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SYNTHESIS OF THE LASER DYES, AC2F AND AC3F, AND RELATED COMPOUN--ETC(U)
JUN 77 R A HENRY , P R HAMMOND

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Synthesis of the Laser Dyes, AC2F and AC3F, and Related Compounds

by
Ronald A. Henry
and
Peter R. Hammond
Research Department

JUNE 1977

Naval Weapons Center
CHINA LAKE, CALIFORNIA 93555

Naval Weapons Center

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R. M. Hillyer ..... Technical Director (Acting)

FOREWORD

One of the programs at the Naval Electronics Laboratory, San Diego, requires stable, blue-green lasing dyes. This report describes in detail the preparation of two closely related compounds, AC2F and AC3F, which have proved to meet this requirement. The work was supported in part during the periods July-September 1976 and April-May 1977 under Task Area No. F54583.

A few of the precursors were prepared earlier under another program for the Laser Isotope Separation Group, University of California's Lawrence Livermore Laboratory, Interagency Agreement SANL 284-001.

This report was reviewed for technical accuracy by Ronald L. Atkins and Aaron N. Fletcher.

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(U) The synthesis of the laser dye, AC2F, which is 2-oxo-6,9-dimethyl-4-trifluoromethyl-6,7,8,9-tetrahydro-2*H*-pyrano[2,3-*b*][1,8]naphthyridine, in nine steps from readily available starting materials is described. AC3F, which is the homologous 6,8,9-trimethyl compound, is made in six steps. Several related azacoumarins and azaquinolones, which fluoresce in the range 393-482 nm in ethanol, have also been prepared. In addition, 2-oxo-6,9-dimethyl-8-phenyl-4-trifluoromethyl-6,7,8,9-tetrahydro-2*H*-pyrano[2,3-*b*][1,8]naphthyridine has been made from 7-hydroxy-1,4-dimethyl-2-phenyl-1,2,3,4-tetrahydro-1,8-naphthyridine and sulfonated to furnish a water-soluble fluorescer (473 nm).

CONTENTS

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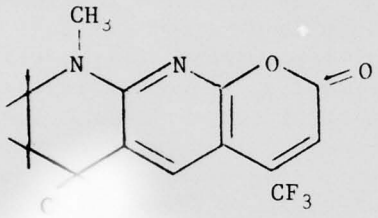
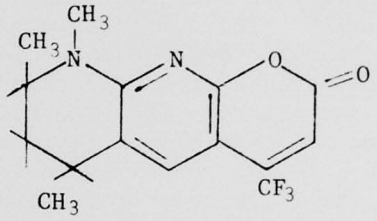
INTRODUCTION

As a consequence of a program to prepare and evaluate fluorescent materials as dyes for lasers,[1-6] two compounds, namely 2-oxo-6,9-dimethyl- and 2-oxo-6,8,9-trimethyl-4-trifluoromethyl-6,7,8,9-tetrahydro-2*H*-pyrano [2,3-*b*][1,8]naphthyridine, AC2F and AC3F, respectively.



AC2F



AC3F

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[1] P. R. Hammond and R. L. Atkins. "2-Keto-4-trifluoromethyl-9-methyl-6,7,8,9-tetrahydro-2*H*-pyrano[3,2-*g*]quinoline, an Efficient, Stable Laser Dye," *J. Heter. Chem.*, Vol. 12 (October 1975), pp. 1061.

[2] E. J. Schimitschek and others. "Laser Performance and Stability of Fluorinated Coumarin Dyes," *Optics Commun.*, Vol. 11, No. 4 (August 1974), pp. 352-355.

[3] E. J. Schimitschek and others. "New Laser Dyes With Blue-Green Emission," *Optics Commun.*, Vol. 16, No. 3 (March 1976), pp. 313-316.

[4] P. R. Hammond and others. "Search for Efficient, Near UV Lasing Dyes. I. Substituent Effects on Bicyclic Dyes," *Appl. Phys.*, Vol. 8 (1975), pp. 311-314.

[5] ------. "Search for Efficient, Near UV Lasing Dyes. II. Aza Substitution in Bicyclic Dyes," *Appl. Phys.*, Vol. 8 (1975), pp. 315-318.

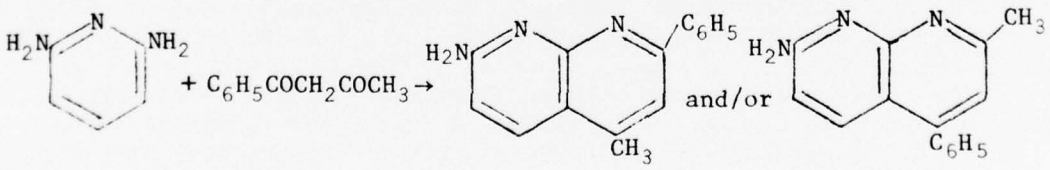
[6] P. R. Hammond and others. "Search for Efficient, Near UV Lasing Dyes. III. Monocyclic and Miscellaneous Dyes," *Appl. Phys.*, Vol. 9 (1976), pp. 67-70.

were shown to possess a relatively high stability (reduced photochemical degradation) toward repeated flash lamp pumping.[3,7,8] This report describes the syntheses of these two compounds, of their precursors, and of some related compounds derived from the same precursors.

Briefly, several new 2-amino- and 2-hydroxy-1,8-naphthyridine compounds were made and then condensed with various β-keto esters, using established methods, to yield derivatives of pyrido- and pyrano-naphthyridines. The reaction sequences are shown in Figure 1; procedures for the synthesis of both the precursors and the dyes are found in the Experimental Section. Table 1 summarizes pertinent information about the preparation and properties of the 1,2-dihydropyrido- and 2*H*-pyrano [2,3-*b*][1,8]naphthyridines. Although ^{1}H nmr spectra were obtained on all new compounds in order to confirm the structure assignments, only a few representative data have been included with the experimental details.

Several features about the reactions involved should be mentioned briefly. The quaternarization of the 7-acetamido-4-methyl- or 2,4-disubstituted-1,8-naphthyridines with methyl *p*-toluenesulfonate, ethyl bromoacetate or benzyl chloride occurred primarily, if not exclusively, on the nitrogen of the pyrido ring with the alkyl substituents. The same ring was also reduced when these quaternary salts were hydrogenated; the C-methyl groups appeared as doublets (splitting by a methine proton) in the ^{1}H nmr spectra. However, when unquaternarized 7-acetamido-2,4-dimethyl-1,8-naphthyridine was hydrogenated under the same conditions, the pyrido ring with the acetamido group was reduced to the tetrahydro derivative. In this case, the C-methyl groups appeared as singlets in the ^{1}H nmr spectrum. Partial hydrogenolysis of the acetamido group also was noted. The mode of hydrolysis of the 7-acetamido-substituted-1,2,3,4-tetrahydro-1,8-naphthyridines was significantly different under acidic and basic conditions, the former giving 7-hydroxy derivatives, the latter 7-amino. Thus convenient entry into two series of compounds was possible from the same precursor.

The condensation of benzoylacetone with 2,6-diaminopyridine could give two isomers:



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[7] S. Edward Neister. "The Dye Laser Dye Update," *Optical Spectra*, February 1977, pp. 34-36.

[8] Aaron N. Fletcher. "Laser Dye Stability. Part 2. Input Energy Per Flash, Dye Concentration, and Mirror Reflectivity Effects," *Appl. Phys.*, Vol. 12 (1977), pp. 327-332.

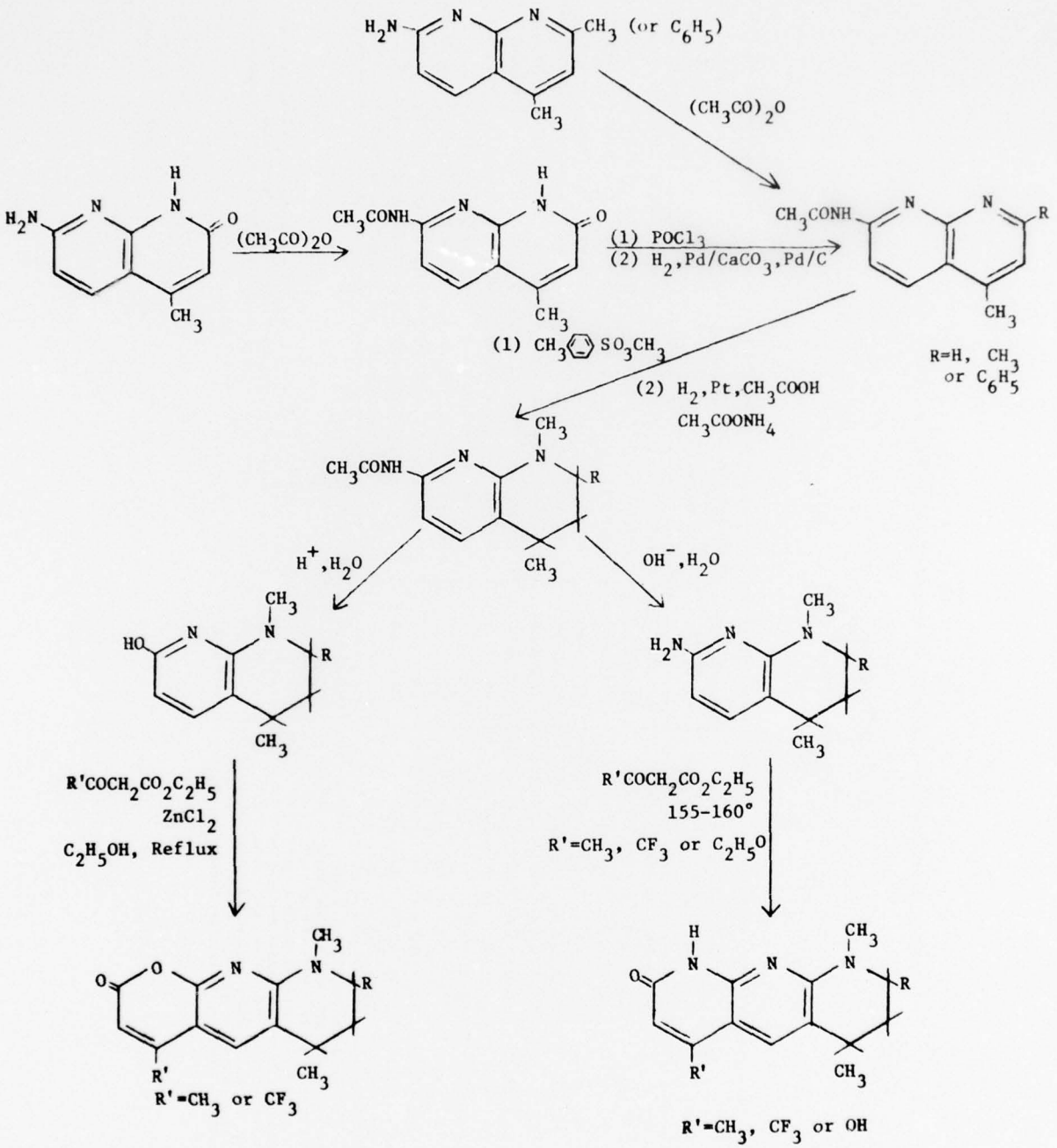
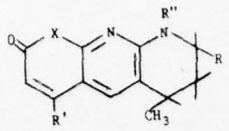


FIGURE 1. Reaction Steps to Substituted-6,7,8,9-tetrahydropyrido- and 2*H*-Pyrano[2,3-*b*]Naphthyridines.

TABLE 1. Substituted 1,2-Dihydropyrido- and 2*H*-Pyrano[2,3-*b*][1,8]Naphthyridines



	X	R′	R	R″	Empirical formula	Yield,[a] %	m.p., °C	Recrystallization solvent	Fluorescence max. in ethanol (Excited, nm)	Analysis			
										C, % (Theory)	H, % (Theory)	N, % (Theory)	F, % (Theory)
	O	H[b]	CH_3	CH_3	$C_{14}H_{16}N_2O_2$	30	111-112	1:1 C_6H_6-C_6H_{12}	437(375)	69.06(68.82)	6.57(6.60)	11.08(11.47)	...
	O	CH_3	CH_3	CH_3	$C_{15}H_{18}N_2O_2$	11	189-190	50% ethanol	430(375)	69.95(69.74)	6.39(7.02)	10.79(10.80)	...
AC2F	O	CF_3	H	CH_3	$C_{14}H_{13}F_3N_2O_2$	95	163.5-164.5	65% ethanol	482(400)	56.2 (56.37)	4.33(4.39)	9.36 (9.39)	19.35(19.11)
	O	CF_3	CH_3	H	$C_{14}H_{12}F_3N_2O_2$	...[c]	210-212	95% ethanol	473(395)	56.05(56.37)	4.51(4.39)	9.22 (9.39)	...
AC3F	O	CF_3	CH_3	CH_3	$C_{15}H_{15}F_3N_2O_2$	91	167-168	75% ethanol	480(394)	57.91(57.69)	5.00(4.84)	8.77 (8.97)	18.54(18.25)
	O	CF_3	CH_3	$CH_2CO_2C_2H_5$	$C_{18}H_{19}F_3N_2O_4$	55	136-138	Cyclohexane	474(390)	56.35(56.25)	4.89(4.98)	7.19 (7.29)	15.00(14.83)
	O	CF_3	C_6H_5	CH_3	$C_{20}H_{17}F_3N_2O_2$	23	146.5-147.5	Cyclohexane	479(395)	64.42(64.16)	4.72(4.58)	7.34 (7.48)	15.40(15.23)
	NH	CH_3	H	CH_3	$C_{14}H_{17}N_3O$[d]	29	254-256	C_6H_6	409(375)	69.26(69.11)	6.93(7.04)	17.32(17.27)	...
	NH	CH_3	CH_3	CH_3	$C_{15}H_{19}N_3O$	26	245-246	C_6H_6	408(370)	69.96(70.01)	7.40(7.44)	16.28(16.33)	...
	NH	CF_3	H	CH_3	$C_{14}H_{14}F_3N_3O$	86	232.5-233.5	C_6H_6	440(390)	56.55(56.56)	4.68(4.75)	14.05(14.14)	18.77(19.17)
	NH	CF_3	CH_3	CH_3	$C_{15}H_{16}F_3N_3O$	90	246-248	C_6H_6	442(390)	57.40(57.87)	5.14(5.18)	13.17(13.50)	...
	NH	OH[e]	H	CH_3	$C_{13}H_{15}N_3O_2$	85	>300	30% ethanol	...	63.58(63.66)	6.06(6.16)	16.92(17.13)	...
	NH	OCH_3[f]	H	CH_3	$C_{14}H_{17}N_3O_2$	49	246-247	Acetone	393(360)	64.39(64.84)	6.57(6.61)	15.96(16.21)	...

[a] For the reaction of the hydroxy or amino-tetrahydro-naphthyridine with the appropriate β-keto ester.

[b] Made from 2 and malic acid in conc. sulfuric acid at 120° for 1 hr. (2 is described on page 11.)

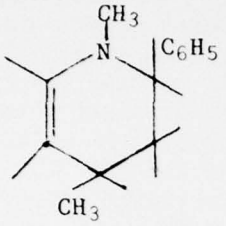
[c] Recovered in low yield as a by-product in the preparation of the compound where R″=$CH_2CO_2C_2H_5$.

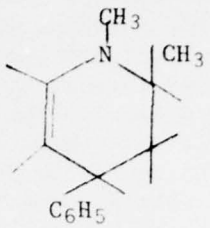
[d] The picrate after recrystallization from ethanol melted 213-214°. Found: N, 17.77; theory, 17.79.

[e] Equivalent amounts of diethyl malonate and 1 were heated with stirring in diphenyl ether at 170-180° for 1 hr; then the temperature was slowly raised during 2.5 hr to 245°. The product, which separated in part from the hot solution, was recovered by diluting the cooled mixture with benzene, chilling, filtering, and washing, first with cold benzene, then with hexane. Based on both the IR and the ^1H nmr the compound exists mainly in the 3-methylene-4 keto form. (1 is described on page 9.)

[f] Made by methylating the previous compound with dimethyl sulfate at 55-60° in basic 33% ethanol.

The former structure was assigned to the product isolated in low yield on the basis of the ^1H nmr of its N-methyl-tetrahydro derivative.





The downfield methine (CH adjacent to N) was always a doubled doublet resulting from the splitting of the methine proton by the H_{axial}-$H_{equatorial}$ protons on the adjacent methylene group. If the methyl rather than the phenyl group had been in this position, this doubled doublet would have been further split by the methyl protons to give a complex multiplet. The stereochemistry of the various tetrahydro compounds was not determined.

The effect of kind and position of substituents on the fluorescence maximum is the same as that observed with other coumarin and quinolone dyes.[4,5] The most pronounced influence on the chromophore is noted with changes in the substituents on the carbonyl-containing ring. When R' is the electron-withdrawing CF_3 group (see formula, Table 1), the fluorescence is red-shifted approximately 50 nm with the azacoumarins and 30-35 nm with the azaquinolones compared to the corresponding compounds with R' = CH_3. An electron-donating group, such as OCH_3, causes a 15-20 nm blue-shift in the fluorescent maximum compared to the analogous methyl compound; even a methyl group produces a small blue-shift when compared with the compound in which R' = H. Changes in R and R" influence only slightly the position of the fluorescence maximum. The fluorescence of the azaquinolone dyes is always blue-shifted 20-40 nm over that of the corresponding azacoumarins.

EXPERIMENTAL

PRECURSORS TO AC2F AND RELATED COMPOUNDS

7-Acetamido-2-chloro-4-methyl-1,8-naphthyridine

This compound was made from 7-acetamido-2-hydroxy-4-methyl-1,8-naphthyridine by the procedure of Petrow, Rewald, and Sturgeon.[9] The latter compound is also described by the same authors.

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[9] V. Petrow, E. L. Rewald, and B. Sturgeon. "The Preparation of 1:8-Naphthyridines from 2:6-Diaminopyridine," *J. Chem. Soc.* (1947), p. 1407.

7-Acetamido-4-methyl-1,8-naphthyridine

The above chloro compound (11.8 g, 0.05 mole) was slurried with 200 ml of 3% potassium hydroxide in 95% ethanol, 2 g of 5% $Pd/CaCO_3$ and 10-20 mg of 10% Pd/C, and hydrogenated at 50 psi (344.8 kPa). After an induction period the pressure rapidly dropped to 46.4 psi (319.9 kPa). The solution was filtered through Celite to remove the catalyst and the cake washed well with ethanol. The filtrate and washings were evaporated to dryness. The residue was slurried with 25 ml of cold water, and the solid filtered, washed with two 10-ml portions of water and dried; 5.8 g (73%), m.p. 201-204°C, of 7-amino-4-methyl-1,8-naphthyridine. Ether extraction of the mother liquors plus washings yielded 0.62 g (8%) more.

Recrystallization of 2.5 g from 130 ml of 9:1 benzene-ethanol gave a mixture of golden needles and white crusts, both of which melted at 204.5-205.5°C and both of which had the same ^1H nmr spectra. The IR spectrum of the golden needles suggested a hydrated form of 7-amino-4-methyl-1,8-naphthyridine (confirmed by analysis).

Anal. Calcd. for $C_9H_9N_3 \cdot 0.5\ H_2O$: C, 64.27; H, 5.99; N, 24.98. Found: C, 64.26; H, 5.97; N, 24.84.

Anal. on white crusts. Calcd. for $C_9H_9N_3$: C, 67.90; H, 5.70; N, 26.40; mol. wt. 159. Found: C, 67.94; H, 5.63; N, 26.43, mol. wt. (mass spec.) 159.

The free 7-amino compound (12.0 g) was reconverted to the 7-acetamido by refluxing with 30 ml of acetic anhydride for 1 hr. The cooled solution was slurried with 100 g of ice plus 100 ml of cold water, neutralized with sodium bicarbonate, warmed to dissolve all solids, then cooled overnight at 5°C. The crystalline product was filtered, washed twice with cold H_2O and dried; 13.3 g (88%); m.p. 248-251°C (dec.). An additional 2.2 g (m.p. 240-250°C) could be recovered by saturating the remaining aqueous phase with solium chloride. When recrystallized from acetonitrile, the compound melted at 252-253°C (dec.).

Anal. Calcd. for $C_{11}H_{11}N_3O$: C, 65.65; H, 5.51; N, 20.88. Found: C, 65.49; H, 5.51, N, 20.72.

A small quantity of a diacetylated product, m.p. 145.5-146.5°C, after recrystallization from benzene/hexane, was isolated from one experiment.

Anal. Calcd. for $C_{13}H_{13}N_3O_2$: C, 64.18; H, 5.39; N, 17.27. Found: C, 64.16; H, 5.45; N, 17.32.

7-Acetamido-1,4-dimethyl-1,8-naphthyridinium *p*-Toluenesulfonate

7-Acetamido-4-methyl-1,8-naphthyridine (13.3 g; 0.066 mole) was refluxed for 8 hr with 12.7 g of methyl *p*-toluenesulfonate in 150 ml of

dry acetonitrile. The dark purple solution was kept at 5°C for several days; 21.8 g (85%) of felted needles, m.p. 200-202°C, was removed. Addition of a large volume of ether to the mother liquors precipitated 2.3 g (9%) more of the salt; m.p. 185-190°C. The ^{1}H nmr was consistent with that expected for the desired product.

7-Acetamido-1,4-dimethyl-1,2,3,4-tetrahydro-1,8-naphthyridine

The previous salt (11.6 g; 0.03 mole) was hydrogenated over 0.15 g of PtO_2 in 100 ml of glacial acetic acid containing 12 g of ammonium acetate. Hydrogen uptake essentially ceased after the pressure dropped from 50 to 45 psi (344.8 to 310.2 kPa) after 4 hr; the purple solution became colorless. The catalyst was removed, washed once with 20 ml of acetic acid and twice with 20 ml of water. The combined solutions were reduced to dryness on a rotary evaporator. The residue was dissolved in 100 ml of water, cooled to 5°C, made basic and ether extracted (2-100 ml); the latter extracts, after washing once with a small volume of water, were dried over K_2CO_3. Evaporation left 5.34 g (81%) of off-white solid, melting sharply at 95-96°C. ^{1}H nmr (60 MHz, $CDCl_3$): δ1.20(d, 3H, $C\underline{H}_3CH$-, J = 7 Hz), 1.5-2.0(m, 2H, H_3, H_3), 2.04(s, 3H, $C\underline{H}_3CO$), 2.6-3.0(m, 1H, $CH_3C\underline{H}$-), 3.03(s, 3H, N-$C\underline{H}_3$), 3.32(t, 2H, H_2, H_2, J = 6 Hz), 7.22(broad s, 2H, H_5, H_6), 8.08(broad s, 1H, -N$\underline{H}$-).

7-Amino-1,4-dimethyl-1,2,3,4-tetrahydro-1,8-naphthyridine (1)

7-Acetamido-1,4-dimethyl-1,2,3,4-tetrahydro-1,8-naphthyridine (3.6 g) in 50 ml of 5% potassium hydroxide in 95% ethanol was refluxed for 8 hr under nitrogen. The solvent was then removed on a rotary evaporator and the residue slurried with 30 ml of water. After cooling to 5°C the solid product was removed, washed three times with cold water and dried; 2.82 g (97%); m.p. 51-53°C. The amide carbonyl absorption had disappeared completely from the IR spectrum, which was also different from that for the 7-hydroxy compound obtained by acid hydrolysis of the amide. Recrystallization from *n*-hexane (0.5 g/10 ml) by cooling to -15°C furnished coarse, white grains; m.p. 52.5-53.5°C. ^{1}H nmr ($CDCl_3$): δ1.17(d, 3H, -CH-$C\underline{H}_3$, J = 7 Hz), 1.69(m, 2H, H_3, H_3), 2.72(m, 1H, H_4), 3.05(s, 3H, N$C\underline{H}_3$), 3.27(t, 2H, H_2, H_2), 4.10(broad s, 2H, N$\underline{H}_2$), 5.72(d, 1H, H_6, J = 8 Hz), 7.02(d, 1H, H_5, J = 8 Hz). $Fl_{(max)}$ EtOH, 373 nm (excited 325 nm); $Fl_{(max)}$ 10^{-3} N $HClO_4$ in EtOH, 416 nm (excited 350 nm).

Anal. Calcd. for $C_{10}H_{15}N_3$: C, 67.76; H, 8.53; N, 23.71. Found: C, 68.19; H, 8.38; N, 23.36.

7-Hydroxy-1,4-dimethyl-1,2,3,4-tetrahydro-1,8-naphthyridine

7-Acetamido-1,4-dimethyl-1,2,3,4-tetrahydro-1,8-naphthyridine (1.27 g) was dissolved in 16 ml of 6N hydrochloric acid, allowed to stand 3 days at 25°C, then heated in the steam bath for 5 hr. The solution was cooled in an ice bath, made basic and the oily product which separated extracted into ether (some ether insoluble solid was removed by filtration). Evaporation of the dried ethereal solution left 0.38 g (37%) of a solid melting at 134-136°C. Golden plates, m.p. 134-135°C, were obtained by recrystallization from cyclohexane. The ^1H nmr spectrum is consistent with the assigned structure.

Anal. Calcd. for $C_{10}H_{14}N_2O$: C, 67.38; H, 7.92; N, 15.72; mol. wt. 178.2. Found: C, 67.36; H, 8.02; N, 15.61; mol. wt. (mass spec.) 178.

PRECURSORS TO AC3F AND RELATED COMPOUNDS

7-Amino-2,4-dimethyl-1,8-naphthyridine

2,6-Diaminopyridine (43.6 g, 0.4 mole), 40.0 g (0.4 mole) of 2,4-pentanedione, 200 ml of glacial acetic acid and 5 ml of 96% sulfuric acid were mixed, then refluxed with stirring for 24 hr. The cold solution was added slowly with good stirring and ice bath cooling to 160 g of sodium hydroxide in enough water to make 600 ml. The brown solid, which crystallized, was filtered after the solution had been cooled overnight at 5°C, washed twice with cold water and dried; 25.3 g, m.p. 125-200°C. This crude material was dissolved in 130 ml of boiling 95% ethanol and the solution chilled overnight at -15°C; 19.5 g (28%), m.p. 215-220°C. This material was suitable for the following experiment. Ochiai and Miyaki[10] reported m.p. 220°C; they performed the condensation at 120-130°C with anhydrous zinc chloride and no solvent.

7-Acetamido-1,2,4-trimethyl-1,2,3,4-tetrahydro-1,8-naphthyridine

This compound was made in 72% yield from the previous material using the same sequence of reactions described above for the corresponding dimethyl derivative: acetylation, methylation, and hydrogenation. The white, felted needles after recrystallization from cyclohexane melted 152.5-153.5°C.

Anal. Calcd. for $C_{13}H_{19}N_3O$: C, 66.92; H, 8.21; N, 18.01. Found: C, 67.03; H, 8.52; N, 17.84.

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[10] E. Ochiai and K. Miyaki. "Synthese von 1.8-Naphthyridin-Homologen und ihre Hydrierung," *Chem. Ber.*, Vol. 74 (1941), p. 1115.

7-Hydroxy-1,2,4-trimethyl-1,2,3,4-tetrahydro-1,8-naphthyridine (2)

The previous compound (3.2 g) was heated for 18 hr on the steam bath with 40 ml of 6N hydrochloric acid. The cooled solution was neutralized with 25% aq. sodium hydroxide; the orange oil which separated soon crystallized. It was removed, washed with water and dried; 2.66 g (100%), m.p. 143-145°C. Recrystallization from 8:2 cyclohexane-benzene, with carbon decolorization, gave white grains, m.p. 146-148°C.

Anal. Calcd. for $C_{11}H_{16}N_2O$: C, 68.71; H, 8.39; N, 14.57. Found: C, 68.20; H, 8.67; N, 14.52.

7-Amino-1,2,4-trimethyl-1,2,3,4-tetrahydro-1,8-naphthyridine

The viscous oil recovered from the alkaline hydrolysis of the corresponding 7-acetamido compound was used without further purification.

SYNTHESIS OF AZACOUMARINS AND AZAQUINOLONES

2-Oxo-6,9-dimethyl-4-trifluoromethyl-6,7,8,9-tetrahydro-2*H*-pyrano[2,3-*b*][1,8]naphthyridine

The following procedure is typical of that used to prepare the various azacoumarins. 7-Hydroxy-1,4-dimethyl-1,2,3,4-tetrahydro-1,8-naphthyridine (0.19 g), 1.2 ml of ethyl trifluoroacetoacetate, 50 mg of anhydrous zinc chloride, and 10 ml of absolute ethanol were refluxed for 40 hr. The cooled solution was poured with stirring into 50 ml of water plus 3 ml of hydrochloric acid; the yellow precipitate was filtered, washed with water, and dried (0.31 g, 95%). Solvent used for recrystallization, melting point, fluorescence data and analytical data are summarized in Table 1. The ^1H nmr spectral data ($CDCl_3$ 100 MHz) on the analogous 6,8,9-trimethyl derivative are: δ1.37(d, 6H, CH_3CH), 1.47(m, 1H, H_7b), 2.10(dt, 1H, H_7a, J = 13 Hz, J = 4 Hz), 2.80(m, 1H, H_6), 3.20(s, 3H, NCH_3), 3.70(m, 1H, H_8), 6.38(s, 1H, H_3), 7.41(q, 1H, H_5, $J_{H_5-CF_3}$ = ~1.5 Hz).

2-Oxo-6,9-dimethyl-4-trifluoromethyl-1,2,6,7,8,9-hexahydro-pyrido[2,3-*b*][1,8]naphthyridine

This is a representative procedure for making azaquinolones. 7-Amino-1,4-dimethyl-1,2,3,4-tetrahydro-1,8-naphthyridine (0.9 g) and 1.0 g of ethyl trifluoroacetoacetate were heated at 145-165°C for 18 hr. The cooled, semisolid mass was slurried with 5 ml of ether, filtered and washed with more ether; 1.3 g, m.p. 225-230°C, wet 200°C. Other data are found in Table 1. ^1H nmr ($CDCl_3$, 100 MHz): δ1.30(d, 3H, CH_3CH, J = 7 Hz), 1.74(m, 1H, H_{7_a} or H_{7_b}), 1.89(m, H, H_{7_a} or H_{7_b}), 3.92(m, 1H, H_6),

3.20(s, 3H, NCH_3), 3.49(t, 2H, H_8, H_8, J = 6 Hz), 6.62(s, 1H, H_3), 7.46(q, 1H, H_5, $J_{H_5-CF_3}$ = ~1.5 Hz), 9.40(broad s, 1H, NH).

RELATED COMPOUNDS

7-Amino-4-methyl-2-phenyl-1,8-naphthyridine

2,6-Diaminopyridine (16.4 g, 0.15 mole), 24 g of benzoylacetone, 75 ml of acetic acid and 1.5 ml of 96% sulfuric acid was refluxed with stirring for 24 hr. The solution was poured slowly with stirring into 50 g of sodium hydroxide in 250 ml of water; the temperature was held 20-30°C by cooling. The tan solid was filtered, washed well with water and dried; 21.8 g. One recrystallization from 100 ml of 95% ethanol gave 6.9 g of coarse needles, m.p. 65-190°C; a second recrystallization from 50 ml of ethanol furnished 2.1 g (6%) of the title compound, m.p. 253-255°C. ^1H nmr ($CDCl_3$ + DMSO-d_6, 60 MHz): δ2.67(s, 3H, CH_3), 6.20(broad exchangeable s, 2H, NH_2), 6.92(d, 1H, H_5, J = 9 Hz), 7.58(d, 1H, H_6), 7.50(m, 3H, meta and para protons on C_6H_5), 8.30(m, 2H, ortho protons on C_6H_5).

Anal. Calcd. for $C_{15}H_{13}N_2$: C, 76.57; H, 5.57; N, 17.86. Found: C, 76.99; H, 5.62; N, 17.96.

From the aqueous mother liquors from which the above compound had been isolated there was recovered upon cooling 6.3 g of an off-white solid. Recrystallization from water gave felted, white needles, melting in part 190-192°C, the balance 205-207°C. The ^1H nmr suggested a mixture of tautomeric and/or isomeric diacetyldiaminopyridines.

Anal. Calcd. for $C_9H_{11}N_3O_2$: N, 21.76. Found: N, 21.54.

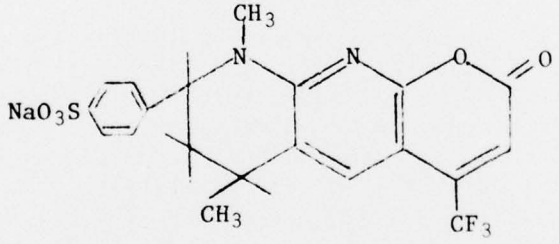
2-Oxo-6,9-dimethyl-8-phenyl-4-trifluoromethyl-6,7,8,9-tetrahydro-2*H*-pyrano[2,3-*b*][1,8]naphthyridine

7-Amino-4-methyl-2-phenyl-1,8-naphthyridine (2.0 g) was mixed with 4 ml of acetic anhydride; the solution was allowed to stand 1 hr at 25°C, refluxed for 3 hr, cooled, and diluted with 15 ml of water. After the excess anhydride hydrolyzed, the solution was made slightly basic with 25% aqueous sodium hydroxide (cooling used). The precipitated solid was filtered, washed well with cold water and dried; 2.3 g (98%), m.p. 209.5-210.5°C after partial melting and resolidification at 150-160°C.

All of the above amide was refluxed for 8 hr in 25 ml of dry acetonitrile with 1.6 g of methyl *p*-toluenesulfonate. Cooling and addition of a large excess of ether yielded 3.34 g (88.5%) of a blue-purple solid. The salt in 25 ml of acetic acid containing 3 g of ammonium acetate was hydrogenated over 0.1 g of PtO_2 at an initial pressure of 50 psi (344.8 kPa);

the theoretical amount (2 mole equivalents) was rapidly absorbed. The catalyst was removed, washed with 3 ml of acetic acid, and two 10-ml portions of water; the combined filtrates were evaporated to thick syrup which was then dissolved in 75 ml of 65% ethanol and made basic with 25% aqueous sodium hydroxide. Water (75 ml) was added to precipitate the product which was filtered off after overnight cooling at 5°C. After washing with cold water, the wet, crude 7-acetamido-1,4-dimethyl-2-phenyl-1,2,3,4-tetrahydro-1,8-naphthyridine was heated overnight on the steam bath with 30 ml of 6N hydrochloric acid. Cooling, followed by careful neutralization with sodium hydroxide solution, furnished 1.2 g of the 7-hydroxy derivative. The latter (a pale orange powder) melted at 211-213°C after one recrystallization from 60 ml of 95:5 benzene-ethanol. ^{1}H nmr ($CDCl_3$, 60 MHz): δ1.30(d, 3H, $C\underline{H}_3CH$, J = 6.5 Hz), 1.6-2.6(m, 3H, H_3, H_3, H_4), 3.10(s, 3H, $NC\underline{H}_3$), 4.72(dd, 1H, H_2, J = 4Hz, J = 10 Hz), 6.19(d, 1H, H_5, J = 9.5 Hz), 7.43(s, 5H, $C_6\underline{H}_5$), 7.60(d, 1H, H_6, J = 9.5 Hz), 12.1(broad s, 1H, O$\underline{H}$, or N$\underline{H}$).

A solution consisting of 0.7 g of the 7-hydroxy-1,4-dimethyl-2-phenyl-1,2,3,4-tetrahydro-1,8-naphthyridine, 3 ml of ethyl trifluoroacetoacetate, 20 ml of abs. ethanol and 0.47 g of anhydrous zinc chloride was refluxed for 64 hr. After cooling, the solution was diluted with 20 ml of water plus 1 ml of conc. hydrochloric acid. The yellow solid which precipitated was filtered, washed with water and dried; 0.24 g (23%). Other data can be found in Table 1. The position of the phenyl group in this compound was assigned on the basis of the analysis of the ^{1}H nmr spectrum of its precursor and of the following sulfonated derivative.



The yellow solid was sulfonated with 20% oleum (15-20°C, 4 hr). After quenching on ice, neutralizing with sodium bicarbonate and evaporating the solution to dryness, the sulfonate was extracted with boiling 95% ethanol. The product crystallized from the cooled extracts upon the addition of diethyl ether (40 ethanol - 30 ether). Fl(max), H_2O: 473 nm (excited, 390 nm). The phenyl group was assigned to the 8-position rather than the 6-position based on the following ^{1}H nmr evidence: the downfield methine proton again appeared as a quartet (splitting by the H_7 axial and H_7 equatorial protons) rather than a very complex multiplet one would expect if a methyl group were in the 8-position.

Anal. Calcd. for $C_{20}H_{16}F_3N_2O_5SNa \cdot 2.5\ H_2O$: F, 10.93; N, 5.37; S, 6.15. Found: F, 10.96; N, 5.27; S, 6.18.

7-Acetamido-2,4-dimethyl-5,6,7,8-tetrahydro-1,8-naphthyridine and 2,4-dimethyl-5,6,7,8-tetrahydro-1,8-naphthyridine

7-Acetamido-2,4-dimethyl-1,8-naphthyridine (5.6 g) was hydrogenated over platinum oxide (0.12 g) in acetic acid (70 ml) containing ammonium acetate (10 g); about 5 hrs were required to absorb the theoretical amount of hydrogen. The basic product recovered in the usual manner was a gum; extraction with boiling benzene left a poorly soluble white solid, wetting at 190°C and melting 197-198°C. Cooling the benzene extracts yielded white crusts also melting 193-197°C. The ^1H nmr on this solid indicated reduction of the pyrido ring possessing the acetamido group rather than the one with the methyl groups; the methyl signals were sharp singlets, rather than the doublets (J = 6-7 Hz) normally seen when the methyl-containing ring was reduced.

Anal. Calcd. for $C_{12}H_{17}N_3O$: C, 65.72; H, 7.82; N, 19.16; mol. wt., 219.28. Found: C, 65.90; H, 7.88; N, 19.04, 19.14; mol. wt. (mass spec.), 219.

What appears to be another epimer was isolated in low yield from another experiment; flat needles, m.p. 155-160°C after recrystallization of 1:1 benzene/cyclohexane. The IR spectrum was different than that for the above compound. Its picrate melted 163-164°C after recrystallization from ethanol.

Anal. Calcd. for $C_{18}H_{20}N_6O_8$: C, 48.21; H, 4.50; N, 18.75. Found: C, 48.14; H, 4.82; N, 18.58.

Evaporation of the benzene mother liquors left a low melting solid which was recrystallized several times from *n*-hexane; flat needles, m.p. 115-116°C. No amide carbonyl was present in the IR spectrum. The ^1H nmr indicated that this compound was 2,4-dimethyl-5,6,7,8-tetrahydro-1,8-naphthyridine, which resulted from the hydrogenolysis of the acetamido group. ^1H nmr ($CDCl_3$, 100 MHz): δ1.8-2.2(multiplet, 2H, H_6, H_6); 2.10(s, 3H, 4-$C\underline{H}_3$), 2.27(s, 3H, 2-$C\underline{H}_3$), 2.70(t, 2H, H_5, H_5, J = 6 Hz), 3.35(sextet, 2H, H_7, H_7, $J_{H_6H_7}$ = 6 Hz, J_{NH-H_7} = 2.5 Hz, collapses to a triplet when exchanged with D_2O), 4.72(broad, exchangeable peak, 1H, N$\underline{H}$), 6.28(s, 1H, H_3).

Anal. Calcd. for $C_{10}H_{14}N_2$; mol. wt., 162.23. Found: Mol. wt. (mass spec.), 162.

7-Acetamido-1-carboethoxymethylene-2,4-dimethyl-1,2,3,4-tetrahydro-1,8-naphthyridine

The reaction product (9.4 g) of ethyl bromoacetate and 7-acetamido-2,4-dimethyl-1,8-naphthyridine was hydrogenated by the same procedure used for the analogous methyl compounds. Work-up in a similar manner

gave 5.3 g (71%) of crude product, m.p. 100-104°C. One recrystallization from *n*-hexane gave pale yellow blades, m.p. 110-111°C.

Anal. Calcd. for $C_{16}H_{23}N_3O_3$: C, 62.93; H, 7.59; N, 13.76. Found: C, 62.94; H, 7.57; N, 13.69.

The crude 7-hydroxy compound obtained by acid hydrolysis was used for the preparation of the azacoumarin without purification.

7-Acetamido-2,4-dimethyl-1,8-naphthyridine Hydrobromide

After recrystallization from acetonitrile this salt decomposed 252-254°C.

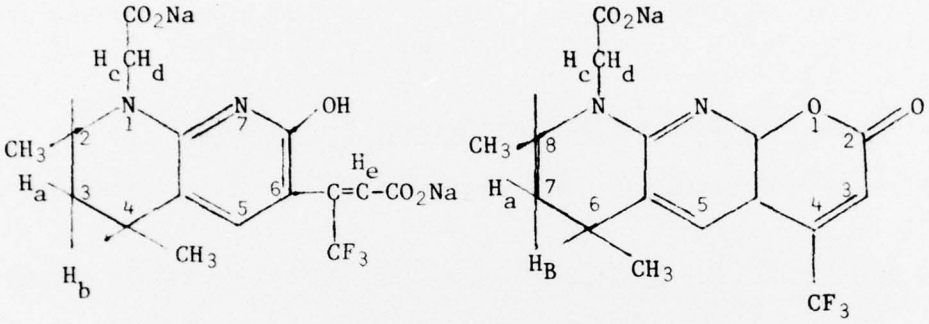
Anal. Calcd. for $C_{12}H_{14}BrN_3O \cdot H_2O$: Br, 25.43; N, 13.37: Found: Br, 25.59; N, 13.29.

7-Acetamido-1-benzyl-2,4-dimethyl-1,8-naphthyridine Chloride

7-Acetamido-2,4-dimethyl-1,8-naphthyridine (6.45 g), 4 g of benzyl chloride and 80 ml of dry acetonitrile were refluxed for 88.5 hours. Complete solution was never attained. After cooling to 5°C the solid was removed and washed with four 50-ml portions of ether; 5.3 g (82%) of starting amide. Cooling the combined filtrate and ether washings yielded 1.2 g (11%) of the title compound. Recrystallization from ethanol-ether gave dark green crusts; m.p. 185-190°C (dec). ^{1}H nmr (DMSO-d_6, 60 MHz): δ2.23(s, 3H, $C\underline{H}_3CO$), 2.92(s, 6H, $C\underline{H}_3C$), 6.49(s, 2H, $C\underline{H}_2$), 7.39(s, 5H, $C_6\underline{H}_5$), 8.10(s, 1H, $\underline{H}_3$), 8.64(d, 1H, $\underline{H}_5$, J = 9 Hz), 9.08(d, 1H, H_6, J = 9 Hz), 11.90(s, 1H, N$\underline{H}$).

Anal. Calcd. for $C_{19}H_{20}ClN_3O \cdot 1.5\ H_2O$: Cl, 9.61; N, 11.39. Found: Cl, 9.75; N, 11.46.

Disodium 3-(6-[2,4-Dimethyl-1-carboxymethylene-7-hydroxy-1,2,3,4-tetrahydro-1,8-naphthyridyl]) 4,4,4-Trifluorocrotonate and Sodium 2-Oxo-6,8-dimethyl-9-carboxymethylene-4-trifluoromethyl-6,7,8,9-tetrahydro-2*H*-pyrano[2,3-*b*][1,8]naphthyridine



2-Oxo-6,8-dimethyl-9-carboethoxymethylene-4-trifluoromethyl-6,7,8,9-tetrahydro-2*H*-pyrano[2,3-*b*][1,8]-naphthyridine (0.5 g) was dissolved in a solution consisting of 0.9 g of sodium hydroxide in 10 ml of 50% ethanol and allowed to stand overnight at 2°C. The solution was diluted with 5 ml of ethanol, made acid with 2 ml of conc. hydrochloric acid; after standing 4 days at r.t., 20 ml of water was added and the pH adjusted to neutral with sodium bicarbonate. The small amount of insoluble which remained was removed and the filtrate evaporated to dryness. The residue was extracted twice with 30-ml portions of boiling 95% ethanol; the combined extracts were cooled to 25°C, refiltered, then cooled for several days at 5°C. Almost colorless crystals of the first compound slowly formed; they were removed, washed with cold ethanol, then ether, and dried. Addition of ether to the mother liquors until a permanent turbidity developed, followed by further cooling gave more of the same compound; the filtrate was saved (see below). A solution of this solid in water was only very weakly fluorescent (probably contamination by the following compound). ^{1}H nmr (D_2O, 100 MHz): δ1.20(d, 3H, 4-C$\underline{H}_3$, J = ~6.5 Hz), 1.25(d, 3H, 2-C$\underline{H}_3$, J = ~6.5 Hz), 1.45(dd, 1H, H_{3a}, J_{3a3b} = 13.5 Hz, J_{3aHx} = 11 Hz), 2.04(dt, 1H, H_{3b}, J_{3a3b} = 13.5 Hz, J_{3bHx} = J_{3bHy} = 4 Hz), 2.67(m, 1H, H_4), 3.58(m, 1H, H_2), 3.87(d, 1H, H_c, $J_{H_cH_d}$ = 18 Hz), 4.07(d, 1H, H_d, $J_{H_cH_d}$ = 18 Hz), 6.75(q, 1H, H_e, $J_{CF_3-H_e}$ = 1.6 Hz), 7.31(s, 1H, H_5).

Anal. Calcd. for $C_{16}H_{15}F_3N_2O_4 \cdot H_2O$: C, 44.04; H, 3.93; F, 13.06; N, 6.42. Found: C, 44.80; H, 3.99; F, 12.86; N, 6.42, 6.35.

The alcohol-ether mother liquors from above were evaporated; the residue was slurried with 10 ml of 2-propanol, filtered, and the filtrate treated with 50 ml of ether. The off-white solid which precipitated was removed and dried. An aqueous solution fluoresced at 498 nm (excited 400 nm). ^{1}H nmr (D_2O, 100 MHz): δ1.17(d, 3H, 6-C$\underline{H}_3$, J = 6.5 Hz),

1.28(d, 3H, 8-$C\underline{H}_3$, J = 6.5 Hz), 1.40(m, 1H, H_{7a}, J_{7a7b} = 14 Hz), 2.04(m, 1H, H_7 , J_{7a7b} = 14 Hz), 2.66(m, 1H, H_6), 3.74(m, 1H, H_8), 4.00(d, 1H, H_c, J_{HcHd} = 17.5 Hz), 4.51(d, 1H, H_d, J_{HcHd} = 17.5 Hz), 6.28(s, 1H, H_3), 7.29(q, 1H, H_5, $J_{CF_3-H_5}$ = 1.5 Hz).

The result was essentially the same when some of the ethyl ester was hydrolyzed in 80% sulfuric acid at 25°C. Quenching in ice, followed by neutralization with sodium bicarbonate and isolation as above, gave largely the non-fluorescing substituted crotonate.

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  - Dr. John MacCallum, Jr. (1)
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2 Office of Naval Research Branch Office, Pasadena
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3 Pacific Missile Test Center, Point Mugu
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1 Navy Laser Liaison Office, Air Force Weapons Laboratory, Kirtland Air Force Base ((HELP-LO), Dr. John Walsh)

2 Office Chief of Research and Development
- DARD-ARP-P, Dr. Watson (1)
- DARD-MSA (1)

1 Army Combat Developments Command, Air Defense Agency, Fort Bliss

1 Army Combat Developments Command, CBR Agency, Fort McClellan (CDCCBR-MR, F. D. Poer)

1 Army Combat Developments Command, Fort Leavenworth (Combat Systems Group, Col. McFall)

2 Army Electronics Command, Fort Monmouth
- AMSEL-CT-L-G, T. Ewanizky (1)
- AMSEL-XL-H, R. G. Buser (1)

2 Army Materiel Development and Readiness Command
- AMCRD-TP, Dr. B. Zarwyn (1)
- Paul Chernoff (1)

3 Army Missile Command, Redstone Arsenal
  Research and Development Division
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    Walter Jennings (1)
1 Army Weapons Command, Rock Island Arsenal (SWERR-R, J. W. McGarvey)
3 Army Ballistic Missile Defense Program Office, Arlington (Albert J. Bast, Jr.)
3 Army Ballistics Research Laboratory, Aberdeen Proving Ground
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3 Ballistic Missile Defense Advanced Technology Center, Huntsville
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  AF-RDPS, Col. Parsons (1)
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2 Air Force Systems Command, Andrews Air Force Base
  DLTW, Lt. Col. Anthony J. Chiota (1)
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1 Aerospace Research Laboratories, Wright-Patterson Air Force Base (Maj. Malcolm R. Fossett, Jr.)
1 Air Force Aerospace Propulsion Laboratory, Wright-Patterson Air Force Base (CC, Col. Walter Moe)
2 Air Force Avionics Laboratory, Wright-Patterson Air Force Base
  TEO-1, Capt. S. Johnson, Jr. (1)
  TEL, K. Hutchinson (1)
4 Air Force Cambridge Research Laboratories, Laurence G. Hanscom Field
  Dr. John Garing (1)
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1 Air Force Rocket Propulsion Laboratory, Edwards Air Force Base (LKCG, B. R. Bornhorst)
1 Air Force Rocket Propulsion Laboratory, Edwards Air Force Base (PYSP, Capt. S. Thompson (1))
2 Electronics Systems Division, Laurence G. Hanscom Field
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  XRT, Alfred E. Anderson (1)

2 Foreign Technology Division, Wright-Patterson Air Force Base
  PDTA (1)
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1 Rome Air Development Center, Griffiss Air Force Base (Frank J. Rehm)
1 Space and Missile Systems Organization, Los Angeles (AFUPO, XRTD, Lt. Dorian DeMaio)
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2 Director of Defense Research and Engineering
  Assistant Director I & C (1)
  SW, Ben T. Plymale (1)
3 Defense Advanced Research Projects Agency, Arlington
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1 Arms Control and Disarmament Agency (Dr. Charles Henkin)
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1 Lewis Research Center (Aerospace Research Engineer, Dr. John W. Dunning, Jr.)
2 AVCO Research Laboratory, Everett, MA
1 Aerospace Corporation, Los Angeles, CA (Dr. G. P. Millburn)
1 Airesearch Manufacturing Company, Los Angeles, CA (A. Colin Stancliffe)
1 Analytic Services, Inc., Falls Church, VA (Dr. John Davis)
2 Applied Physics Laboratory, JHU, Laurel, MD
  Dr. R. E. Gorozdos (1)
  Dr. Albert Stone (1)
1 Atlantic Research Corporation, Alexandria, VA (Propulsion Division, R. F. Hoglund)
3 Autonetics, A Division of North American Rockwell Corporation, Anaheim, CA
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2 Battelle Memorial Institute, Pacific Northwest Laboratory, Richland, WA
  DSB 3000 Area, Dr. R. S. Gordon (1)
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1 Electro-Optical Systems, Pasadena, CA (Dr. Andrew Jensen)
1 General Electric Company, Defense Electronics Division, Pittsfield, MA (D. G. Harrington, Room 1044)
1 General Electric Company, Missile Space Vehicle Department, Philadelphia, PA (Space Division, W. J. East)