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A NMR STUDY OF BARRIERS TO INTERNAL ROTATION
IN 3-DIAZO-2-BUTANONE

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It is recognized that in α -diazoketones free rotation about the central C-C bond might be hindered through positive overlap of the carbonyl π -system with the p orbital on the α -carbon part of the CNN fragment.^{1,2}

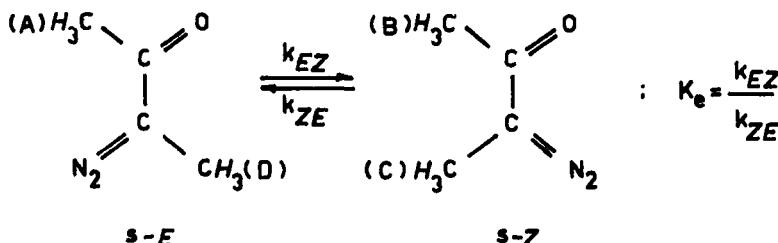
By using NMR spectroscopy, Kaplan and Meloy presented conclusive evidence that a number of α -diazoketones of the type $\text{RCO}-\text{CH}=\text{N}_2$ exist in solution as an equilibrium mixture of two conformational isomers having cisoid (i.e., s-Z) and transoid (s-E) configurations. For 3-diazo-2-propanone $\text{CH}_3\text{CO}-\text{CH}=\text{N}_2$ (1) in CDCl_3 solution at 25° , ΔG^\neq values for the $\text{E} \rightarrow \text{Z}$ and $\text{Z} \rightarrow \text{E}$ interconversion were estimated to be 14.1 and 15.4 kcal.mol^{-1} respectively.² Thus, the s-Z form appears to be thermodynamically more stable than the s-E form by ca. 1.3 kcal.mol^{-1}

The observed dipole moment of 1 in benzene at 25° was found to be 3.37 D;³ on basis of calculated dipole moments of 1.76 and 3.93 D for the s-E and s-Z form respectively, a $[\text{s-Z}]_0/[\text{s-E}]_0$ ratio of 4.5 was estimated for 1 in this solvent.³ For this compound the prevalence of the s-Z form at equilibrium was rationalized invoking the unfavorable steric interaction between the methyl and the diazo-group arising in the s-E form; this must be such as to overcome the unpropitious opposition of dipoles presented by conformer s-Z.

A dipole moment of 2.45 has been found for 3-diazo-2-butanone $\text{CH}_3\text{CO}-\text{C}(\text{CH}_3)=\text{N}_2$ (2) in benzene at 25° .⁴ On comparison with the calculated dipole moments of the E and Z configurations, 1.7 and

3.9 D respectively, the hypothesis was advanced that this compound exists either as a single highly distorted structure (fixed or with restricted internal rotation) or as mixture of distorted E and Z forms.⁴

Consistent with early reports,⁵ we find that the ¹H-NMR spectra of 2 show temperature dependence both in CDCl_3 and CCl_4 . At $+40^\circ$ the methyl protons resonances appear as two rate-broadened singlets; the singlet at lower field must be attributed to the $\text{O}=\text{C}-\text{CH}_3$ resonance.⁵ As the temperature is lowered, each of these singlets broadens further and then separates into two distinct, unequally intense singlets (see Figure 1 and Table 1). This clearly shows that 2 exists as an equilibrium mixture of two interconverting conformers:



In order to decide which form is prevalent,⁵ we have measured the spectra of 2 in the presence of $\text{Eu}(\text{fod})_3$, a lanthanide shift reagent,⁶ at temperatures below coalescence. As expected,^{6,7} with lanthanide to substrate molar ratio > 0.1 the intensity of signals corresponding to the minor component increases with respect to that of signals of the major component with increasing $[\text{Eu}(\text{fod})_3]_0 / [\underline{2}]_0$ ratio. However, the two conformers display a different dependence of induced shifts on $\text{Eu}(\text{fod})_3$ concentration.^{7,8} For example, at -13° and $[\text{Eu}(\text{fod})_3]_0 / [\underline{2}]_0 \approx 0.6$ the $\text{N}_2=\text{C}-\text{CH}_3$ resonances of the major component show a larger induced shift (5.60 ppm) than do those of the minor component (3.23 ppm) (Table 1 and Figure 1). On basis of this evidence, assuming that bonding of the shift reagent to the α -diazoketone occurs largely at the carbonyl oxygen,^{7,8} one should conclude that in 2 the prevalent conformer has the s-E and not^{5,9} the s-Z configuration.

Thus, it appears that for 2 the situation has been reversed with respect to α -diazoketone 1. It is likely that both unfavorable steric

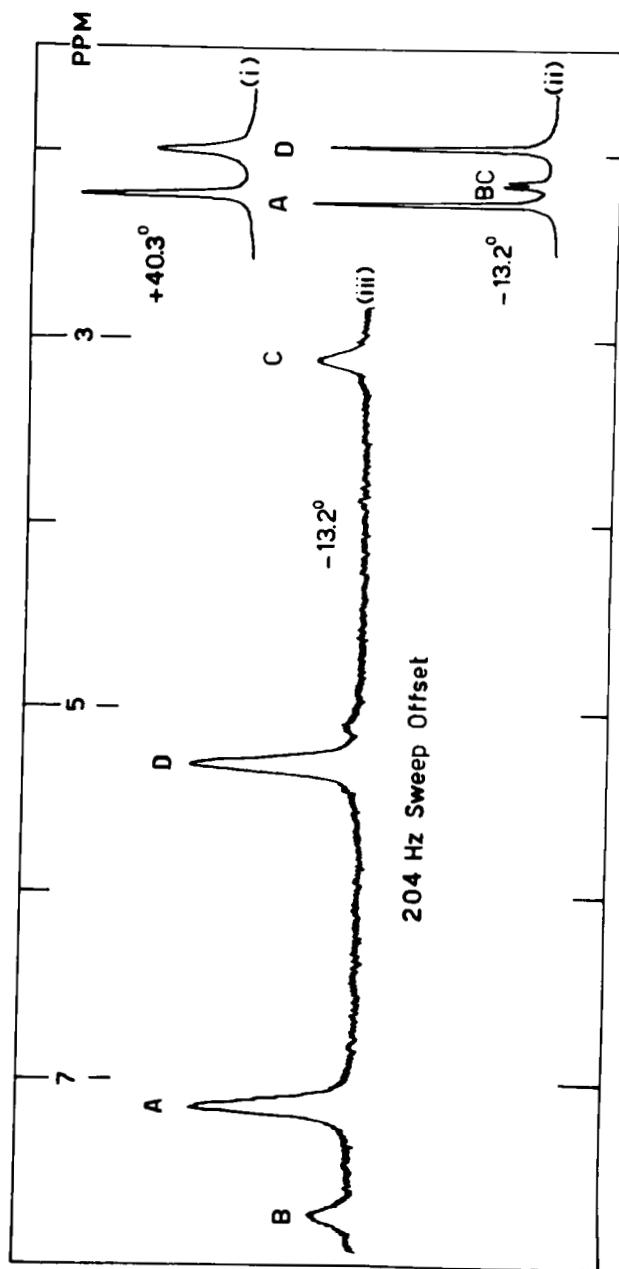


FIG. 1 - Proton Resonance Spectra (90 MHz) of 3-Diazo-2-butanone : (i) and (ii) 0.4 M in CDCl_3 ; (iii) 0.4 M in CDCl_3 , in the presence of 0.25 M $\text{Eu}(\text{fod})_3$.

TABLE 1

Chemical Shifts (δ)^a of Methyl Protons Resonances of the s-E and s-Z Conformers of 3-Diazo-2-butanone.^b

Solvent	$t, {}^{\circ}\text{C}$	δ_A	δ_{av}	δ_B	δ_C	δ_{av}	δ_D	$T_c, {}^{\circ}\text{C}$ ^c
CDCl_3	-30	2.28		2.18	2.16		1.96	+21
	+46		2.20			1.97		
	-13	2.27		2.18	2.15		1.96	
$\text{CDCl}_3 +$ $\text{Eu}(\text{fod})_3^d$	-13	9.41		9.99	5.38		7.56	
CCl_4	-30	2.19		2.16	2.07		1.92	+13
	+46		2.14			1.93		

^a In ppm (TMS internal standard). ^b In all experiments the concentration of 2 was $\approx 0.4 \text{ M}$. ^c Estimated coalescence temperature (90 MHz). ^d $[\text{Eu}(\text{fod})_3]/[\underline{2}]_0 \approx 0.6$.

interaction between the methyl groups and opposition of $\text{C}=\text{O}$ and $\text{C}=\text{N}_2$ dipoles arising in the s-Z form contribute to render conformer s-E prevalent in 2.

To obtain the relative energies of the two conformers and energy barrier to internal rotation, we performed a detailed line-shape analysis of the temperature-dependent methyl resonances of 2, corresponding to two unequally populated AB(DC) exchange cases with common reaction rates.¹⁰ The dependence of chemical shifts with temperature was also taken into account. High-resolution spectra were recorded at several temperatures on a Bruker HFX-10 spectrometer and calibrated to $\pm 0.1 \text{ Hz}$ with a frequency counter. Sample temperatures were measured to $\pm 0.2^{\circ}$ using methanol standard¹¹ and corrected by the method of Van Geet.¹² Spectra were digitized point by point and the digits used for input to a DNMR program.^{10,11} Visual fitting of the computer-plotted to experimental spectra gave relative populations, lifetimes τ and hence the individual interconversion rates (to $\pm 5\%$) at each temperature. Typical fits are shown in Figure 2.

TABLE 2

Temperature Dependence of Fractional Populations, Equilibrium Constants and Rates of Interconversion of the s-E and s-Z Forms of $\underline{\underline{2}}$.^a

Solvent	$t, {}^{\circ}\text{C}$	p_E	p_Z	$1/K_e$	k_{ZE}	k_{EZ}
CDCl_3	-34.9	0.862 ^b	0.138 ^b	6.25	-	-
	-29.8	0.848 ^b	0.152 ^b	5.58	-	-
	-25.2	0.842 ^b	0.158 ^b	5.33	-	-
	-15.2	0.836 ^b	0.164 ^b	5.10	-	-
	-5.1	0.821	0.179	4.58	2.38	0.520
	0.7	0.814	0.186	4.38	4.07	0.930
	5.4	0.803	0.197	4.08	9.64	2.36
	10.9	0.794	0.206	3.85	13.1	3.40
	15.2	0.789	0.214	3.69	17.7	4.80
	20.8	0.774	0.227	3.41	27.6	8.10
	30.5	0.762	0.239	3.19	63.2	19.8
	40.3	0.746	0.251	2.97	131.	44.0
	46.4	0.737	0.260	2.80	229.	81.0
CCl_4	-20.1	0.903	0.097	9.31	0.144	0.016
	-15.5	0.897	0.103	8.71	0.359	0.041
	-10.1	0.871	0.129	6.75	0.871	0.129
	0.4	0.856	0.144	5.94	5.14	0.865
	10.4	0.821	0.179	4.59	22.2	4.84
	30.0	0.750	0.250	3.00	120.	40.
	35.4	0.742	0.258	2.88	271.	94.1
	40.9	0.692	0.308	2.25	287.	127.

^a Concentration of $\underline{\underline{2}}$ was $\approx 0.4 \text{ M}$; k values are in sec^{-1} .

^b Estimated by integration of resonance peaks.

Assuming a transmission coefficient of unity, statistical least-squares treatment of Eyring plots¹⁰ provided approximate ΔH^{\neq} and ΔS^{\neq} values, hence ΔG^{\neq} values at 298°K . Similarly, plots of $\ln(1/K_e)$ vs. $1/T$ gave ΔH_{EZ}^0 values, whereas ΔG_{EZ}^0 was calculated as $-RT\ln K_e$. Thermodynamic and activation parameters are collected in Table 3 together with their uncertainties. Systematic errors, however, could result in errors larger than these estimates.

Noteworthy, significant increases in ΔH^{\neq} values on passing from CDCl_3 to CCl_4 solvent are not accompanied by corresponding increases in ΔG^{\neq} .

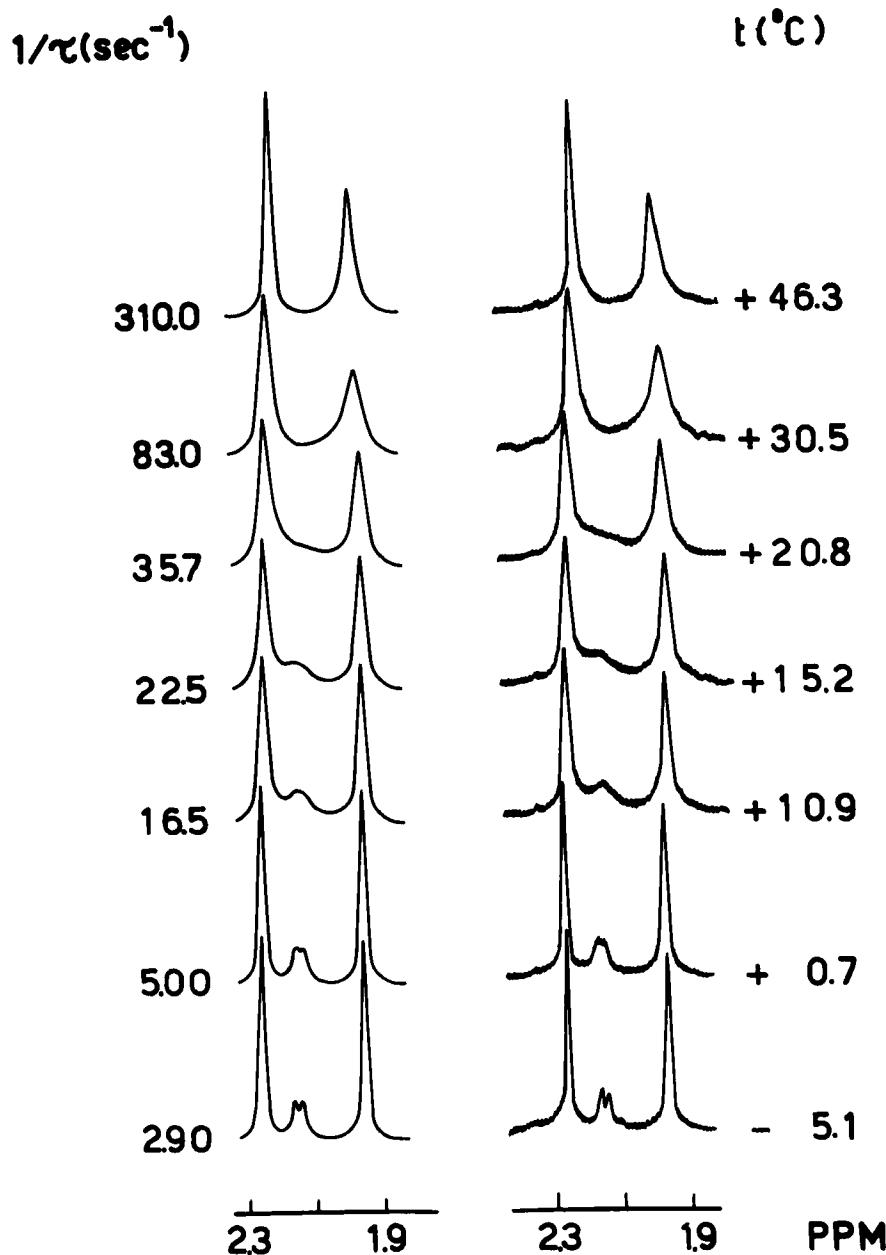


FIG. 2 - Experimental (right) and Computer-plotted (left) proton resonance spectra of ca. 0.4 M 3-Diazo-2-butanone in CDCl_3 at various temperatures.

TABLE 3

Differences in Conformational Energy and Activation Parameters
of Interconversion for the s-E and s-Z Forms of 2.^a

Solvent :	CCl ₄	CDCl ₃
ΔH_{EZ}^0	3.50 \pm 0.15	1.45 \pm 0.15
ΔG_{EZ}^0 (298°K)	0.71 \pm 0.22	0.72 \pm 0.15
ΔH_{EZ}^\neq	22.9 \pm 0.7	15.6 \pm 0.5
ΔH_{ZE}^\neq	19.3 \pm 0.8	14.0 \pm 0.5
ΔS_{EZ}^\neq	24.5 \pm 3	-1 \pm 2
ΔS_{ZE}^\neq	15. \pm 3	-4 \pm 2
ΔG_{EZ}^\neq (298°K)	15.6 \pm 1.	15.9 \pm 0.6
ΔG_{ZE}^\neq (298°K)	14.9 \pm 1.	15.2 \pm 0.6

^a Free-energy and enthalpy changes are in kcal mol⁻¹; entropy changes are in cal mol⁻¹deg⁻¹.

Inspection of data in Table 3 reveals that this occurs largely at expenses of activation entropies. Thus, while at 0° the interconversion rates are nearly equal in the two solvents, the ratio of rate in CCl₄ to rate in CDCl₃ would be ca. 4 at +50° and ca. 0.1 at -50°.

Clearly, reordering of solvent molecules around the C=O and C=N₂ groups on going from ground to transition state is considerably more costly in terms of entropy in CDCl₃ than in CCl₄. This is not surprising in view of the capability of chloroform (a weakly acidic solvent)¹³ to give specific solvation interactions (via hydrogen-bonding) with several organic substrates.

The magnitude of the barriers to internal rotation in 2 compares favorably with that found for α -diazoketones RCO-CH=N₂,² for aromatic α -diazoketones ArCO- $\text{CR}=\text{N}_2$,⁷ as well as with theoretical calculations.¹⁴ It is unlikely, therefore, that dramatic distortions of planar arrangement of O=C-C=N₂ moiety occur in each of the two conformers of 2.

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