The nmr and infrared spectra of the reaction product show that it is homogeneous. It contains 97% D- and 3% L-mandelonitrile (lit.[4] $[\alpha]_D$ +48.7° ($CHCl_3$) for optically pure D-(+)-mandelonitrile).

The method described for the synthesis of D-(+)-mandelonitrile can be used for the conversion of many aliphatic, aromatic, and heteroaromatic aldehydes into D-α-hydroxynitriles, which can be readily transformed into optically active D-α-hydroxycarboxylic acids, substituted ethanolamines,[5] or acyloins.[6] A table showing the aldehydes that can be used is given in ref 2.

Since both the reaction rate and the solubility in the reaction medium vary according to the aldehyde, the quantity of catalyst, flow rate, concentration of the reactants, and methanol–water ratio must be matched to the substrate in question in order to obtain optimum yields. A suitable pH range has been found to be 4.8–5.2; the H^+ concentration can be adjusted with volatile acids or bases.

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A Volatile Inorganic Salt, $Cs[Y(CF_3COCHCOCF_3)_4]$

Sir:

In the course of our investigation of a series of eight-coordinate β-diketonate complexes of yttrium and the rare earths, we made the rather surprising discovery that $Cs[Y(HFA)_4]$ (HFA = hexafluoroacetylacetonate) sublimes both in air and *in vacuo* without decomposition at temperatures ranging from 180 to 230°. In order to obtain further information about the identity of the chemical species in the vapor phase and in view of the current interest[1–5] in the mass spectra of various transition metal complexes, we have measured the mass spectrum of $Cs[Y(HFA)_4]$. Some preliminary results are reported here.

Analytically pure crystalline $Cs[Y(HFA)_4]$ was prepared in 60% yield from the reaction of Cs(HFA) with YCl_3 (4:1) in aqueous ethanol. *Anal.* Calcd for $CsYC_{20}H_4O_8F_{24}$: C, 22.86; H, 0.38; F, 43.43. Found: C, 22.9; H, 0.60; F, 42.6. A small quantity of the product was sublimed at 170° *in vacuo* (0.02 mm) onto a probe cooled with running water using the apparatus described previously.[6] The material obtained was analyzed (Found: C, 22.53; H, 0.58) and used in the mass spectrometric investigation.

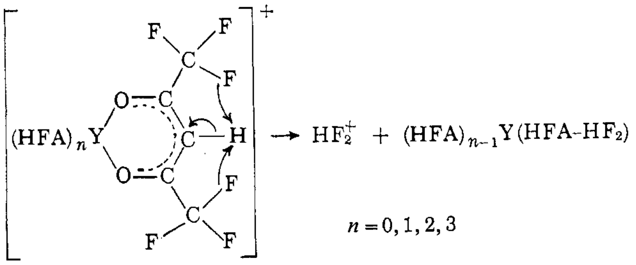
A list of several of the peaks observed in the mass spectrum of $Cs[Y(HFA)_4]$ may be found in Table I, along with their tentative assignments.[7] In addition to the peaks expected for the "molecular ion," $Cs[Y(HFA)_4]^+$, and its most likely decomposition daughters, Cs^+ and $Y(HFA)_4^+$, peaks corresponding to stepwise loss of ligand molecules to give $Y(HFA)_3^+$, $Y(HFA)_2^+$, and $Y(HFA)^+$ are quite prominent. The loss of β-diketonate ligand radicals has been previously observed for the iron, chromium, and aluminum acetylacetonates.[3,4]

Table I. Partial List of Peaks in the Mass Spectrum of $Cs[Y(HFA)_4]$

Mass number	Assignment	Intensity[a]
1050 ± 5	$Cs[Y(HFA)_4]^+$	vvw
917 ± 2	$Y(HFA)_4^+$	w
843	$Cs[Y(HFA)_3]^+$	s
807	$(CF_3CO)Y(HFA)_3^+$	m
738	$(CO)Y(HFA)_3^+$	s
710	$Y(HFA)_3^+$	s
641	$(COCHCOCF_3)Y(HFA)_2^+$	s
503	$Y(HFA)_2^+$	s
434	$(COCHCOCF_3)Y(HFA)^+$	w–m
340	Cs(HFA)	w
296	$Y(HFA)^+$	w–m
208	$H(HFA)^+$ (?)	w–m
133	Cs^+	vvs
69	CF_3^+	vvs
39	HF_2^+	vvs

[a] s = strong, m = medium, w = weak, v = very.

Of significance is the intense peak at mass 843 which may be assigned to the $Cs[Y(HFA)_3]^+$ ion. Apparently the cesium ion is held so strongly to the β-diketonate complex anion that loss of a ligand molecule can readily occur without the prior departure of Cs^+. This interaction may be formulated as a strong ion pair existing between the monopositive cesium ion and the sheath of electronegative fluorine atoms of the chelating ligands which surround the yttrium atom. Alternatively, the cesium ion could be bound directly to the methylene (=CH—) carbon atom of one of the β-diketonate ligands in a manner analogous to the interaction of silver ions with the β-diketonate anions chelated to nickel in the crystal structure of $AgNi(CH_3COCHCOCH_3)_3 \cdot 2AgNO_3 \cdot H_2O$.[8] Another interesting feature of the mass spectrum is the very strong peak at mass 39, which we tentatively assign to the HF_2^+ ion. This species may result in the following manner



a process made favorable by the close proximity of the hydrogen and two fluorine atoms of a chelated (*vs.* a free) HFA group.

The X-ray crystal structure of $Cs[Y(HFA)_4]$ is currently being determined in our laboratory,[9] the results

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of which will be reported, along with a more detailed analysis and discussion of the mass spectrum, in future publications.

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A New Approach to Conformational Analysis. Carbon-13 Nuclear Magnetic Resonance[1,2]

Sir:

Since the first report of marked conformational effects on proton chemical shifts,[3] the use of nmr spectroscopy for the investigation of stereochemistry and molecular conformation has become increasingly popular. A variety of applications has been described[4] and the use of nuclei other than protons has been illustrated, prominent among which are ^{19}F and ^{13}C studies.[2,5,6] The feature common to all of these published approaches is that the shielding or the spin coupling of the particular nucleus which is examined directly must vary with its orientation within the molecule (*e.g.*, axial *vs.* equatorial protons in cyclohexyl systems or dihedral angle for vicinal couplings). The magnitude of the variation with position governs the precision with which conformational parameters may be determined. We wish to report that in cyclohexanol derivatives the shieldings of the readily identified carbinol carbons are markedly dependent on the orientation of the oxygen functions and, consequently, these data are useful for conformational analysis. These differences are due *solely* to substituent orientation since the position of the carbon nucleus itself is unchanged relative to the other atoms in the molecule. Because these differences are relatively large, the method, when refined techniques are employed, is capable of higher precision than other nmr methods.

The ^{13}C spectra of the *cis*- and *trans*-4-*t*-butylcyclohexanols and their methyl ethers and acetates reveal that the chemical shifts of the carbinol carbons (C-1) differ substantially for each pair in this series.[7] Shielding differences of up to 5 ppm are found between carbinol carbons bearing axial and equatorial oxygen functions and, in each case, the carbon having an axial substituent absorbs at the higher field (Table I). To demonstrate that the 4-*t*-butyl group exerts a negligible effect on the chemical shift of the carbinol carbon, the *trans*-4-methyl- and 4-isopropyl-substituted derivatives were also examined. These data are included in Table I.

Table I. Carbinol Carbon Shieldings[a] of Some Cyclohexyl Systems, *cis*- and *trans*-4-R-$C_6H_{10}OR^1$

		Orientation of OR^1		
R	R^1	Axial[c]	Equatorial[d]	$\Delta\delta_c$,[b] ppm
t-Bu	H	126.4	121.5	4.9
	Ac	123.6	119.6	4.0
	Me	117.5	112.6	4.9
i-Pr	H		121.8	
	Ac		119.2	
	Me		112.6	
Me	H		121.4	
	Ac		119.8	
	Me		113.0	

[a] In parts per million from CS_2 (δ_c = 0 ppm). [b] Shielding difference due to substituent orientation ($\delta_c^{axial} - \delta_c^{equat}$). [c] *cis* isomer. [d] *trans* isomer.

These results establish the existence of substantial conformational effects on ^{13}C shieldings and suggest a number of possible applications in addition to their usefulness for stereochemical elucidations. One of these is the determination of conformational free energies for various substituents. For example, determination of the chemical shift of the carbinol carbon for cyclohexanol provides a measure of the relative populations of its two available chair conformations. Its carbinol absorption at δ_c = 122.8 ppm indicates that cyclohexanol is 74% equatorial on the basis of the data in Table I. This result corresponds to a conformational equilibrium constant of *ca.* 2.8 and a $-\Delta G°$ value of 0.6 kcal/mole. The latter value lies well within the range 0.4–1.2 kcal/mole found by other means.[9] In a similar manner $-\Delta G°$ values for the OMe and OAc groups on cyclohexane rings were determined and are given in Table II together with other published values.[9]

Table II. Some $-\Delta G°$ Values for OR Groups in Cyclohexyl Systems[a]

	Method of estimation		
OR	^{13}C	^1H[b]	Other[b]
OH	0.6	0.6–1.2	0.3–1.0
OAc	0.65	0.6–0.8	0.4–1.6
OMe	0.6	0.6	0.74

[a] In kcal/mole. [b] From ref 9.

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