preferential stabilization of lipoprotein particles of about 200-Å diameter, CD spectra consistent with β-strand structure both in solution and at interfaces, a high tendency to self-associate in aqueous media, and an very high affinity for lipid surfaces. For these reasons we feel our model peptide will provide us with an excellent tool to investigate the specific lipid–protein interactions that occur in low-density lipoproteins.

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Registry No. NH_2ValGluValOrnValGluValOrnValGluValQrnVa-lCO2H, 92269-72-2.

Chemical Modification of Nucleic Acid Components: Conversion of Guanosine by Methyl *N*-Cyanomethanimidate to a Tricyclic, Fluorescent Analogue of Adenosine

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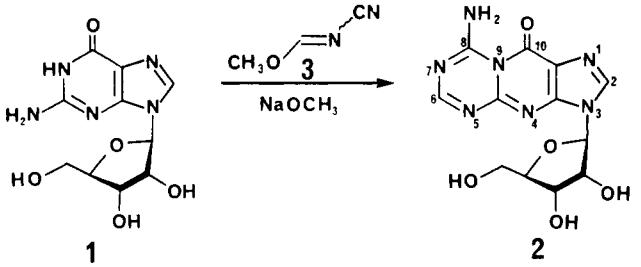
We have accomplished the goal of converting a natural *N*-ribonucleoside into an entity whose structure more closely resembles, in the periphery, that of a different natural *N*-ribonucleoside, for example, guanosine (**1**) into a product that bears a peripheral resemblance to adenosine, as in **2**. Best results were



obtained with methyl *N*-cyanomethanimidate (**3**)[2-6] in the presence of sodium methoxide. The structure of the fluorescent product from **1** and **3** was established by spectroscopic means as 8-amino-9,10-dihydro-10-oxo-3-β-D-ribofuranosyl-3*H*-1,3,5-triazino[1,2-*a*]purine (**2**), or IA′-metamorphosine.[7]

Compound **2**, which possesses an imidazole ring, ribosyl moiety, and the major hydrogen-bonding functionalities generally considered important for the expression of the biological activity of the purine ribonucleosides and ribonucleotides,[8,9] is a laterally extended adenosine analogue in which the terminal rings are

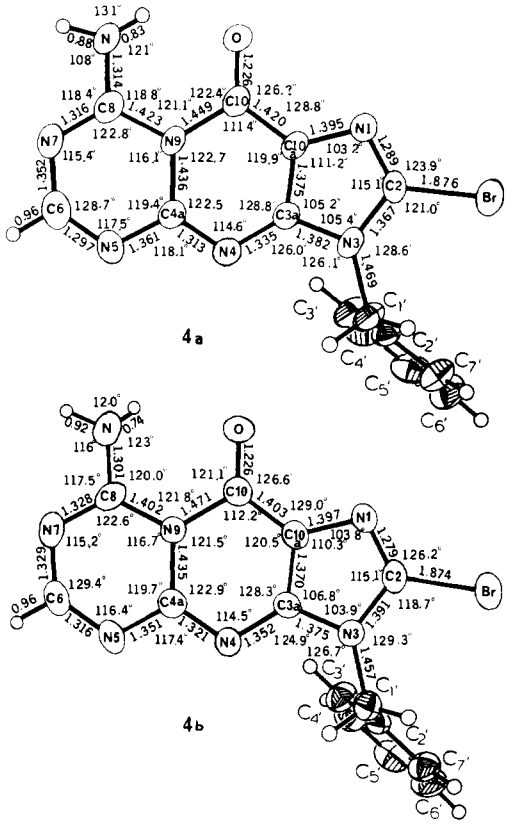


Figure 1. Single-perspective ORTEP drawings simplified.

displaced by approximately 2.4 Å relative to adenosine. As such, it bears resemblance to lin-benzoadenosine,[10,11] with related potential for application in enzyme studies. Conversion of N-bicyclic to N-tricyclic ribonucleosides by simple reagents has already provided interesting results and useful applications.[12-18]

Methyl *N*-cyanomethanimidate (**3**) (7 equiv)[2-6] was introduced through a hypodermic syringe into guanosine (**1**) and sodium methoxide (2 equiv) in methanol, and the mixture was stirred at 20 °C for 24 h. Purification was effected by partial evaporation, filtration, and pressure chromatography on Woelm silica gel using acetone as eluant. Evaporation gave a colorless solid, mp 247–249 °C dec, $C_{12}H_{13}N_7O_5$,[19] in 39% yield (66% based on unrecovered guanosine). The same product, characterized spectroscopically by ^{13}C and ^1H NMR in $(CD_3)_2SO$, was obtainable from guanosine, NaH, and **3** in DMF at 60 °C for 6 h in about the same yield. We could differentiate between the ^1H NMR chemical shifts for the 2-H (δ 8.3) and 6-H (δ 8.03) in the assigned formula **2** by synthesis of the isotopically labeled analogues (a) from **3** and [8-^{2}H]guanosine, made by heating guanosine in D_2O under reflux for 7 h, and (b) from **1** and methyl [1-^{2}H]-*N*-cyanomethanimidate, made from trimethyl [1-^{2}H]orthoformate[6] and cyanamide in cyclohexane at reflux. The D_2O-exchangeable N–H's were

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nonidentical, as shown by the clearly differentiated δ values of 10.2 and 9.39, which suggests hydrogen bonding between the peri carbonyl and the proximate exocyclic N-H. The UV spectrum (EtOH) was indicative of the extended ring system: λ_{max} (ϵ) 331 (9500), 309 (8700), 253 sh (7200), 245 sh (9800).

While the analytical and spectroscopic data were consistent with proposed structure **2**, they were not completely definitive for distinguishing it from the three other possible isomeric products arising from different modes of condensation-cyclization of **1** (**1**-N^2 vs. N^2-**3**) and **3** (C=N vs. C≡N). Therefore, we obtained confirmation of structure **2** by a pair of parallel spectroscopic matches involving **2** and its 2-bromo derivative with the product of 9-benzylguanine[20] with **3** and its corresponding bromo derivative. Single-crystal X-ray analysis showed the presence of two crystallographically independent molecules in the solid-state structure of 8-amino-3-benzyl-2-bromo-9,10-dihydro-10-oxo-3*H*-1,3,5-triazino[1,2-*a*]purine ($C_{14}H_{10}BrN_7O$),[19] mp 282-284 °C dec.[21] Molecules **4a** and **4b** in Figure 1 are nearly planar through the entire tricyclic base moiety.

IA′-Metamorphosine (**2**) exhibits fluorescence on a TLC plate (silica gel); however, in aqueous solution at 20 °C, Φ is only 0.003 (compared with rhodamine G) for λ_{max}^{ex} 350 nm, λ_{max}^{em} 361-590 nm (br), and τ (by phase) = 0.38 ns. In glycerol at 20 °C, by contrast, Φ = 0.19, λ_{max}^{em} 444 nm, τ = 1.31 ns (by phase), and 1.38 ns (by modulation), and at -38 °C, Φ = 0.985 and λ_{max}^{em} 450 nm. These changes probably reflect a change in the facility of adiabatic proton transfer from NH_2 to the peri carbonyl as well as a decrease in energy release via vibrational processes. The reagent described herein, methyl *N*-cyanomethanimidate and NaOMe in methanol, has potential application as a spray reagent for thin-layer or paper chromatography. Observed fluorescence develops on heating a sprayed chromatogram at the location of guanosine and adenosine but not at cytidine or uridine. Since only adenine- or adenosine-containing compounds react with chloroacetaldehyde as a spray reagent to develop fluorescence,[22] the two spray reagents can be used in parallel for full differentiation. IA′-Metamorphosine functions as a competitive inhibitor, K_i = $(2.3 \pm 0.3) \times 10^{-4}$, of adenosine with adenosine deaminase.[23] It is nonmutagenic in the bacterial mutagen (Ames) screening test.[24]

Compound **2** can serve also as a "protected" guanosine (**1**) since quantitative reconversion of **2** to **1** occurs upon treatment with 0.1 N NaOH at 20 °C within 5 min. The modification of guanosine to an N-tricyclic derivative, as in **2**, by means of methyl *N*-cyanomethanimidate and nonaqueous base, can be extended to other guanine-containing substrates.

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Registry No. 1, 118-00-3; **2**, 92220-57-0; **3**, 51688-22-3; **4**, 58-61-7.

Supplementary Material Available: Complete crystallographic data for 8-amino-3-benzyl-2-bromo-9,10-dihydro-10-oxo-3*H*-1,3,5-triazino[1,2-*a*]purine (**4a,b**), including tables listing atomic positional and thermal parameters, bond angles, torsional angles, intermolecular contact distances, weighted least-squares planes, and observed and calculated structure factors (44 pages). Ordering information is given on any current masthead page.

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(Trimethylphosphine)cobalt(I) Complexes. 3. $Co(PMe_3)_2(BPh_4)$, the First Structural Example of Tetraphenylborate Anion π-Coordinated to a First-Row Metal Ion

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The tetraphenylborate anion is widely used as an "inert" counterion to isolate cationic species from solutions. However, its role is sometimes not as passive as those of the perchlorate, tetrafluoroborate, or hexafluorophosphate anions, since it can coordinate to transition metals via π-bonded interaction with one of its phenyl groups.[2,3] This type of bonding has been observed for $ML_2(BPh_4)$ complexes (M = Rh(I) and Ir(I) and L = diene, PR_3, etc.).[4] The presence of a π-bonded BPh_4^- group has been shown by X-ray diffraction for $Rh(P(OMe)_3)_2(BPh_4)$[5] and, more recently, for the analogous compounds in which the phosphites are replaced by a bidentate diphos ligand.[6] The Rh(I) and Ir(I) compounds are known as inert d^8 compounds with low, if any, catalytic activity.[7]

During our investigation of the basic chemistry of Co^I-PR_3 systems, it appeared to us that such complexes are also present when $CoX(PR_3)_3$ compounds are reacted in presence of $NaBPh_4$. The only reported Co(I) complex of this type, $Co(P(OEt)_3)_2(BPh_4)$, has been synthesized by this method.[8] The chemical and structural characterization of the trimethylphosphine complex $Co(PMe_3)_2(BPh_4)$ is herein reported.

Addition of sodium tetraphenylborate to a methanol or acetone solution of $CoBr(PMe_3)_3$ gives rise to two species, $[Co(PMe_3)_4]BPh_4$ and $Co(PMe_3)_2(BPh_4)$, according to reaction 1. They were separated by fractional crystallization.

$$2CoBr(PMe_3)_3 + 2NaBPh_4 \rightarrow [Co(PMe_3)_4]BPh_4 + Co(PMe_3)_2(BPh_4) + 2NaBr \quad (1)$$

$[Co(PMe_3)_4]BPh_4$, obtained as blue-green crystals, is a paramagnetic tetracoordinate species (μ_{eff} = 2.8 μ_B at 295 K). Its X-ray structure[9] indicates a distorted tetrahedral coordination with normal Co-P bonds (av 2.227 Å) and one P-Co-P angle (125.4 (1)°) noticeably greater than the other five (101.1 (1)-113.1 (1)°). A similar structure has been observed for the d^9 $[Ni(PMe_3)_4]BPh_4$ compound.[11] The geometry of the BPh_4^- ion is normal.

Dark brown crystals of the diamagnetic $Co(PMe_3)_2(BPh_4)$ complex can be handled in air without transformation into phosphine oxide complexes. They are reasonably stable in acetone

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