tion of nonaqueous component before "falling apart." This is in keeping with our previously stated hypothesis[5] of the origin of the extrema.

Although a number of $\Delta \bar{C}_{\mathrm{p_s}}$ measurements have been reported for electrolytes[10,11] and a few nonelectrolytes[12] in water, we are aware of no previous study of a medium effect on heat capacity. The results described here suggest that solvent–temperature studies of heats of solution, activation, and reaction may be a useful specialized tool for the study of reactions.[9]

Measurements of $\Delta \bar{H}_s$ at 4° were made in a calorimeter such as we have described previously.[5] The entire calorimeter apparatus was enveloped in a metal casing and held conveniently at 4° by immersion in an ice–water slush. We attach no unique significance to results obtained at this temperature.

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Received August 26, 1966

Nuclear Magnetic Resonance Evidence for a Three-Well Torsional Potential in Vinylcyclopropane

Sir:

We have observed the nmr spectrum of vinylcyclopropane as a function of temperature from −60° to +76°, in *ca.* 10% v/v solutions, using a Varian HA-100 spectrometer. The four-spin system of the vinyl and adjacent ring protons (Figure 1) was analyzed using the computer program TWOSUM,[1] a development of the program NMRIT described by Ferguson and Marquardt.[2] A method of analysis was adopted which treats the other ring protons as a first-order perturbation. Only three parameters, τ_2, τ_4, and J_{12}, are strongly temperature dependent; these are presented in Table I. A downfield shift of approximately 0.02 ppm on going from CS_2 to CCl_4 at constant temperature was observed for all protons.

Table I. Spectral Parameters

Solvent	Temp, °C	τ_2, ppm	τ_4, ppm	J_{12}, cps
CS_2	−60	4.944	5.017	9.64
CS_2	−30	4.873	5.027	9.13
CS_2	0	4.809	5.035	8.73
CS_2	+31	4.745	5.045	8.34
CCl_4	−30	4.850	5.004	9.10
CCl_4	+31	4.729	5.029	8.38
CCl_4	+53	4.691	5.036	8.16
CCl_4	+76	4.655	5.042	7.94

The uncertainty of each coupling presented is less than 0.1 cps; that of each shielding is less than 0.001 ppm.

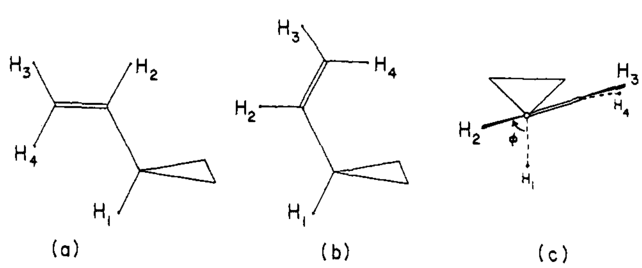

Figure 1. Conformations of vinylcyclopropane.

Chemical shifts in a large number of cyclopropyl derivatives have been interpreted in terms of the anisotropic diamagnetic polarizability of the ring,[3] with the larger component of $\Delta\chi$ normal to the ring. The linear dependence of both proton shifts τ_2 and τ_4 on the coupling J_{12} supports the hypothesis that all of these depend on the same mechanism, a thermal redistribution among conformers related by rotation about the C–C single bond. In this and related systems the low-energy conformer appears to be the *s-trans* form,[4] in which the dihedral angle relating H_1 and H_2 is 180° (Figure 1a). The abnormally high shielding of H_2 at low temperatures would thus reflect its location near the symmetry axis of the ring polarizability tensor.

The relative magnitudes of the H_2 and H_4 shielding shifts, $\Delta\sigma_2$ and $\Delta\sigma_4$, are sensitive to the dihedral angle, ϕ (Figure 1c), of the high-energy conformer or conformers (for dihedral angles other than 0 and 180° these must occur in symmetrically related pairs). Using the point-dipole ring-current approximation we have computed the reduced shieldings, $\sigma_2/\Delta\chi$ and $\sigma_4/\Delta\chi$, and the ratio of their shifts, $\Delta\sigma_4/\Delta\sigma_2$, which is independent of the magnitude of the anisotropy. These values are plotted as a function of the dihedral angle of the upper state, ϕ, in Figure 2.

A graph of τ_4 *vs.* τ_2 should give a straight line whose slope is $\Delta\sigma_4/\Delta\sigma_2$. Our shielding data give two well-defined straight lines, one for each solvent. Their slopes differ significantly, being −0.197 in CCl_4 and −0.138 in CS_2, suggesting upper-state dihedral angles (see Figure 2) of 79 and 86°, respectively. These compare to electron-diffraction values of *ca.* 40° for bicyclopropyl[5] and 0° (the *s-cis* form) for cyclopropylaldehyde.[6] Note that if the upper state of vinylcyclopropane were the *s-cis* form, the shift ratio (Figure 2) would be *ca.* −1.2, an order of magnitude larger than that observed, because of the high shielding of H_4 in that conformer (Figure 1b). The predicted values of the shift ratio do not involve any assumption about the magnitude of the anisotropy, nor would a more refined geometric model (*e.g.*, treating the polarization as a current loop[7]) significantly alter these conclusions.

If the coupling between protons 1 and 2 takes the value J_l in the lower energy conformer and J_u in each

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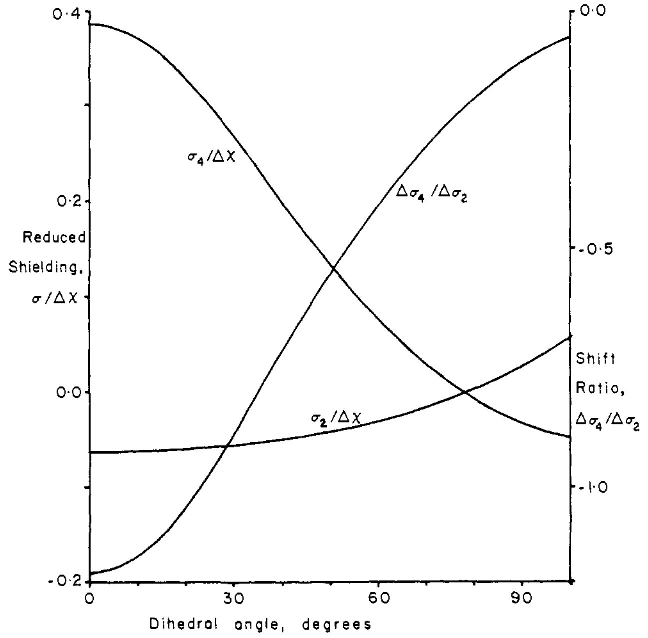

Figure 2. Computed shieldings arising from the ring anisotropy.

of the two upper ones, the observed population-weighted average value, J_{12}, may be used to deduce the fractional population, x, in upper states.

$$x = (J_1 - J_{12})/(J_1 - J_u)$$

A plot of the logarithm of $x/(1 - x)$ *vs.* $1/T$ yields the energy separation of the conformers, ΔE; the rate of change of τ_2 or τ_4 with x yields the anisotropy, $\Delta\chi$. The values deduced depend on the assumed conformer couplings, J_1 and J_u. Table II presents ΔE and $\Delta\chi$ as functions of reasonable choices of the conformer couplings, which are consistent with those in related systems[8] and which also appear to give the most linear $1/T$ plots. The energy separations are consistent with other determinations;[4,9] the values of the anisotropy are somewhat larger than those derived by less direct methods.[3]

Table II. Energy Difference (ΔE) and Anisotropy ($\Delta\chi$) *vs.* Conformer Couplings, J_1 and J_u

J_1, cps	J_u, cps	ΔE, kcal	$\Delta\chi \times 10^{30}$, cm^3
11.5	1.5	0.93	51.
12.5	0.5	0.73	62.
12.5	1.5	0.79	57.
12.5	2.5	0.77	52.
13.5	1.5	0.66	62.

Acknowledgment. We wish to acknowledge the assistance of D. M. Cameron, L. G. Walker, R. D. Green, B. Sykes, and Miss J. Maynes. This work was supported in part by the National Research Council of Canada (Grant No. A-2051).

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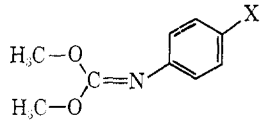
Received August 15, 1966

Isomerization Rates of Iminocarbonates

Sir:

Until recently, examples of geometric isomerism due to restricted rotation around a carbon–nitrogen double bond were observed only for those in which an electronegative atom such as oxygen, nitrogen, or halogen was bonded to the imino nitrogen. The isolation of geometric isomers of imines by Curtin[1] was the first unequivocal demonstration of the existence of stereoisomeric compounds in which a carbon atom was bonded to the imino nitrogen. The extraordinary susceptibility of the configurational stability to the group bonded to imino nitrogen in compounds such as $Ar_2C{=}N{-}X$ is exemplified by the fact that the isomerization rate is faster by a factor of 10^{14} for the compound where $X = C_6H_5$ than for that where $X = OCH_3$.[2]

We now wish to report the first stereochemical study of an analogous class of compounds, the iminocarbonates (I). The distinguishing feature of iminocarbonates[3] is that they contain an electronegative hetero atom bonded to the imino carbon. The nmr spectra of compounds I all show a single methoxyl resonance at room temperature. Cooling the sample results first in a broadening of the methyl signal and then in the formation of a distinct doublet. The pertinent nmr and kinetic data are given in Table I.



I

The first three entries in Table I demonstrate that the process obeys a first-order rate law and is attributed to inversion of the aryl group. The data also show that substituents on the phenyl group have very little effect on the isomerization rate. In acetone solution, there is less than a threefold difference in the first-order rate constants between the chloro- and methyl-substituted compounds. The rate ratio in chloroform is only 1.3. This is unlike the results obtained on isomerization rates of imines for which a ρ value of between +1 and +2 was found.[4] The most important feature of the data is the remarkably low E_a values. Only for the isomerization of a perfluoroalkylimine has an E_a value as low as 13 kcal/mole been obtained.[5] The anils of substituted benzophenones have isomerization E_a values ranging from 17 to 20 kcal/mole, while that of acetone anil measured in quinoline is 21 kcal/mole.[6] A comparison of rates extrapolated to 60°

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(3) The previously unreported *p*-chloro compound (*Anal.* Found: C, 54.23; H, 5.16; N, 6.97) and the *p*-methoxy compound (*Anal.* Found: C, 67.20; H, 7.34; N, 7.68) were prepared by the method described by H. Tieckelmann, and H. W. Post, *J. Org. Chem.*, **13**, 268 (1948), and purified by chromatography through neutral alumina and then distilled at 53° (0.02 mm) and 55° (0.07 mm), respectively. The infrared and integrated nmr spectra were consistent with the assigned structures.

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