Evaporation of the solvent gave garosamine hydrochloride identical with authentic material.

Acknowledgments. We thank our colleagues for helpful discussions and Messrs. J. Morton, J. McGlotten, and P. Bartner for spectral data.

Registry No.—**4,** 65483-48-9; **8,** 65483-49-0; **9,** 65483-50-3; **10,** 65483-51-4; **13,** 65483-52-5; **14,** 65483-53-6; **15,** 65483-54-7; **19,** 65483-55-8; **21,** 65483-56-9; **22,** 65483-57-0; **24,** 65483-58-1; **25,** 65483-59-2; **26,** 65483-60-5; **27,** 65504-54-3; garosamine, 29914-71-4; *N*-acetyl-3-amino-3-deoxy-1,2:5,6-diisopropylidine-α-D-galactofuranose, 19131-09-0.

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Poly(iminomethylenes). 6.[1] Synthesis and Polymerization of α- and β-D-Glucopyranosyl Isocyanide

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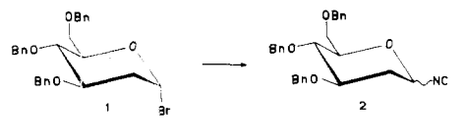
Both anomers of 2,3,4,6-tetra-*O*-benzoyl-D-glucopyranosyl isocyanide have been synthesized starting from 2,3,4,6-tetra-*O*-benzoyl-α-D-glucopyranosyl bromide. This bromide was converted into the β-azide which after hydrogenation to the amine and formylation afforded *N*-formyl-2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosylamine. Dehydration of the latter compound gave the isocyanides in an α to β ratio of 1:9. Polymerization of the isocyanides was performed with nickel chloride. From the optical rotations it was concluded that the helical polymers obtained from the anomeric monomers are opposites in a screw sense.

Poly(isocyanides), more systematically named poly(iminomethylenes), $[RN{=}C<]_n$, are rigid rod polymers[2] with a helical configuration.[3,4] In general, they are easily prepared from the monomeric isocyanides, RN=C, with nickel chloride or a nickel(II) complex as catalyst.[5,6] Stereoselective formation of either a right-handed (*P*) or left-handed (*M*) helix can be expected when the monomeric isocyanide is one enantiomer of R*N=C, in which R* is chiral.

Because of their ready availability and optical purity natural compounds often are the starting materials of choice for stereoselective syntheses. Our first entry into this field was the synthesis of a poly(iminomethylene) derived from L-histidine.[1] In the present paper we wish to report the synthesis of such polymers derived from glucose. An additional motive for the synthesis of these compounds is the fact that polymer-bounded sugars[7] and especially sugar residues linked to polymer-bounded amino acids may be interesting models in immunological studies.[8]

Results and Discussion

Reaction of silver cyanide with benzyl protected glucopyranosyl halides (1) was recently reported[9] to give formerly unknown isocyano sugars (2).



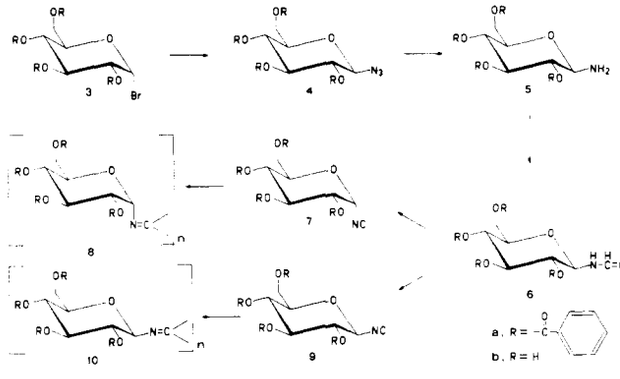
1 2

In our hands, however, this reaction afforded unseparable mixtures of α and β anomers and other unidentified products.

We have synthesized the α and β anomers of D-glucopyranosyl isocyanide, compounds **7** and **9,** via amine **5** and N-substituted formamide **6** according to Scheme I.

A convenient route for the synthesis of per-*O*-acylglycosylamines is provided by the reduction of the corresponding *O*-acylglycosyl azides.[10] Sproviero[11] synthesized 2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl azide (**4a**) in 66% yield from 2,3,4,6-tetra-*O*-benzoyl-α-D-glucopyranosyl bromide (**3a**) by a nucleophilic displacement reaction with sodium azide in boiling acetonitrile. We have carried out this reaction by using phase-transfer catalysis in a mixture of chloroform and water. Compound **4a** was isolated in quantitative yield; its β-D-gluco configuration was confirmed by the ^{1}H-NMR spectrum, in which the signal for the anomeric proton appeared as a doublet at 4.95 ppm ($J_{1,2}$ = 8.7 Hz).

Scheme I



Catalytic hydrogenation of the glycosyl azide **4a** over palladium on carbon afforded 1,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosylamine (**5a**) as a white foam. The latter amine was converted into its debenzoylated form (**5b**) by reaction with sodium methanolate in methanol. The infrared absorption spectrum of **5b** showed that this compound was uncontaminated by *N*-benzoylglucopyranosylamine,[12] proving that in the reduction step no O → N benzoyl migration had oc-

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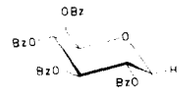
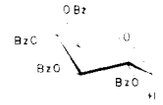
Table I. Optical Rotation Data of Poly(iminomethylenes) [RN=C<]$_n$, and Monomers, RN=C

R	Monomer $[\alpha]^{22}_D$[a]	Polymer $[\alpha]^{22}_D$[a]	Contribution of helix to $[\alpha]$	Screw sense of helix
	+70.4°[b]	>+80°[c]	(+)	*M*
	+44.7°[d]	0.0°[e]	(−)	*P*

[a] In chloroform; the rotation of the polymer is expressed per repeating unit. [b] *c* 1.47. [c] *c* 0.42. [d] *c* 2.52. [e] *c* 0.73.

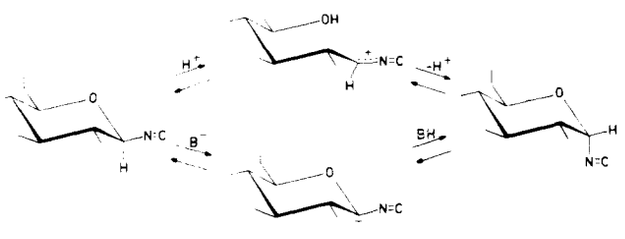
curred.[11] On treatment with formic acetic anhydride, the glycosylamine **5a** gave *N*-formyl-2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosylamine (**6a**). In the infrared and NMR spectra of **6a** the characteristic absorptions of the *N*-formyl function were partly masked by absorption peaks of the benzoyl protecting groups. After removal of the latter groups to give free *N*-formylglucopyranosylamine (**6b**) the former absorptions became visible. The coupling constant $J_{1,2}$ in the ^{1}H-NMR spectrum of **6b** amounted to 8.4 Hz. This is indicative of a β-D-gluco configuration.[13] In view of its axial position the signal of the anomeric proton appeared at a rather low field (δ 5.08 ppm). The low field shift is probably due to the electron-withdrawing character of the *N*-formyl group attached to the anomeric center. A similar chemical shift value has been found for the anomeric proton in 2-acetamido-1-*N*-(4-L-aspartyl)-2-deoxy-β-D-glucopyranosylamine.[13]

The glycosyl isocyanides **7a** and **9a** were obtained in 90% yield by dehydration of the *N*-formylglucopyranosylamine **6a** using phosphorus oxychloride and triethylamine as the dehydrating agent.[14] Substitution of pyridine for triethylamine as the base lowered the yield to 15%. Other dehydrating agents like thionyl chloride in *N,N*-dimethylformamide[15] and triphenylphosphine–carbon tetrachloride[16] gave no or only traces of isocyanide. Compounds **7a** and **9a** were separated by column chromatography and isolated as almost odorless, white solids in a ratio of 1:9. They were soluble in apolar solvents, moderately soluble in alcohols, and insoluble in water. The infrared absorption spectra of the solids showed characteristic isocyanide stretching vibrations at 2124 cm^{-1} (α anomer) and 2142 cm^{-1} (β anomer). In the ^{13}C-NMR spectra of **7a** and **9a** the ^{13}C resonances of the isocyano carbons were observed at 166.1 and 165.1 ppm, respectively.[9] The structure of isocyanides **7a** and **9a** was further established by elemental analysis, ^{1}H NMR, and mass spectroscopy.

Compound **9a** could be converted into free β-D-glucopyranosyl isocyanide (**9b**) without affecting the NC function. Aliphatic isocyanides with free hydroxylic groups have not been described before.[17]

The isolation of both α- and β-isocyanide from *N*-formyl-β-D-glucopyranosylamine might indicate anomerization of these compounds under the reaction conditions employed. Anomerization is conceivable to occur through acid- and base-catalyzed pathways (Scheme II).

Scheme II



Preliminary experiments, however, showed that neither triethylammonium chloride nor triethylamine could effect anomerization of **7a** and **9a**. Elevated temperatures and strong bases like 1,8-bis(dimethylamino)naphthalene ("proton sponge") and 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) were ineffective as well. Enhancement of the electron-withdrawing effect of the isocyano group through coordination of **7a** and **9a** to copper(II) tetrafluoroborate and subsequent treatment with strong base was not successful either. The results above suggest that anomerization is most likely to occur in some stage of the dehydration of the *N*-formylglucopyranosylamine by phosphorus oxychloride.

Both glycosyl isocyanides **7a** and **9a** were polymerized by 1 mol % nickel chloride[5] in chloroform–methanol 1:1 (v/v). Under these conditions the rate of polymerization of **7a** was very slow, probably as a result of steric hindrance; its isocyano group is in axial position. As judged by TLC, polymerization of **7a** was accompanied by anomerization. The poly(iminomethylenes) were isolated as creamish brown solids. They were soluble in apolar solvents and insoluble in alcohols and water. Their infrared absorption spectra showed partly obscured –N=C< stretching vibrations at approximately 1640 cm^{-1}. The polymers showed an intrinsic viscosity in the order of 0.025 dL/g (toluene, 30.0 °C). Applying the Mark–Houwink equation as determined[2] for poly(1-phenylethyliminomethylene), a molecular weight of 6000 is calculated. Higher degrees of polymerization can be expected at higher isocyanide catalyst ratios.[18]

Removal of the protecting groups in **10a** and subsequent ultrafiltration and freeze drying of the resulting solution afforded poly(β-D-glucopyranosyliminomethylene), **10b**, as a light-brown solid. In its infrared spectrum a distinct –N=C< stretching vibration was visible at 1630 cm^{-1}. Compound **10b** was soluble only in water.

In earlier papers[3,4] we showed that poly(iminomethylenes) have a helical configuration. On polymerization of a chiral isocyanide an excess of one screw sense can be expected. The preferred screw sense can be predicted by application of our S–M–L rule which will be described in a forthcoming paper.[19] S–M–L stands for small, medium, and large in isocyanide C(S)(M)(L)–N=C, respectively. The reverse direction of rotation S → M → L in **7** and **9** gives rise to an opposed screw sense of their polymers, viz., right handed (*P*) for **10a** and left handed (*M*) for **8a**. We know[4] that a *P* screw gives rise to a (−) contribution to the optical rotation. Since the side chain in polymer **10a** will probably have the same sign of optical rotation as in the monomer, the contributions by main chain and side chain are opposing. The total rotation can be expected to be small; in fact, it is not significantly different from zero (Table I). In polymer **8a** the contributions by main chain and side chain are both predicted to be (+). The experimental value of 80° (Table I) is probably still somewhat too low for pure **8a**. Because of the anomerization mentioned above, our sample of **8a** will contain **10a** or be a copolymer of **7a** and **9a**.

Experimental Section

General. Melting points were determined on a Mettler FP5/FP51 photoelectric melting point apparatus. Rotations were measured on a Perkin-Elmer 141 polarimeter. Infrared (IR) spectra were recorded on a Perkin-Elmer 457 spectrophotometer. ^{1}H-NMR and ^{13}C-NMR spectra were obtained on Varian EM-390 and Varian CFT-20 instruments, respectively. Chemical shifts (δ) are given in ppm downfield from internal tetramethylsilane or sodium 2,2,3,3-tetradeutero-3-(trimethylsilyl)propionate. Abbreviations used are: s = singlet, d = doublet, m = multiplet, br = broad. Mass spectra were recorded on an AEI MS-902 mass spectrometer. Elemental analyses were carried out by the Element Analytical Section of the Institute for Organic Chemistry TNO, Utrecht, The Netherlands, under supervision of W. J. Buis. TLC was performed on silica (Schleicher and Schüll TLC Ready Plastic Foil FR-1500) and detection was effected by UV and/or spraying with 20% sulfuric acid in methanol and charring at 120 °C for 10 min. Column chromatography was performed on silica (Merck Kieselgel 60, 230–400 mesh).

2,3,4,6-Tetra-*O*-benzoyl-α-D-glucopyranosyl Bromide (3a). This compound was prepared as described in the literature.[20]

2,3,4,6-Tetra-*O*-benzoyl-β-D-glucopyranosyl Azide (4a). To a solution of 13.2 g (20 mmol) of **3a** in 100 mL of chloroform was added 26 g (400 mmol) of sodium azide in 100 mL of water and 300 mg of benzyltriethylammonium chloride. The mixture was vigorously stirred for 2 h at 70 °C. Hereafter another 26 g of sodium azide and 300 mg of benzyltriethylammonium chloride were added and stirring was continued until TLC (benzene–isopropyl alcohol, 100:1) indicated complete conversion of **3a** (6–15 h). The aqueous layer was separated and extracted twice with chloroform. The combined organic layers were washed, dried over sodium sulfate, and concentrated in vacuo to give 12.6 g of white solid **4a**. Recrystallization from absolute ethanol afforded a purified sample: mp 113–114 °C; $[\alpha]^{22}_D$ −0.54° (*c* 5.0, $CHCl_3$) [lit. $[\alpha]^{22}_D$ +42.0° (*c* 1.0, $CHCl_3$);[11] to us this value seems less reliable]; IR (KBr) 2120 (N_3), 1725 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ 7.90 and 7.40 (2 × m, 20, benzoyl), 6.00–6.40 (m, 3, H-2,3,4), 4.95 (d, $J_{1,2}$ = 8.7 Hz, 1, H-1), 4.80–4.40 (m, 2, H-6,6′), 4.40–4.15 (m, 1, H-5). Anal. Calcd for $C_{34}H_{27}N_3O_9$: C, 65.70; H, 4.38; N, 6.76; O, 23.16. Found: C, 65.54; H, 4.23; N, 6.82; O, 23.19.

2,3,4,6-Tetra-*O*-benzoyl-β-D-glucopyranosylamine (5a). An amount of 15.8 g (25.4 mmol) of **4a** in 350 mL of ethyl acetate was hydrogenated over 1.8 g of 10% palladium on carbon under a slow stream of hydrogen. When TLC (chloroform–methanol, 25:1) showed that starting material was no longer present, the reaction mixture was filtered and used directly for the synthesis of **6a**. For characterization a sample was drawn and evaporated to give a white foam: IR (KBr) 3350 (NH_2), 1725 cm^{-1} (C=O) and absence of N_3; ^{1}H NMR ($CDCl_3$) δ 7.95 and 7.35 (2 × m, 20, benzoyl), 6.05–5.25 (m, 3, H-2,3,4), 4.70–4.35 (m, 2, H-6,6′), 4.55 (d, $J_{1,2}$ = 8.1 Hz, 1, H-1), 4.30–4.05 (m, 1, H-5). A broad signal at δ 2.30 was attributed to the NH_2 group, although the integration value was too low for two protons.

***N*-Formyl-2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosylamine (6a).** To the solution of **5a** in ethyl acetate was added at room temperature 17 mL (210 mmol) of formic acetic anhydride. After 6 h TLC (chloroform–methanol, 25:1) revealed the complete conversion of **5a**. The volatile compounds were removed under reduced pressure followed by several codistillations with absolute ethanol in vacuo. After drying in vacuo (0.02 mm) 16.0 g (100%) of **6a** was obtained. For analytical purposes a small amount was recrystallized from absolute ethanol: mp 178.5–179.5 °C; $[\alpha]^{22}_D$ +61.1° (*c* 1.0, $CHCl_3$); IR (KBr) 3400 (NH), 1720 (C=O benzoyl), 1690 cm^{-1} (C=O formyl); ^{1}H NMR ($CDCl_3$) δ 8.15 (s, 1, CHO), 7.95 and 7.30 (2 × m, 21, benzoyl and NH), 6.20–5.45 (m, 3, H-2,3,4), 5.60 (d, $J_{1,2}$ = 9.0 Hz, 1, H-1), 4.80–4.20 (m, 3, H-5,6,6′). Anal. Calcd for $C_{35}H_{29}NO_{10}$: C, 67.41; H, 4.69; N, 2.25; O, 25.66. Found: C, 67.06; H, 4.83; N, 2.13; O, 25.89.

***N*-Formyl-β-D-glucopyranosylamine (6b).** To a suspension of 520 mg (0.83 mmol) of **6a** in 100 mL of dry methanol was added a solution of sodium methanolate in methanol until the reaction mixture had pH 8 (wet indicator paper). After being stirred for 2 h at room temperature TLC (chloroform–methanol, 25:1) indicated that conversion was complete. The reaction mixture was neutralized by Dowex 50W (H^+) resin, filtered, and concentrated in vacuo (0.02 mm) to yield 172 mg (100%) of **6b**: IR (KBr) 3300–3400 (OH, NH), 1680 cm^{-1} (C=O formyl); ^{1}H NMR (D_2O) δ 8.30 (s, 1, CHO formyl), 5.08 (d, $J_{1,2}$ = 8.4 Hz, 1, H-1), 3.90–3.30 (m, 6, remaining CH's).

α and β-Anomers of 2,3,4,6-Tetra-*O*-benzoyl-D-glucopyranosyl isocyanide (7a and 9a). An amount of 2.5 g (4.0 mmol) of **6a** was suspended in 20 mL of triethylamine and 10 mL of methylene chloride; 4.8 g (31 mmol) of phosphorus oxychloride was added dropwise with stirring at 0 °C. The mixture was stirred overnight at room temperature. Subsequently, 25 mL of methylene chloride was added and the mixture was poured into an ice-cold saturated solution of sodium bicarbonate in water. The layers were separated and the aqueous layer was extracted three times with 25 mL of methylene chloride. The combined organic layers were washed with water, dried over sodium sulfate, and evaporated to dryness in vacuo, yielding a crude mixture of **7a** and **9a**. This mixture was separated by chromatography on a column of silicagel (30 cm long, 4 cm i.d.) with chloroform as eluent. In this way 0.12 g of **7a**, 0.17 g of a mixture of **7a** and **9a**, and 1.78 g of **9a** were obtained. Total yield 86%.

Pure **7a** had mp 54–56 °C: $[\alpha]^{22}_D$ +70.4° (*c* 1.5, $CHCl_3$); IR (KBr) 2124 ± 1 (NC, CO was used for calibration), 1725 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ 8.00 and 7.35 (2 × m, 20, benzoyl), 6.25 (d of d, 1) and 5.85 (d of d, 1, H-3,4), 5.90 (d, $J_{1,2}$ = 4.5 Hz, 1, H-1), 5.50 (d of d, 1, H-2), 5.00–4.40 (m, 3, H-5,6,6′); ^{13}C NMR ($CDCl_3$) δ 166.1 (NC), 165.7, 165.2, 165.1 and 164.8 (C=O), 133.8, 133.5, 133.2, and 133.1 (arom C-4), 129.9–129.5 and 128.4–128.0 (2 × m, remaining arom C's), 78.8 (C-2), 71.5 (C-1), 69.6 (C-3), 69.4 (C-5), 67.9 (C-4), 61.8 (C-6). ^{13}C assignments were made by comparison with reported values of per-*O*-acetylglucopyranose[21] and isocyanides;[22] the position of C-6 was confirmed by an ^{1}H off-resonance decoupling experiment.

Pure **9a** had mp 88–90 °C: $[\alpha]^{22}_D$ +44.7° (*c* 2.5, $CHCl_3$); IR (KBr) 2142 ± 1 (NC), 1725 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ 8.00 and 7.45 (2 × m, 20, benzoyl), 6.05–5.65 (m, 3, H-2,3,4), 5.20 (d, $J_{1,2}$ = 8.4 Hz, 1, H-1), 4.80–4.45 (m, 2, H-6,6′), 4.45–4.15 (m, 1, H-5); ^{13}C NMR ($CDCl_3$) δ 165.1 (NC), 165.9, 165.4, 164.8, and 164.6 (C=O), 133.6, 133.5, 133.4, and 133.1 (arom C-4), 129.8–129.7 and 128.3–128.1 (2 × m, remaining arom C's); 79.6 (C-2), 74.9 (C-1), 72.1 (C-3), 71.6 (C-5), 68.4 (C-4), and 62.3 (C-6). ^{13}C assignments are tentative vide supra; MS *m/e* 605 (M^+), 428 (M − benzoic acid − HC(O)NC), 361 (M − 2 benzoic acid), 352 (M − benzoic acid anhydride − HCN), 334 (M − 2 benzoic acid − HCN), 321 (M − $PhCOOCH_2$· − benzoic acid − −HCN). Anal. Calcd for $C_{35}H_{27}NO_9$: C, 69.42; H, 4.49; N, 2.31; O, 23.78. Found: C, 69.47; H, 4.77; N, 2.35; O, 23.41.

β-D-Glucopyranosyl Isocyanide (9b). Debenzoylation of **9a** as described for **6a** afforded **9b** in quantitative yield. The product was isolated by freeze drying: IR (KBr) 3400 (OH), 2150 cm^{-1} (NC), no C=O present; ^{1}H NMR (CD_3OD) δ 4.60 (H-1, partly masked by solvent), 3.85–3.25 (m, remaining H's).

Polymerization of 2,3,4,6-Tetra-*O*-benzoyl-β-D-glucopyranosyl Isocyanide (9a). To a solution of 1.59 g (2.63 mmol) of **9a** in 4 mL of chloroform was added a solution of 6.1 mg (0.026 mmol) of nickel chloride hexahydrate in 4 mL of methanol. The mixture was stirred for 2 days at room temperature. The solvent was removed under diminished pressure and the resulting red-brown solid was dissolved in 15 mL of chloroform. This solution was added dropwise, with vigorous stirring, to 500 mL of methanol–water 4:1. The precipitate was filtered off and dried in vacuo yielding 1.56 g (98%) of pale yellow **10a**: $[\alpha]^{22}_D$ 0.0° (*c* 0.7, $CHCl_3$); IR (KBr) 1730 (C=O), 1640 cm^{-1} (N=C); ^{1}H NMR ($CDCl_3$) δ 7.9 ($\Delta\nu_{1/2}$ 45 Hz) and 7.4 ($\Delta\nu_{1/2}$ 45 Hz) (2 × br, 20, benzoyl), 5.8 ($\Delta\nu_{1/2}$ 105 Hz, br, 4, tentative assignment H-1,2,3,4), 4.6 ($\Delta\nu_{1/2}$ 90 Hz, br, 3, tentative assignment H-5,6,6′). Anal. Calcd for $C_{35}H_{27}NO_9$: C, 69.42; H, 4.49; N, 2.31; O, 23.78. Found: C, 68.63; H, 4.64; N, 2.67; O, 24.06.

Polymerization of 2,3,4,6-Tetra-*O*-benzoyl-α-D-glucopyranosyl Isocyanide (7a). A procedure analogous to that described for the polymerization of **9a** was followed, except that the temperature of the reaction mixture was kept at 45 °C. After a reaction time of 7 days a 35% yield of polymer was obtained: $[\alpha]^{22}_D$ +80° (*c* 0.42, $CHCl_3$). After another 5 days the yield had increased to 88%: $[\alpha]^{22}_D$ +71°. Spectroscopic properties as for **10a**.

Poly(β-D-glucopyranosyliminomethylene) (10b). To a solution of 162 mg (0.27 mmol) of **10a** in 40 mL of dry THF was added sodium methanolate in methanol until the reaction mixture had pH 8. After being stirred for 2 h at room temperature, TLC revealed complete removal of the benzoyl groups. Diluted hydrochloric acid was added dropwise until the mixture had pH 6. After removal of the organic solvents in vacuo, the residue was diluted with water and after several extractions with ether subjected to ultrafiltration (Diaflo Ultra-Filter, UM-2). Freeze drying of the resulting solution afforded 35 mg (68%) of a creamish powder: $[\alpha]^{22}_D$ 0° (*c* 0.7, D_2O); IR (KBr) 3500–3200 (OH), 1630 cm^{-1} (NC); ^{1}H NMR (D_2O) δ 5.1 (H-1, partly masked by solvent), 4.4 ($\Delta\nu_{1/2}$ 20 Hz, br) and 4.1 ppm ($\Delta\nu_{1/2}$ 30 Hz, br, remaining protons).

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Registry No.—3a, 1428-11-2; **4a**, 33639-93-9; **5a**, 33639-91-7; **6a**, 65293-31-4; **6b**, 65293-32-5; **7a**, 65375-78-2; **8a**, 65292-96-8; **9a**, 65375-79-3; **9b**, 65292-94-6; **10a**, 65292-93-5; **10b**, 65292-95-7; sodium azide, 26628-22-8; formic acetic anhydride, 2258-42-6.

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Substituted Coumarins and Azacoumarins. Synthesis and Fluorescent Properties

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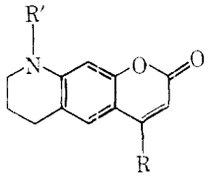
A number of new substituted 7-amino- and 8-aza-7-amino coumarins have been synthesized. Substituent effects on fluorescence properties (maxima and quantum yields) are reported. Substitution by fluorine in the 4-methyl position and by nitrogen in the benzo ring has been found to reduce fluorescence quantum yields. Nitrogen substitution in the benzo ring provides a blue shift in the fluorescence while fluorine substitution at the 4-methyl position gives pronounced red shifts.

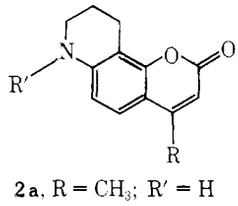
Recent synthesis programs in this laboratory have resulted in the preparation of a large number of substituted coumarins and azacoumarins for use as emission sources for dye laser applications. The effects of substituents on the lasing characteristics of these compounds have been reported.[1-4] This report describes the synthesis of several new laser dyes and the effects of substituents on their fluorescence maxima and fluorescence quantum yields.

The new coumarin dyes prepared in the present work are shown below. Results are summarized in Table I. The syntheses led to several new results of chemical interest.

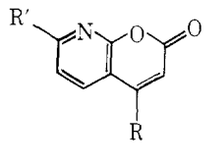
Synthesis. The preparation of 8-aza-7-hydroxy-4-methylcoumarin (**3c**) by the method of von Pechmann[5,6] from 2,6-dihydroxypridine (**4**) and ethyl acetoacetate gave in addition to the desired product small amounts of the bis addition product 10-aza-2,8-dioxo-4,6-dimethyl-2*H*,8*H*-benzo[1,2-*b*:5,4-*b*]dipyran (**5**) (detected by mass spectroscopy; M^+ ion at *m/e* 243). Merchant and co-workers[7] also noted the formation of trace amounts of a similar bis addition product in the reaction of ethyl acetoacetate with resorcinol. When the condensation of 2,6-dihydroxypyridine (**4**) is carried out in



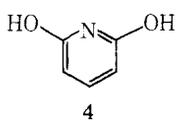
1a, R = CH_3; R′ = H
b, R = CF_3; R′ = H
c, R = CH_3; R′ = CH_3
d, R = CF_3; R′ = CH_3



2a, R = CH_3; R′ = H
b, R = CF_3; R′ = H
c, R = CH_3; R′ = CH_3
d, R = CF_3; R′ = CH_3



3a, R = CH_3; R′ = NH_2
b, R = CH_3; R′ = $N(CH_3)_2$
c, R = CH_3; R′ = OH
d, R = CF_3; R′ = 
e, R = CH_3; R′ = 



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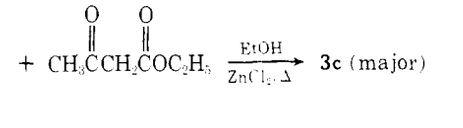

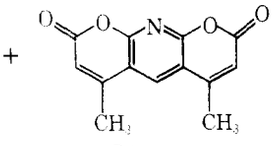

5 (trace)