

It is believed that these spectral changes are due to a slowing of the ring-inversion process for the following reasons. The resonances for the 3-, 4-, and 5-methylene groups develop into two resonances separated by 0.45 ppm. One may compare this value to 0.48 ppm found for the chemical shift difference between axial and equatorial protons in cyclohexane.² The upfield resonance of this set, at 1.29 ppm, is assigned to three axial protons and is somewhat broader than the one at lower field. Qualitatively, the same variation in line widths is found in cyclohexane. Similarly, the 2,6-methylene signal unfolds into two peaks separated by ~ 0.27 ppm, a value close to 0.24 ppm found for the chemical shift difference between axial and equatorial protons in the methylene groups adjacent to the double bond in cyclohexene.⁸ Again, the upfield (axial) resonance is considerably broader than the downfield (equatorial) peak. The vinyl portion of the spectrum undergoes no change beyond slight viscosity broadening over the entire temperature range investigated. That the vinyl protons remain magnetically equivalent even when the conformational rate process is slow tends to rule out the presence of appreciable amounts of certain twist-boat and twist-chair conformations that, *a priori*, have nonequivalent methylene environments.

The signals at 1.74 and 1.29 ppm coalesce at $\sim -105^\circ$, and it is estimated that the rate of the interconversion is $2 \times 10^2 \text{ sec}^{-1}$ at this temperature, a rate that corresponds to $\Delta F^\ddagger = 7.7 \text{ kcal/mole}$.¹⁰ It thus appears that replacement of a single sp^3 carbon atom in cyclohexane with an sp^2 carbon results in a lower barrier to chair-chair interconversion, probably because the number of repulsive H-H nonbonded interactions are reduced. A more accurate assessment of the nature of the conformations of methylenecyclohexane and the energetics of their interconversion will have to await the results of studies with certain deuterated analogs of this molecule.

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(10) Estimated from the formula $k = 2^{1/2}\pi\Delta\nu$; cf. E. F. Caldin, "Fast Reactions in Solution," John Wiley and Sons, Inc., New York, N. Y., 1964, p 237.

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The Barrier to the Inversion of Six-Membered Rings Containing an sp^2 -Hybridized Carbon

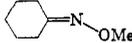
Sir:

Although the barriers to the ring inversion of cyclohexane and cyclohexene derivatives have been studied by variable-temperature nmr, no barrier for a six-membered ring containing only one sp^2 -hybridized carbon atom has been reported. (From epr studies a barrier to the ring inversion of the cyclohexyl radical was estimated to be $4.9 \pm 0.5 \text{ kcal/mole}$;¹ however,

the exact hybridization of this species is uncertain.) Previous investigations of cyclohexanone have shown that at -140° the conformers appear to be rapidly interconverting on the nmr time scale.²

Changes have now been observed in the nmr spectra of cyclohexanone, tetradeuteriocyclohexanone, methylenecyclohexane, and O-methylcyclohexanone oxime at low temperatures. From these changes barriers to the interconversion of these compounds have been calculated (Table I).

Table I. Barriers for Chair-Twist Interconversions of Six-Membered Ring Compounds Containing a Trigonal Carbon Atom

Compound	ΔF^\ddagger , kcal/mole	T, °C
	7.7 ± 0.5	-115
	5.6 ± 0.5	-152
	$< 5.1^a$	-170
	$< 5.2^a$	-168

^a From the data, barriers of 4.9 kcal/mole were calculated, but because of viscosity effects only upper limits could be obtained with confidence.

Clear transitions were observed in the variable-temperature nmr spectra of methylenecyclohexane and O-methylcyclohexanone oxime. For methylenecyclohexane (Figure 1) the two broad peaks of the ring protons, which are observed at room temperature, upon cooling below -109° change into a very complicated set of peaks. Because of the complexity of the spectrum, only maximum and minimum barriers to the interconversion were obtained. (All of the barriers were calculated assuming an intermediate occurs which has a 0.5 probability of becoming product. The reported barriers are to the formation of this intermediate.) From the low-temperature spectrum it is seen that the maximum peak separations lie between 10 and 40 Hz. At -109° (Figure 1b) no separation for any signal is observed; however, assuming the separation is already half complete for a signal whose final maximum separation is 10 Hz, a maximum ΔF^\ddagger of 8.2 kcal/mole can be calculated. Similarly at -119° (Figure 1c) the peaks appear almost completely separated, but assuming that a signal whose maximum separation is 40 Hz is only half-separated at this temperature, a minimum ΔF^\ddagger of 7.2 kcal/mole is obtained. Thus at -114° , $\Delta F^\ddagger = 7.7 \pm 0.5 \text{ kcal/mole}$ assuming an intermediate occurs having a 0.5 probability of becoming product.

Similarly, the barrier for the interconversion of O-methylcyclohexanone oxime was determined to be $5.6 \pm 0.5 \text{ kcal/mole}$ at -152° .

For cyclohexanone (20% by volume in vinyl chloride) and tetradeuteriocyclohexanone (20% by volume in a mixture of vinyl chloride and trifluorochloroethylene),

(1) S. Ogawa and R. W. Fessenden, *J. Chem. Phys.*, **41**, 994 (1964).

(2) J. E. Anderson, D. D. MacNicol, and B. D. Batts, unpublished results as quoted by J. E. Anderson, *Quart. Rev. (London)*, **19**, 426 (1965).

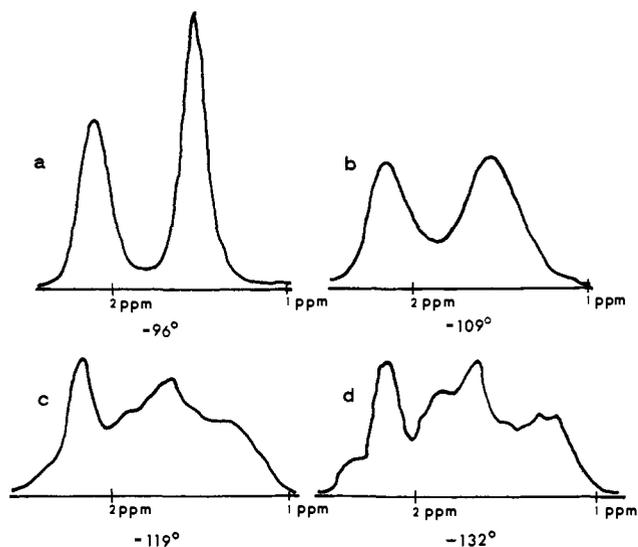


Figure 1. The 60-MHz spectrum of methylenecyclohexane at various temperatures.

below -140° their signals were observed to broaden more rapidly than the peak which corresponds to the TMS internal standard. At -172° , however, the peaks from both the ketone and TMS were extremely broad due to the viscosity of the solution. In neither compound was peak separation observed. The minimum $\nu_{\text{axial}} - \nu_{\text{equatorial}}$ separation which can account for the broadening not attributable to viscosity effects is about 10 Hz. For the deuterated cyclohexanone, the highest temperature at which the spectrum could be at half-maximum separation for this chemical shift difference is -168° . Therefore, the maximum barrier for this process is 5.2 kcal/mole at this temperature. Similar considerations applied to the cyclohexanone spectrum indicate that the maximum ΔF^\ddagger for this process at -170° is 5.1 kcal/mole. The most probable value for these barriers is $\Delta F^\ddagger = 4.9 \pm 0.3$ kcal/mole.

As in the case of cyclohexane, the entropy of activation can very likely be estimated more accurately than it can be measured.^{3,4} The degeneracy for the chair-twist conversion for these compounds is likely two,⁴ which would give an entropy of activation of 1.4 eu. Thus, ΔH^\ddagger differs from ΔF^\ddagger by 1.4 kcal/mole.

The differences in the barriers for methylenecyclohexane and cyclohexanone appear in part to be analogous to those observed in the rotational barriers for propene and acetaldehyde.⁵ This and other contributing factors will be discussed in the full paper.

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(4) B. H. Beck, Ph.D. Dissertation, University of California, Berkeley, Calif., 1967.

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The Molecular and Electronic Structure of the Dichlorobis(diarsine)nickel Monocation¹

Sir:

We have begun detailed studies of the spectroscopic and magnetic behavior of several complexes of the ligand *o*-phenylenebisdimethylarsine (diars), in order to elucidate the key features of their electronic structures. In this communication, we report the results of an X-ray structural determination and esr data that lead to an initial formulation of the electronic structure of the spin-doublet complex $[\text{Ni}(\text{diars})_2\text{Cl}_2]\text{Cl}$.

Brown monoclinic crystals of $[\text{Ni}(\text{diars})_2\text{Cl}_2]\text{Cl}^2$ were grown from ethanol solution. Weissenberg photographs indicate the space group $P2_1/c$, with a cell of dimensions $a = 9.33 \pm 0.01 \text{ \AA}$, $b = 9.69 \pm 0.07 \text{ \AA}$, $c = 14.87 \pm 0.02 \text{ \AA}$, and $\beta = 98.6 \pm 0.1^\circ$. The measured density of 1.87 g cm^{-3} is in exact agreement with the density calculated for two cations and two anions per unit cell. In the space group $P2_1/c$, the two nickel atoms and the two chloride ions must occupy special positions on centers of symmetry.

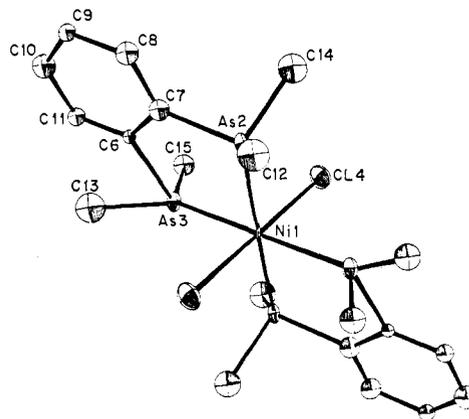


Figure 1. Structure of dichlorobis(diarsine)nickel monocation. The ellipsoids representing the Ni, As, and Cl atoms illustrate the thermal motions implied by the anisotropic temperature factors of these atoms. The carbon atoms are represented by spheres, since their temperature factors were constrained to be isotropic during the refinement of the structure.

All intensity data were collected by the equiinclination Weissenberg method using $\text{Cu K}\alpha$ radiation. Intensities were estimated visually and scaled by standard methods. The atomic form factors for nickel and arsenic were corrected by 3.1 and 1.2 electrons, respectively, for anomalous dispersion. The structure was solved by standard Patterson and Fourier methods and refined by least squares. Eighty parameters were adjusted: coordinates of 13 As, Cl, and C atoms in general positions; anisotropic temperature factors for the Ni, Cl, and As atoms; isotropic temperature factors for the C atoms; and a scale factor. The final R factor is 0.14 for 1366 observed reflections.

The monocation $\text{Ni}(\text{diars})_2\text{Cl}_2^+$ is monomeric and has the structure shown in Figure 1. The four arsenic atoms of two diars ligands surround the nickel atom in

(1) Acknowledgment is made to the National Science Foundation for support of this research. We thank Professor Barbara W. Low for use of equipment, Dr. Maurice Lovell for helpful discussions, and Dr. Steven Weiner for help with some of the esr measurements.

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