comparison of their retention times with those of the authentic primary and secondary iodides.

Procedure for Gas-Phase Reaction. Reactions were carried out in 100-, 500-, and 1000-mL reaction vessles. Iodine monochloride was weighed into a small glass tube and placed in a reaction vessel which had been wrapped with aluminum foil. Similarly, the appropriate amount of cyclohexane was weighed into the vessel. The reaction vessel was then attached to a vacuum line and degassed by using the freeze-thaw method. in the case of the reactions with neopentane or propane a known amount of alkane was distilled into the reaction vessel. The vessel was then sealed under vacuum and placed in a thermostatically controlled water bath set at 36 °C. After adequate time to reach thermal equilibrium (15 min) was allowed, the vessel was irradiated for 10 min with a 300-W incandescent light.

The reactants were frozen (−198 °C), the vessel opened, a known amount of an external standard (undecane) added, and the contents extracted with Freon 113. The resulting solution was analyzed with an HP5840 gas chromatograph fitted with a 50-m methylsilicone capillary column. Yields of compounds were calculated by using calibration factors determined with known mixtures of standard and the authentic compounds. Results are summarized in Tables I and II.

The Liquid-Phase Reaction with Cyclohexane. A 2-mL aliquot of a 0.25 M iodine chloride solution in carbon tetrachloride was added to 2 mL of cyclohexane in a Pyrex ampule. After being degassed, sealed, under vacuum, and equilibrated in a water bath at 10 °C, the ampule was irradiated with a 140-W Hanovia UV lamp for 5 h. Other ampules were wrapped in aluminum foil and placed in the water bath at the same temperature for the same time. Solutions were analyzed by gas chromatography; results are summarized in Table I.

The Liquid-Phase Reaction with Iodocyclohexane. Solutions of iodine monochloride (0.00341 mmol) and iodocyclohexane (0.0065 mmol) in carbon tetrachloride (5 mL) were prepared. Aliquots of each (2 mL) were added to Pyrex ampules at −78 °C. The ampules were wrapped in foil, evacuated, sealed under vacuum, and then placed in a water bath at 10 °C for 5 h. The products were determined by GC analysis; results are given in Table I.

Registry No. ICl, 7790-99-0; cyclohexane, 110-82-7; neopentane, 463-82-1; propane, 74-98-6; iodocyclohexane, 626-62-0; chlorocyclohexane, 542-18-7; *trans*-1,2-dichlorocyclohexane, 822-86-6; *trans*-1-iodo-2-chlorocyclohexane, 33427-17-7; neopentyl iodide, 15501-33-4; 2-chloro-2-methylbutane, 594-36-5; 2,3-dichloro-2-methylbutane, 507-45-9; cyclohexene, 110-83-8; neopentyl alcohol, 75-84-3; 2-iodopropane, 75-30-9; 1-iodopropane, 107-08-4.

Modification of Chemical Reactivity via Inclusion Complex Formation: Photochemistry of Dibenzyl Ketones and Benzyl Phenylacetates

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In the context of employing "inclusion complexes" as a medium for organic photochemical reactions, we have investigated the photochemical behavior of dibenzyl ketones and benzyl phenylacetates using deoxycholic acid (DCA), Dianin's compound, and cyclodextrin (CD) as hosts in the solid state. Results on cage effect suggest that the translational motion of the benzyl radical pairs is restricted in all three media and totally in Dianin's compound. Products resulting from rearrangement of dibenzyl ketones were formed upon photolysis in Dianin's compound and cyclodextrin and were absent in deoxycholic acid. The absence of rearrangement in DCA and its presence to varied extents in Dianin's compound and cyclodextrin is suggested to be an indication of the restriction imposed by the host on the reorientational process of geminate radical pairs.

In the context of the study of reactivities of guest molecules and the way in which this reactivity is governed by the environment, the field of "inclusion complex" holds considerable promise. An essential characteristic of the host in the inclusion complex is its ability to form a solid structure with hollow spaces of large enough dimension to house prospective guests. Crystalline inclusion compounds may be subclassified as true clathrate-type, in which the guest molecules are imprisoned in discrete closed cavities or cages (Dianin's compound, cyclodextrin), the channel-type, in which the guest species are accommodated in continuous canals running through the crystal (deoxycholic acid, urea), and the layer-type where the guest component is situated between bands of the host structure (graphite). Zeolites belong to an intermediate class possessing cavities interconnected by channels. Significant changes in reaction product ratios have been effected by carrying out photochemical reactions in DCA and related matrices.[1] Thus the way was opened for employing inclusion complexes as a medium for organic photochemical studies.[2] Results described below on photochemical studies of dibenzyl ketones and benzyl phenylacetates using deoxycholic acid (DCA), Dianin's compound, and cyclodextrin (CD) as the host in the solid state represent our further interest in exploring the "host–guest" chemistry

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Table I. Product Distribution upon Photolysis of Dibenzyl Ketones in Various Host Media in Solid State

host	guest:host[a] ratio	complex, mp, °C	% products[b]				cage effect,[d] %
			AA	AB	BB	RP[c]	
		Dibenzyl Ketone					
α-CD	1:1.3		99			1	
β-CD	1:1	263	91			9	
γ-CD	1:1		81			19	
DCA	1:8	155	99			0	
Dianin's compd	1:45	169	95			5	
		p-Methylbenzyl Benzyl Ketone					
β-CD	1:1.4	229	1	86	1.5	12	95
DCA	1:8	170	1.5	97	1.5	0	94
Dianin's compd	1:22	166–167		98		2	100
		α-Methylbenzyl Benzyl Ketone					
β-CD	1:1	251	1.6	95	1.3	2	94
DCA	1:8	163	1.0	98	1.0	0	96
Dianin's compd	1:46	166–167		98		2	100

[a] Estimated on the basis of GC analysis; yields calcualted with respect to reacted ketone. [b] Estimated by GC with an internal standard; error limit ±2%. [c] RP corresponds to rearranged products 1-phenyl-4′-methylacetophenones and 1-phenyl-2′-methylacetophenones. [d] Calculated according to the formula (AB − (AA + BB))/(AA + AB + BB) × 100%.

Table II. Product Distribution upon Photolyses of Benzyl Phenylacetates in Various Host Media in Solid State

host	guest:host[a] ratio	complex mp, °C	% products[b]		
			AA	AB	BB
		p-Methylbenzyl Phenylacetate			
β-CD	1:1	258	<1	≥99	<1
DCA	1:8	184	<1	≥99	<1
Dianin's compd	1:51	164	<1	≥99	<1
		Benzyl (*p*-Methoxyphenyl)acetate			
β-CD	1:1.3	262	<1	≥99	<1
DCA	1:8	185	<1	≥99	<1
Dianin's compd	1:51	166	<1	≥99	<1
		p-Methylbenzyl (*p*-Methoxyphenyl)acetate			
β-CD	1:1.4	256	<1	≥99	<1
DCA	1:8	182	<1	≥99	<1
Dianin's compd	1:54	163	<1	≥99	<1

[a] Estimated on the basis of GC analysis; yields calculated with respect to reacted ketone. [b] Estimated GC with an internal standard; error limit ±2%.

to achieve selectivity in photochemical reactions.

The photodecarbonylation of dibenzyl ketones in homogeneous fluid solution occurs via a free-radical pathway in which coupling products (1,2-diarylethanes) are formed in quantitative yield.[3] For an unsymmetrical dibenzyl ketone (ACOB) the coupling products AA, AB, and BB are formed in the expected statistical ratio of 1:2:1. The solution photolysis of unsymmetrical benzyl phenylacetate yields 1,2-diarylethanes, but a marked cage effect has been noted in the more viscous solvents (e.g., 4-methylbenzyl 4-methoxyphenylacetate, 1:2.5:1 in dioxane and 1:5:1 in 2-propanol).[4] Photolysis of dibenzyl ketones and benzyl phenylacetates have been exploited extensively in several anisotropic environments—micellar solution,[5] silica surfaces,[6] uncoated glass surfaces,[7] and liquid crystalline media.[8] The reaction has been shown to result in enhanced cage recombination of geminate radical pairs and in marked ^{13}C enrichment of recovered starting ketones. Useful information regarding these anisotropic media has also been obtained through the use of the above reaction. In the present study the photochemical behavior of three dibenzyl ketones (**1**–**3**) and three benzyl phenyl acetates (**4**–**6**) has been explored for understanding the influence of cavity or canal upon chemical reactions. Our results presented below indicate that generation of the two radicals A° and B° in the cavity or canal effectively sequesters these reactive species in which translational and rotational motions are restricted. This results in a dramatic enhancement of selectivity in formation of AB over AA and BB.

Results

Addition of dibenzyl ketones and benzyl phenylacetates to saturated aqueous solutions of β-cyclodextrin precipitated a white solid. The solid was washed with excess of water and hexane and dried at 55 °C. Microcrystals of the inclusion complexes of DCA with the above carbonyl compounds were obtained by slow evaporation of methanol from an ice-cold solution containing excess of DCA. Dianin's compound complexes were prepared by slow crystallization from solutions of "empty" Dianin's compound in excess of liquid guest molecules. In some cases mild heating (~40 °C) was required to maintain the guest molecules in the molten state. DCA and Dianin's compound complexes were washed several times with excess of hexane and dried at 55 °C. All three complexes (cyclodextrin, DCA, and Dianin's compound) were obtained as white dry microcrystalline solids and were used as such for photolysis. Existence of true complexes in all cases was inferred from their mp, X-ray powder diffraction pattern, and solid-state NMR spectra. The X-ray powder pattern of the precipitated solid complex differed from those of

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the hosts. The solid-state ^{13}C NMR spectra exhibited peaks corresponding to the guests in addition to the hosts. The host–guest ratio in each case was determined as follows. The amount of the guest present in a weighed sample of the complex was determined by GC using internal standard after extracting the guest with suitable solvent. Results are presented in Tables I and II. Close to a 1:1 ratio observed with cyclodextrin is consistent with our belief that the majority of the host molecules contain one guest molecule in their cavity. DCA is known[9] to form complexes with host–guest ratios ranging from 1:1 to 8:1. Formation of an 8:1 complex is known with long chain fatty acids (C_{15}–C_{29}) as guests, and the canal length in these cases is believed to be ~28.9 Å. Although, generally the host-guest ratio in the case of Dianin's compound[10] is ~6, the unexpectedly large value obtained here is an indication of either the poor method of complex preparation or distortion of the host structure by the guest molecule. It is quite likely that large size of the guests imposes strain on the system and thus keeps most of the pockets empty. Since none of the complexes gave suitable single crystals for X-ray crystallographic studies, no such investigation was pursued.

Photolyses of the solid complexes were done with 450-W medium-pressure mercury lamp either in degassed and sealed Pyrex tubes (in the case of dibenzyl ketones) or in quartz tubes (for benzyl phenylacetates). After irradiation, the products were extracted by dissolving the complex in suitable solvents and analyzed by GC. Product ratios in various media are summarized in Tables I and II. In addition to the decarbonylated products, small amounts of rearranged ketones 1-phenyl-4′-methylacetophenone and 1-phenyl-2′-methylacetophenone were obtained upon photolysis of dibenzyl ketone 1 in nonhomogeneous media such as micellar solution,[11] silica surface,[6] and zeolite.[2] Similar rearranged products are also expected for other dibenzyl ketones. In the present study, rearranged products were obtained in cyclodextrin and Dianin's compound and were absent (within GC detection limit, 1% of reacted ketone) in DCA matrix. Another interesting feature to come to light was the absence of cage escape products in Dianin's compound and their very minor amounts in cyclodextrin and DCA matrix (~1–2%). However, with benzyl phenylacetates only one product (AB) was obtained in quantitative yield in all three media.

Discussion

In the absence of structural data on the inclusion complexes under investigation we base our arguements on the structural details available for the inclusion complexes of DCA, Dianin's compound, and cyclodextrin with other guest molecules. The cavity/canal characteristics of these are briefly described below. DCA[12] crystallizes in such a manner as to leave a canal in which the guest can be closely confined. The DCA–guest interactions are hydrophobic, and thus the best fit depends principally on the size and shape of the guest molecule. The channel size in the *ab* plane is ~4 × 6 Å, and the length of the channel varies (*c* axis) depending on the guest molecule. The mole ratio of the DCA to guest component depends upon the size of the guest molecule and so varies from 1 to 8. Six molecules of Dianin's compound form a cage, and the cages are of an hourglass shape that has been cut horizontally across the middle of each globe.[13] The cavity has a length of approximately 11 Å with a midpoint width of 4.2 Å and maximum upper and lower widths of 6.3 Å. The ends of each cage have a width of 2.8 Å and are formed by six hydrogen-bonded hydroxyl groups. Cyclodextrins,[14] one of the most commonly used "host" systems possess hydrophobic cavities that are able to include a variety of organic compounds whose character may vary from hydrophobic to ionic. Internal diameters and depth of cyclohexaamylose or α-cyclodextrin (4.2–8.8 and 7.8 Å), cycloheptaamylose or β-cyclodextrin (5.6–10.8 and 7.8 Å), and cyclooctaamylose or γ-cyclodextrin (6.8–12.0 and 7.8 Å) provide cavities for appropriately sized guest molecules. Cavity shapes and dimensions of the above three host systems that are used in the present study are illustrated in the Figure 1. While DCA and Dianin's compound belong to a category of polymolecular inclusion compounds, cyclodextrin belongs to monomolecular inclusion compounds.

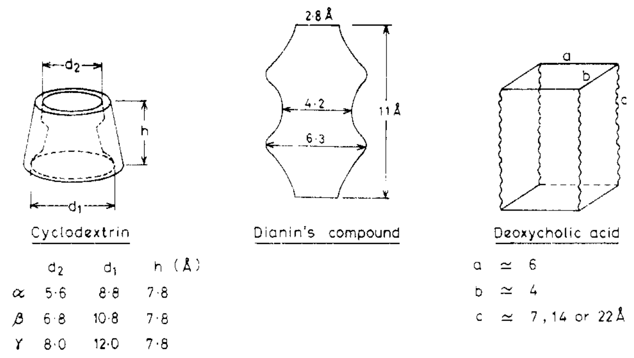
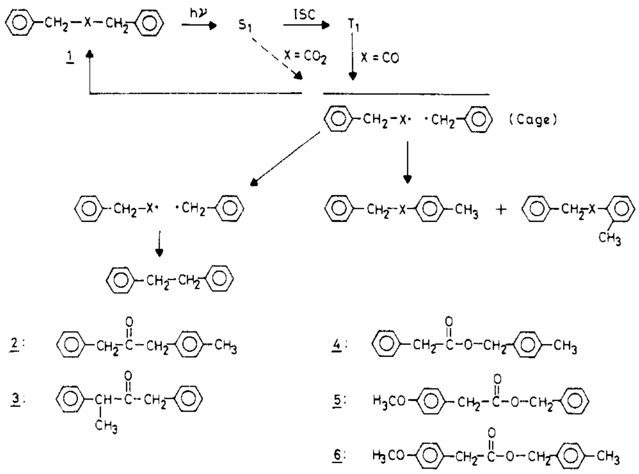


Figure 1. Cavity shapes and dimensions of the three host systems.

Scheme I



Some of the interesting results that need elaboration are the following. The cage effect is total (100%) for benzyl phenylacetates, whereas it is so only in Dianin's compound for dibenzyl ketones. Very small amounts of noncage products (~2%) are formed in the DCA and cyclodextrin matrixes (Table II). Rearranged products are formed only in Dianin's compound and cyclodextrin. Surprisingly they were absent in DCA medium. A mechanism for photolysis of 1–6 is presented in Scheme I. The difference in cage effect between benzyl phenylacetates and dibenzyl ketones may also be understood on the basis of the different spin states involved in the reaction. The decomposition of 1–3

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is established[3] as being via triplet, while analogous esters[4] are believed to follow a singlet pathway. Long lifetime of the triplet benzyl radical pairs (derived from dibenzyl ketones) probably allows them to move farther in the host matrix and thus may result in a small percentage of noncage products.

Unit cage effect observed for **1**–**3** in Dianin's compound is completely in accord with the structure of the Dianin's compound. Although the cavity size is large enough to accommodate **1**–**3**, the ends of the cavity are narrow and therefore the radical pair cannot escape from the cavity. Indeed 100% cage effect is expected. Small noncage products (~2%) observed in DCA and cyclodextrin are unexpected as one would have expected 100% cage effect in solid matrix. However, the packing arrangements in both systems are such that there is a canal present. Therefore, a small percent of escape of the geminate radical pairs via the canals is not surprising. Another possibility is that a few percent of noncage products may also derive from small pockets of bulk liquid trapped by polycrystalline sample. This possibility cannot be ruled out on the basis of available structural information. Thus the results on cage effect suggest that the translational motion of the benzyl radical pairs is restricted in all three media.

Rearranged products (substituted acetophenone) were formed upon photolysis of dibenzyl ketones in Dianin's compound and cyclodextrin. These products have been proposed to arise via recombination of the original acyl benzyl radical pair with subsequent rearomatization (Scheme I).[6,11] In the case of dibenzyl ketone and α-methylbenzyl benzyl ketone para and ortho coupling products are expected, whereas *p*-methylbenzyl benzyl ketone could give more than two, depending upon the site of cleavage. Only in the case of dibenzyl ketone was unequivocal identification of 1-phenyl-4′-methylacetophenone made by comparison with an authentic sample. In other cases products eluting in the GC very close to the starting ketone were presumed to be rearranged products. The opportunity for rearrangement would be enhanced by the longer lifetime of the geminate radical pair (phenylacetyl radical and benzyl radical) and by their freedom to undergo rotational motion within the restricted space. There is as yet little information about motional processes of guest molecules in complex clathrates. In the absence of such knowledge, chemical studies such as this can be informative. The large cage effect observed in all three media for **1**–**3** certainly suggests that the host medium is greatly restricting the movement of benzyl radicals. Therefore, the absence of rearrangement in DCA and its presence to varied extents in Dianin's compound and cyclodextrin is probably an indication of the restriction imposed by the host on the reorientational process of geminate radical pairs. The rotational process required for the rearrangement certainly seems to depend on the space available for the guest molecule. Yield of 1-phenyl-4′-methylacetophenone from dibenzyl ketone increases with the cavity size of the cyclodextrin (γ > β > α). Therefore absence of rearrangement in DCA is possibly due to the small size (4 × 6 Å) of the canal. Dianin's compound having slightly larger cavity (6.3-Å diameter) allows for rearrangement but not to the same extent as cyclodextrin (7–11-Å diameter).

Thus the results presented here illustrate that interesting effects can be obtained by carrying out photochemical reactions using organic host lattices. In view of the possibilities of predesigning a host from our knowledge of the thousands that have been proposed or prepared,[15] it becomes immediately obvious that the field of selective photochemistry through clathration stretches limitlessly ahead.

Experimental Section

Materials. Dibenzyl ketone (Aldrich) was twice distilled prior to use. Dibenzyl ketones **2** and **3** and benzyl phenylacetates **4**–**6** were prepared by following reported procedures.[4,16] All samples were purified by preparative TLC (silica gel, hexane–benzene). Cyclodextrins (α, β, and γ) and deoxycholic acid were obtained from Sigma and were used as received. Dianin's compound was prepared by following the literature method.[17] unsolvated Dianin's compound was obtained by dissolving the above compound in hot aqueous NaOH and passing CO_2 through the solution for about 30 min.

Apparatus. UV–vis absorption spectra were recorded on a Shimadzu UV-180 double-beam spectrometer. IR data were obtained with a Perkin-Elmer infrared spectrometer (Model 730). Varian T-60 and Bruker HW-270 FT NMR spectrometers were used for recording ^1H and ^{13}C NMR spectra, respectively. Solid-state ^{13}C NMR spectra were obtained by Dr. J. Ripmeester using a Bruker FT CXP-200 instrument. X-Ray powder photographs were recorded with a Phillips powder diffractometer employing monochromated Cu Kα radiation. Gas chromatographic analyses were carried out on a Chemito GC instrument (Model 3800) fitted with a SE-30 5% column (8 ft × $^1/_8$ in.) and a thermal conductivity detector. Irradiations were carried out with either a 450-W medium-pressure mercury lamp or a Rayonet reactor (RPR-100) fitted with 254-nm lamps.

Preparation of Inclusion Complexes. Cyclodextrin complexes were prepared as below. To a saturated aqueous solution of cyclodextrin, equimolar amounts of the guest molecule were added and stirred for 24 h. The white precipitate that formed was filtered, washed with cold water and ether, and dried at 50 °C for 10 h. Microcrystals of DCA complexes were obtained by slow evaporation of the solvent from a methanol solution of DCA (4 mM) and guest compound (1 mM). DCA complexes were washed several times with cold hexane and dried. Dianin's complexes with **1**–**6** were prepared by slow crystallization of unsolvated Dianin's compound from the guest liquids **1**–**6**. In certain cases heating to 80 °C was required to dissolve the host. Microcrystalline complexes thus obtained were washed several times with hexane and dried. Inclusion complexes were characterized by their mp, X-ray powder photographs, and solid ^{13}C NMR spectra. The host–guest ratio was determined by GC analysis. The amount of **1**–**6** present in a known amount of the complex were determined by the GC integration of the guest peak with respect to the added internal standard (diphenyl ethane).

Photolysis. Irradiation of dibenzyl ketone complexes were carried out in a Pyrex tube using a 450-W medium-pressure mercury lamp and that of benzyl phenylacetates complexes in quartz tubes using a Rayonet reactor fitted with 254-nm lamps. Samples were degassed (10^{-3} mm) prior to irradiation and were rotated periodically during irradiation. Generally irradiations were stopped at ~20% conversion (8–12 h), and products were extracted as follows. Cyclodextrin complexes were dissolved in warm water and extracted with chloroform. DCA and Dianin's complexes were dissolved in hot aqueous methanol and extracted with hexane–chloroform mixture (9:1). Products were analyzed by GC and ^1H NMR.

Acknowledgment. V.R. thanks the Council of Scientific and Industrial Research, Government of India, and N.J.T. the National Science Foundation and the Air Force Office of Scientific Research for financial support. Dr. J. Ripmeester is thanked for ^{13}C NMR spectra of the solid complexes.

Registry No. Dibenzyl ketone–(α-CD) (1:1.3), 99766-03-7; dibenzyl ketone–(β-CD) (1:1), 99765-87-4; dibenzyl ketone–(γ-CD)

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(1:1), 99765-88-5; dibenzyl ketone–DCA (1:8), 99765-89-6; dibenzyl ketone–Dianin's compound (1:45), 99765-90-9; *p*-methylbenzyl benzyl ketone–(β-CD) (1:1.4), 99766-04-8; *p*-methylbenzyl benzyl ketone–DCA (1:8), 99765-91-0; *p*-methylbenzyl benzyl ketone–Dianin's compound (1:22), 99765-92-1; α-methylbenzyl benzyl ketone–(β-CD) (1:1), 99765-93-2; α-methylbenzyl benzyl ketone–DCA (1:8), 99765-94-3; α-methylbenzyl benzyl ketone–Dianin's compound (1:46), 99765-95-4; *p*-methylbenzyl phenylacetate–(β-CD) (1:1), 99765-96-5; *p*-methylbenzyl phenylacetate–DCA (1:8), 99765-97-6; *p*-methylbenzyl phenylacetate–Dianin's compound (1:51), 99765-98-7; benzyl (*p*-methoxyphenyl)acetate–(β-CD) (1:1.3), 99766-05-9; benzyl (*p*-methoxyphenyl)acetate–DCA (1:8), 99765-99-8; benzyl (*p*-methoxyphenyl)acetate–Dianin's compound (1:51), 99766-00-4; *p*-methylbenzyl (*p*-methoxyphenyl)acetate–(β-CD) (1:1.4), 99766-06-0; *p*-methylbenzyl (*p*-methoxyphenyl)acetate–DCA (1:8), 99766-01-5; *p*-methylbenzyl (*p*-methoxyphenyl)acetate–Dianin's compound (1:54), 99766-02-6.

NMR Analysis of Boromycin Sodium Complex and Sodium Desvalinoboromycinate

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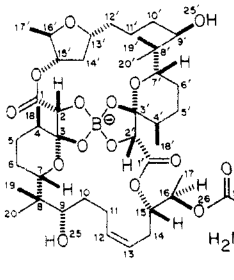
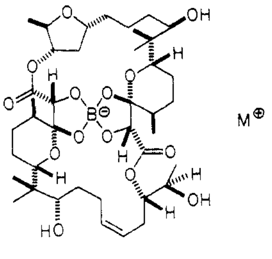
Detailed ^1H and ^{13}C NMR assignments were made to the sodium complex of boromycin (7) by using two-dimensional chemical shift correlation, NOE difference spectroscopy, and long-range heteronuclear shift correlation (LR-HETCOR). The latter technique was shown to provide a valuable means for assigning ^{13}C signals, including the three carbonyl groups of 7, by establishing connectivities across quaternary carbons. Similar protocols were used for assigning ^1H NMR signals to the sodium derivative of desvalinoboromycin (8). The results of NOE experiments on 7 are consistent with a solution conformation that approximates the tertiary structure of 2, as revealed by an X-ray crystal structure.

Boromycin (1), first isolated from *Streptomyces antibioticus* (Waksman et Woodruff) obtained from an African soil sample,[2] has been encountered in several antibiotic screens, where its activity against gram-positive bacteria, certain fungi, and protozoae has been evaluated.[3] Although early investigation of 1 as a potential coccidiostat has not led to its commercial development,[4] interest in the properties of this ionophore has continued unabated. In particular, the ability of 1 to encapsulate alkali metal cations and transport them across artificial membrane systems has provided a useful tool for studying the mode of action of this antibiotic, which has been shown to reduce the permeability barrier of the cytoplasmic membrane toward potassium ions.[5]



1, M = H
7, M = Na

Structural studies of boromycin by Dunitz, Prelog, et al.[6] revealed that the molecular architecture of this substance is exquisitely designed for its role as an ionophore. An X-ray crystallographic analysis of the rubidium complex 2, obtained by selective removal of the D-valine residue from 1, established the complete stereostructure of the macrodiolide, and showed that inward directed oxygen atoms provide an ideal geometry for accommodation of the metal ion. Conversely, the hydrophobic segments of the structure form a nonpolar exterior surface. A similar conformation is observed in the X-ray crystal structure of 3, in which the borate is absent.[7]



2, M = Rb
8, M = Na

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[1] (a) Oregon State University. (b) The Ohio State University. (c) Purdue University.

[2] Hutter, R.; Keller-Schierlein, W.; Knüsel, F.; Prelog, V.; Rodgers, G. C., Jr.; Suter, P.; Vogel, G.; Voser, W.; Zahner, H. *Helv. Chim. Acta* **1967**, *50*, 1533.

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