-0.84; this correction plus that for *p*-chloro substitution gives $pK_{a3} = 13.3$. At ionic strength 1.0 the value of pK_{a3} may be decreased by 0.1–0.2 unit; these estimates are based on reference pK_a values at low or zero ionic strength. The estimates of pK_{a1} and pK_{a2} are based on measured pK_a values of reference compounds at ionic strength 1.0.

(iv) From the relationship among the equilibria of eq 3, pK_{a4} for the dissociation of $T^{\pm}$ is equal to $pK_{a1} + pK_{a3} - pK_{a2} = (-1.6 + 13.0 - 8.3) = 3.1$.

The value of log K_z for the interconversion of T^0 and $T^{\pm}$ calculated from these ionization constants is -9.9 ± 1.0. A value of log $K_z = -9.4$, consistent with this estimate, is obtained by the following extrapolation from the value of log $K_z = -1.9$ at 35° estimated from the data of Hine and coworkers[54] for the analogous equilibrium between the zwitterionic and neutral forms of the carbinolamine derived from isobutyraldehyde and methylamine. The assumption is made that substituent effects at the central carbon atom are equal for the ionization of the oxygen- and nitrogen-bound protons and hence do not affect K_z. The use of $pK_a = 10.62$ for methylammonium ion at 25°[63] gives log $K_z = -1.8$ for the methylamine adduct of isobutyraldehyde at 25°. Changing the amine from methylamine to methylthiosemicarbazide will decrease pK_{a4} with a β value of 1.0, assuming that substituent effects are additive; the effect of nitrogen substituents on K_{a3} will be attenuated by transmission through a nitrogen and a carbon atom, giving a β value for this equilibrium of approximately 1/(2.5)(2.0) or 0.2. Hence, the β value for K_z is approximately 0.8, and log K_z for the methylthiosemicarbazide adduct is $-1.9 - (0.8)(10.6 - 1.2)$ or -9.4.

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Base Hydrolysis of Coordinated Acetonitrile

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Abstract: The base hydrolysis of acetonitrile to acetamide is catalyzed by a factor of 2×10^6 on coordination to $Co(NH_3)_5^{3+}$. Hydroxide appears to attack the carbon atom of the nitrile group, while in a separate and concurrent process the methyl protons exchange. On addition of acid to the acetamido complex produced, protonation occurs on the carbonyl oxygen ($pK_a = 3.02$; $\mu = 1.0$ *M*, $NaClO_4$; $T = 25°$) rather than on the amide nitrogen atom.

The metal ion promoted hydrolysis of nitriles has been studied for several nitriles.[1-3] In cases where valid comparisons can be made, the corresponding N-bonded carboxamide product is formed at a rate 10^6–10^7 faster than for the base hydrolysis of the noncoordinated nitrile.[1,3]

However, in the system $[Co(en)_2X(NCCH_2NH_2)]^{2+}$ (X = Cl, Br) a different reaction occurs under basic conditions, and a tridentate amidine complex is formed by attack of a coordinated amide ion (formed by deprotonation of an amine proton of en) at the nitrile C atom.[4] Consequently, it was of interest to determine whether $[Co(NH_3)_5(N{\equiv}CCH_3)]^{3+}$ would react by direct hydroxide ion attack at the nitrile group to give the N-bonded acetamido complex, or by attack of a deprotonated ammine on the nitrile group to produce coordinated acetamidine. The present paper reports the investigation of the base hydrolysis of $[Co(NH_3)_5(N{\equiv}CCH_3)]^{3+}$, and of the properties of the hydrolysis product.

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Experimental Section

Analytical reagents were used without further purification. $[Co(NH_3)_5(N{\equiv}CC_6H_5)](ClO_4)_3$ and $[Co(NH_3)_5(NHCOC_6H_5)]I_2$ (and the protonated species as the chloride salt) were obtained as described previously.[3] Electronic spectra were measured on a Cary 14 spectrophotometer, and pmr spectra on either a Varian HA-100 or a JEOL MH-100 spectrometer using TMS as external reference or *tert*-butyl alcohol as internal reference.

Preparation of $[Co(NH_3)_5(N{\equiv}CCH_3)](ClO_4)_3$ was effected as previously reported in the literature,[5] or on a larger scale by the following method. $[Co(NH_3)_5I](ClO_4)_2$[6] (9.42 g, 0.02 mol) and $AgClO_4$ (4.2 g, 0.02 mol) were stirred for 5 min in dried acetone (15 ml). Acetonitrile (50 ml) was added and the mixture stirred overnight at room temperature. Ether (50 ml) was added, and the yellow product and precipitated silver iodide were filtered off. The complex was extracted with warm water (40 ml), acidified with a few drops of acetic acid, and precipitated by the addition of $NaClO_4$ and cooling. $[Co(NH_3)_5(N{\equiv}CCH_3)](ClO_4)_3$ (8.2 g, 85%) was filtered off, washed with ethanol and ether, and air dried. The complex was recrystallized from warm acidified water. The visible spectrum of the complex in 10^{-3} *M* $HClO_4$ gave ϵ_{467}^{max} 63 and ϵ_{333}^{max} 56. *Anal.* Calcd for $CoN_6C_2H_{15}Cl_3O_{12}$: Co, 12.19; C, 4.97; H, 3.75; N, 17.38. Found: Co, 12.21; C, 5.21; H, 4.07; N, 17.06.

Isolation of Base Hydrolysis Product. $[Co(NH_3)_5(N{\equiv}CCH_3)](ClO_4)_3$ (1.21 g, 0.0025 mol) was dissolved in water (25 ml) and NaOH solution added (2.5 ml of 1.2 *M*, 0.0030 mol). After 10 sec excess $NaClO_4$ was added to precipitate the red hydrolysis product,

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which was filtered and washed with ethanol, yield 0.82 g, 82%. Recrystallization was achieved from warm water (pH ~9, 8 ml) by the addition of $NaClO_4$ and cooling. Electronic spectra showed ϵ_{485}^{max} 73, ϵ_{351}^{max} 87, and ϵ_{252}^{max} 2.47×10^3 in 0.01 *M* NaOH, and ϵ_{476}^{max} 63 and ϵ_{342}^{max} 60 in 0.1 *M* $HClO_4$. *Anal.* Calcd for $CoN_6C_2H_{19}Cl_2O_9$: Co, 14.69; C, 5.99; H, 4.78; N, 20.96; Cl, 17.68. Found: Co, 14.58; C, 6.21; H, 4.92; N, 20.98; Cl, 17.60.

The complex was isolated in a protonated form (yellow) by precipitation with $NaClO_4$ from an acidified solution of the red base hydrolysis product, but the analytical results were poor and indicated some unprotonated form.

Analysis of Water Content of Base Hydrolysis Product. The base hydrolysis product was analyzed for water by the Karl Fischer method. The complex (322 mg) was dissolved in dry dimethylformamide (3 ml) and aliquots (1 ml) of this solution were added to dried methanol (10 ml) and titrated with Karl Fischer reagent. The average titer of 0.10 ml (1 ml of KF reagent ≡ 5.73 mg of H_2O) indicated <1% water content in the complex.

Kinetics of Base Hydrolysis of $[Co(NH_3)_5(N{\equiv}CCH_3)](ClO_4)_3$. A solution of the complex (2×10^{-4} *M*) in water was mixed with an equal volume of standard NaOH solution (μ = 2.0 *M*, $NaClO_4$) using a stopped-flow apparatus. The reaction was followed at λ 240 nm on a Cary 16K spectrophotometer at a cell temperature of 25.0°. The rate of hydrolysis was also followed by nmr techniques in a 1 *M* Tris-$DClO_4$ (D_2O) buffer (μ = 0.1 *M*; measured pH = 9.20, pD = 9.60[7]) at the probe temperature (33°).

$[Co(NH_3)_5(N{\equiv}CCH_3)](ClO_4)_3$ (*ca.* 0.1 g) and *tert*-butyl alcohol (0.02 ml) were dissolved in the buffer solution (1 ml), and pmr spectra were recorded over 4 half-lives. The methyl signals of the reactant complex (2.62 ppm) and of the product (2.12 ppm) were superimposed on the tail of the large resonance due to the buffer, and the results were plotted as the disappearance of the methyl resonance of the reactant measured in terms of peak height relative to the standard *t*-BuOH. A plot of log (peak height − peak height$_\infty$) *vs.* time was linear over $2 \times t_{1/2}$.

The extent of the proton exchange process on the CH_3 group was measured separately by recording the pmr spectrum of a solution of $[Co(NH_3)_5(N{\equiv}CCH_3)](ClO_4)_3$ in D_2O (0.1 g in 1 ml) with *tert*-butyl alcohol (0.02 ml) as a standard, then adding 0.1 ml of 1 *M* NaOD solution and recording the pmr of the base hydrolysis product. The integrals of the two methyl signals (relative to *tert*-butyl alcohol) gave the extent of proton exchange in the course of hydrolysis.

Determination of pK_a. The pK_a of the acetamide complex was obtained spectrophotometrically at 350 nm by adding aliquots of 1.0 *M* $HClO_4$ to a solution of the complex in 0.01 *M* NaOH (μ = 1.0 *M*, $NaClO_4$). The pK_a was evaluated by the procedure of Albert and Serjeant.[8]

Results and Discussion

The complex $[Co(NH_3)_5(N{\equiv}CCH_3)]^{3+}$ hydrolyzed in basic conditions according to the rate law, $v = k_{OH} \cdot [\text{nitrile}][OH^-]$. The kinetic results are given in Table I.

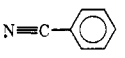
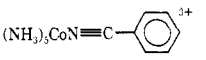
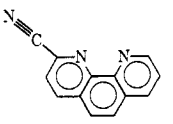
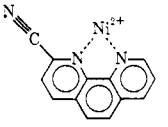
Table I. Kinetic Results for Base Hydrolysis of $[Co(NH_3)_5(N{\equiv}CCH_3)]^{3+}$ at 25°[a]

$[OH^-]$, *M*	k_{obsd}, sec^{-1}	$k_{OH} = k_{obsd}/[OH^-]$, M^{-1} sec^{-1}
0.10	3.48×10^{-1}	3.5
0.050	1.70×10^{-1}	3.4
0.010	3.40×10^{-2}	3.4
0.0050	1.68×10^{-2}	3.4

[a] μ = 1.0 *M* ($NaClO_4$); [Co] = 1.2×10^{-4} *M*.

The hydrolysis rate (3.40 M^{-1} sec^{-1}) is 2×10^6 faster than base hydrolysis of free acetonitrile to acetamide (1.60×10^{-6} M^{-1} sec^{-1}),[9] a factor which is practically identical with the enhancement of the rate of benzonitrile hydrolysis by the $(NH_3)_5Co^{3+}$ moiety,[3] and similar to the factor of 10^7 observed for the Ni(II)–2-cyano-1,10-phenanthroline system[1] (Table II).

Table II. Comparison of the Rates of Base Hydrolysis of Nitriles

Nitrile	k_{OH}, M^{-1} sec^{-1}
$N{\equiv}CCH_3$	1.60×10^{-6} [a]
$(NH_3)_5CoN{\equiv}CCH_3^{3+}$	3.40[a]
	8.2×10^{-6} [b]
	18.8[b,c]
	2.6×10^{-3} [a]
	2.4×10^{4} [a,d]

[a] T = 25.0°. [b] T = 25.6°. [c] Reference 3. [d] Reference 1.

Before considering the mechanism of base hydrolysis, some discussion of the composition of the product is necessary to establish whether the N-bonded acetamide complex of $(NH_3)_5Co^{3+}$ or the acetamidine complex of $(NH_3)_4Co^{3+}$ is formed. The product of the base hydrolysis reaction analyzes to contain an additional hydroxyl (or water) group compared with the acetonitrile complex. Such a formulation would be consistent with the acetamido product $[(NH_3)_5Co(NHCOCH_3)](ClO_4)_2$ or alternatively with the acetamidino complex crystallized with one molecule of lattice water, *i.e.*, $[(NH_3)_4Co(NH{=}C(NH_2)CH_3)](ClO_4)_2 \cdot H_2O$. A Karl Fischer determination of water contained in the complex showed no such water, so that the former of these two possibilities must be the product.

The nmr data obtained on this system is consistent with this assignment. The parent $[Co(NH_3)_5(N{\equiv}CCH_3)]^{3+}$ ion has the pmr spectrum in D_2O–D^+ shown in Figure 1A, where the NH_3 protons are resolved by nitrogen spin decoupling into the ammine groups cis (12 protons) and trans (3 protons) to the acetonitrile ligand. The two types of ammine nitrogen atoms were also observed in the ^{14}N spectrum of the complex using the indor technique,[10] with resonances at Ξ = 7,223,269 (±10) (cis) and 7,223,207 (±10) (trans) Hz.[11]

For the base hydrolysis product, $[Co(NH_3)_5(NHCOCH_3)]^{2+}$, the pmr spectrum is given in Figure 1B, where the NH and NH_3 proton resonances are not separated. On nitrogen spin decoupling, the NH and NH_3 resonances are separated but the cis and trans ammonia proton resonances are not distinguished. The ^{14}N nmr spectrum showed the amide nitrogen atom and the five ammine nitrogen atoms at Ξ = 7,223,247 (±10) and 7,223,217 (±10) Hz, respectively. In this respect the spectral resolution from the ^{14}N indor

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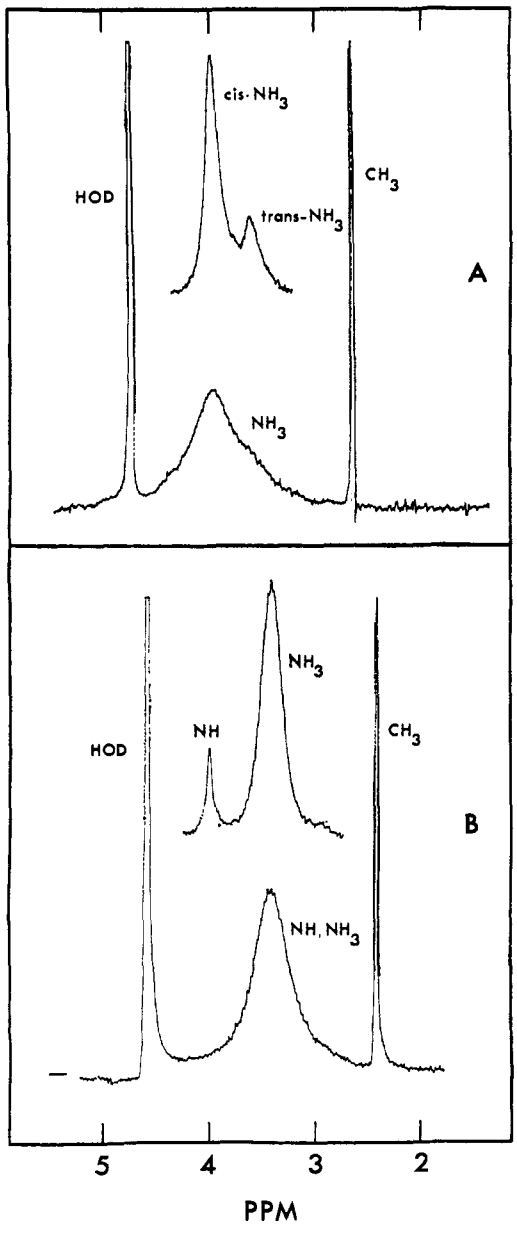

Figure 1. The 100-MHz pmr spectra, and ^{14}N decoupled ammine regions, for (A) $[Co(NH_3)_5(N{\equiv}CCH_3)](ClO_4)_3$ in 1% DCl (TMS external reference), and (B) $[Co(NH_3)_5(NHCOCH_3)](ClO_4)_2$ in 2% D_2SO_4 solution (*t*-BuOH internal reference).

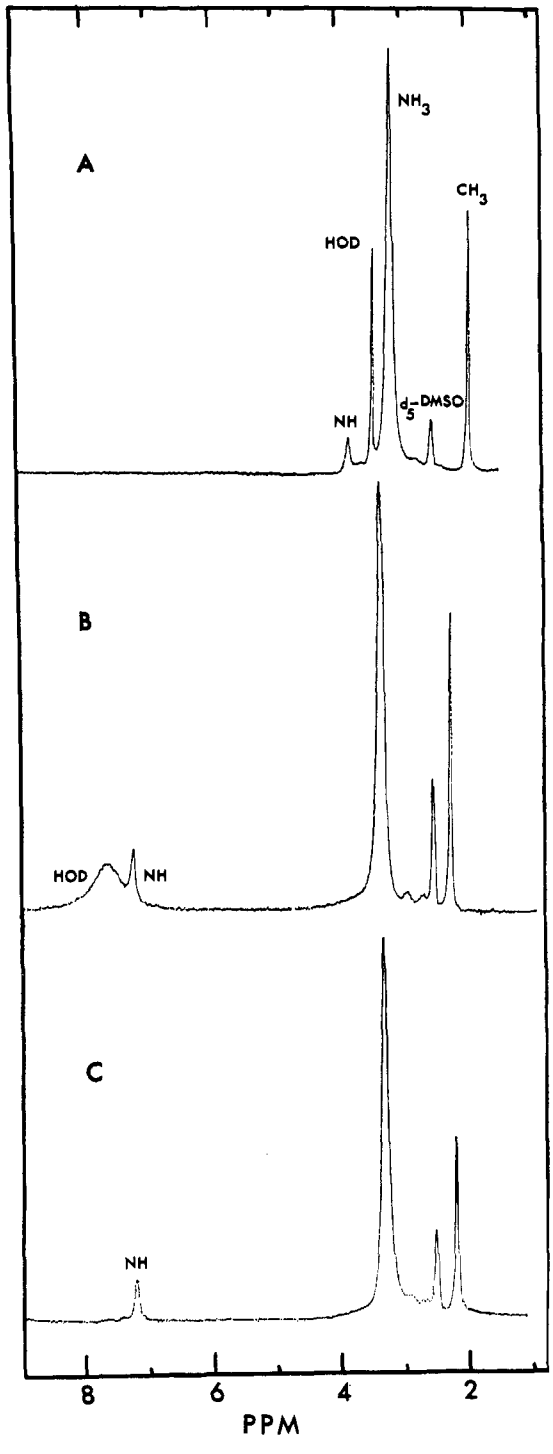

Figure 2. The 100-MHz pmr spectrum of $[Co(NH_3)_5(NHCOCH_3)](ClO_4)_2$ in DMSO-d_6 (A), and with increasing amounts of H_2SO_4 (B and C). External reference TMS.

technique was somewhat disappointing. Even so, the results are consistent with the acetamido formulation where three resonances were expected and two were observed, one for the ammonia residues and one for the amide moiety. For the acetamidino formulation five resonances could be expected, two involving the amide moiety and three for the ammonia residues.

The pmr spectrum of the base hydrolysis product is also shown in DMSO-d_6 (Figure 2A) where the resonances δ_{CH_3} 1.93, δ_{NH_3} 4.19, and δ_{NH} 4.77 (all relative to δ_{DMSO} centered at δ 2.51 ppm) are in agreement with the pmr of $[Co(NH_3)_5(NHCOCH_3)]^{2+}$ prepared directly from acetamide.[12] On the addition of increasing amounts of H^+ the HOD and NH signals move downfield, with the NH signal remaining at 7.25 ppm on full protonation of the complex (Figure 2B and C). The magnitude of this resonance corresponds to one proton throughout. This can be explained if protonation occurs on the carbonyl oxygen atom. The NH

$$CoNH{-}\overset{\overset{O}{\|}}{C}{-}CH_3 \xrightarrow{H^+} CoNH{=}\overset{\overset{OH}{|}}{C}{-}CH_3$$

proton is thereby more effectively deshielded by the anisotropy of the >C=N– compared with the >C=O double bond, and so resonates at lower field in the protonated complex. The carbonyl group, however, is weakly basic and the protonated species would be a strong acid and would exchange the proton rapidly

(12) R. B. Jordan, private communication.

with H_2O in the solvent. Similar behavior has also been observed for protonation of $[Co(NH_3)_4(NH_2CH_2CONH)]^{2+}$,[13] and protonation of the carbonyl oxygen rather than the nitrogen atom is also claimed for uncoordinated acetamide.[14]

In the present case, some slow decomposition occurs in acidified DMSO with the liberation of free acetamide and the formation of $[Co(NH_3)_5(DMSO)]^{3+}$. The pmr signals associated with these products have not been included in Figure 2 for simplicity.

The pK_a of the protonated acetamide complex in aqueous solution is 3.02 (μ = 1.0 M, $NaClO_4$; T = 25°) which is slightly higher than those of the benzamide (pK_a = 1.65)[3] and formamide (pK_a = 2.16)[15] complexes of $Co(NH_3)_5^{3+}$, where protonation was indicated to be at the amide nitrogen atom. In view of the present work, it seems more likely that protonation will occur in these complexes at the carbonyl oxygen atom, and the pmr spectrum of the protonated benzamido complex in 1 M DCl solution confirms that there is only one proton at the nitrogen atom.

The rate law for the hydrolysis reaction is consistent with direct attack of hydroxide ion at the carbon atom of the nitrile group, giving rise to the acetamido complex, in the same way as proposed for the benzonitrile system.[3]

$$(NH_3)_5CoN{\equiv}CCH_3^{3+} + OH^- \longrightarrow (NH_3)_5CoNH{-}\overset{\overset{O}{\|}}{C}{-}CH_3^{2+}$$

However, unlike the nitriles previously studied,[1-3] acetonitrile has hydrogen atoms on the carbon atom α to the cyano group. Pmr studies indicate that during the hydrolysis process, exchange of about half of the methyl protons occurs. (The rate of exchange of methyl protons in the acetamido complex is extremely slow.) Consequently, the rate of disappearance of the methyl signal of $[Co(NH_3)_5(N{\equiv}CCH_3)]^{3+}$ (k_{obsd} = 1.36 × 10^{-3} sec^{-1}) exceeds that of the hydrolysis (k_{obsd} = 9.7 × 10^{-4} sec^{-1}, measured spectrophotometrically) under the same conditions (Tris–$DClO_4$ buffer in D_2O, T = 33°, pD = 9.60) since in the former case both hydrolysis and exchange are observed. It is therefore possible that deprotonation may be a prerequisite to hydrolysis.

$$\begin{array}{ccc} (NH_3)_5CoN{=}CCH_3^{3+} & \xrightarrow{OH^-} & (NH_3)_5CoN{\equiv}C\bar{C}H_2^{2+} \\ & & \uparrow \\ (NH_3)_5CoNH{-}\overset{\overset{O}{\|}}{C}{-}CH_3^{2+} & \xleftarrow{H_2O} & (NH_3)_5Co{-}\bar{N}{=}C{=}CH_2^{2+} \end{array}$$

In the present instance, the rate of exchange is such that slightly more than one exchange occurs for every hydrolysis act. Alternatively, the two processes may be independent.

For the benzonitrile analog, similar studies reveal that exchange does not occur during hydrolysis so that no deprotonation of the phenyl protons is involved, presumably as no stabilization of the carbanion is possible. Thus, hydrolysis by direct attack of hydroxide ion on the nitrile carbon atom is most likely. The similarity in catalysis of the hydrolyses of benzonitrile and acetonitrile by $(NH_3)_5Co^{3+}$ (*ca.* 2 × 10^6) suggests some identity in the mechanisms, so that hydrolysis of acetonitrile in the pentaamminecobalt(III) complex would appear to occur by direct hydroxide attack also, with exchange being an independent process.

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The [8]Paracyclophane Ring System. Structure and Spectroscopic Properties of 4-Carboxy[8]paracyclophane[1-3]

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Abstract: An improved synthesis of 4-carboxy[8]paracyclophane is described. The nmr spectrum shows a highly shielded proton at δ −0.25. The X-ray crystal structure (R value 0.05 for 2187 unique nonzero maxima) shows that the molecule has normal bond lengths, but most of the C–C–C bond angles in the side chain are opened in an effort to bridge the ring. The ring is a boat, with the p carbons attached to the side chains 9° out of the plane of the other four ring carbons. There are many distances between atoms in the side chain and atoms in the ring which are less than the sum of the van der Waals radii.

Compounds having the [8]paracyclophane ring system have been known for some time.[4-7] These molecules are known from their ultraviolet spectra to possess a nonplanar benzene ring; however, in no case has the actual geometry of the benzene ring been re-

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