interaction occurs in these molecules. The smaller shift difference between the two different nitroso nitrogen in **3b** as compared to **3c** (5.5 vs. 14.7 ppm) probably reflects the reduced amount of interaction between the syn nitro oxygen and anti nitroso nitrogen.

We believe that the foregoing explanation, based on the weak bonding interaction between the suitable juxtaposed nitrosamine groups, provides a conceptually simple and correct explanation for both the unusual isomer distribution observed in **3** and the large variation in chemical shifts of the nitroso nitrogen in **3a-d** and **1**.

Experimental Section

The NMR spectra were recorded on a Nicolet WB-360 MHz spectrometer. The ^1H and ^{13}C NMR spectra are referenced to internal Me_4Si. The ^{15}N NMR spectra are reported on the ammonia scale (NH_3 = 0 ppm). The reference standard was dimethylformamide; a conversion term of 103.81 ppm[14] was used to convert the data to the ammonia scale.

1,4,5,8-Tetranitroso-1,4,5,8-tetraazadecalin (3). A solution of 3.45 g (50 mmol) of sodium nitrite and 1.42 g (10 mol) of 1,4,5,8-tetraazadecalin was prepared in a 125-mL Erlenmeyer flask. The temperature of this solution was not allowed to exceed 5 °C. The solution was cooled to −2 °C, and 50 mL of 1 N hydrochloric acid was added over 60 s. A white precipitate formed immediately. The mixture was stirred at 0 °C for 30 min and then at room temperature for 1 h. The product was collected by vacuum filtration and was washed well with water. It was dried overnight in a vacuum oven to give an off-white powder (2.35 g, 9.1 mmol, 91%, decomposed at 211–212 °C). It was recrystallized from DMF/H_2O to yield fine light yellow neddles: IR (KBr) 2900 (w), 1475 (m), 1450 (sh), 1410 (m), 1370 (m), 1310 (m), 1300 (m), 1275 (m), 1260 (m), 1210 (m), 1190 (m), 1110 (m), 1050 (m), 975 (w), 935 (m), 895 (w), 830 (w), 735 (m); ^1H NMR Me_2SO-d_6, 80 °C) δ 3.80–4.10 (cm, 4 H), 4.95 (cm, 2 H), 5.55 (cm, 2 H), 6.76(s, 2 H, $H_{9,10}$). Anal. Calcd. for $C_6H_{10}N_8O_4$: C, 27.90; H, 3.91; N, 43.40. Found: C, 27.92; H, 3.91; N, 43.53.

The ^{15}N-labeled **3** was synthesized by substituting labeled sodium nitrite for the natural material in the preparation.

Registry No. 1, 140-79-4; *trans*-**3**, 81898-35-3; *trans*-1,4,5,8-tetraazadecalin, 67919-28-2.

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Inclusional Association of a Fluorescence Detergent Probe with Cyclodextrins. Microscopic Environment of the Interior of a Cyclodextrin Cavity. Pressure Effects

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Abstract: The fluorescence parameters (peak maximum, lifetime, relative intensity, and depolarization) of aqueous solutions of a cationic detergent probe, 11-(3-hexyl-1-indolyl)undecyltrimethylammonium bromide (6-In-11$^+$), have been measured in the presence of α-, β-, and γ-cyclodextrins (α-CD, β-CD, and γ-CD) at ambient and elevated pressures. The results are consistent with the formation of complexes of 6-In-11$^+$ and the CD's. NMR measurements confirm the existence of 6-In-11$^+$/CD complexes. It is concluded that the probe experiences a somewhat different environment in each complex. The results are compared to those for the same probe in the environment of ionic micelles and of the macroions of polyelectrolytes.

The properties of cyclodextrin (CD) inclusion complexes in aqueous solution have served as important models for the attainment of knowledge relevant to hydrophobic interactions, such as those that determine many of the critical properties of biological systems, i.e., the selectivity and catalytic efficiency of enzyme action.[2] Both the static and the dynamic properties of CD complexes may be investigated by means of luminescence probes.[3] The main goals of this work were to first determine the environmental polarity and mobility of a probe that is included in a CD cavity and then to establish how these properties vary as a function of applied pressure. A fluorescent detergent probe, 11-(3-hexyl-1-indolyl)undecyltrimethylammonium bromide (6-In-11$^+$), was selected because the values of $\lambda^F_{max} \sim 370$ nm and $\tau_F \sim 15$ ns are typical of a highly polar, aqueous environment and values of $\lambda^F_{max} \sim 350$ nm and $\tau_F \sim 7$ ns are typical of a less polar, hydrophobic environment.[5] Furthermore, the fluorescence depolarization of 6-In-11$^+$ affords a measure of the microviscosity of the environment experienced by the probe.[6]

In addition to the above points, the fact that 6-In-11$^+$ is at once a fluorescence probe and a detergent allows the examination of how a detergent structure can influence the binding to a CD,[7] and finally, the effect of applied pressure on the luminescence parameters of 6-In-11$^+$ in CD's is of interest because of the possible relation of such information to the influence of pressure on "soft" and "hard" binding sites that cause reversible structural transitions in proteins[8] and to the influence of pressure on hydrophobic interactions.

Experimental Section

Spectroscopic Measurements. Fluorescence spectra were obtained on a SPEX Fluorolog fluorimeter. Fluorescence lifetimes were measured by the single-photon counting technique. The details on the fluorescence depolarization measurements[6] and the high-pressure cell[9] were described in preceding papers. The UV absorbance spectra and ^1H NMR spectra were taken on a Cary 18 spectrophotometer and a Bruker WM-300 MHz NMR spectrometer.

Materials. 11-(3-Hexyl-1-indolyl)undecyltrimethylammonium bromide, 6-In-11$^+$, was available from previous studies.[4] α-, β-, and γ-cy-

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(9) Turro, N. J.; Okubo, T. *J. Am. Chem. Soc.* **1981**, *103*, 7224.

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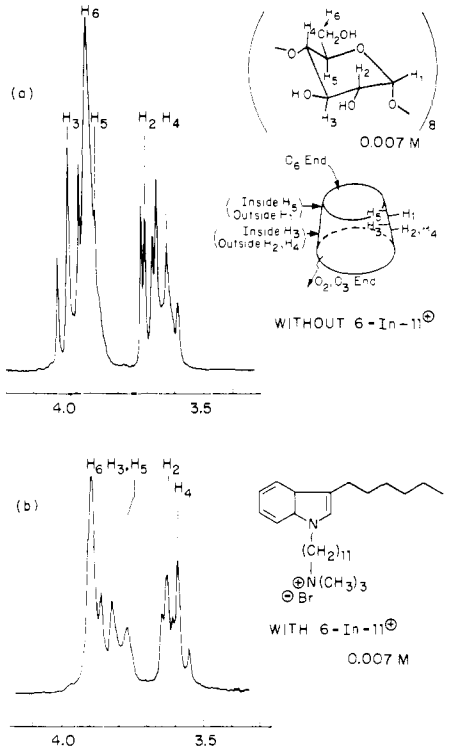

Figure 1. 300-MHz ^1H NMR spectra of γ-cyclodextrin in the (a) absence and (b) presence of 6-In-11$^+$ in D_2O. [γ-CD] = 0.007 M; [6-In-11$^+$] = 0.007 M. Intensities are relative.

clodextrins (Aldrich) were used as received.

Results

^1H NMR Spectroscopy. The NMR spectrum of the CD's has been analyzed,[2b,10] and several "outside" (H_2 and H_4) and "inside" (H_3 and H_5) protons (see Figure 1) have been assigned, as have been the H_6 protons (associated with the CH_2OH group at the "bottom" or smaller opening). If an aromatic group complexes with a CD, it is expected that some of the CD protons will experience a chemical shift that depends on the average location of the probe with respect to the CD structure. ^1H NMR analysis of aqueous solutions of 6-In-11$^+$ and α-CD, β-CD, and γ-CD reveals substantial differences of the ^1H resonance of both the probe and the CD. We shall assume that these shifts result from the formation of complexes of 6-In-11$^+$ and the CD's. In the cases of the 6-In-11$^+$/α-CD complex and the 6-In-11$^+$/β-CD complex, the H_5 protons show substantial major shifts (~0.2 ppm), and the H_3 and H_6 protons show a somewhat smaller upfield shift (~0.09 ppm). On the other hand, the H_2 and H_4 protons show negligible shifts (<0.03 ppm). Furthermore, the "sharpness" (half-widths) of the resonances of the probe protons is comparable in water and in the α-CD or β-CD complexes.

In the case of the 6-In-11$^+$/γ-CD complex (Figure 1), the H_3 proton shows the most substantial upfield chemical shift (~0.2 ppm), with H_2 and H_5 showing a somewhat smaller shift (~0.09 ppm). Protons of the indolyl group of 6-In-11$^+$ were shifted toward a lower magnetic field upon addition of γ-CD into 6-In-11$^+$ solution, whereas all protons of other moieties of 6-In-11$^+$ did not show any significant shift (Figure 2). Furthermore, the "sharpness" of the resonances of the indole protons is substantially reduced (Figure 2b) relative to the resonances in water (Figure 2a).

Fluorescence Spectra. The position of the fluorescence maximum (λ_{max}) of 6-In-11$^+$ is a convenient parameter for evaluating the hydrophobicity or polarity around the probe.[5] The λ_{max} value in pure water is 374 nm and shifts to shorter wavelengths when the probe is located in a hydrophobic atmosphere such as that provided by the interior of micelles and hydrophobic macroions, for example.[4-7] The λ_{max} values of 6-In-11$^+$ shifted from the water values toward shorter wavelengths upon addition of CD (Figure 3). The limiting values of λ_{max} for the α-CD (~366 nm) and β-CD (~360 nm) complexes appeared to be closely approached at ~10^{-2} M CD. However, the limiting value of λ_{max} for the 6-In-11$^+$/γ-CD complex is not reached at 10^{-2} M γ-CD (~352 nm) but is approaching the value found in a strongly hydrophobic environment (λ_{max} = 353 nm in CH_3OH and λ_{max} = 338 nm in cyclohexane).[5]

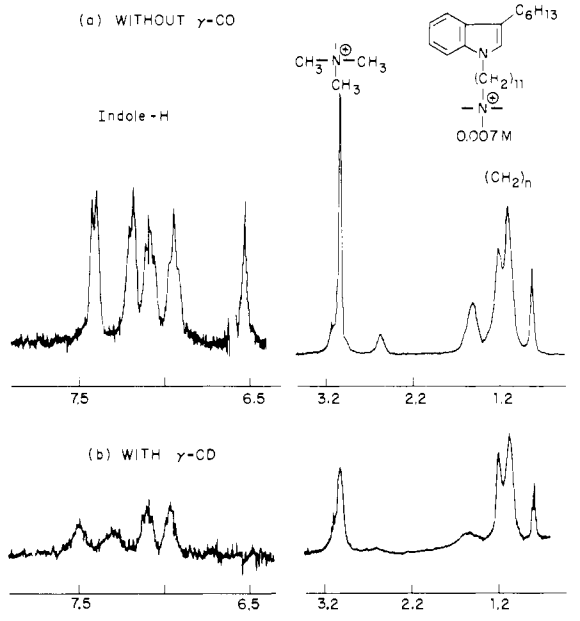

Figure 2. 300-MHz ^1H NMR spectra of 6-In-11$^+$ in the (a) absence and (b) presence of γ-CD in D_2O. [6-In-11$^+$] = 0.007 M; [γ-CD] = 0.007 M.

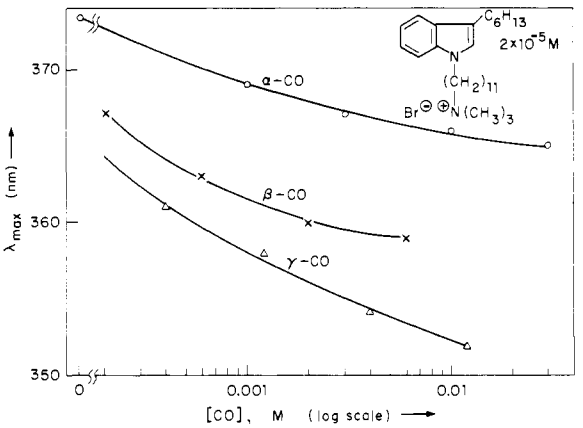

Figure 3. λ_{max} vs. [CD] plots for 6-In-11$^+$ with α-CD (○), β-CD (×), and γ-CD (△) at 25 °C. [6-In-11$^+$] = 2 × 10^{-5} M. Comparison of the position of corrected maxima of fluorescence of triphenylene in cyclohexane (λ_{max} 355, 362, and 372 nm) with our values (λ_{max} 354, 362, and 372 nm) demonstrated that no instrument response correction is necessary in the range studied. See: Berlman, I. B. "Handbook of Fluorescence Spectra of Aromatic Molecules"; Plenum Press: New York, 1971.

Fluorescence Lifetimes. The magnitude of the fluorescence lifetime (τ) of 6-In-11$^+$ has been correlated with the hydrophobicity about the probe. The value of τ in pure water is ~15 ns and decreases to shorter values (~7 ns) when the probe is located in a hydrophobic environment. The τ values of the 6-In-11$^+$ probe in the presence of excess α-CD, β-CD, or γ-CD are in the range of 6–9 ns.

Fluorescence Depolarization. The degree of loss of fluorescence polarization of a probe such as 6-In-11$^+$ provides a means for the evaluation of the freedom of motion experienced by the probe during its singlet lifetime. Measurement of fluorescence depo-

(10) Wood, D. J.; Hruska, F. E.; Saenger, W. *J. Am. Chem. Soc.* **1977**, *99*, 1735.

Table I. Molecular Anisotropy and Lifetimes as a Function of Macroscopic Viscosity[a]

[β-CD]	[methyl α-glucoside]	r	τ, ns	η, cP[b]	η, cP[c]
0	0	0 ± 0.0015	15.5	1	1 ± 30
0.0025 M	0	0.014 ± 0.004	6.5		145 ± 50
0.0025 M	0.1 M	0.013 ± 0.003	6.7		135 ± 40
0.0025 M	1 M	0.016 ± 0.005	6.4	2	165 ± 60
0.0025 M	saturated (~10 M)	0.013 ± 0.004	6.9	8	140 ± 50

[a] [6-In-11$^+$] = 2.0 × 10^{-5} M. [b] Relative macroscopic viscosity determined by viscometer measurements. [c] "Microscopic viscosity" determined by polarization (see text).

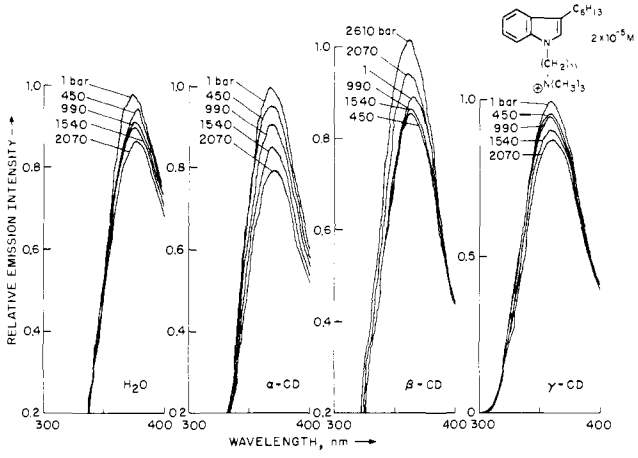

Figure 4. High-pressure influence on the fluorescence spectra of 6-In-11$^+$ in pure water and α-CD, β-CD, and γ-CD solutions.

larization allows calculation of the molecular anisotropy (r) via standard relationships.[11] The molecular anisotropy, in turn, may be related to an "apparent microviscosity",[6] i.e., a quantity that is a measure of the "friction" experienced by the probe as it moves in its environment. The "microviscosities" of 6-In-11$^+$, determined from fluorescence depolarization, were found (±20% error) to be 80, 150, and 100 cP for the α-CD, β-CD, and γ-CD complexes, respectively.

In order to decide whether the polarization measurements refer to the motions of the probe in the complex or to the complex as a whole, we increased the macroscopic viscosity of β-CD/6-In-11$^+$ system by nearly a factor of ~10 by addition of methyl α-glucoside, which should have minimal influence on the viscosity experienced by the probe and maximal influence on the viscosity experienced by the complex as a whole. Since neither the lifetime nor emission maximum of 6-In-11$^+$ changed, within the experimental error (Table I), upon addition of methyl α-glucoside, we conclude that the included probe is unaware of the viscosity change that is occurring in the aqueous phase. Furthermore, since the polarization loss experienced by the probe is also unaffected by an increase of the macroscopic viscosity by nearly an order of magnitude, we conclude that the polarization loss is due entirely to the motion of the probe within the CD cavity and not to the motion of the complex as a whole.

Effect of Pressure. As displayed in Figure 4, the influence of increased pressure leads to a similar slight red shift of λ_{max} and a decrease in fluorescence intensity for the 6-In-11$^+$ probe in water and in the α-CD and γ-CD complexes. A small (<20%) increase in lifetime was noted as the pressure was increased for these systems. In the case of the 6-In-11$^+$/β-CD complex, for increasing pressures up to ~1000 bar, the value of λ_{max} shows a slight red shift and the fluorescence intensity is lower than that for the probe in water. For increasing pressure ≳1500 bar, the value of λ_{max} begins to shift to the blue and the fluorescence intensity increases. Due to excessive light scattering by the high-pressure cell, meaningful depolarization measurements could not be made.

Equilibrium Constants for Complex Formation. The magnitude of the equilibrium (K_{eq}) for the 6-In-11$^+$/CD complexes can be established by measuring optical densities (OD) or emission intensities (EI) of the probe as a function of concentrations and then applying standard Benesi–Hildebrant relationships[12] to evaluate K_{eq}. For the 6-In-11$^+$ complex with α-CD and β-CD, the values of K_{eq} (M^{-1}) were found to be 500 ± 100 (OD) or 410 ± 100 (EI) and 2100 ± 700 (OD) or 3500 ± 100 (EI), respectively. Because of technical difficulties, only an aproximate value of ~3000 (OD) was obtained for the 6-In-11$^+$/γ-CD complex.

Discussion

The results of several spectroscopic measurements leave no doubt that 6-In-11$^+$ forms association complexes with α-CD, β-CD, and γ-CD. Measurements of K_{eq} suggest that the 6-In-11$^+$ forms comparably stable complexes with β-CD and with γ-CD, and a weaker complex with α-CD. NMR data suggest a difference between the 6-In-11$^+$ complex with γ-CD and the other two complexes (NMR shift and line broadening data). From the chemical shift data, it appears that the *indole* portion of the 6-In-11$^+$ probe is near the H_3, H_5, and H_6 protons of α-CD and β-CD and near the H_2, H_3, and H_5 protons of γ-CD. These results provide strong evidence that the probe is included with the indole moiety located near the bottom of the α-CD and β-CD cavity and near the top of the γ-CD cavity. Fluorescence parameters (λ_{max}, τ, r) all are consistent with a structure of the complex that places the indole moiety in a hydrophobic environment. The value of λ_{max}, which is probably the more reliable of these parameters for determination of environmental polarity, suggests that the indole group experiences a more hydrophobic environment in the γ-CD complex (λ_{max} ~ 352 nm) than in either the α-CD (λ_{max} ~ 366 nm) or the β-CD (λ_{max} ~ 360 nm) complex. These results, when considered along with the observation that significant NMR line broadening occurs for the 6-In-11$^+$/γ-CD complex, but not for the α-CD or β-CD complexes, are consistent with complete inclusion of the indole moiety within the γ-CD cavity, whereas for the α-CD and β-CD complexes, the indole group is not completely included. Inspection of molecular models indicates that only the six-carbon side chain, but not the indole moiety or the detergent chain, may be included in the α-CD cavity. However, the indole moiety can "fit" in either the β-CD or γ-CD cavity.

It is of interest to compare the results reported here with those for association of 6-In-11$^+$ with other hydrophobic complexing environments, such as micelles[5] and polyelectrolytes.[13] For example, from the λ_{max} criterion, the order of "reported" hydrophobicity of the environment is H_2O (~374 nm) < α-CD (~366 nm) < β-CD (~360 nm) < HDTBr micelles (~355 nm) < sodium poly(styrenesulfonate) (~351 nm) ≈ γ-CD (~352 nm) < cyclohexane (~340 nm).

Concerning the effect of pressure on the 6-In-11$^+$/CD complexes, first we note that in an investigation[14] of the influence of high pressure on the fluorescence of several indoles in homogeneous solutions leads to the conclusion that an increase in pressure causes an increase in the dielectric constant of the solvent. Furthermore, the nonradiative rates scale with increasing dielectric constant. Next, we note that the results of a study[8] of the influence of pressure on a fluorescence probe/CD complex were consistent with the inclusion of the probe in a hydrophobic environment. The differing behavior of the fluorescence parameters of 6-In-11$^+$ complexes with α-CD and γ-CD compared to those of the 6-In-11$^+$/β-CD complex may be tentatively explained in light of these reports. If the equilibrium of eq 1 is assumed, increasing pressure

$$\text{CD}\cdot n\text{H}_2\text{O} + \text{6-In-11}^+ \rightleftharpoons \text{CD}\cdot\text{6-In-11}^+ + n\text{H}_2\text{O} \quad (1)$$

is expected to shift the equilibrium toward the more compressible

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state. The results show that for the α-CD and γ-CD complexes, the effects of pressure on the fluorescence parameters are similar to those in pure water, whereas the effects of pressure on the fluorescence parameters of the β-CD complex are different from those in pure water. We can interpret these results in terms of an increase in dielectric constant with increasing pressure, which results in a slight red shift in λ_{max} and a decrease in fluorescence intensity due to an increased rate of radiationless deactivation for the α-CD and γ-CD complexes. In the β-CD complex, we propose that as pressure is applied, there is an initial increase in the dielectric constant experienced by the probe leading to a (slight) red shift in λ_{max} and decrease in emission intensity, followed by a decrease in the dielectric constant leading to a blue shift.

This "turnaround" in fluorescence behavior can be explained if the conformation of the probe in the β-CD complex is more readily compressible than it is in the α-CD or γ-CD complexes, i.e., possibly because of an easier folding of the C_{11} detergent.

The order of magnitude of the microviscosity experienced by the 6-In-11$^+$ probe in water, typical micelles, sodium poly(styrenesulfonate) (NaPSS), and the cavity of cyclodextrins (present work), which were evaluated from various methods, is found to be as follows: H_2O (~1 cP) < SDS (~15 cP)[9,13] < HDTBr (~40 cP)[6,9] < α-CD (~80 cP) < γ-CD (~100 cP) < β-CD (~150 cP) < NaPSS (~150 cP)[13] < HDTBr + cetyl alcohol (200–300 cP)[11] < HDTBr + 1-hexadecanesulfonate (~400 cP).[11] It is clear that the apparent microviscosity of 6-In-11$^+$ is fairly large when it is included in cyclodextrins. The microviscosity values derived for α-CD and β-CD suggest that the location of the indolyl group is not simply "hanging free" in the water for these complexes but is weakly bound near the exterior of the cavity of the cyclodextrin via hydrophobic interactions of the side chain(s). Models suggest that the α- and β-CD cavity is too small to allow inclusions of the 11-carbon hydrocarbon group and that only the hexyl group is small enough to be inserted into the cavity. On the other hand, in the case of γ-CD, the entire probe is capable of fitting in the cavity.

Conclusion

It should be stressed that except for the NMR studies, the results of this investigation are derived from measurements of an *electronically excited probe* and not the ground state. The time scales of the measurements are sufficiently short (≲10 ns) that we expect that the results will reflect the initial general spatial location of the probes: i.e., the exit rate of the included probe is much slower than the rate of emission. However, the polarity of the electronically excited indolyl chromophore of 6-In-11$^+$ is expected to be different from that of the ground state, so that properties that depend on polar interactions surely will be different for the two states. Thus, the λ_{max} and τ measurements probably reflect the equilibrium position of the excited probe, and the η evaluations refer to the tumbling state.

Acknowledgment. We express our gratitude to the National Science Foundation for its generous support of this work and to Professor Gregorio Weber for an important discussion of this research and for suggesting an experiment to differentiate intracavity motions of the probe from those of the complex of probe and CD.

Registry No. 6-In-11$^+$, 51097-79-1; α-CD, 10016-20-3; β-CD, 7585-39-9; γ-CD, 17465-86-0.

Structure and Conformation of 8-Bromo-9-β-D-xylofuranosyladenine in the Solid State and in Solution[1]

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Abstract: The three-dimensional structure of 8-bromo-9-β-D-xylofuranosyladenine, an analogue of the antimetabolite xylofuranosyladenine, was determined by X-ray crystallography. The crystals belong to the triclinic space group $P1$, and the cell dimensions are a = 8.946 (1), b = 16.510 (8), and c = 7.140 (1) Å; α = 90.76 (3), β = 89.10 (6), and γ = 103.72 (1)°. In the unit cell there are three molecules of the nucleoside ($C_{10}H_{12}N_5O_4Br$) and two molecules of water. The structure was solved by the heavy-atom method and the refinement converged at R = 0.037 for 4200 observed reflections. All three nucleoside molecules adopt the syn conformation about the glycosidic bond. In two of the molecules the xylose ring has the C(4′)exo–C(3′)endo pucker, and there is an intramolecular O(3′)–H···N(3) hydrogen bond. In the third molecule the sugar ring pucker is C(2′)endo, and there is an O(5′)–H···N(3) intramolecular bond. The solid-state data, together with a new modified version of the Karplus relationship, were profited from to refine the results of previous NMR analyses of the solution conformations of 9-β-D-xylofuranosyladenine and its 8-bromo analogue. The new relationship, proposed by Haasnoot et al. (*Org. Magn. Reson.* **1981**, *15*, 43–52), proved distinctly superior to previous versions for conformational analyses of xylofuranosyl nucleosides.

The solution conformations of 9-β-D-xylofuranosyladenine (xyloA),[3] of some of its *O*′-methyl derivatives, and of 8-Br-xyloA have been determined with the aid of ^{1}H NMR spectroscopy.[4,5] The present article describes the solid-state structure and conformation of 8-Br-xyloA and a comparison with solution data. This is the first report on the solid-state structure of a β-D-xylofuranosyl nucleoside.

Purine nucleosides with bulky substituents at C(8) are usually constrained by steric hindrance to the syn conformation about the glycosidic bond. The earliest crystallographic study specifically

(1) Issued as NRCC No. 19984.
(2) (a) National Research Council of Canada. (b) University of Warsaw.
(3) Abbreviations employed are the following: xyloA, 9-β-D-xylofuranosyladenine; 8-Br-xyloA, 8-bromo-9-β-D-xylofuranosyladenine.
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