spectra were consistent with the structure postulated.

N,N'-Dipentyl-2-pentylaminomalonamide (12).—A 1-l. Monel autoclave was charged with 160 ml (8.0 mol) of HF and 33 g (48 ml, 1.2 mol) of HCN. 1-Pentene (70 g, 1.0 mol) was pumped into the reactor at 18° over a period of 42 min. It was then heated at 45–50° for 2 hr; the heating was followed by cooling and addition of 300 ml of water and 200 ml of CH_2Cl_2. The CH_2Cl_2 layer was collected and the aqueous acid layer was extracted with CH_2Cl_2. The organic layers were combined and shaken with $NaOH$–H_2O giving an emulsion which was broken by filtration. Removal of the CH_2Cl_2 after separation and drying over

$MgSO_4$ gave 90.4 g of a brown viscous liquid. Crystallization was achieved by immersing the flask in ice and adding 150 ml of hexane. Filtration and two additional crystallizations (hexane) gave a total of 4.2 g of white crystals, mp 76–78°.

Anal. Calcd for $C_{18}H_{37}N_3O_2$: C, 66.01; H, 11.39; N, 12.83; mol wt, 327. Found: C, 66.16; H, 11.42; N, 12.86; mol wt, 324 (osmometry).

Reaction of Ethylene with HCN–HF.—The 1-l. autoclave was charged with 160 ml of HF and 50 ml of HCN and pressured to 500 psig (39 g) with ethylene. The mixture was heated at 50° for 3 hr and the pressure dropped to 280 psig at 51°. It was repressured to 500 psig (21 g) and stirred an additional 1 hr. Work-up was similar to those described previously with only 2.5 g being obtained on various extractions with CH_2Cl_2. Possibly the product which would arise would be very water soluble and not be extractable by these methods.

Reaction of 1-Octene with HCN–HF.—When 160 ml of HF, 48 ml of HCN, and 112 g (1.0 mol) of 1-octene were used under conditions described above, 139.5 g of a dark viscous residue was obtained. No identifiable materials, except a small amount of N-octylformamide, could be detected either by crystallization or distillation procedures.

Reaction of 2-Methyl-2-butene with HCN–HF.—Using 160 ml of HF, 48 ml of HCN, and 70.0 g (1.0 mol) of 2-methyl-2-butene under conditions described above, 30.5 g of a black tar was isolated. No identifiable products could be isolated.

Registry No.—Hydrogen fluoride, 7664-39-3; **3,** 23604-71-9; **4,** 23604-72-0; **5** (2-pentyl), 23604-73-1; **5** (3-pentyl), 23604-84-4; **6,** 23604-74-2; **8,** 23604-75-3; **8** (acetylated), 23604-76-4; **9,** 23604-77-5; **9** (methiodide), 23758-69-2; **10,** 23604-78-6; **11,** 23604-79-7; **12,** 23604-80-0; **14,** 23604-81-1; **15,** 23604-82-2; **16** (HCl), 23604-83-3.

Crystal Structure of 10-Methylisoalloxazinium Bromide Dihydrate

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The title compound, a model for protonated riboflavin, exists in the crystal in the tautomeric form I. There is minor deviation from coplanarity in the ring system, with a slight general bow along the long axis. The molecules are arranged in sheets of P_g symmetry with intrasheet hydrogen bonding.

In spite of the importance of riboflavin and its derivatives FMN and FAD in biological redox systems, bond parameters have been measured on only a few substances containing the riboflavin ring system.[1] This is undoubtedly due to the failure of many derivatives of interest to form crystals suitable for X-ray study. The title substance, however, which contains the cation depicted below, forms excellent crystals,
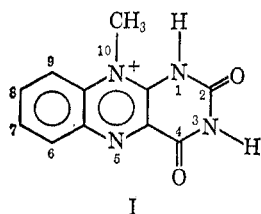
and we wish to report the results of an X-ray study on them.[2]

Experimental Section

Cooling of a solution of 10-methylisoalloxazine in concentrated hydrobromic acid gave many-faced, olive green crystals of 10-methylisoalloxazinium bromide dihydrate.

Anal. Calcd for $C_{11}H_{13}N_4O_4Br$: C, 38.51; H, 3.86; N, 16.10; O, 18.54; Br, 23.89. Found: C, 38.29; H, 3.79; N, 16.24; O, 18.55; Br, 23.16.

I

(1) (a) P. Kierkegaard, *et al., Chem. Commun.*, **288** (1967); (b) N. Tanaka, *et al., Bull. Chem. Soc. Jap.*, **40,** 1739 (1967); (c) C. J. Fritchie, Jr., and B. L. Trus, *Chem. Commun.*, 1486 (1968).

(2) Fritchie and Trus[1c] have communicated their results on the same substance, and our parameters appear to be in close agreement with theirs. Our preliminary results with this structure (not then fully refined) were reported: Abstracts, 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 1967, No. O-149.
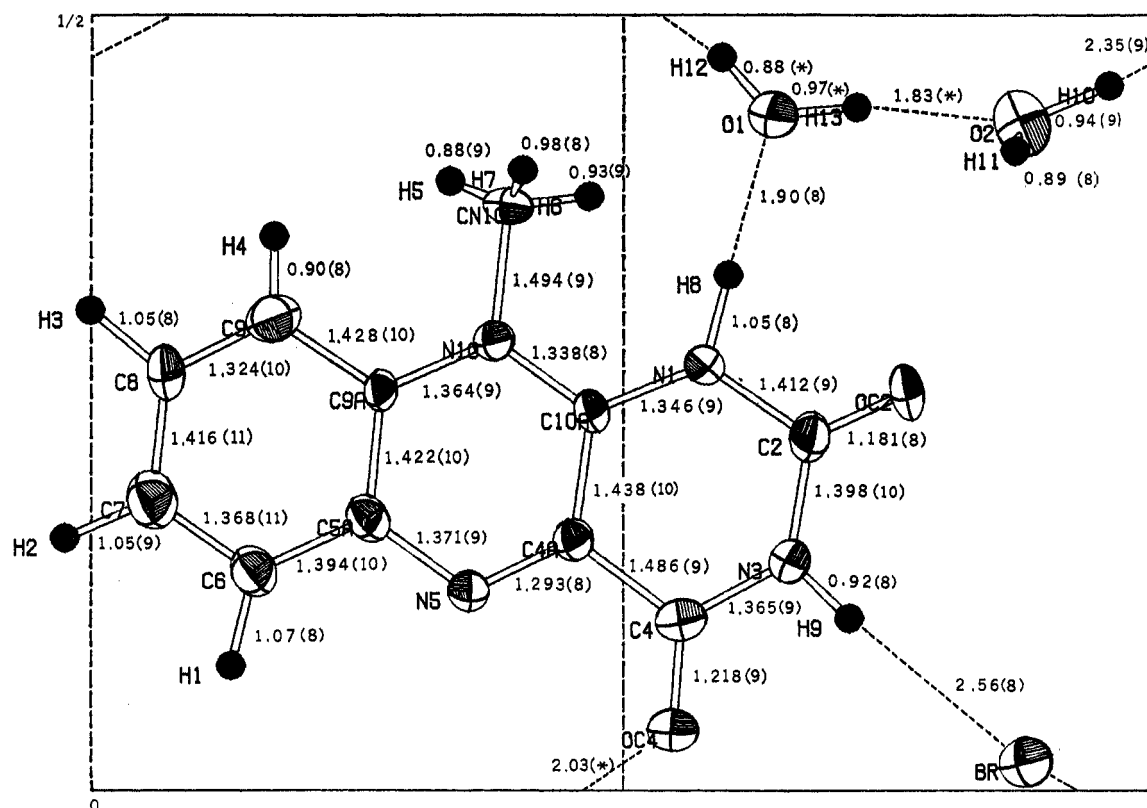
Figure 1.—An ORTEP plot of an asymmetric unit, viewed perpendicular to the 102 plane. Bond distances and their standard deviations are given in angstroms, and the intrasheet hydrogen bonds are shown as dotted lines. Standard deviations were not available in the starred cases owing to the failure of H-12 and H-13 to refine satisfactorily. Thermal ellipsoids enclose 50% probability.

Cell constants, determined from oscillation and Weissenberg photographs using a traveling microscope, follow: a = 9.38 Å (3), b = 11.77 Å (3), c = 13.57 Å (3), and β = 118.26° (10). The space group is P2$_1$/c. The unit cell volume calculated from these data is 1320 Å^3, and the density based on Z = 4 is 1.737 g/cm^3; the crystal density measured by flotation was 1.724 g/cm^3.

Intensity data were collected around the b axis of a 0.2 × 0.3 × 0.3 mm crystal on a Supper automatic diffractometer using a fine-focus Cu tube with a Ni filter. A 3° scan at 2°/min was used, with 45-sec background counts before and after. Reflections were accepted if the intensity was at least twice the square root of the sum of the scan and background counts. On levels 0–9, 1624 of a possible 2102 reflections (77%) were observed.[3] No absorption corrections were made.

The bromine atom was readily located on a three-dimensional Patterson map, and structure factors based on this atom gave an R of 39.9. All of the atoms except the hydrogens were clearly visible in the first Fourier map, and their inclusion in structure factor calculations lowered R to 22.4. Isotropic refinement gave an R of 12.3, which was lowered to 10.3 by anisotropic refinement.[4] A difference map revealed all of the hydrogens except H-13. At this point a data-processing error was corrected; isotropic refinement—including hydrogens—gave an R of 7.3, and anisotropic refinement led to a final R of 5.3. In these re-

TABLE I
BOND ANGLES

Angle	Degrees	Angle	Degrees
C-10a-N-1-C-2	123.6 (5)	OC-4-C-4-N-3	122.2 (6)
N-1-C-2-N-3	115.6 (6)	OC-4-C-4-C-4a	122.3 (6)
C-2-N-3-C-4	126.7 (6)	C-4-C-4a-N-5	117.5 (6)
N-3-C-4-C-4a	115.4 (5)	N-5-C-5a-C-6	119.4 (6)
C-4-C-4a-C-10a	118.6 (6)	H-1-C-6-C-5a	129 (5)
C-4a-C-10a-N-1	119.9 (5)	H-1-C-6-C-7	111 (5)
C-10a-C-4a-N-5	123.8 (6)	H-2-C-7-C-6	121 (4)
C-4a-N-5-C-5a	118.2 (5)	H-2-C-7-C-8	120 (4)
N-5-C-5a-C-9a	120.5 (6)	H-3-C-8-C-7	124 (6)
C-5a-C-9a-N-10	119.0 (5)	H-3-C-8-C-9	114 (5)
C-9a-N-10-C-10a	120.4 (5)	H-4-C-9-C-8	117 (5)
N-10-C-10a-C-4a	117.9 (6)	H-4-C-9-C-9a	123 (5)
C-9a-C-5a-C-6	120.1 (6)	C-9-C-9a-N-10	122.8 (6)
C-5a-C-6-C-7	120.3 (6)	CN-10-N-10-C-9a	119.6 (5)
C-6-C-7-C-8	119.2 (7)	CN-10-N-10-C-10a	119.8 (6)
C-7-C-8-C-9	122.5 (7)	N-10-C-10a-N-1	122.2 (6)
C-8-C-9-C-9a	119.8 (6)	N-10-CN-10-C-5	106 (5)
C-9-C-9a-C-5a	118.2 (6)	N-10-CN-10-C-6	103 (5)
H-8-N-1-C-10a	125 (5)	N-10-CN-10-C-7	112 (5)
H-8-N-1-C-2	110 (5)	C-5-CN-10-C-6	114 (8)
OC-2-C-2-N-1	121.1 (6)	C-5-CN-10-C-7	122 (8)
OC-2-C-2-N-3	123.3 (6)	C-6-CN-10-C-7	98 (9)
H-9-N-3-C-2	123 (6)	H-10-O-1-H-11	111 (12)
H-9-N-3-C-4	108 (7)	H-12-O-2-H-13	119 (a)

[a] The standard deviation in this angle is unknown, since H-12 and H-13 did not refine satisfactorily.

finements, hydrogens were given the same temperature factors as the atoms to which they were attached, and hydrogen temperature factors were not refined. All of the hydrogen positions refined satisfactorily except for H-12 and H-13, which refined into O-1 and a position roughly halfway between O-1 and O-2, respectively. As the most reasonable hydrogen-bonding scheme

requires H-12 and H-13 to be in the positions shown, they were placed there for the final refinement cycles and for Figure 1.

Bond lengths calculated using ORFFE[5] are given on an ORTEP[6] plot in Figure 1, and bond angles are listed in Table I.

Discussion

In the crystals under study, as has been postulated for solutions,[7] 10-methylisoalloxazine is protonated on N-1. Other riboflavin derivatives have also been shown to be protonated at this position in the crystalline state.[1]

The bond lengths found for the cation are very close to those reported by Fritchie and Trus[1c] and close to those in related structures.[1a,b] The long C-4–C-4a bond and the short C-4a–N-5 bond have been observed in all three of these structures.

All of the atoms except H-11 lie close to sheets of P_g symmetry parallel to the 102 plane. There are parts of six such sheets in the unit cell chosen, spaced 3.264 Å apart, starting from 408. The least squares plane calculated from the 17 nonhydrogen atoms of the cation is inclined 1.6° from the 102 plane. The standard deviation of the atoms defining the plane from the plane is only 0.053, with the deviations occurring primarily as a slight bow along the long axis of the molecule. This bow, which is quite possibly absent in solution, is probably present in the crystal to permit reasonable distances between bromide ion and N-3 in adjacent sheets [these atoms are 3.463(9) Å apart] and bromide and N-10 in adjacent sheets in the other direction [3.364(9) Å apart].

Figure 1 shows the intrasheet hydrogen bonds as dotted lines. The distances between nonhydrogen atoms joined through hydrogen bonds are unexceptional. The values in angstroms are: N-1–O-1, 2.883 (13); O-1–O(C-4), 2.886 (10); O-1–O-2, 2.767 (11); N-3–Br, 3.433 (10); O-2–Br, 3.291 (10).

The stacking arrangement of the sheets is governed primarily by the intersheet hydrogen bond involving H-11. The formation of strong intersheet hydrogen bonds requires the water oxygens to move closer to one another [intersheet O-1–O-2 distance, 2.983 (11) Å; H-11–O-1 distance, 2.09 (8) Å], and accounts for their large deviations from the molecular plane. O-1 moves farther out of the plane than O-2, presumably to give both oxygens better tetrahedral coordination [the fourth coordination for O-2 is provided by interaction with N-10, 3.235 (10) Å away]. The bromine is sandwiched between two nitrogens with partial positive charges, N-3 and N-10, as noted above. It also serves as a hydrogen-bond acceptor for N-3 and O-2, giving it roughly square-planar coordination. An H-2 and H-4 in the same sheet are nearly close enough [2.79 (8) and 2.85 (8) Å, respectively] and at the right angle to complete an octahedral arrangement around bromide ion.

(5) W. R. Busing, K. O. Martin, and H. A. Levy, ORNL-TM-306, Oak Ridge National Laboratory, 1964.

(6) C. K. Johnson, ORNL-3794.

(7) K. Dudley, A. Ehrenberg, P. Henmerich, and F. Muller, *Helv. Chim. Acta*, **47**, 1354 (1964).

Conversion of Some Bicycloheptanols into Chlorides Using Triphenylphosphine–Carbon Tetrachloride. Stereochemistry and Mechanistic Implications

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The reaction of triphenylphosphine and carbon tetrachloride with *exo,exo*-2,3-dideuterio-*anti*-7-hydroxybicyclo-[2.2.1]heptane affords *exo,exo*-2,3-dideuterio-*syn*-7-chlorobicyclo[2.2.1]heptane, exclusively. The isolated products from *exo,exo*-3,4-dideuterio-*exo*-2-hydroxybicyclo[3.2.0]heptane are *exo,exo*-3,4-dideuterio-*endo*-2-chlorobicyclo-[3.2.0]heptane and *exo,exo*-2,3-dideuterio-*anti*-7-chlorobicyclo[2.2.1]heptane. With the aid of a comparison between the inversion found in these reactions and the predominant retention of configuration found in the products of solvolysis of the esters of the above alcohols, a *tentative* mechanistic rationale is presented to account for our observations.

A previous report[1b] has demonstrated that the reaction of triphenylphosphine and carbon tetrachloride with alcohols to give alkyl chlorides has remarkable

$$ROH + Ph_3P + CCl_4 \longrightarrow RCl + Ph_3PO + CHCl_3$$
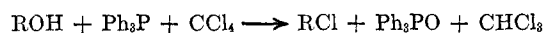
tendency for inversion, even in cases where solvolysis of the corresponding esters is largely or completely

assisted and the solvolysis products exhibit retained configurations. It is known also that such conversions occur with little or no skeletal rearrangement in those systems where SN1 reactions afford extensively rearranged products.[1b,2] To further elucidate the scope of this reaction, the course of reaction with alcohols 1 and 2 was determined.

(1) (a) To whom correspondence should be addressed: East Tennessee State University, Johnson City, Tenn. 37601. (b) R. G. Weiss and E. I. Snyder, *Chem. Commun.*, 1358 (1968).

(2) R. G. Weiss, Ph.D. Thesis, University of Connecticut, 1969; I. M. Downie, J. B. Holmes, and J. B. Lee, *Chem. Ind.* (London), 900 (1966).