determined as 3.5; pK_I of benzimidazole was found as 5.4. Since at these pH values α_1 for both is equal to 1.0, the increase of rate with pH results from α_2 mainly.

The enhanced rates of the polymers *vs.* the monomers in these particular cases is therefore mainly due to a modified contribution of the *anionic* fractions of the polymers.

With poly-4(5)-vinylimidazole and the negatively charged substrate NABA the results were similar to those previously observed by Letsinger and Savereide[12] for analogous systems. The protonated sites (α_0), which do not catalyze the hydrolysis of PNPA, serve as binding sites for NABA. As a result a bell-shaped pH–rate profile was observed (Fig. 2) with a strong maximum near pH 7.5. At this point the catalytic rate of poly-4(5)-vinylimidazole is five times faster than that of imidazole with NABA, and *ca.* 12 times the latter's rate with PNPA. On the other hand, while at pH 8.0 the catalytic activity of poly-5(6)-vinylbenzimidazole with NABA was found comparable to that of benzimidazole, at pH 10.0 the polymer was found to be 50-fold faster than the monomer. Since at these pH values α_0 for this polymer is zero, the enhancement in this case can be only explained as for the neutral substrate.

Acknowledgment.—The authors are indebted to Professor Herbert Morawetz for his stimulating and helpful advice. Financial support by the United States Chemical Corps is gratefully acknowledged.

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Conformer Populations and Thermodynamic Data from Temperature Dependent Circular Dichroism Measurements[1,2]

Sir:

Recent measurements[3] of circular dichroism (C.D.) curves over relatively large ranges of temperature open a new door to comparatively accurate information on the population of conformers in flexible, optically active molecules. Under favorable circumstances, $\Delta G°$, $\Delta H°$, and $\Delta S°$ pertinent to the distribution of conformers may be derived from the C.D. data. In addition, similar information relating to solvation of an optically active species can sometimes be obtained. We confine ourselves in the present note to a quantitative treatment of a two-conformer equilibrium, and adapt to our purposes a type of analysis used previously in connection with monochromatic rotations.[4]

For a particular absorption band, the *observed* total rotational strength R_0^T at temperature T can be derived[5] from the relevant C.D. curve. If R_a and R_b denote the rotational strengths associated with the lower energy conformer a and the higher energy conformer b, respectively, then assumption of a Boltz-

(1) Paper XCIII in the Stanford series "Optical Rotatory Dispersion Studies." For preceding article see C. Djerassi, J. Burakevich, J. W. Chamberlin, D. Elad, T. Toda, and G. Stork, *J. Am. Chem. Soc.*, in press.

(2) Financial support from the Alfred P. Sloan Foundation (A.M.) and the National Science Foundation (Grant G-19905 to Stanford University) is gratefully acknowledged.

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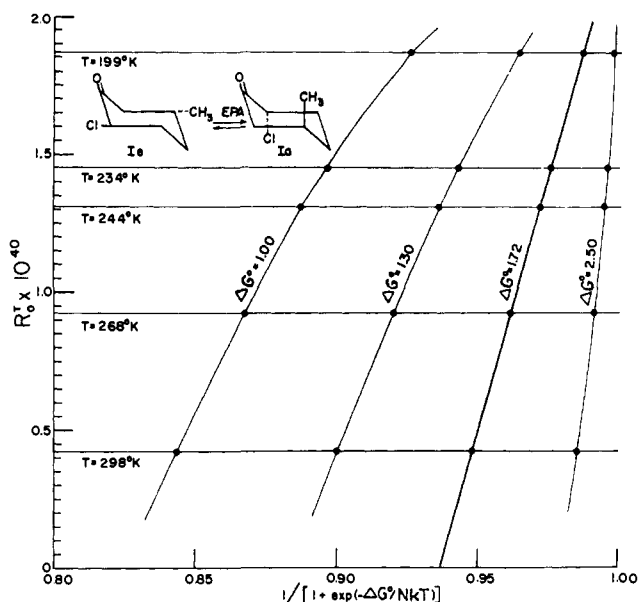(5) C. Djerassi, "Optical Rotatory Dispersion," McGraw–Hill Book Co., New York, N. Y., 1960, p. 164.

mann distribution for the conformers leads to the following expression relating R_0^T to R_a and R_b

$$R_0^T = (R_a - R_b)[1 + \exp(-\Delta G°/NkT)]^{-1} + R_b \quad (1)$$

Here N is Avogadro's number, k is Boltzmann's constant, and $\Delta G°$ is the standard Gibbs free energy change for the reaction a $\rightleftharpoons$ b. The equilibrium constant K can be written as

$$K = (R_a - R_0^T)/(R_0^T - R_b) \quad (2)$$

According to eq. 1, a plot of R_0^T *vs.* $1/[1 + \exp(-\Delta G°/NkT)]$ should yield a straight line for the proper temperature-dependent values of $\Delta G°$. If $\Delta G°$ is in fact a constant over the temperature range studied, then substitution of various trial values for $\Delta G°$ into eq. 1 yields a family of curves, only one of which (that for the proper $\Delta G°$) is a straight line.[6,7] From the slope and intercept of this line one can obtain the correct values for R_a and R_b, which, when substituted into eq. 2, provide an explicit temperature-dependent expression for K in terms of the experimental R_0^T.

It is noteworthy that one obtains specific values for the rotational strengths (R_a and R_b) of the nonisolatable forms a and b. Without solvent corrections, these values refer to the apparent rotational strengths in solution, rather than to their values *in vacuo.* However, because K appears as a ratio of R-values, the equilibrium constant can be shown to be largely independent of these solvent corrections if the solvation effects themselves are not markedly temperature dependent, as often seems to be the case.[8] Hence the K-value obtained is a reasonable reflection of the population of conformers present. Moreover, it follows as a corollary that once one obtains R_a and R_b values in one solvent, K can be found in any other solvent at any temperature T simply by measuring R_0^T for that solvent. *A facile means for obtaining K in a variety of solvents is therefore available.*

By way of specific example, we consider the equilibrium $I_e \rightleftharpoons I_a$ in $(+)$-*trans*-2-chloro-5-methylcyclohexanone in EPA.[3] Some of the curves corresponding to the plot of eq. 1 are indicated in Fig. 1. An optimized[6] straight line is obtained for $\Delta G° = 1.72$ kcal./mole, with $R_a = +2.34 \times 10^{-40}$ c.g.s. and $R_b = -34.7 \times 10^{-40}$ c.g.s. This value for $\Delta G°$ is good to ± 0.09 kcal./mole. Since $\Delta G°$ is assumed to be temperature-independent, $\Delta H° = \Delta G°$, and $\Delta S° = 0$ for the equilibrium $I_e \rightleftharpoons I_a$.

Conformer populations in various solvents at 25°, calculated from the preceding values of R_a and R_b in conjunction with measured[3] values of R_0^{298}, are given in Table I along with estimates obtained previously from ultraviolet and optical rotatory dispersion data. The three sets of percentages agree within the stated error limits.

(6) A minimal least-squares fit to a straight line can be used to obtain a better value for $\Delta G°$ than can be achieved visually from the plot. In the example of *trans*-2-chloro-5-methylcyclohexanone (1) discussed later, we used such a least-squares procedure. In this case, the eye could distinguish easily to better than 0.05 kcal./mole.

(7) Equations of the mathematical forms 1 and 2 appear in connection with a variety of kinetic and spectroscopic measurements [see E. L. Eliel, *J. Chem. Educ.*, **37**, 126 (1960)]. Data from such measurements are amenable to the present method of analysis so long as the quantities analogous to R_a and R_b, (*e.g.*, n.m.r. chemical shifts for pure conformers) are temperature independent, and the other stated assumptions are met.

(8) Calculation of R_0^T from the raw experimental data must take account of the concentration changes accompanying the volume variation with temperature, which also produce changes in the index of refraction of the medium. According to the simple $(n^2 + 2)/3$ Lorentz-type correction factor, this implies a further correction for R_0^T. However, in those steroids studied so far which one may expect to be rigid, the differences between R_0^T at 25° and $-192°$ generally represent changes of less than 4%, and these differences have been both positive and negative. Hence, in the absence of further information, we have ignored any corrections due to changes in the index of refraction with temperature.

Fig. 1.—Plot of eq. 1 for various trial values of $\Delta G°$ (kcal./mole).

A variation of R_0^T with temperature can also be found in situations where rigidity of the molecular framework would seem to preclude the possibility of radical conformational changes. For example, we have observed such temperature variations for R_0^T in camphor and norcamphor. In these cases, no temperature-independent value for $\Delta G°$ would yield a straight line

TABLE I

| | | % Diequatorial conformer | | |
Solvent	$R_0^{298} \times 10^{40}$	Present C.D. data	Ultra-violet[a]	O.R.D.[a]
Methanol	+1.40	97 ± 2	100	99
Dioxane	+0.89	96 ± 2	88	100
EPA	+0.42	95 ± 2		
CCl₄	−1.21	90 ± 3		
Isooctane	−1.87	89 ± 3	82	82

[a] From J. Allinger, N. L. Allinger, L. E. Geller, and C. Djerassi, J. Org. Chem., 26, 3521 (1961). These authors indicate an accuracy of about ±10%.

in the plot suggested for eq. 1, and these results are indicative of nonnegligible $\Delta S°$ values, such as one might expect in the case of asymmetric solvation.[9] The analysis of these data in terms of this hypothesis and the problems posed by a multiplicity of conformers will be treated in a later paper.

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Nuclear Magnetic Resonance Spectroscopy and (p → d) π-Bonding in Silicon Compounds

Sir:

In several studies of the n.m.r. spectra of substituted methylsilanes, it has been concluded that the results can best be explained in terms of (p → d) π-bonding between silicon and electronegative atoms or groups.[1–5]

(1) H. Schmidbaur and M. Schmidt, J. Am. Chem. Soc., 84, 1069 (1962).

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The evidence cited includes the "small" low-field shifts of the proton resonances in hexamethyldisiloxane[1] and tris(trimethylsilyl)amine[2] as against tetramethylsilane; the smaller low-field shifts with increasing n in the series $(CH_3)_{4-n}MCl_n$ and $(CH_3)_{3-n}MHCl_n$ when M is Si than when M is C[3,4]; the decrease in shielding along the series $(CH_3)_3SiX$, X = F, Cl, Br, I[5]; and the increase in $J(^{13}CH_3)$ in $(^{13}CH_3)SiX(^{12}CH_3)_2$ and in $J(^{29}SiH)$ in $(^{12}CH_3)_3{}^{29}SiX$ along the series CH₃ < F < Cl < Br < I.[5] We have recently studied several substituted methylsilanes and related alkanes; from the results, taken with published work, we conclude that many of the so-called anomalies in the spectra of silicon compounds are also to be found in the spectra of similar derivatives of carbon, and that it is at present unjustified to use these effects as evidence in favor of the occurrence of π-bonding in silicon compounds.

The β-proton shieldings in the series of compounds CH_3SiH_2X decrease along the series X = H, N, O, F (which is consistent with increasing inductive deshielding), but increase along the series X = I, Br, Cl, F[6]; a similar effect is observed both in the dimethylsilyl[7] and trimethylsilyl[5] halides, and has been explained for the last named derivatives in terms of increasing (p → d) π-bonding between silicon and the halogen atoms in the order I < Br < Cl < F. The same effect, however, has been observed in ethyl,[8,9] isopropyl,[8,9] t-butyl,[8] and cyclohexyl[10] halides. At present there is no satisfactory explanation for this, but since it occurs in compounds in which the α-atom is carbon, it is unlikely to be caused by (p → d) π-bonding.

It is now clearly established that SiHXYZ resonance chemical shifts are less sensitive than are CHXYZ shifts to changes in the rest of the molecule[6,7]; this is true not only when the substituents are potentially strongly π-bonding groups, such as –OR or –Cl, but also for others (like –I, –Br, and –SR) which are unlikely to be involved in strong π-bonds. It is therefore not surprising that CH_3SiXYZ resonances are less sensitive than CH_3CXYZ resonances to changes in X, Y, and Z. Substitution of –I (or –Br) for (Si)H in the three methylsilanes, for instance, shifts the β-proton resonance 0.7 (or 0.5) p.p.m. to low field, while in alkanes the analogous substitution shifts are about 0.9 and 0.7 p.p.m., respectively.[9] For polar, potentially strongly π-bonding groups, the shifts follow the same pattern: –F or –OR substitution shifts in the methylsilanes are about 0.15 and 0.05 p.p.m. to low field, respectively,[6] as against substitution shifts for the same substituents in alkanes of some 0.3 and 0.1 p.p.m.[9] There is no reason to conclude from these data that there is any unusual bonding in the silicon compounds.

Rather more convincing evidence indicating (p → d) π-bonding comes from the high-field shifts of the SiH proton resonances of fluorosilane (0.05 p.p.m.),[11] difluorosilane (0.20),[11] and methylfluorosilane (0.03)[7]; and of the β-proton resonances of methylfluorosilane (0.05)[7] and dimethylfluorosilane (0.02)[7] on substitution of one of the (Si)H atoms by –F. Even this, however, is by no means decisive. It is very dangerous to draw conclusions from changes in SiH chemical

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