Steric Interactions of Double Bonds

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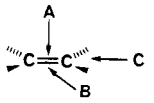
The double bond is a highly anisotropic structural entity, with three major avenues of steric approach (1).



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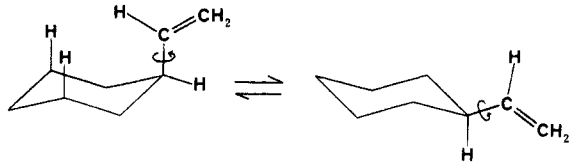
An interacting group may approach the face of the double bond (avenue A in 1), the π node along the side (avenue B), or the π node at the end (avenue C). In contrast, a spherically shaped group such as halogen or (roughly) methyl has only one major mode of approach, and a cylindrically shaped group such as nitrile has two (side-on and end-on, although the latter is excluded by the attached substituent in acetylenes). Consequently, conformational interactions of a double bond should depend critically on the direction of approach of the interacting group to the double bond.

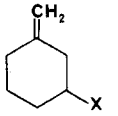
These complexities may be seen in the standard system for studying conformational interactions, the monosubstituted cyclohexane (2). Free rotation of the



2a 2b

vinyl group about the bond to the ring generates six rotamers, four of which are different and one of which is shown for the axial (**2a**) and equatorial (**2b**) rotamers in vinylcyclohexane. These rotamers differ in whether the C—H or the C=C portion of the double bond is eclipsed with the C—H or the C—C bond of the ring (in the illustrated rotamer, C=C of the substituent is eclipsed with C—H of the ring). The relative stabilities of the rotamers are determined by the magnitude of the eclipsing energies and of through space interactions (in the illustrated rotamer of **2a** the dominant through space interaction occurs between the 3- and 5-axial ring protons and the C—H group of the substituent double bond).

Our focus has been on the through space interactions, which are commonly referred to as steric or conformational interactions. Eclipsing interactions have been considered thoroughly in studies of rotational conformations of unsaturated systems. In order to remove eclipsing interactions from consideration, the rotational degree of freedom permitted in **2** (rotation about the vinyl-ring single bond, H_2C=CH—C) must be frozen out. This objective may be accomplished by embedding the double bond in a carbocycle, in either an exocyclic (**3**) or an endocyclic (**4**) fashion. These double bonds



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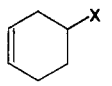

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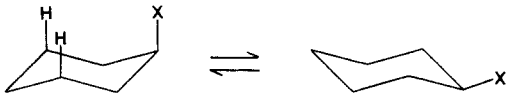
do not possess the rotational freedom of the vinyl group, so that eclipsing interactions are no longer a point of discussion. Placement of a substituent on the second carbon removed from the double bond (X in **3** and **4**) introduces steric or conformational interactions between the substituent and the double bond. We have been examining the nature of these interactions in both the exo- and the endocyclic systems and have uncovered a host of unexpected results, which we describe in this Account.

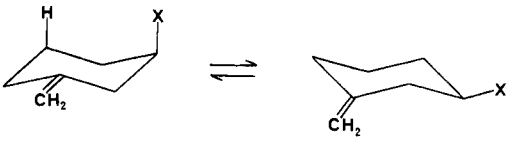
The Exocyclic Double Bond

Conformational equilibria of monosubstituted cyclohexanes are generally considered to be controlled by interactions between the axial substituent and the syn-axial protons at the 3 and 5 positions with respect to it, as in eq 1. Because the dipoles of the axial and



(1)

equatorial conformers are nearly identical, the equilibrium constant is altered very little by solvent. A slight decrease in the proportion of the axial conformer in eq 1 in polar solvents may result from differences in the quadrupoles of the two conformers.[1] In the methylenecyclohexane system (**3**) with a substituent at the 3 position with respect to the double bond, as in eq 2, one of the syn-axial interactions in the axial conformer of eq 1 has been removed. In its stead is an undefined interaction between the axial substituent and the exocyclic double bond; cf. eq 1 and eq 2.



(2)

(1) Abraham, R. J.; Bretschneider, E. *Internal Rotation in Molecules*; Orville-Thomas, W. J., Ed.; Wiley: London, 1974; pp 481-584.

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Table I.
Free Energy Differences for Axial-Equatorial Equilibria in 3-Substituted *exo*-Methylenecyclohexanes (3)

substituent	A,[a] kcal mol^{-1}	$-\Delta G°(CF_2Cl_2)$,[b] kcal mol^{-1}	$-\Delta G°(CHFCl_2)$,[b] kcal mol^{-1}
CD_3	1.6	0.80 ± 0.10[c]	0.70 ± 0.15[c]
OH	0.61	1.12 ± 0.04	0.69 ± 0.03
$O(CO)CH_3$	0.71	0.61 ± 0.03	0.38 ± 0.02
$O(SO_2)CH_3$	0.56		0.39 ± 0.02
OTs	0.52		0.44 ± 0.05
OCD_3	0.55	0.80 ± 0.02	0.11 ± 0.01
CN	0.24	0.26 ± 0.04	0.07 ± 0.02
SCH_3	1.07	1.22 ± 0.02	0.65 ± 0.04

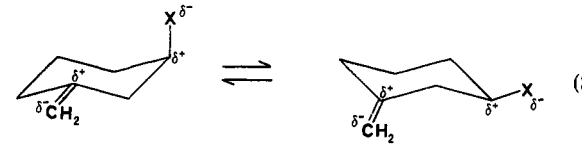
[a] $-\log K$ for eq 1 in CS_2 or $CS_2/CDCl_3$, taken from Jensen, F. R.; Bushweller, C. H.; Beck, B. H. *J. Am. Chem. Soc.* **1969**, *91*, 344–351; Abraham, R. J.; Siverns, T. M. *J. Chem. Soc., Perkin Trans. 2* **1972**, 1587–1594; Bushweller, C. H.; Beach, J. A.; O'Neil, J. W.; Rao, G. U. *J. Org. Chem.* **1970**, *35*, 2086–2087; for OH the solvent is dilute CCl_4 or cyclohexane, taken from ref 6. [b] References 2 and 3. [c] Calculated from the temperature dependence of the chemical shift; all other values were obtained by direct, low-temperature integration.

In order to understand this interaction, we have measured equilibrium constants for eq 2 for several substituents X and compared them with the known results for the equilibrium of eq 1.[2,3] We used the direct NMR method for measuring these quantities, whereby the sample is cooled below the coalescence temperature for ring reversal. Separate resonances for the axial and equatorial conformers then are obtained, and the equilibrium constant is measured by integration. We used the resonance of the proton that is geminal to the single substituent, since that resonance usually is well removed from others. The coalescence temperatures were usually around −95 °C. In order to determine the effect of solvent polarity, the relatively nonpolar CF_2Cl_2 ($\epsilon = 2.13$) and the highly polar $CHFCl_2$ were used. The inherent, intramolecular interactions are best seen in the nonpolar solvent, and the polar solvent provides a useful test to determine which conformer is more polar. The results for several substituents are given in Table I, along with literature values for monosubstituted cyclohexanes.

The effect of the *exo*-methylene double bond on the conformational preference of methyl is somewhat reminiscent of the analogous effect of an oxo group, which was termed the *3-alkyl ketone effect*.[4] There is considerably more axial methyl in **3** (X = CH_3), and the effect is independent of solvent (Table I). The approximate halving of the free energy difference between conformers seems to indicate that methyl has essentially no interaction with the double bond. The equilibrium of eq 2 (X = CH_3) then is determined primarily by the single remaining syn–axial H···X nonbonded interaction.

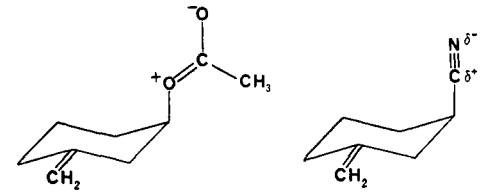
All other substituents in Table I are polar and do not show the substantial increase in the axial conformer observed in the case of methyl. In the nearly nonpolar solvent CF_2Cl_2, in fact, almost every substituent shows a decrease in the amount of axial conformer, i.e., *the exo-methylene substituent is operationally more repulsive than the axial hydrogen of the cyclohexyl equilibrium* (eq 1). Thus the free energy difference for OH increases from 0.61 (eq 1) to 1.12 kcal mol^{-1} (eq 2), for OCD_3 from 0.55 to 0.80 kcal mol^{-1}, and for SCH_3 from 1.07 to 1.22 kcal mol^{-1}.

The changes in free energy suggest that the interaction is electrostatic. Because of the unsymmetrical substituent pattern on the double bond, it possesses a small dipole (0.50 D for isobutylene). This dipole interacts repulsively with the dipole of the axial substituent (eq 3). Because methyl lacks polar properties,



(3)

it does not have this repulsive interaction and hence can exist more in the axial position. The size of the effect is roughly proportional to the polarity of the substituent. Thus the two oxygen substituents (OH and OCD_3) have the largest polarity and show the greatest decrease in the axial conformer. The methylthio group is much less polar and shows only a slight decrease in the axial conformer. The polarity of the acetoxy group is reduced by ester resonance (**5**), so that the effect is substantially offset. A similar situation occurs with nitrile.[3] The



5 **6**

negative end of the nitrile dipole is considerably farther away (**6**) than that for hydroxyl, for example. Although for OAc and CN the free energy difference of eq 2 is slightly reduced from that for cyclohexyl (eq 1), nonetheless a repulsive interaction is suggested by comparison with the case of methyl, in which the free energy difference is reduced more substantially.

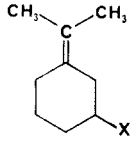
Although the mechanism of the steric interaction between the axial substituent and the *exo*-methylene substructure appears to be dipolar in origin, other mechanisms should be considered. A van der Waals interaction (induced dipoles) seems not to be appropriate, since the distances are too long (>3 Å). Moreover, a van der Waals effect should increase when OCD_3 is replaced by SCH_3, since the latter is more polarizable. The opposite is observed: OCD_3 is more repulsive, in agreement with its higher polarity. Through bond interactions should favor the axial form, contrary to observation. The nearly W arrangement in the equatorial form permits optimal repulsive interaction between X and the double bond in eq 2.[5] Our observation, however, is of increased equatorial conformer. We have carried out molecular mechanics calculations on this system. Although the calculations were consistent with our observations, they provided little insight into the mechanism of the interactions.

Thus a classical dipole–dipole interaction provides the best explanation of our results. This hypothesis may be tested in various ways. A change of solvent from nonpolar to polar should bring about a large change in the equilibrium constant, in contrast to the case for monosubstituted cyclohexyl systems. The results in the

(2) Lambert, J. B.; Clikeman, R. R. *J. Am. Chem. Soc.* **1976**, *98*, 4203–4211.
(3) Lambert, J. B.; Taba, K. M. *J. Org. Chem.* **1980**, *45*, 452–455.
(4) Rickborn, B. *J. Am. Chem. Soc.* **1962**, *84*, 2414–2417. Allinger, N. L.; Freiberg, L. A. *Ibid.* **1962**, *84*, 2201–2203.
(5) Bingham, R. C. *J. Am. Chem. Soc.* **1976**, *98*, 535–540.

polar solvent $CHFCl_2$ are in accord with this expectation (Table I). The nonpolar group CH_3 shows no solvent effect, but all the polar substituents show vastly decreased free energy differences in $CHFCl_2$; i.e., the axial form is more favored. As seen in eq 3, the axial form is indeed the more polar and hence should be favored in the more polar solvent. Even acetoxyl and nitrile show substantial reductions in the free energy difference in $CHFCl_2$. Thus the values in CF_2Cl_2 for these two substituents must reflect a substantial repulsive interaction, although less than that of OH or OCD_3. These large solvent effects are very unusual for cyclohexane equilibria. Even for a hydrogen-bonding substituent such as hydroxyl, the range of the free energy difference for eq 1 does not exceed 0.3 kcal mol^{-1} for solvents ranging from cyclohexane to 2-propanol.[6] For the *exo*-methylene system (eq 2), the free energy differences change 0.5–0.7 kcal mol^{-1} for OH, OCD_3, and SCH_3 between CF_2Cl_2 and $CHFCl_2$.

A second method to test for the presence of a dipolar interaction is to alter the dipole of the double bond. We carried out this approach by replacing the hydrogens on the exocyclic carbon with a substituent. For example, replacement with methyl produces system **7**, in which the ring now carries an isopropylidene substituent. Full symmetrization of the double bond eliminates



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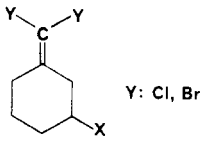

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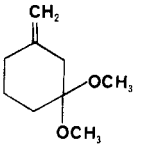
any dipole (thus 2,3-dimethyl-2-butene has no dipole moment). Therefore, the double bond of **7** should have little or no interaction with methoxyl (X = OCH_3) at the 3 position.[7] In the nonpolar solvent CF_2Cl_2, the axial–equatorial free energy difference for OCH_3 was found to be only 0.19 ± 0.01 kcal mol^{-1} **7**, compared with 0.80 for the *exo*-methylene system **3**. Moreover, the change to the polar solvent $CHFCl_2$ for system **7** (X = OCH_3) brought about only a small change in the free energy difference, to 0.08 ± 0.01 kcal mol^{-1}. Thus isopropylidene, in contrast to *exo*-methylene, shows little repulsive interaction, so that considerably more axial conformer is permitted. Without a dipole, the double bond indeed exhibits little interaction with 3 substituents. This experiment also demonstrates that the dipole of polar 3 substituents interacts repulsively with the *dipole* of the double bond, not its quadrupole. The experiments with **3** do not distinguish between dipole–dipole and dipole–quadrupole interactions. System **7**, however, retains the quadrupole of the double bond but loses the major part of the repulsive interaction. This observation is consistent with dipolar rather than quadrupolar properties of the double bond.

We have made preliminary observations with the halogen systems **8** (Y = Br and Cl), and the results appear not to fit into this simple electrostatic model. We expected that the heightened dipole of the halogen-substituted double bond would increase dipolar repulsion with the 3-methoxy substituent, but the reverse was observed. For **8** (Y = Br, X = OCH_3), the free energy difference is 0.01 ± 0.01 kcal mol^{-1} in CF_2Cl_2 and 0.04 ± 0.01 in $CHFCl_2$. For **8** (Y = Cl, X = OCH_3), it is 0.07 ± 0.01 and 0.08 ± 0.02, respectively, in the two solvents. Thus both increasing and decreasing the dipole of the double bond increases the proportion of axial conformer. An electrostatic explanation alone cannot explain all these observations. We believe that the exomethylene system **3** indeed is governed by a repulsive dipole–dipole interaction between the double bond and polar 3 substituents, that the isopropylidene system **7** is devoid of a strong interaction between the molecular components, but that the halogen systems, **8**, are governed by an attractive, through space interaction in the axial conformer.

The through space n → π* interaction depends on the ability of the oxygen lone pair to donate electrons to the lowest unoccupied molecular orbital (LUMO) of the double bond. The LUMO is made increasingly accessible as the double bond is substituted with electron-withdrawing groups. It may be that the LUMO is too high in energy in the *exo*-methylene and isopropylidene cases, but the halogen-substituted double bonds come within range of a feasible n → π* interaction. Thus the orbital interaction supersedes the electrostatic interaction. The absence of a significant solvent effect is consistent with the orbital rather than the electrostatic interaction. At present this explanation for the halogen systems is only a hypothesis. No experiments have been carried out to test its validity.

We have, however, tested the electrostatic interactions in the *exo*-methylene system **3** (X = OCH_3) by examination of the ultraviolet photoelectron spectrum (UPS).[8] These experiments in the gas phase are carried out on the equilibrium mixture of axial and equatorial conformers, so that for **3**, in which there is very little axial conformer, the observed electron ionization potential (IP) corresponds to that of the equatorial conformer. In order to measure the IP for the axial conformer, it is necessary to use a system that has a substantial axial population. Consequently, we prepared the geminally disubstituted ether related systems **9** and **10**, in which there is an axial oxygen atom in either ring-flipped form. The IPs in these molecules must be compared with those in methylenecyclohexane (**11**) and in 3-methoxy(1-methylene)cyclohexane (**3**, X = OCH_3), which has a predominantly equatorial methoxy group.



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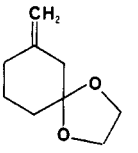

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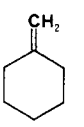


11

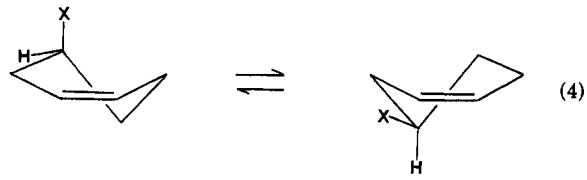
The IP for **11** (no methoxy group) is 9.18 eV. Introduction of the equatorial methoxy group in **3** has little or no effect on the IP (9.17 eV). In the systems with an axial oxygen, however, the IP drops to 9.07 eV for **9** and to 8.99 eV for **10**, indicating a raising of the π orbital energy. These trends are reproduced by ab initio and semiempirical calculations.[8] Thus both experiment and calculation show that the axial oxygen atom destabilizes the energy of the π orbital of the

(6) Eliel, E. L.; Gilbert, E. C. *J. Am. Chem. Soc.* **1969**, *91*, 5487–5495.
(7) Lambert, J. B.; Taba, K. M. *J. Am. Chem. Soc.* **1981**, *103*, 5828–5832.
(8) Lambert, J. B.; Xue, L.; Bosch, R. J.; Taba, K. M.; Marko, D. E.; Urano, S.; LeBreton, P. R. *J. Am. Chem. Soc.* **1986**, *108*, 7575–7579.

exomethylene double bond, in accord with the repulsive interaction between the double bond and axial methoxyl indicated by the NMR measurements. It would be of interest to carry out UPS experiments on the isopropylidene and halogen-substituted systems (**7** and **8**), but these have not been done (synthesis of the systems analogous to **9** and **10** would be necessary).

The Endocyclic Double Bond

The exocyclic double bond of **3** in the axial form is positioned more or less along the axis of the C=C bond, as in approach C in **1** but with off-axis approach (B and A) mixed in. In order to explore the spatial dependence of the steric interactions of the double bond, we have also examined 4-substituted cyclohexenes (**4**), in which the double bond is endocyclic and the axial substituent (eq 4) is more or less along the nodal side of the double bond (approach B in **1**, with some admixture of A and C). Cyclohexenes exist in a mobile equilibrium between two half-chair forms (eq 4).



(4)

There are several differences between the relationship of the axial substituent and the double bond in the endocyclic and exocyclic systems. The polar properties of the cyclohexenes are reduced in comparison with those of the methylenecyclohexanes; thus the dipole moment of *cis*-2-butene is 0.33 D and that of isobutylene is 0.50 D.[9] An axial group is somewhat closer to the midpoint of the double bond in cyclohexenes: 2.88 Å for cyclohexene and 3.23 Å for methylenecyclohexane for X = H in eq 2 and 4.[10] In both systems, the equatorial substituent is well removed from the double bond (3.99 Å for eq 2, 3.66 Å for eq 4), so that through space interactions in the equatorial form may be ignored. These distance relationships were corroborated in the methoxy-substituted systems (eq 2 and 4, X = OCH_3) by MM2 calculations.

In order to examine the interactions in 4-substituted cyclohexenes, we prepared a series of such molecules (**4**) and measured the axial–equatorial equilibrium constants by NMR spectroscopy.[11] The intramolecular interactions may be studied only in a nonpolar solvent such as CF_2Cl_2. An earlier study of halogen-substituted cyclohexenes used a polar solvent, vinyl chloride, in which solvent interactions would be important.[12] Table II contains the results of our experiments.

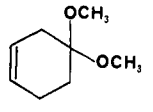
The most remarkable characteristic of the endocyclic free energy differences in Table II is that they are much smaller than the values for the exocyclic system in Table I, e.g., 1.12 and 0.22 kcal mol^{-1}, respectively, for OH. The values for the cyclohexenes are uniformly smaller than the *A* values measured for monosubstituted cyclohexanes. Clearly, the axial substituent is allowed to approach much more closely to the endocyclic than to the exocyclic double bond without experiencing a strongly repulsive interaction. The most likely explanation is that the cis-disubstituted double bond of **4** is of lower polarity than is the 1,1-disubstituted double bond of **3**. Alternatively, there may be a more fundamental difference that results from the differences in the angle of approach.

Table II.
Free Energy Difference for Axial–Equatorial Equilibria in 4-Substituted Cyclohexenes (4)

substituent	$-\Delta G°(CF_2Cl_2)$,[a] kcal mol^{-1}	$-\Delta G°(CHFCl_2)$,[a] kcal mol^{-1}
Cl	0.31	−0.02
Br	0.27	
I	0.16	
OH	0.22	
$OSiMe_3$	0.31	
CN	0.15	0.02
Cl[b]	0.38	0.06
Br[b]	0.30	
I[b]	0.20	
CN[b]	0.14	0.14

[a] Reference 12; error is ±0.03 kcal mol^{-1}. [b] These measurements are on the 1,2-dimethylcyclohexene system.

We have used three methods to test whether the electrostatic interaction of the endocyclic double bond is lower than that of the exocyclic double bond. (1) A change to the more polar solvent $CHFCl_2$ should have a smaller effect than in the exocyclic system. We obtained only limited data on this point, for X = Cl and CN. The solvent effects are generally smaller in Table II than in Table I, but they are not absent. Either a residual dipole–dipole interaction or a dipole–quadrupole interaction, albeit smaller for endocyclic than exocyclic, might be responsible for the small solvent effects of Table II. (2) Placement of methyl groups on the cyclohexene double bond, as in 1,2-dimethylcyclohexene, should nullify any dipolar effects of the double bond. As seen in the data of Table II, dimethyl substitution has no appreciable effect on the free energy differences. This observation is in agreement with the small size of the electrostatic effect and contrasts with the large size of the effect of exo dimethyl substitution in the exocyclic case. (3) In the photoelectron spectrum, the presence of an axial ether-like oxygen does not lower the IP of the π orbital, again in contrast to the exocyclic case. Instead, introduction of the axial oxygen has the effect of raising the IP (lowering the π orbital energy), from 9.09 eV in cyclohexene to 9.31 eV in **12** and 9.47 eV in **13**. This is the normal direction of the inductive



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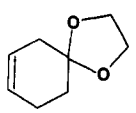

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effect of an electron-withdrawing substituent. There is apparently no through space effect that lowers the IP.

Thus the low dipolar interaction of the endocyclic double bond is indicated by the small free energy differences, the small solvent effect, the absence of much effect of 1,2-dimethyl substituent, and the raising of the IP.

(9) Boggs, J. E.; Crain, C. M.; Whiteford, J. E. *J. Phys. Chem.* **1957**, *61*, 482–484.
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Summary

The double bond displays a complex set of steric effects that depend on a number of factors.

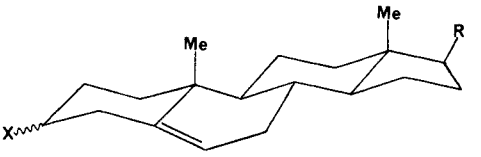
(1) **Nature of the Intruding Group.** At the distances we have examined, methyl has no apparent interaction with the exocyclic double bond in **3**. The interaction becomes demonstrably repulsive as the polarity of the 3 substituent increases. Thus methylthio shows a pronounced repulsion, and hydroxyl and methoxyl show even larger repulsions. The repulsive interaction is manifested by a decreased proportion of the 3-axial conformer in these methylenecyclohexanes.

(2) **Solvent.** The repulsion between double bond and polar groups shows the classic solvent response of a dipole–dipole interaction. Thus an increase in polarity of the solvent favors the more polar conformer in eq 2, which is the axial form. Studies of the steric interactions of double bonds therefore are best carried out in nonpolar solvents in order to focus on intramolecular interactions.

(3) **Substitution Pattern on the Double Bond.** The geminally disubstituted (exomethylene) double bond in **3** is sufficiently polar to show large dipolar interactions with 3 substituents. Tetrasubstitution, as in **7**, removes the dipole and eliminates most vestiges of polar effects. Conformational analysis of unsaturated systems thus must consider the precise substitution pattern for any given case. Introduction of groups of higher polarity, as in **8**, may even bring in an entirely different mechanism of interaction between the double bond and 3 substituents. If the LUMO of the double bond is lowered sufficiently by electron-withdrawing substituents, the $n \rightarrow \pi^*$ transannular interaction may cause the overall interaction to reverse sign and become attractive, resulting in increased amounts of the axial conformer.

(4) **Orientation of Approach of the Intruding Group (See 1).** The side-on approach of axial substituents in 4-substituted cyclohexenes results in a much less repulsive interaction than the end-on approach in 3-substituted *exo*-methylenecyclohexanes. Although this difference may simply reflect differences in polarity of the two double bonds, there may be a subtler dependence of the steric interaction on the angle of approach.

The work described in this account provides only a beginning in understanding the conformational properties of unsaturated segments of a molecule. We still must explore a wider range of substituents, the details of the effects of polar substituents attached to the double bond (like cyano), and a variety of other modes of approach of the perturbing group to the double bond (see **1**). The work up to now, however, already shows that the double bond cannot be ignored simply as part of the hydrocarbon framework. Thus in 3-substituted cholest-5-enes (**14**), careful consideration of the effect of this trisubstituted double bond must be carried out in order to understand the α/β ratio for the X substituents.



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