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Substituent Effects in the Hydrolysis of Quinoline–Boranes

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Rates of hydrolysis of quinoline–boranes (QB) in aqueous dioxane are dramatically influenced by substitution in both the hetero and all-carbon ring systems. Effects of 3-, 4-, and 6-substituents appear to be due to electronic induction. Rates obtained at 25 °C with 3- and 4-substituted quinoline–boranes correlate with Hammett σ_m and σ_p parameters for both acid-independent and acid-catalyzed pathways, which are depicted respectively by k_1 and k_2 in the expression $-d[QB]/dt = [QB](k_1 + k_2[H^+])$. Results are consistent with previously proposed mechanisms involving, for the first-order process, dissociative loss of BH_3 and, for the acid-catalyzed reaction, electrophilic displacement of BH_3 via cis attack of hydrogen ion at nitrogen. Methyl substitution at C-2 enhances k_1 presumably through a steric effect and k_2 through an inductive effect. A significant steric effect of the peri hydrogen at C-8 is suggested through a comparison of kinetic parameters for substituted quinoline–boranes with those of isoquinoline–borane, wherein k_1 may be observed to change by over 4 orders of magnitude. Such substituent effects are significant in the projected synthetic use of heteroaromatic amine–boranes in protic media.

Introduction

Substituted quinoline–boranes are utilized in the preparation of tetrahydroquinolines, which are employed in the synthesis of natural products and also used in studies of mechanisms of selected reactions.[1-3] As expected, the reactivities of quinoline–boranes and corresponding tetrahydroborate derivatives are influenced by the nature and position of substituent groups in both the hetero and all-carbon ring systems. Since many such transformations are studied in protic media, the influence of ring substitution on the hydrolytic kinetic stability of quinoline–boranes is of particular relevance. The present study was undertaken to elucidate such effects and is an extension of investigations of effects of B- and N-substitution on the kinetics and mechanism of hydrolysis and hydride oxidation in amine–boranes.[4-16]

Experimental Section

Materials. Quinoline and isoquinoline were obtained from Matheson Coleman and Bell, 3-methyl- and 6-nitroquinoline were obtained from Lancaster Syntheses Ltd., 8-methylquinoline was obtained from K and K Laboratories, and other substituted quinolines were obtained from Aldrich. Tetrahydrofuran (THF), obtained from Fisher or Mallinckrodt, was doubly distilled, once from CaH_2 and subsequently from sodium and benzophenone. A 1 M solution of tetrahydrofuran–borane (THF·BH_3) in THF was obtained from Aldrich. 1,4-Dioxane, obtained from Mallinckrodt, was boiled under reflux with HCl (20 mL of concentrated HCl/L of dioxane) for about 2 h. The solution was then refluxed for several hours over KOH pellets (60 g of KOH/L of dioxane) and, on cooling, was decanted from KOH and refluxed and distilled from $LiAlH_4$ solution. Analytical reagent grade KIO_3 was obtained from Mallinckrodt or MCB, KI from Mallinckrodt, Fisher, or Kodak, and Vitex starch from G. Frederick Smith Co. Solutions 0.02 N in $Na_2S_2O_3$ were prepared by using reagent grade $Na_2S_2O_3 \cdot 5H_2O$ (Mallinckrodt) or by dilution of 0.1 N Acculute solutions obtained from Anachemia Chemicals Ltd., and subsequently standardized against 0.05 N KIO_3.

Preparation of Amine–Boranes. Amine–boranes derived from quinoline, 3-methylquinoline, 4-methylquinoline, 6-methylquinoline, 6-methoxyquinoline, and isoquinoline were each synthesized according to a general procedure exemplified below for the preparation of 6-methylquinoline–*N*-borane. The remaining examples were not sufficiently stable to survive the aqueous workup and/or purification by recrystallization. These were synthesized by modifying the procedure to use a minimum amount of solvent thus allowing (ideally) the amine–borane to crystallize directly from the reaction mixture at low temperature. Addition of a slight molar excess of neat 2-methylquinoline to 1 M BH_3·THF in THF, according to the description below, produced a crude product, which was spectrally pure by NMR. Application of the method to 8-methylquinoline gave a free-flowing granular white solid with a sharp melting point, which nevertheless contained 12 mol % of occluded free amine. The NMR spectrum of crude 3-bromoquinoline–*N*-borane prepared similarly indicated a trace amount of an unidentified impurity containing aliphatic hydrogens. In all cases, the ^{11}B NMR spectrum showed only one boron absorption (quartet).

The preparations of 4-chloro- and 6-nitroquinoline–*N*-borane involved the addition of slightly less than 1 molar equiv of 1 M BH_3·THF in THF to a saturated solution of the solid amine in THF at 0 °C. The inverse mode of addition was necessary in the latter case to avoid reduction of the nitro group. These amine–boranes failed to precipitate at −78 °C and were isolated simply by removing the solvent in vacuo. Virtually pure 4-chloroquinoline–*N*-borane was obtained by recrystallization of the crude product from isopropyl alcohol but with substantial loss of material. Crude 6-nitroquinoline–*N*-borane, containing 40 mol % of the corresponding free base, was used directly without complication since all hydrolysis reactions were carried out under pseudo-first-order conditions. Again, only one boron-containing compound was present in these mixtures.

See Tables I–III for physical, analytical, and spectral information. All NMR data were recorded by using a Varian XL-300 spectrometer operating at 299.94 MHz for ^1H, 75.43 MHz for ^{13}C, and 96.23 MHz for ^{11}B.

Preparation of 6-Methylquinoline–*N*-Borane. To a magnetically stirred solution of 1.61 g (11.2 mmol) of 6-methylquinoline in 50 mL of anhydrous THF under N_2 atmosphere at −78 °C was added 12.0 mL of 1.0 M BH_3·THF complex in THF (12.0 mmol) via syringe. After 30 min at −78 °C, the entire reaction mixture was poured into a separatory funnel containing 50 mL of water. The product was removed by extraction with CH_2Cl_2 (1 × 55 mL and 1 × 10 mL), and the combined organic extracts were dried over Na_2SO_4. Rotary evaporation of the solvent yielded a solid, which was recrystallized from approximately 40 mL of isopropyl alcohol to give 1.38 g (79%) of pure 6-methylquinoline–*N*-borane, mp 105.0–106.5 °C.

Preparation of 2-Methylquinoline–*N*-Borane. Freshly distilled 2-methylquinoline (2.30 g, 16.0 mmol) was added dropwise via syringe to 15.0 mL (15.0 mmol) of 1.0 M BH_3·THF complex in THF (stirred magnetically) under N_2 at 0 °C. The milky suspension was cooled to −78 °C and rapidly vacuum-filtered through a medium frit under N_2. The filtrate was washed with 5 mL of cold ether and dried under vacuum (0.1 mm, 25 °C, 2 h). The crude white amorphous product (1.71 g, 72%; mp 133.0–134.0 °C) was spectrally pure by NMR analysis.

Kinetic Experiments. All aqueous dioxane solutions were prepared with calibrated pipets and are reported as % by volume. Each hydrolysis

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Table I. Physical and Analytical Data for Amine–Boranes

amine	mp, °C	% yield[a]	anal.	^{11}B NMR,[b] ppm (J_{BH}, Hz)
quinoline	84.0–85.0	78	calcd: 75.59% C, 7.05% H found: 75.44% C, 6.96% H	−13.78 (96.4)
2-methylquinoline	133.0–134.0	72 (crude)	calcd: 76.49% C, 7.70% H found: 75.98% C, 7.86% H	−18.49 (97.7)
3-methylquinoline	114.0–116.0	38	calcd: 76.49% C, 7.70% H found: 76.89% C, 7.66% H	−13.86 (95.2)
4-methylquinoline	118.5–120.0	49	calcd: 76.49% C, 7.70% H found: 76.49% C, 7.63% H	−13.95 (94.3)
6-methylquinoline	105.0–106.5	79	calcd: 76.49% C, 7.70% H found: 76.43% C, 7.66% H	−13.87 (96.4)
8-methylquinoline	77.0–78.5	70 (crude)	88 mol % *N*-borane 12 mol % 8-methylquinoline	−8.81 (100.1)
3-bromoquinoline	100 dec	75 (crude)	>92% pure by integration (internal standard)	−13.06 (95.2)
4-chloroquinoline	65 dec	38 (100 crude)	>96% pure by integration (internal standard)	−13.60 (95.2)
6-methoxyquinoline	139.0–141.0	83	calcd: 69.42% C, 6.99% H found: 69.22% C, 6.93% H	−13.82 (90.3)
6-nitroquinoline	140 dec	100 (crude)	60 mol % *N*-borane 40 mol % 6-nitroquinoline	−13.12 (95.6)
isoquinoline	62.0–63.0	81	calcd: 75.59% C, 7.05% H found: 75.47% C, 7.23% H	−12.39 (95.2)

[a] Recrystallized unless otherwise indicated. [b] Relative to $BF_3 \cdot Et_2O$.

Table II. Proton Chemical Shifts (ppm vs. Me_4Si) of Amine–Boranes in $CDCl_3$ (10% w/v)[a]

	position								
amine	1	2	3	4	5	6	7	8	CH_3
quinoline		9.11	7.50	8.42	7.91	7.68	7.88	8.92	
2-methylquinoline			7.38	8.17	7.78	7.57	7.78	9.18	2.99
3-methylquinoline		8.95		8.15	7.80	7.63	7.79	8.84	2.50
4-methylquinoline		8.92	7.30		8.01	7.67	7.83	8.90	2.76
6-methylquinoline		9.00	7.44	8.29	7.63		7.67	8.77	2.54
8-methylquinoline		9.21	7.37	8.30	7.69	7.47	7.64		3.29
3-bromoquinoline		9.21		8.57	7.86	7.74	7.91	8.89	
4-chloroquinoline		9.05	7.63		8.29	7.80	7.96	8.96	
6-methoxyquinoline		8.89	7.41	8.26	7.10		7.47	8.79	3.94
6-nitroquinoline		9.37	7.78	8.71	8.91		8.65	9.19	
isoquinoline	9.26		8.36	7.82	7.93	7.88	7.75	8.02	

[a] protons attached to boron appeared as an extremely broad quartet in all cases between 2.1 and 3.6 ppm.

Table III. Carbon Chemical Shifts (ppm vs. Me_4Si) of Amine–Boranes in $CDCl_3$ (10% w/v)

	position										
amine	1	2	3	4	5	6	7	8	9	10	CH_3
quinoline		150.44	120.68	141.26	128.33	128.25	132.08	124.71	142.76	128.82	
2-methylquinoline		160.78	124.27	139.77	128.20	126.98	131.49	125.09	143.96	127.40	26.62
3-methylquinoline		152.05	130.63	139.89	127.61	128.15	130.93	124.42	141.13	128.72	18.58
4-methylquinoline		149.78	121.50	150.81	124.30	127.84	131.45	125.25	142.28	128.48	19.29
6-methylquinoline		149.43	120.60	140.48	127.00	138.53	134.26	124.32	141.31	128.94	21.35
8-methylquinoline		153.58	119.76	142.14	127.50	127.61	136.37	135.32	144.38	130.85	26.20
3-bromoquinoline		151.61	114.84	142.38	127.49	129.35	132.37	124.98	141.33	129.46	
4-chloroquinoline		149.92	121.10	143.44	124.71	129.22	132.92	125.54	147.57	126.94	
6-methoxyquinoline		147.77	121.01	139.71	105.39	158.67	124.67	126.13	138.70	130.38	55.76
6-nitroquinoline		153.59	122.94	142.94	124.47	146.45	125.30	127.45	144.80	128.01	
isoquinoline	150.41		139.53	122.93	126.57	133.44	129.35	128.49	127.94	135.61	

study was started by dissolving a weighed sample of amine–borane in about 100 mL of a specified aqueous dioxane solution contained in a thermostated Sargent or Freas Precision constant-temperature bath. For the 3-bromo and 8-methyl derivatives, an improved solubilization procedure involved dissolving the amine–borane in a prescribed volume of dioxane followed by the addition of a measured volume of H_2O. The temperature of the hydrolysate was maintained to ±0.05 °C.

Measurement of the rate of reaction was based upon determination of unreacted amine–borane according to a previously reported iodometric determination of soluble hydride.[8,17] Ten-milliliter portions of hydrolysate were periodically withdrawn and added to solutions containing known amounts of KIO_3. Hydrolysis was quenched by the addition of about 1 g KI followed by 5 mL of 6 *N* H_2SO_4. In each case, the KIO_3 was sufficient to generate I_2 in excess of that required to oxidized unreacted hydride according to $H^- + I_2 \rightarrow 2I^- + H^+$. For hydrolysates containing HCl, I_2 generation occurred immediately upon addition of KI. Residual I_2 was measured by titration with 0.02 N $Na_2S_2O_3$ using Vitrex starch indicator. Amine–borane concentrations were calculated from a knowledge of the hydride content obtained from a calculation of the consumed I_2.

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Results and Discussion

Amine–borane hydrolysis involves aqueous oxidation of hydridic (boron-bonded) hydrogen and is accompanied by formation of free amine and borate equilibrated between respective acidic and basic forms. Consistent with previous studies on alkyl, aryl and selected heterocyclic amine–boranes,[8] the hydrolysis of substituted quinoline–boranes (QB) proceeds via two pathways as depicted in (1). A study of the rate in the absence of added acid allows

$$-d[QB]/dt = [QB](k_1 + k_2[H^+]) \quad (1)$$

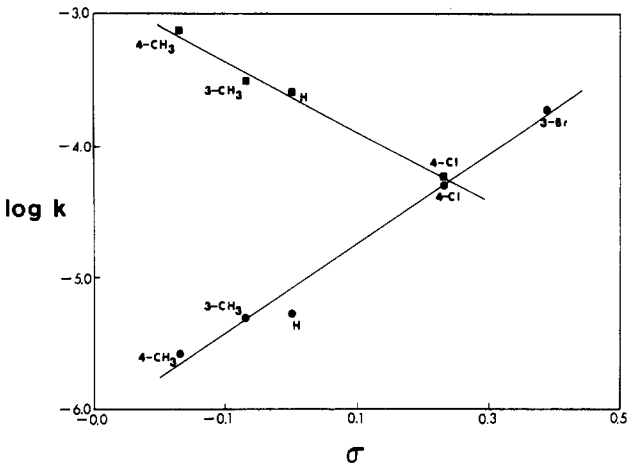

Figure 1. Correlation of hydrolysis rates with the Hammett equation, $\log (k/k_0) = \rho\sigma$: (●) $\log k_1$; (■) $\log k_2$. Data for 3- and 4-substituted quinoline–boranes are plotted vs. respective σ_m and σ_p parameters. σ values: *p*-CH_3, −0.17; *m*-CH_3, −0.07; H, 0.00; *p*-Cl, 0.23; *m*-Br, 0.39. For k_1, ρ = 3.41 (cc = 0.991); for k_2, ρ = −2.67 (cc = 0.994).

Table IV. Hydrolysis Rates of Substituted Quinoline–Boranes (QB) and Isoquinoline–Borane (IsQB) in 50% Aqueous Dioxane at 25 °C

substrate	10^5k_1,[a] s^{-1}	10^4k_2,[a] M^{-1} s^{-1}
QB	0.54	2.6
2-MeQB	18.4	6.3
3-MeQB	0.49	3.1
4-MeQB	0.28	7.4
6-MeQB	0.36	4.0
6-MeOQB	0.44	2.9
3-BrQB	19.2	
4-ClQB	5.1	
6-O_2NQB	9.1	
8-MeQB	700	
IsQB	0.046	15.6

[a] From eq 1.

direct determination of k_1, whereas k_2 is readily obtained from the slope of the line derived from the hydrogen ion dependence of the pseudo-first-order rate constant for a series of studies conducted in the presence of known excess hydrogen ion concentrations.

The effects of substituents in the 3- and 4-positions of the heterocyclic ring system parallel effects observed on substitution in meta and para positions of the aromatic ring in the hydrolysis of aniline–boranes in aqueous dioxane in that, relative to (unsubstituted) quinoline–borane, electron-withdrawing groups enhance the k_1 term whereas electron-releasing groups enhance k_2 (Table IV).[8] In Figure 1, such rates are shown correlated with Hammett σ parameters[18] for five derivatives for the first-order reaction and four derivatives for the acid-dependent pathway. Here σ_m and σ_p values are plotted against rate data obtained for the respective 3- and 4-substituted quinoline–boranes.

Such effects are consistent with previously proposed mechanisms of amine–borane hydrolysis[6-9,14] (summarized in Scheme I), in which the acid-independent pathway is presumed to involve rate-limiting loss of BH_3 via dissociative activation, with the k_2 term reflecting bimolecular electrophilic displacement of BH_3 through cis attack of solvated hydrogen ion at nitrogen,[9] perhaps at the electron density of the B–N bond. Evidence for general-acid catalysis of the latter process has been previously presented.[8] In each process, rapid hydrolysis of solvated BH_3 has been proposed, with no implication as to the lifetime of a solvated borane or even its existence as a kinetically significant intermediate. Electron-withdrawing substituents are expected to enhance a transition-state configuration involving development of increased electron density at nitrogen whereas electron-releasing groups expectedly favor the development of positive charge in the incipient quinolinium ion.

Scheme I

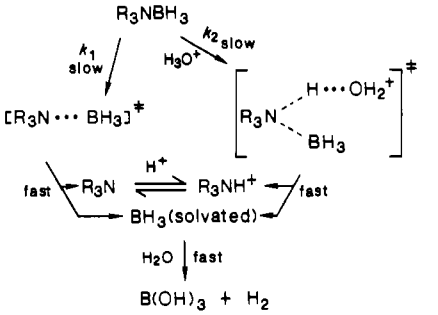

Table V. Effect of Solvent Composition on the Acid-Independent Hydrolysis of Quinoline–Borane and Derivatives at 25 °C

substrate	vol % dioxane/H_2O	10^5k_1,[a] s^{-1}	Y[b]	m[b]
QB	40/60	0.42	1.95	
	50/50	0.54	1.36	
	67/33	0.83	0.245	−0.19
	75/25	1.14	−0.373	
2-MeQB	40/60	14.3	1.95	
	50/50	18.4	1.36	
	60/40	24.0	0.715	−0.18
	70/30	31.8	0.013	
6-MeOQB	40/60	0.32	1.95	
	50/50	0.44	1.36	
	67/33	0.66	0.245	−0.20
	75/25	0.97	−0.373	
3-BrQB	40/60	15.9	1.95	
	50/50	19.2	1.36	
	60/40	25.1	0.715	−0.17
	67/33	33	0.245	
	75/25	44	−0.373	

[a] From eq 1. [b] $\log (k/k_0) = mY$.[20]

Table VI. Temperature Dependence of k_1 for Quinoline–Borane and 6-Methoxyquinoline–Borane in 50% Aqueous Dioxane

	10^5k_1, s^{-1}	
t, °C	QB	6-MeOQB
25.0	0.54	0.44
34.9	1.97	1.61
43.6	5.64	4.68
53.2	16.6	
53.5		15.1

A dissociative pathway for the first-order reaction is also supported by rate studies in solvents varying in dioxane–water content (Table V). As in previously reported investigations with *p*-toluidine–borane,[8] a linear correlation of $\log k_1$ with Grunwald–Winstein Y values,[20,21] produces a negative slope suggesting a transition-state configuration involving dissipation of the B–N dipole of the amine–borane. Whether the process should be regarded as purely dissociative (D), or a dissociative interchange (I_d) reaction[22] is uncertain in the absence of evidence as to the role of water in the activated complex.

The temperature dependence of k_1 for quinoline–borane and the 6-methoxy derivative (Table VI) yields activation parameters $\Delta H^\ddagger$ = 96.8 kJ mol^{-1} and $\Delta S^\ddagger$ = −21.7 J deg^{-1} mol^{-1} and $\Delta H^\ddagger$ = 98.7 kJ mol^{-1} and $\Delta S^\ddagger$ = −16.7 J deg^{-1} mol^{-1}, respectively. It

(18) Hammett, L. P. *Physical Organic Chemistry*; McGraw-Hill: New York, 1940.
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is possible that the negative entropy term is the result of a positive entropy contribution accompanying a dissociative process being offset by a solvation requirement for the incipient BH_3 group and free amine in the transition state.

Previous applications of the Hammett equation to reactions of quinoline derivatives have included a study of variations of reactivity, with position, of side-chain acid and ester functions.[23] Its application here must be considered with caution inasmuch as this linear free-energy relationship is designed for correlation of rates and equilibria of reactions occurring at aryl side chains. Nevertheless, a correlation of kinetic data for 3- and 4-substituted quinoline–boranes is probably not surprising if one considers the primary reaction site to be the electron pair of the B–N bond, and although quinoline–borane hydrolysis is quite sensitive to electronic inductive effects of hetero ring substituents ($\rho = 3.4$ for the acid-independent contribution), there appears to be no imposition of electronic demand that would necessitate the use of modified substituent constants beyond those σ values which are defined on the basis of benzoic acid dissociation.[18,20,24-27]

The effect of the 2-methyl group in producing an approximate 30-fold increase in k_1, relative to unsubstituted quinoline–borane, is attributed to steric enhancement of a dissociative pathway involving a change in the coordination number of nitrogen from four in the amine–borane to three in the incipient free amine. Interestingly, 2-methyl substitution also causes a greater than 2-fold *increase* in k_2, presumably reflecting the greater importance of the electronic inductive effect of the methyl group over its capacity to hinder approach of solvated proton to the coordination sphere of nitrogen. A small effect on k_1 and k_2 is also observed on introduction of methyl or methoxy in the 6-position, suggesting some transmission of electronic induction from this region of the all-carbon ring. The nearly 20-fold increase in k_1 resulting from insertion of a nitro group at this position is consistent with previous reports of the exceptional effect of the NO_2 function in reactions subject to acceleration by electron-withdrawing substituents, particularly where there is direct conjugation of the nitro group with the reaction site.[27]

It is also interesting to compare kinetic parameters of quinoline–borane and its derivatives with those of isoquinoline–borane. Relative values of k_1 and k_2 suggest, for the quinoline–boranes, a steric influence of the peri hydrogen at C-8, resulting in enhancement of the dissociative pathway and, to a lesser degree, retardation of bimolecular substitution relative to what is exhibited by the isoquinoline derivative. Such an influence is further suggested by the magnitude of the k_1 term in 8-methylquinoline–borane.

These studies provide insight regarding the effects of substituents on the stability of heteroaromatic amine–boranes in protic media. Recognition of these factors is essential to extending the potential synthetic utility of the amine–borane moiety as a convenient protecting group for tertiary nitrogens.[2]

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Registry No. Quinoline–*N*-borane, 13240-36-3; 2-methylquinoline–*N*-borane, 92367-41-4; 3-methylquinoline–*N*-borane, 54304-40-4; 4-methylquinoline–*N*-borane, 94553-41-0; 6-methylquinoline–*N*-borane, 102941-75-3; 8-methylquinoline–*N*-borane, 54304-36-8; 3-bromoquinoline–*N*-borane, 102941-76-4; 4-chloroquinoline–*N*-borane, 102941-77-5; 6-methoxyquinoline–*N*-borane, 102941-78-6; 6-nitroquinoline–*N*-borane, 102941-79-7; isoquinoline–*N*-borane, 54304-37-9.

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Vibrational Fine Structure of the Lowest Spin-Allowed Absorption Band of *trans*-$[Co(CN)_2(tn)_2]^+$ (tn = 1,3-Propanediamine). Structures of *trans*-$[Co(CN)_2(tn)_2]Cl\cdot H_2O$ and *trans*-$[Co(CN)_2(tn)_2]Cl\cdot 3H_2O$

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The results of X-ray structure analyses of *trans*-$[Co(CN)_2(tn)_2]Cl\cdot H_2O$ and *trans*-$[Co(CN)_2(tn)_2]Cl\cdot 3H_2O$ are presented. In these crystal lattice systems the cationic complex exists in two forms. In the trihydrate crystal both six-membered metal chelate rings of the complex ion *trans*-$[Co(CN)_2(tn)_2]^+$ assume the chair form, while in the monohydrate crystal one is present in the chair and the other one in the skew-boat form. This change in geometry of the complex ion is made manifest by high-resolution, polarized absorption spectroscopy. This shows that the spectrum of the monohydrate yields much less information in the region of the lowest spin-allowed transition $^1A(C_1)[^1A_{2g}(D_{4h})] \leftarrow {}^1A$ than does the spectrum of the $^1B_g(C_{2h})[^1A_{2g}(D_{4h})] \leftarrow {}^1A_g$ transition in the trihydrate crystal. Analysis of the vibronic structure in these spectral regions, supported by the results of a normal-coordinate analysis, shows that the complex ion undergoes a distortion in its electronic excited state ^1B_g (trihydrate) and ^1A (monohydrate). This results in a flattening of the chelate rings in the equatorial direction, as well as a contraction along the vertical axis containing the cyanide ligands. This flattening produces an expansion of ~0.06 Å in the Co–N bond lengths. Support for the experimentally determined excited-state distortion is provided by MO calculations of the forces exerted in the excited state of *trans*-$[Co(CN)_2(tn)_2]^+$.

I. Introduction

In previous studies,[1,2] we had estimated the distortion of *trans*-$[Co(CN)_2(NH_3)_4]^+$ and *trans*-$[Co(CN)_2(en)_2]^+$ in their ligand field excited states $^1A_{2g}(D_{4h})$ and $^1B_g(C_{2h})[^1A_{2g}(D_{4h})]$, respectively. This was done through analysis of the vibrational fine structure and the intensity distribution of the single-crystal absorption bands combined with a normal-coordinate analysis of the distorting (accepting) modes of the chromophores. It was found that the *trans*-$[Co(CN)_2(en)_2]^+$ complex undergoes dis-

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