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ROTATIONAL ISOMERISM BETWEEN THE E AND Z FORMS OF o-SUBSTITUTED BENZO-N-METHYL HYDROXAMIC ACIDS IN STRONG ACID

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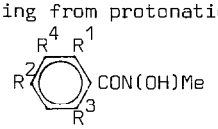
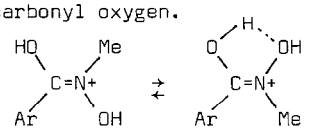
Summary The E ⇄ Z equilibrium of the cations of benzo hydroxamic acids, in mineral acid, was studied utilising ^{1}H NMR spectroscopy, NOEDS and MNDO calculations.

Whereas the protonation of amides[1] has been extensively studied, hydroxamic acids, which are structurally similar, have received only scant attention in this respect. Recently, evidence was provided that aliphatic hydroxamic acids are protonated on the carbonyl oxygen in strong acid medium.[2] We have extended our study to the behaviour of various substituted benzo hydroxamic acids in strong acid and the results are collected in the TABLE. With the exception of compounds Ia and Ib, the ^{1}H NMR spectra of all other hydroxamic acids exhibited two distinct N-methyl resonances, signals which are to be attributed to the presence of two isomeric cations, E and Z, resulting from protonation on the carbonyl oxygen.

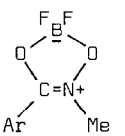


(I)

a) $R^1=R^2=R^3=R^4=H$
b) $R^1=R^3=R^4=H, R^2=Me$
c) $R^1=R^2=R^3=Me, R^4=H$
d) $R^1=R^2=Me, R^3=R^4=H$
e) $R^1=R^2=R^4=H, R^3=Br$
f) $R^1=R^2=R^4=H, R^3=Cl$
g) $R^1=R^2=R^4=H, R^3=NO_2$
h) $R^1=R^2=R^4=H, R^3=OMe$
i) $R^1=R^2=H, R^3=NO_2, R^4=Me$



E ⇄ Z



(II)

The N-methyl resonances in the 250 MHz ^{1}H NMR spectrum of Ii were assigned using nuclear Overhauser effect difference spectroscopy(NOEDS).[3] Pre-irradiation of the ortho protons in Ii significantly decreased[4] the intensity of the highfield N-methyl resonance compared with the low-field N-methyl resonance.[5] Conversely, a greater decrease in the intensity of the ortho proton resonances in Ii was observed with pre-irradiation of the highfield N-methyl group than with pre-irradiation of the low N-methyl group. Since the N-methyl and the ortho protons are closer geometrically in the Z isomer of Ii than in the E isomer, these effects suggest that the highfield N-methyl signal should be assigned to the former isomer and the lowfield signal to the latter isomer. The N-methyl resonances of Ic-Ih were assigned by analogy with the chemical shifts of Ii. The chemical shift of the N-methyl resonance of Ib, when compared with the resonance of the corresponding

TABLE[a]

Compound	δ_E[b]	δ_Z[b]	δ[c]	%Z	T_c(K)[d]	$\Delta G^{\ddagger}_E$ (kcal mol^{-1})[e]	$\Delta G^{\ddagger}_Z$ (kcal mol^{-1})[e]
Ia	3.80		-	>99	-	-	-
Ib	3.80		3.78	>99	-	-	-
Ic	3.76	3.42	3.40	84	>373[f]	>19	
Id	3.75	3.53	3.54	89	>373[f]	>19	
Ie	3.78	3.53	3.52	85	403	19.4	20.8
If	3.75	3.51	3.53	83	399	19.3	20.5
Ig	3.78	3.50	3.47	53	393	18.9	19.0
Ih	3.71	3.50	3.48	69	395	19.1	20.3
Ii	3.78	3.50	-	58	-	-	-

a) All spectra were recorded on a JEOL JNM-PS-100 spectrometer, in concentrated D_2SO_4, after equilibration at 303 K, and relative to an external reference of TMS. b) Observed chemical shifts for the N-methyl groups. c) N-methyl resonance of the corresponding BF_2-complex, in $CDCl_3$-TMS. d) Represents the coalescence temperature for the N-methyl resonances. e) $\Delta G^{\ddagger}_Z = \Delta G^{\ddagger}$ for the conversion of major isomer Z to minor isomer E. f) Rapid decomposition occurred before the coalescence temperature could be reached.

boron complex II, suggests that it exists entirely as the Z isomer.[6] Theoretical MNDO[7] calculation of ΔH^f_{298} for compound Ia, including optimization of all geometrical variables with respect to the potential energy, predict that the Z isomer is more stable than the E isomer by 0.6 kcal mol^{-1}. Since the MNDO method is known to underestimate the strength of hydrogen bond, a true value is likely to be greater; a value of 2.4 kcal mol^{-1} would result in a population ratio of approximately 97:3 and would thus account for the experimental observation of only one resonance in the spectra of Ia. Using the equation of Shanan-Atidi and Bar-Eli[8], it is possible to obtain free energies of activation, $\Delta G^{\ddagger}$, for the $E \rightleftarrows Z$ interconversion (TABLE). The absence of an obvious correlation between the Hammet values of the ortho substituents in the aromatic ring and the $\Delta G^{\ddagger}$ for rotation[9] is possibly due to steric inhibition of electronic resonance between the phenyl ring and the carbonyl group. This situation would in turn lead to increased electron donation by the nitrogen atom to the protonated carbonyl group and to the high energy barriers observed.

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