solution was treated with chloroform, a partial fractionation occurred. Elemental analysis and mass spectrum of the solid that was not readily soluble in chloroform confirmed molecular formula for a nitroso dimer $C_{12}H_{20}N_2O_2Cl_2$, and the uv and ir spectra (uv$_{max}$ (EtOH) 278.0 nm (ϵ 7640); ir (KBr) 1420, 1300, 1110, 1045 cm^{-1}) indicated that this was a *Z* dimer. In ethanol, on standing, the intensity of the absorption at 278.0 nm gradually decreased and finally disappeared while at the same time a new absorption at 294.5 nm appeared, showing that the isomerization of the *Z* dimer to the thermodynamically more stable *E* isomer was taking place. On further standing the intensity of the absorption at 294.5 nm gradually decreased, and, when it had completely disappeared, the solution contained 2-chlorocyclohexanone oxime. Furthermore, a 100-MHz proton NMR spectrum of the crude reaction product in sulfur dioxide at 0° clearly showed that the crude reaction product was a mixture of both the (*Z*)- and (*E*)-1,1'-dioxidodiazenediylbis(*trans*-2-chlorocyclohexanes), which on standing underwent relatively fast isomerization to both *E* isomers, **1** and **2**, and a small amount of **3**.

(19) Numerous reports dealing with nitroso dimers have disregarded the possibility that the dimers investigated may exist as mixtures of the corresponding *dl* and meso compounds; e.g., (a) J. B. Miller, *J. Org. Chem.*, **26**, 4905 (1961); (b) J. Meinwald, Y. C. Meinwald, and T. N. Baker, III, *J. Am. Chem. Soc.*, **86**, 4074 (1964); (c) K. H. Bell, *Aust. J. Chem.*, **24**, 1089 (1971); (d) B. W. Ponder and P. W. Wheat, *J. Org. Chem.*, **37**, 543 (1972); (e) Y. L. Chow, S. C. Chen, and D. W. L. Chang, *Can. J. Chem.*, **48**, 157 (1970); (f) C. Shive and L. B. Clapp, *J. Org. Chem.*, **36**, 1169 (1971); (g) K. A. Ogloblin and V. P. Semenov, *Dokl. Akad. Nauk SSSR*, **155**, 145 (1964); (h) H. C. Hamann and D. Swern, *J. Am. Chem. Soc.*, **90**, 6481 (1968); also references 1-7, 11, and many others. That the lack of understanding of the basic principles involved is not restricted only to the dimerization of nitroso compounds is illustrated by a recent paper by D. D. Tanner, N. Nychka, and T. Ochiai, *Can. J. Chem.*, **52**, 2573 (1974).

(20) However, from the available information it is not possible to decide which one of the two isolated diastereoisomers is the *dl* pair and which one is the meso compound. ^{13}C NMR spectra of (*E*)-1,1'-dioxidodiazenediylbis(*trans*-2-chlorocyclohexanes) and several other diastereoisomeric nitroso dimers will be presented elsewhere.

(21) Due to the great ease with which the *Z* isomers isomerize in solution to the *E* isomers,[11] it was not possible to achieve a similar separation of the diastereoisomeric (*Z*)-*dl*-pair and (*Z*)-meso compound.

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Conformational Equilibrium Trapping by High-Vacuum Cryogenic Deposition

Sir:

High-energy conformations are difficult to study directly because of their low equilibrium concentrations at room or low temperatures. This problem is especially serious when the barrier separating two conformations is relatively low, e.g., <15 kcal/mol, and the minor form lies more than 1 kcal/mol or so above the major one. Low temperatures are required under these conditions to avoid averaging effects in NMR spectroscopy, but this results in a very small population of the minor form. We now report a method for observing the NMR spectra of high-energy conformations for systems which have barriers of about 8 kcal/mol or higher.

The apparatus used is very similar to that employed in flash vacuum pyrolysis.[1] The compound, as a low pressure gas (ca. 0.2 Torr), is heated by passing it through a glass or quartz tube (2 × 30 mm) that is surrounded by an electrically heated resistance wire. The gas, which contains a relatively high proportion of the minor form because of its high temperature, is allowed to impinge in a high vacuum on a copper surface cooled to liquid nitrogen or other temperature. The deposited compound cools so rapdily that the conformational equilibrium set up at the high temperature is trapped.[2] The nonequilibrium population of the minor form remains unchanged for a time that depends on the temperature and the barrier separating the minor from the major form. At −170°, a free energy barrier of 8 kcal/mol gives a half-life of 8 hr, which is ample for NMR observation or other physical measurements. The NMR spectrum of a deposited sample is obtained by slowly condensing a suitable solvent onto the cold sample and allowing the solution to drip into a cold NMR tube, which is then transferred to a precooled NMR probe.

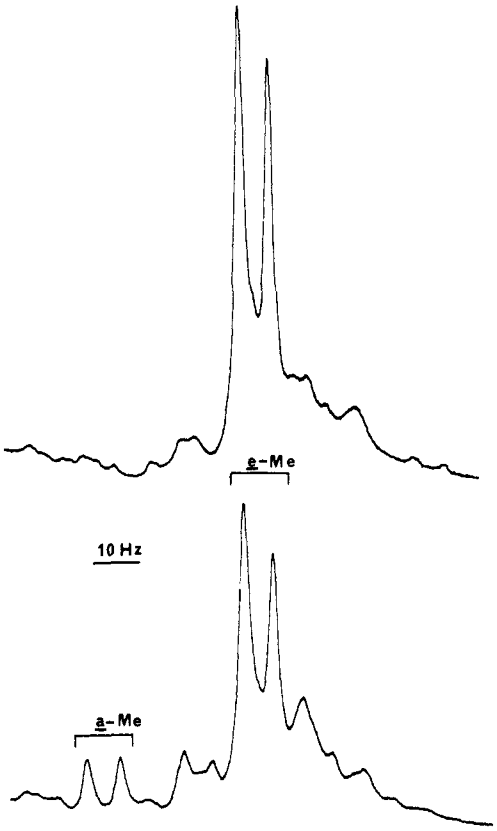
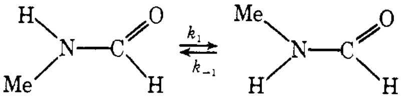


Figure 1. Bottom: 251-MHz ^{1}H NMR spectrum at −160° of methylcyclohexane obtained by high-vacuum deposition from a temperature of 500° onto a surface cooled to −175° (only the high-field region is shown). Top: same sample as at bottom after warming to −128° and recooling to −160°.

The instrumentation described above has been used to study the cis-trans isomerism in *N*-methylformamide (I) and the axial-equatorial equilibrium in methylcyclohexane, two systems that were chosen to test the practicality of the method. Compound I was deposited at −65° from a temperature of 540° and the ^{1}H NMR spectrum was measured in 1,2-dichloroethane. Integration of the signals showed 25% of the minor (cis) form[3] and this corresponds to a $\Delta G°$ (see below) in the gas phase at 540° of −2.2 kcal/mol, provided that the equilibrium is perfectly trapped. The equilibrium constant and the rate for return to equilibrium at −10.4° were measured and gave $K_{\text{equil}} = 16$, $\Delta G° = -1.44$ kcal/mol, $k_1 = 3.5 \times 10^{-4}$ sec^{-1}, $k_{-1} = 2.2 \times 10^{-5}$ sec^{-1}, $\Delta G^{\ddagger}{}_1 = 19.48$ kcal/mol, $\Delta G^{\ddagger}{}_{-1} = 20.92$ kcal/mol for the following reaction.



I-cis I-trans

Measurements of K between −10 and 40° gave $\Delta G°$'s that are almost independent of temperature ($\Delta H°_1 = -1.46 \pm 0.04$ kcal/mol, $\Delta S°_1 = 0.1 \pm 0.1$ eu). Previous NMR lineshape measurements[4] on I at 60° in the same solvent gave $\Delta G^{\ddagger}{}_1 = 19.0$ and $\Delta G^{\ddagger}{}_{-1} = 20.6$ kcal/mol, from which $\Delta G°$ can be calculated to be −1.6 kcal/mol, in satisfactory agreement with the present work. By combining the line-shape data at 60° with the equilibrium data at −10° and using the relationship $\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger$ with $\Delta H^\ddagger$ and $\Delta S^\ddagger$ as temperature-independent quantities, we obtain $\Delta H^\ddagger{}_1 = 20.6 \pm 0.2$, $\Delta H^\ddagger{}_{-1} = 22.1 \pm 0.2$ kcal/mol, $\Delta S^\ddagger{}_1 = 4.4 \pm 0.7$, $\Delta S^\ddagger{}_{-1} = 4.5 \pm 0.7$ eu. These values are much more accurate than those obtained from the NMR line-shape data alone because of the limited temperature range over which rate constants can be determined by line-shape studies.[4]

The efficiency of the equilibrium trapping cannot be calculated from the present data since the assumption of temperature-independent $\Delta H°$ and $\Delta S°$ terms is probably not valid over a large temperature range, and in any event, $\Delta G°$'s in the gas phase and in solution may well be different. It is clear, however, that substantially perturbed populations over the equilibrium values can be obtained.

Methylcyclohexane was deposited at −175° from a temperature of 500° and the ^{1}H NMR spectrum was observed at −160° in a 1:1 mixture of $CHClF_2$ and CCl_2F_2 (Figure 1). A doublet (δ 1.00), ascribed to the axial methyl group, is visible downfield from the resonance of the equatorial methyl group.[5] The population of the axial form is at least 10% and could be as high as 25%. Overlap of the equatorial methyl group doublet with ring proton bands prevents a more accurate measurement of the axial-equatorial ratio. From the known thermodynamic data on methylcyclohexane,[6] the population of the axial form at 500° should be about 30%. The apparent trapping efficiency in this case may be low owing to adventitious reequilibrium at various stages prior to NMR measurements. Further experiments involving ^{13}C NMR and ^{1}H NMR of undeuterated and partially deuterated methylcyclohexane are in progress.

It appears that high-vacuum cryogenic deposition will become a valuable tool in conformational analysis.[7] The method should be applicable to systems with barriers as low as 4-5 kcal/mol by deposition near liquid helium temperatures and observation by infrared or other suitable spectroscopic techniques, and such experiments are underway.

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References and Notes

(1) E. Hedaya and D. McNeil, *J. Am. Chem. Soc.*, **89**, 4213 (1967).

(2) The trapping efficiency should be very good provided that the barrier which prevents reversion of the minor to the major form is much greater than *RT.* (*T* = temperature of the hot gas). There are scattered reports (e.g., R. G. Snyder and J. H. Schachtschneider, *J. Mol. Spectrosc.*, **30**, 290 (1969); G. A. Crowder and H. K. Mao, *J. Mol. Struct.*, **18**, 33 (1973); G. A. Crowder and P. Priettlangkura, *Ibid.*, **18**, 177 (1973)) that compounds deposited as films at cryogenic temperatures from the vapor state at *room temperature* consist of nonequilibrium mixtures of rotamers. This phenomenon has generally been considered as a nuisance which can be overcome by suitable annealing of the deposited film. A recent review dealing with matrix isolation (H. E. Hallam in "Vibrational Spectroscopy of Trapped Species", H. E. Hallam, Ed., Wiley, New York, N.Y., 1973, pp 115 and 116) mentions that the rotameric populations obtained by cryogenic deposition from *room temperature* possibly reflect the equilibrium at the latter temperature, but that proof of this is lacking.

(3) L. A. La Planche and M. T. Rogers, *J. Am. Chem. Soc.*, **86**, 337 (1964).

(4) T. Drakenberg and S. Forsén, *Chem. Commun.*, 1404 (1971). The errors in ΔG, ΔH, and ΔS given by these authors are ±0.3 kcal/mol, ±1.8 kcal/mol, and ±5 eu, respectively; however, it can be calculated from the errors given for the rate constant and temperature in the above reference that the error in ΔG must be no greater than 0.03 kcal/mol. Errors in ΔH and ΔS are correlated and can be quite large if ΔG is obtained over a small temperature range, even if ΔG is quite accurate (K. B. Wiberg, "Physical Organic Chemistry", Wiley, New York, N.Y., 1964, p 378).

(5) The equatorial methyl group has a chemical shift of 0.86 ppm. *cis*-1,4-Dimethylcyclohexane under the same conditions exhibits methyl resonances at 0.96 (a-Me) and 0.86 ppm (e-Me).

(6) F. A. L. Anet and V. J. Basus, to be submitted for publication; see also F. A. L. Anet, C. H. Bradley, and G. W. Buchanan, *J. Am. Chem. Soc.*, **93**, 258 (1971).

(7) Nonequilibrium populations of conformations have been obtained by dissolving conformationally homogeneous crystals in solvents at low temperatures and by related techniques (F. R. Jensen and C. H. Bushweller, *J. Am. Chem. Soc.*, **91**, 3223 (1969)). These methods are difficult or impossible to apply to conformations whose populations are very small.

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Spectroscopic Detection of the Twist-Boat Conformation of Cyclohexane. A Direct Measurement of the Free Energy Difference between the Chair and the Twist-Boat

Sir:

Theoretical calculations on cyclohexane[1] and experimental data on some highly constrained cyclohexane derivatives[1a,2] indicate that the twist-boat conformation of cyclohexane lies about 5-6 kcal/mol above the chair conformation. The equilibrium proportion of cyclohexane twist-boat form at room temperature should be of the order of 0.1% or less,[3] and thus it is not surprising that no direct observation of this form has been reported. However, thermodynamic considerations based on the expected values of $\Delta H°$ and $\Delta S°$ between the chair and twist-boat forms indicate that the concentration of the twist-boat becomes quite substantial at high temperatures, e.g., 30% at 800°.[4] Detection of boat forms at high temperatures by infrared or Raman spectroscopy presents difficulties because of the possible presence of "hot" bands arising from the chair form. We have therefore chosen to trap the high-temperature equilibrium by a high-vacuum deposition technique[5] before carrying out a spectroscopic investigation. The infrared spectrum of the mixture of chair and twist-boat conformations can then be observed at very low temperatures and can be compared with that of the chair form in the pure state. The rate at which the twist-boat returns to the chair can also be obtained by raising the temperature to a suitable value. Since the energy barrier for the isomerization of the twist-boat to the chair is expected to be about 5 kcal/mol,[1] the twist-boat should have a virtually infinite life at 20°K, but should be fairly rapidly transformed to the chair at liquid nitrogen temperature (77°K).

The considerations described above led us to carry out the following experiments. Cyclohexane gas at about 0.2 Torr pressure was heated to ca. 800° (contact times ≃ 10 msec) and allowed to deposit, either in the neat state or in the presence of a large excess of argon (also at 800°) onto a CsI plate cooled to 20°K. The same type of experiment was also carried out with the cyclohexane (and the argon, if used) initially at room temperature instead of at 800°. A well-resolved infrared spectrum (measured at 10°K) of the pure chair conformation is obtained by deposition at 20°K of room-temperature cyclohexane vapor in the presence of argon (mole ratio 1:500). The matrix-isolated chair cyclohexane shows bands (between 600 and 2000 cm^{-1}) at the following frequencies (relative intensities are given in parentheses): 861 (0.38), 865 (0.39), 906 (0.42), 1021 (0.10), 1034 (0.07), 1047 (0.10), 1262 (0.20), 1454 (0.60), and 1457 (1.0). This spectrum is similar to that reported for crystalline (phase II) cyclohexane at liquid nitrogen temperature[6] but is missing some bands[7] because of the absence of intermolecular crystal effects in the argon matrix.[8]

The infrared spectrum at 10°K of cyclohexane deposited from 800° in the presence of argon shows all the bands de-