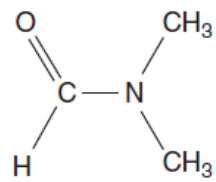
Lecture # 21

5.2.1 Hindered Rotation

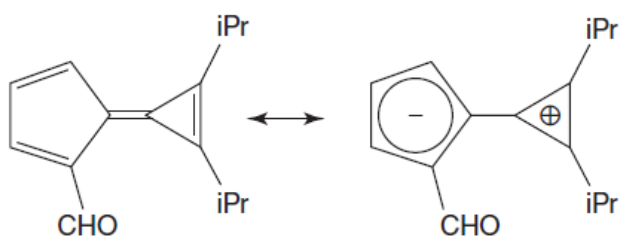
Normally, rotation around single bonds has a barrier below 5 kcal mol^{-1} and occurs faster than the NMR time scale. Rotation around the double bond of alkenes, on the other hand, has a barrier that is normally above 50 kcal mol^{-1} and is slow on the NMR time scale. There are numerous examples of intermediate bond orders, however, whose rotation occurs within the NMR time scale. Hindered rotation about the C—N bond in amides such as *N*,*N*-dimethylformamide (**5.4**)



5.4

provides a classic example of site exchange. At room temperature, exchange is slow and two methyl resonances are observed, whereas, above 100 °C, exchange is fast and a single resonance is observed. The measured barrier is about 22 kcal mol^{-1}.

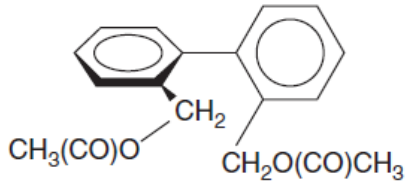
Hindered rotation occurs on the NMR time scale for numerous other systems with partial double bonds, including carbamates, thioamides, enamines, nitrosamines, alkyl nitrites, diazoketones, aminoboranes, and aromatic aldehydes. Formal double bonds can exhibit free rotation when alternative resonance structures suggest partial single bonding. The calicene **5.5**,



5.5

for example, has a barrier to rotation about the central bond of only 20 kcal mol^{-1}.

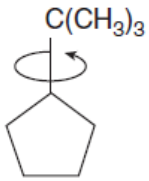
Steric congestion can raise the barrier about single bonds enough to bring it into the NMR range. Rotation about the single bond in the biphenyl **5.6**



5.6

is raised to a measurable 13 kcal mol^{-1} by the presence of the ortho substituents, which also provide diastereotopic methylene protons as the dynamic probe.

Hindered rotation about an sp^3—sp^3 bond can sometimes be observed when at least one of the carbons is quaternary. Thus, at −150 °C, the *tert*-butyl group in *tert*-butylcyclopentane (**5.7**) gives two resonances in the ratio of 2 : 1, since two of the methyl groups are different from the third (**5.7a**).



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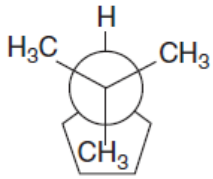
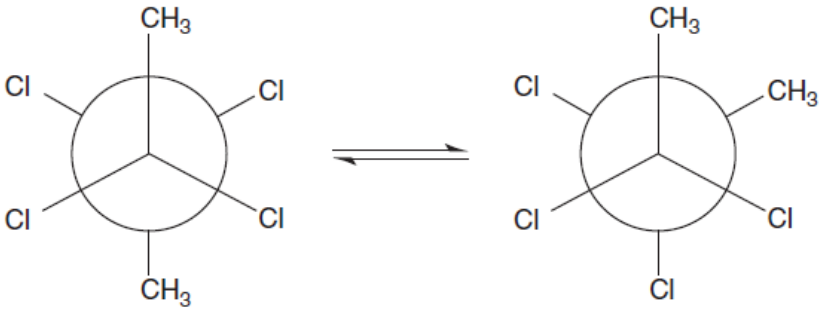


5.7a

Hindered rotation has frequently been observed in halogenated alkanes. The increased barrier probably arises from a combination of steric and electrostatic interactions. 2,2,3,3-Tetrachlorobutane (**5.8**)



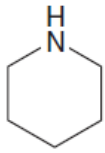
5.8

exhibits a 2 : 1 doublet below −40 °C from anti and gauche rotamers that are rotating slowly on the NMR time scale.

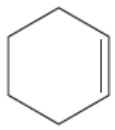
When both atoms that constitute a single bond possess nonbonding electron pairs, the barrier often is in the observable range. The high barrier may be due to electrostatic interactions or repulsions between lone pairs. For example, the barrier to rotation about the sulfur–sulfur bond in dibenzyl disulfide ($C_6H_5CH_2S—SCH_2C_6H_5$) is 7 kcal mol^{-1}. Similar high barriers have been observed in hydrazines (N—N), sulfenamides (S—N), and aminophosphines (N—P).

5.2.2 Ring Reversal

Axial–equatorial interconversion through ring reversal has been studied in a wide variety of systems in addition to cyclohexane, including heterocycles such as piperidine (**5.9**),



5.9



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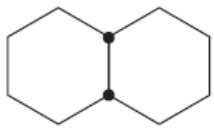

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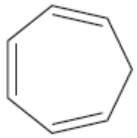
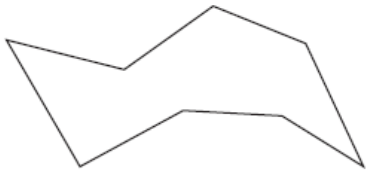


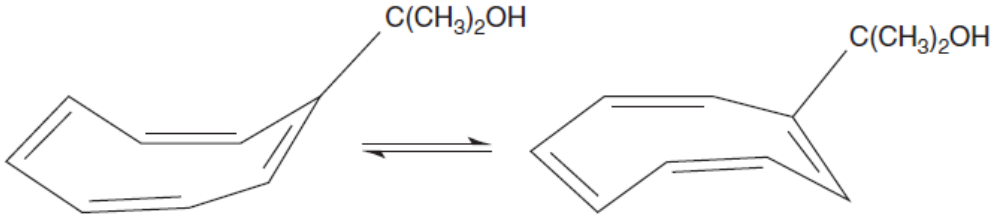
5.12

unsaturated rings such as cyclohexene (**5.10**), fused rings like *cis*-decalin (**5.11**), and rings of other than six members, such as cycloheptatriene (**5.12**). Cyclooctane and other eight-membered rings have been examined extensively. The pentadecadeutero derivative of the parent compound exhibits dynamic behavior below −100 °C, with a free energy of activation of 7.7 kcal mol^{-1}. The dominate conformation appears to be the boat–chair (**5.13**).



5.13

Cyclooctatetraene (**5.14**)



5.14

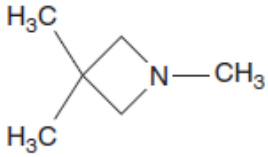
undergoes a boat–boat ring reversal. The methyl groups on the side chain provide the diastereotopic probe and reveal a barrier of 14.7 kcal mol^{-1}. The favored transition state is a planar form with alternating single and double bonds.

5.2.3 Atomic Inversion

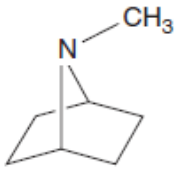
Trisubstituted atoms with a lone pair, such as amines, may undergo the process of pyramidal atomic inversion on the NMR time scale. The resonances of the two methyls in the aziridine **5.15**

5.15

become equivalent at elevated temperatures through rapid nitrogen inversion. This barrier is particularly high (18 kcal mol^{-1}) because of angle strain in the three-membered ring, which is higher in the transition state than in the ground state. The effect is observed to a lesser extent in azetidines (**5.16**, 9 kcal mol^{-1}) and in strained bicyclic systems such as **5.17** (10 kcal mol^{-1}).

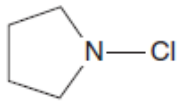


5.16

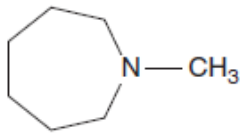


5.17

The inversion barrier may be raised when nitrogen is attached to highly electronegative elements. This substitution increases the s character of the ground-state lone pair. Since the transition-state lone pair must remain p-hybridized, the barrier is higher, as in *N*-chloropyrrolidine (**5.18**).



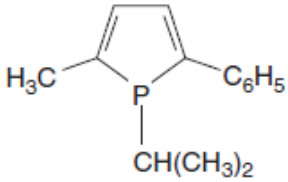
5.18



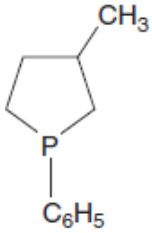
5.19

When neither ring strain nor electronegative substituents are present, barriers are low, but still often measurable, as in *N*-methylazacycloheptane (**5.19**, 7 kcal mol^{-1}) and 2-(diethylamino)propane, $(CH_3CH_2)_2NCH(CH_3)_2$ (6.4 kcal mol^{-1}). In the latter case, the transition state is considered to be a mix of nitrogen inversion and C—N bond rotation.

Inversion barriers for elements in lower rows of the periodic table generally are above the NMR range. Thus chiral phosphines and sulfoxides are isolable. Barriers must be brought into the observable NMR range by substitution with electropositive elements, as in the diphosphine $CH_3(C_6H_5)P—P(C_6H_5)CH_3$, whose barrier of 26 kcal mol^{-1} compares with 32 kcal mol^{-1} in $CH_3(C_6H_5)(C_6H_5CH_2)P$. The former is within the NMR range and the latter is not. The barrier in phosphole **5.20**



5.20



5.21

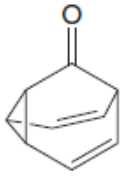
is lowered because the transition state is aromatic. Its barrier of 16 kcal mol^{-1} compares with 36 kcal mol^{-1} in a saturated analogue, **5.21**.

5.2.4 Valence Tautomerizations and Bond Shifts

The barriers to many valence tautomerizations fall into the NMR range. A classic example is the Cope rearrangement of 3,4-homotropilidine (**5.22**).

5.22

At low temperatures, the spectrum has the features expected for the five functionally distinct types of protons (disregarding diastereotopic differences). At higher temperatures, the Cope rearrangement becomes fast on the NMR time scale, and only three types of resonances are observed (14 kcal mol^{-1} for the 1,3,5,7-tetramethyl derivative). When a third bridge is added, as in barbaralone (**5.23**),

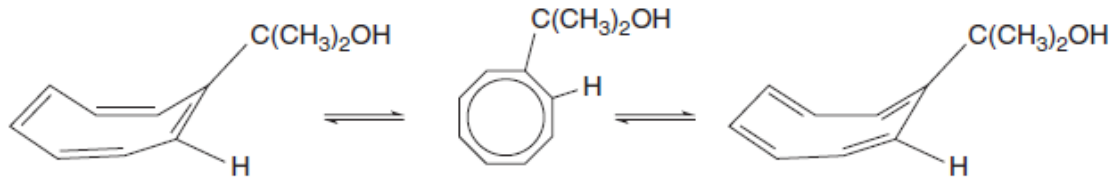


5.23

5.24

steric requirements of the rearrangement are improved, and the barrier is lowered to 9.6 kcal mol^{-1}. When the third bridge is an ethylenic group, the molecule is bullvalene (**5.24**). All three bridges are identical, and a sequence of Cope rearrangements renders all protons (or carbons) equivalent. Indeed, the complex spectrum at room temperature becomes a singlet above 180 °C (12.8 kcal mol^{-1}). Molecules that undergo rapid valence tautomerizations often are said to be *fluxional*.

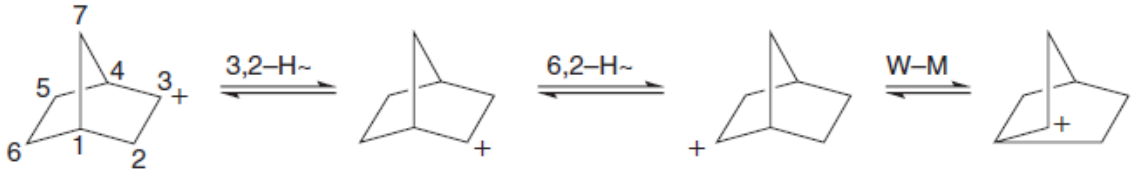
Cyclooctatetraene offers another example of fluxional behavior. In an operation distinct from boat–boat ring reversal depicted in **5.14**, the locations of the single and double bonds are switched via the antiaromatic transition state **5.25b**.



5.25a **5.25b** **5.25c**

The transition state to ring reversal in **5.14** has alternating single and double bonds. The proton adjacent to the substituent is different in the bond-shift isomers **5.25a** and **5.25c**. The barrier to bond switching was determined from the conversion of the proton resonance from two peaks to one (17.1 kcal mol^{-1}). The barrier to bond switching is higher than that to ring reversal because of antiaromatic destabilization that is present in the equal-bond-length transition state **5.25b**.

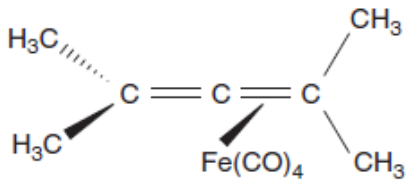
Rearrangements of carbocations also may be studied by NMR methods. The norbornyl cation (**5.26**)



5.26

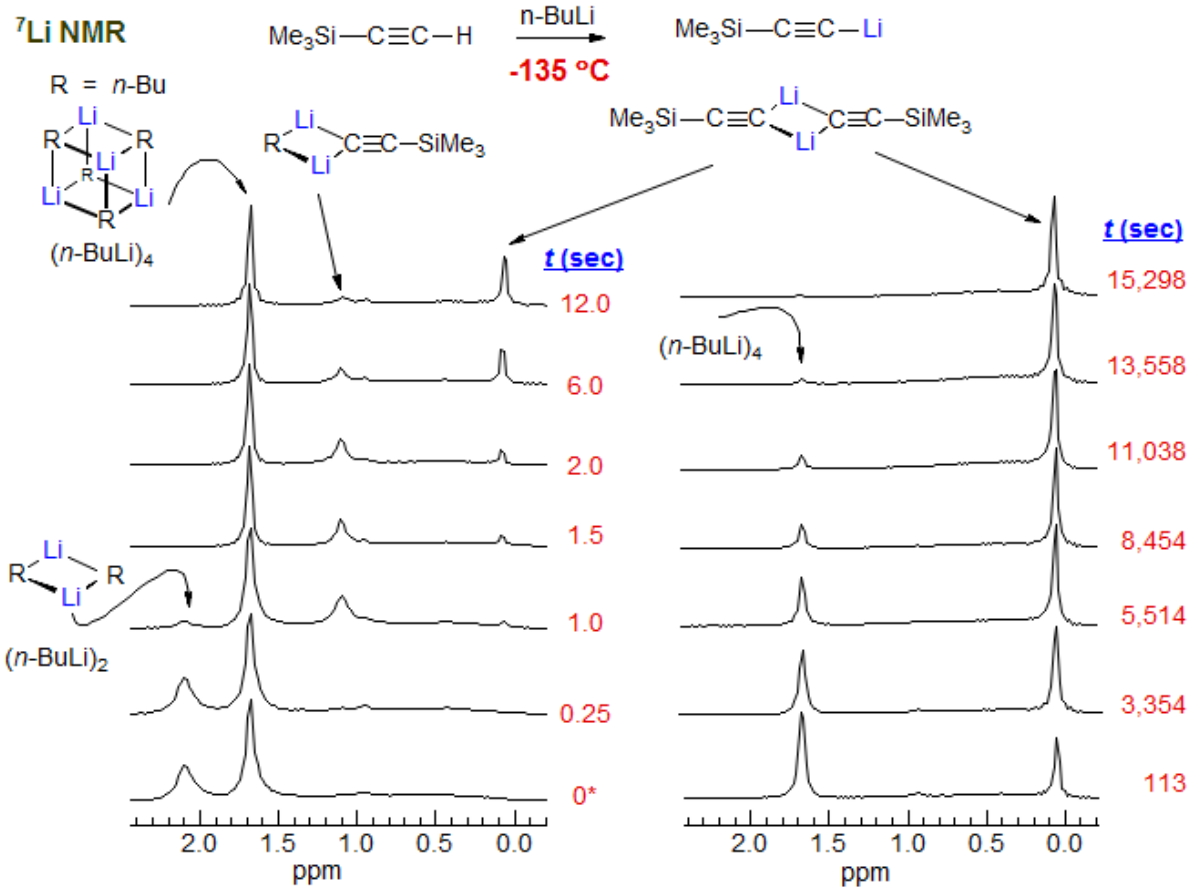
may undergo 3,2- and 6,2-hydride shifts, as well as Wagner–Meerwein (W–M) rearrangements. The sum of these processes renders all protons equivalent, so that the complex spectrum below −80 °C becomes a singlet at room temperature. The slow process appears to be the 3,2-hydride shift, whose barrier was measured to be 11 kcal mol^{-1}.

Many examples of fluxional organometallic species have been investigated. Tetramethylalleneiron tetracarbonyl (**5.27**)

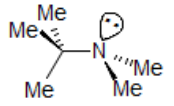


5.27

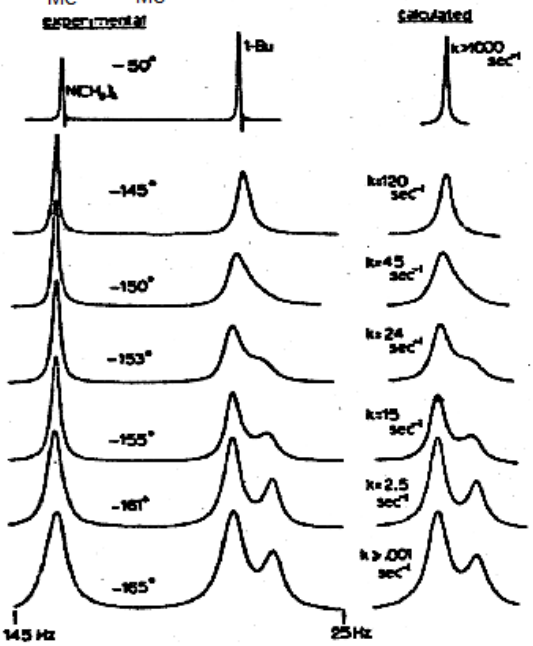
exhibits three distinct methyl resonances in the ratio 1 : 1 : 2 at −60 °C, in agreement with the structure depicted. Above room temperature, however, the spectrum becomes a singlet (9 kcal mol^{-1}) as the $Fe(CO)_4$ unit circulates about the allenic π-electron structure by moving orthogonally from one alkenic unit to the other.



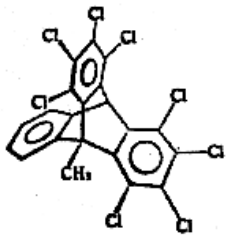
Bushweller, C. H. *Tet.* **1971**, *27*, 5761



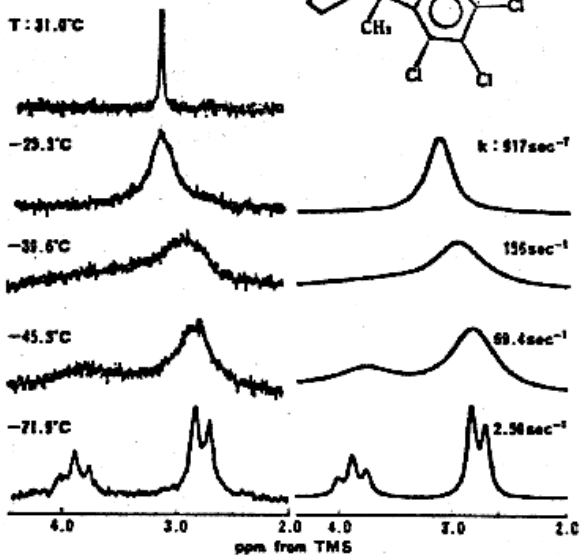
$\Delta G^{\dagger}_{-153}$ = 6.1 kcal/mol

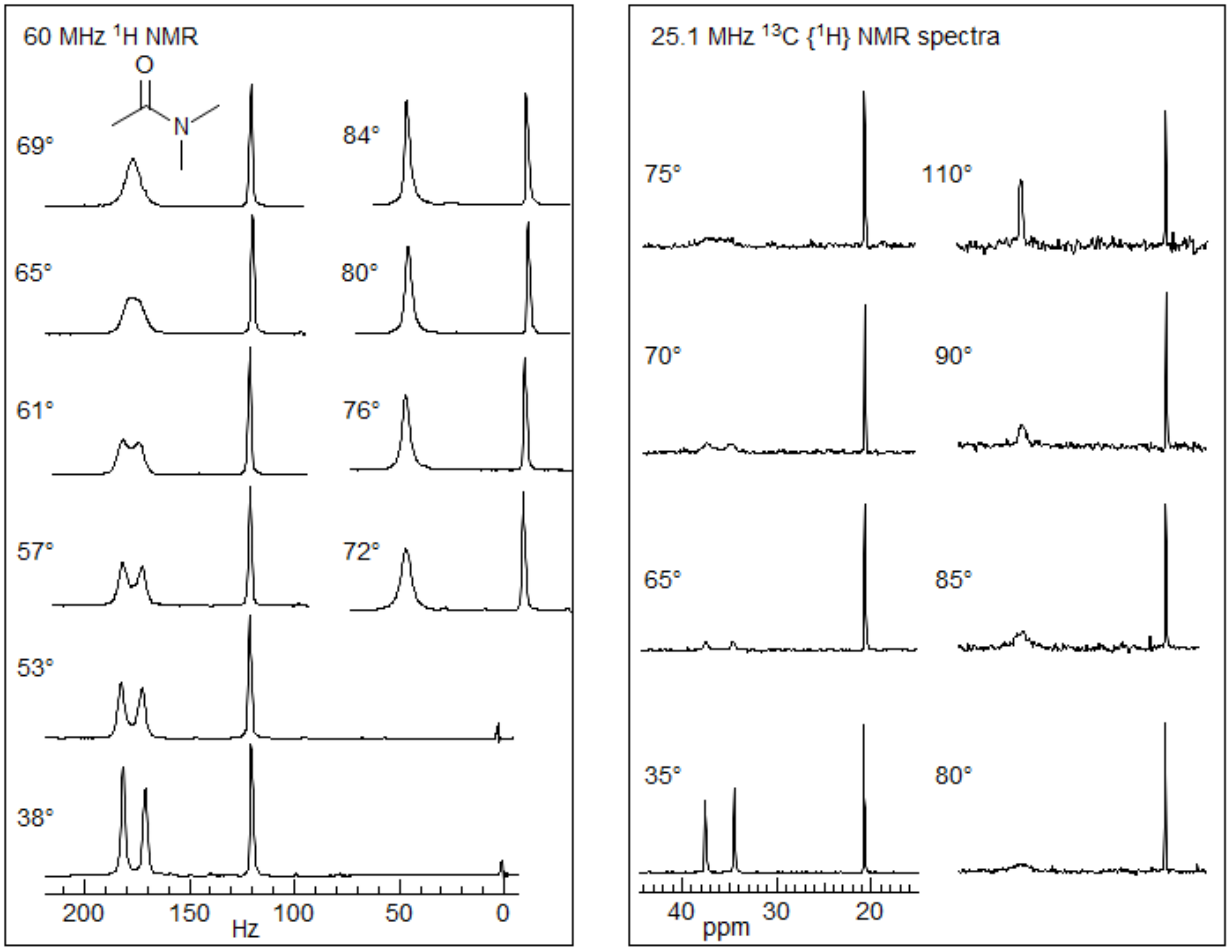


Even he rotation of a methyl group can be slowed in a rigid frmework: Nakamura, M.; Oki, M.; Nakanishi,



$\Delta G^{\dagger}_{-39}$ = 11.2 kcal/mol

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N
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84°
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57°
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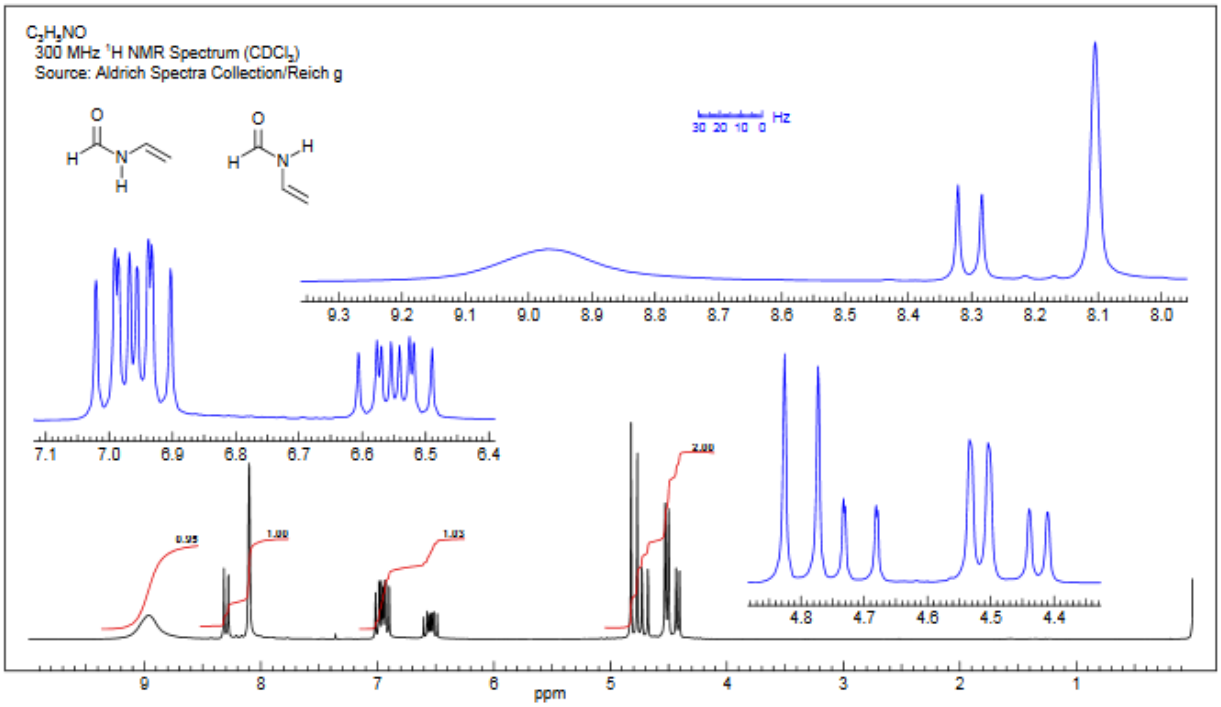
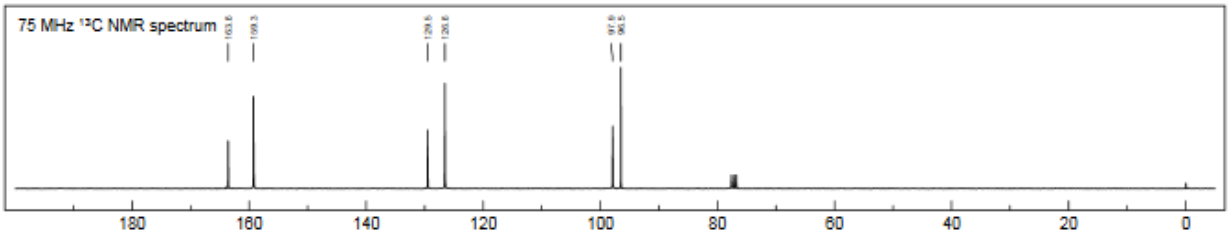
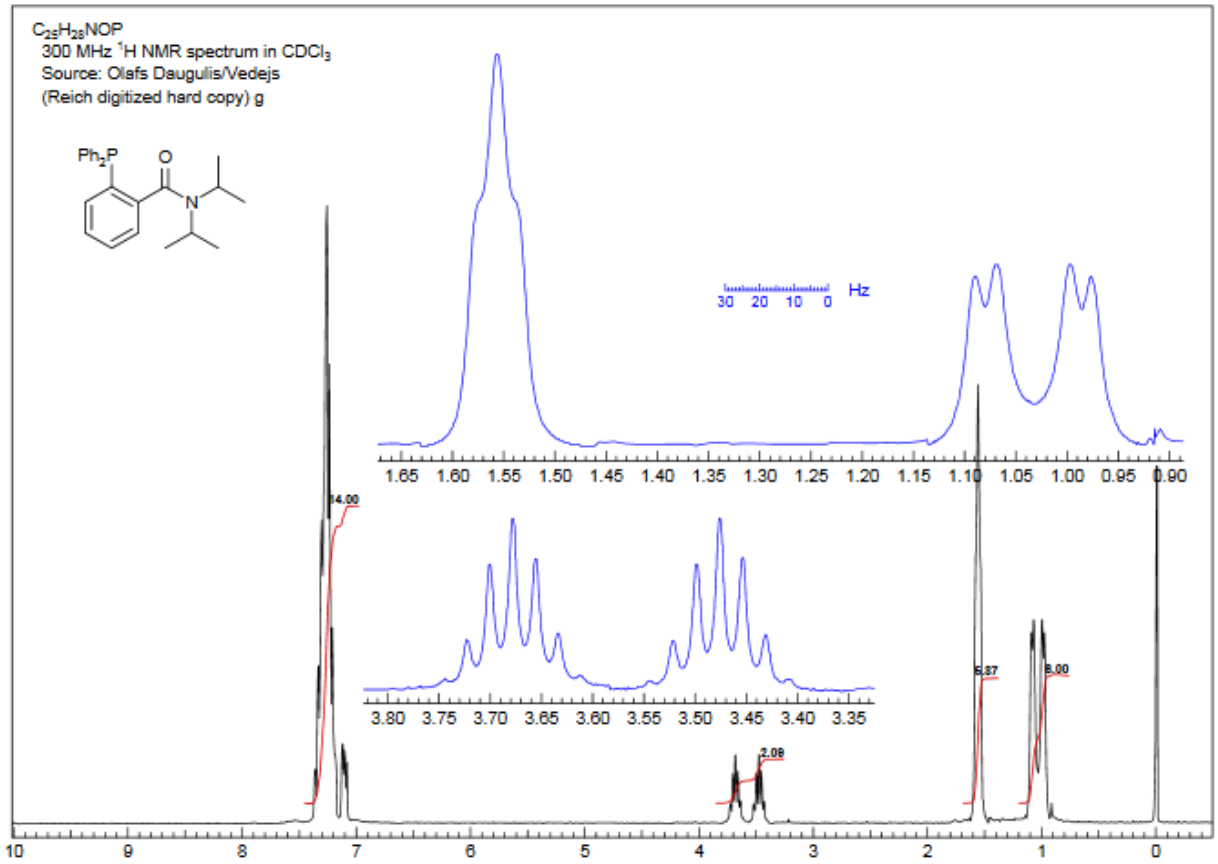
50
0
Hz
25.1 MHz ¹³C {¹H} NMR spectra
75°
110°
70°
90°
65°
85°
35°
80°
40
30
20
ppm

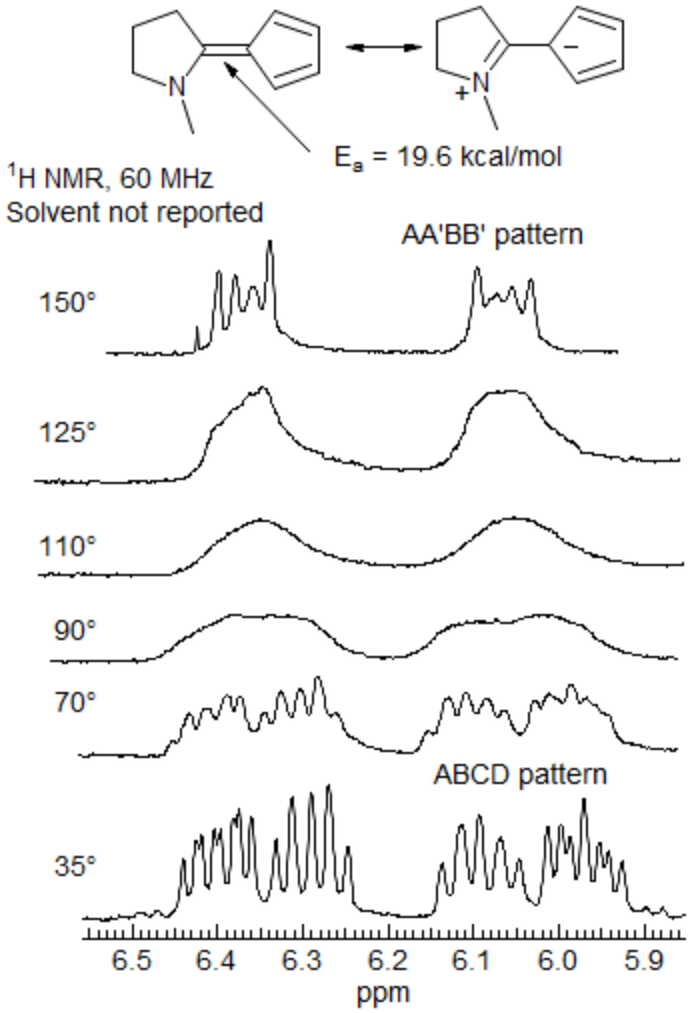
Exercize: Interpret all features of the NMR spectrum of N-vinyl formamide



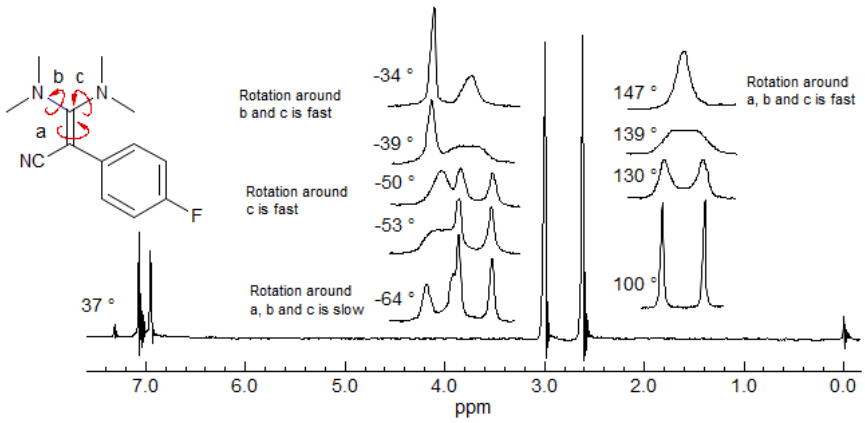


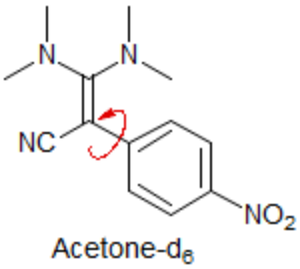
Exercise: (a) Explain the appearance of the CH region around δ 3.6. (b) Explain the appearance of the methyl region. HINT: there is restricted rotation around more than one bond.

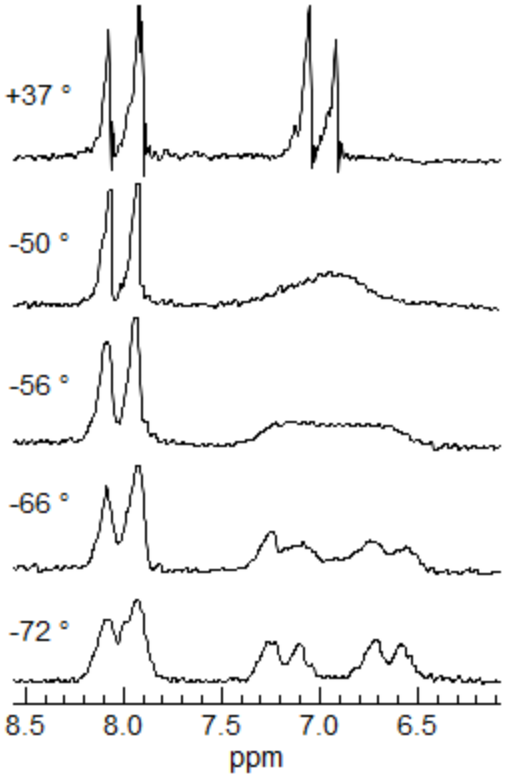


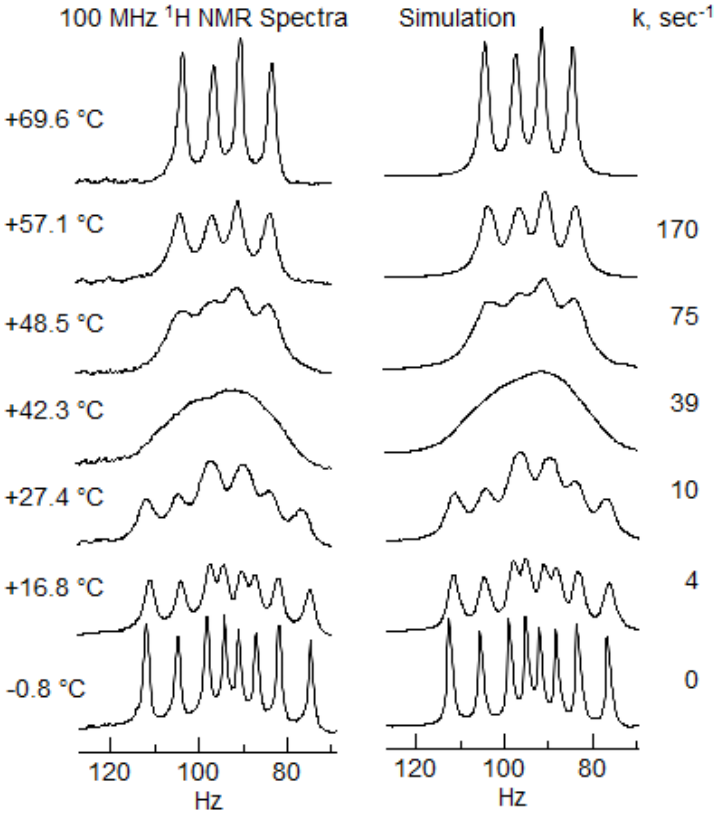


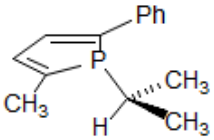
Push-Pull Double Bond Rotation. These diamino cyano alkenes show restricted rotation around 4 different bonds, three of them formal single bonds with double bond character, the fourth a double bond with single bond characater (H. Kessler *Chem. Ber.* **1970**, *103*, 973.)







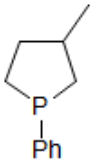




$\Delta G^{\ddagger}$ = 17.1 ± 0.4 kcal/mol

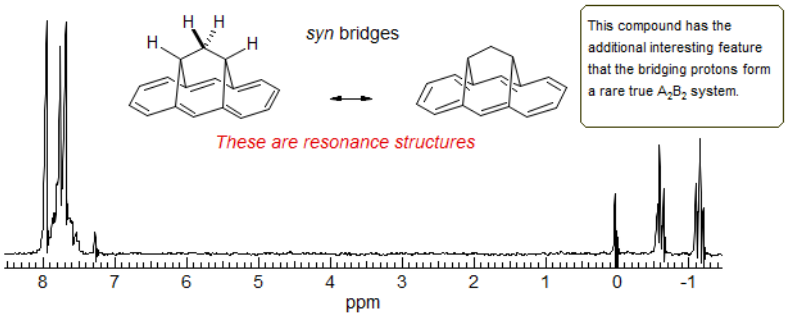
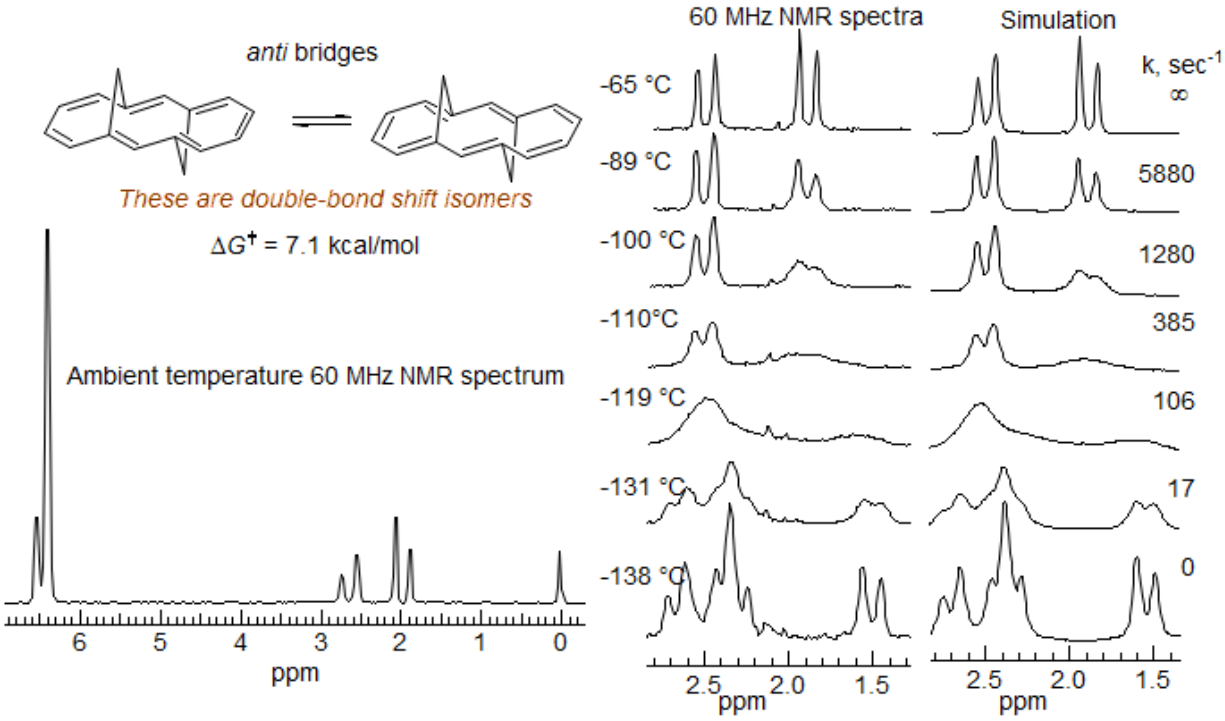
$\Delta S^{\ddagger}$ = 3.1 ± 1.1 eu

Measured by DNMR



$\Delta G^{\ddagger}$ = 38 kcal/mol at 170 °C

Measured by racemization of an optically active phosphine

8-TECH-3.8 Double Bond Shifts

Annulene Double Bond Bhift. The *syn* bridged annulene is a delocalized aromatic (bis-homo anthracene) compound, as shown by the strong upfield shift of the bridging protons (δ -0.6 and -1.1), and the downfield vinyl protons. In the *anti*-bridged annulene conjugation is apparently not possible, since the NMR chemical shifts of the bridge protons are normal (δ 1.9 and 2.5). At room temperature the spectrum of the *anti* compound is symmetric, and shows only a single CH_2 group. However, at lower temperatures decoalescence occurs, and two CH_2 are seen at -138 °C (Vogel, E. *Angew. Chem.* **1970**, *82*, 510, 512). At this temperature the double-bond shift is slow on the NMR time scale. The activation energy for bond-shift is $\Delta G^{\ddagger}$ = 7.1 kcal/mol. Thus the two representations are *resonance structures* for the *syn* compound, but *valence-bond isomers* in the *anti*.