and 81.0 kcal/mol by MINDO/3.[46]

Summary. Methylenecyclopropene is a remarkably polar compound; we estimate that dipolar form **1d** constitutes (in valence bond terms) about $^1/_5$ of the ground state of **1**. However, over $^1/_2$ of the π polarization in **1** results from four-electron repulsion and therefore corresponds to a destabilizing effect. Consequently the π delocalization energy of **1** is probably not greatly different from that for butadiene, and we conclude that it is nonaromatic.

Interestingly, although the polarity of the π system is primarily responsible for the dipole moment of **1**, there is some polarization of the σ system in the opposite direction. In particular, four-electron polarization of σ orbitals on going from **2** or **3** to **1** may contribute to a reduced lengthening of C_3C_4 and undoubtedly causes an enhanced lengthening of C_1C_2 compared to what is expected on the basis of π delocalization alone.

Acknowledgment. This research has been supported by NSF Grants CHE 81-10428 and 83-18188 at the University of Nebraska, by NSF Grant CHE 86-04007 at Carnegie Mellon University, and by NSF Grant CHE 81-08395 at the University of Kansas. T.D.N. acknowledges support of a Maude Hammond Fling Fellowship and a University of Nebraska Presidential Fellowship.

Registry No. Methylenecyclopropene, 4095-06-1.

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A Correlation between β-Hydrogen Isotope Effects on Carbon-13 NMR Chemical Shifts in Unsaturated Systems and the Strength of Hyperconjugative Interactions

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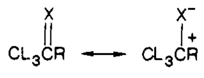
Contribution from the Department of Chemistry, University of Toronto, Toronto, Ontario M5S 1A1, Canada. *Received April 14, 1986*

Abstract: β-Hydrogen isotope effects on the carbon-13 NMR chemical shifts of the trigonal carbon in $CL_3C(R){=}X$ (L = H or D) are reported for 15 substances in which the positive charge density at the trigonal carbon is regulated through systematic variation of R and X. A linear relationship is found between these isotope effects and the chemical shifts of the trigonal carbons, and this is taken as evidence for dependence of the magnitude of these isotope effects upon the strength of the hyperconjugative interaction between CL_3 and $C(R){=}X$. An explanation of hyperconjugative NMR isotope effects in terms of anharmonic carbon-hydrogen bond-bending vibrations is advanced.

Hydrogen isotope effects on carbon-13 NMR chemical shifts of unsaturated carbon atoms produced by isotopic substitution at a β-position have been attributed to isotopic perturbation of hyperconjugation.[1] The evidence for this interpretation includes a conformational dependence of isotope effect appropriate to hyperconjugation,[2-4] transmission of the isotope effect through π-systems,[4-7] and a general parallelism between the magnitude of these isotope effects and the need for hyperconjugative stabilization.[1,3,8] We now present additional evidence which strengthens this last line of reasoning: we have found a correlation between such isotope effects and the chemical shifts of the carbon atoms to which they refer, which implies that the magnitude of the isotope effect depends upon the strength of the hyperconjugative interaction.

We examined a series of compounds with the general formula **1** (L = H or D) in which the demand for hyperconjugative stabilization by the methyl group can be regulated by varying the groups X and R. As the dipolar resonance form **2** becomes more important and the positive charge density at the trigonal carbon atom increases, hyperconjugative stabilization of this positive charge will increase as well. Increases in positive charge density induced by increasing contribution from dipolar resonance forms have also been taken to be the cause of downfield changes in the position of NMR chemical shifts of trigonal carbon atoms in olefins and carbonyl compounds.[9] It follows then, that, if hy-



$$CL_3\overset{X}{\overset{\|}{C}}R \longleftrightarrow CL_3\overset{X^-}{\overset{|}{C^+}}R$$

1 **2**

Table I. Carbon-13 Chemical Shifts and NMR Isotope Effects for $CL_3CR{=}X$

X	R	$\delta^{CH_3}_{C=X}$	$(\delta^{CH_3}_{C=X} - \delta^{CD_3}_{C=X})^a$
$OH^{+\,b}$	CL_3	248	−0.242 ± 0.009[c]
O^d	CL_3	212	−0.173 ± 0.004[c]
O	2,4,6-$(CH_3)_3C_6H_2$	206	−0.147 ± 0.004
O	CL_3	204	−0.154 ± 0.004[c]
O	$C(CH_3)_3$	211	−0.117 ± 0.007
O	H	199	−0.223 ± 0.007
O	C_6H_5	197	−0.128 ± 0.007
$OH^{+\,e}$	OH	191	−0.106 ± 0.007
O	OH	178	−0.040 ± 0.005
O	OC_6H_5	170	−0.021 ± 0.007
O	Cl	170	0.000 ± 0.009
$NNHC_6H_3(NO_2)_2$	CL_3	154	0.000 ± 0.003[c]
$CHCH_3$	CL_3	132	0.086 ± 0.002[c]
CHC_6H_5	H	125	0.113 ± 0.004
$C(CH_3)_2$	CL_3	123	0.095 ± 0.002[c]

[a] Error limits are based upon uncertainties in chemical shifts, which were taken to be equal to the digital resolution. [b] The solvent was SbF_5/FSO_3H and CD_2Cl_2 was used as external reference; sample temperature −30 °C. [c] Isotope effect per CD_3 group, i.e., one-half of the observed value. [d] The solvent was H_2O, and C_6D_6 was used as external reference. [e] The solvent was 96% aqueous H_2SO_4, and C_6D_6 was used as external reference.

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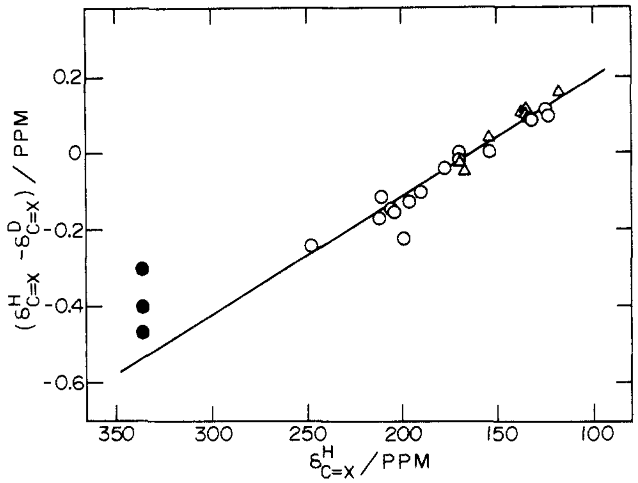


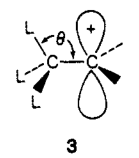
Figure 1. Relationship between the carbon-13 NMR chemical shift of the trigonal carbon atom in $CL_3CR{=}X$ and the β-hydrogen isotope effect on that shift: (○) values determined here, (△) literature values for neutral substrates, (●) literature values for carbocations. Least-squares analysis of ○ and △ points gives $(\delta^{CH_3}_{C=X} - \delta^{CD_3}_{C=X}) = (5.21 \pm 0.32) \times 10^{-1} - (3.24 \pm 0.18) \times 10^{-3}\, \delta^{CH_3}_{C=X}$, $R = 0.968$.

perconjugation is a factor responsible for β-hydrogen isotope effects on the NMR chemical shifts of trigonal carbon atoms, the magnitude of these isotope effects should vary in the same sense as the chemical shifts of the trigonal carbons. This expectation is borne out by the results summarized in Table I: the β-hydrogen isotope effects listed there do increase in magnitude with increasing downfield chemical shift of the trigonal carbon. As Figure 1 shows, there is in fact a good linear relationship between these two variables and thus between the isotope effects and the strength of the hyperconjugative interaction.

Completely deuterated methyl groups were used in this study in order to avoid any conformational bias which isotope effects on hyperconjugative electron release from less symmetrical or less freely rotating groups might have introduced into the system.[2,3] There are some additional data in the literature which conform to this requirement: the effect of changing CH_3 to CD_3 on the chemical shift of an adjacent trigonal carbon atom has been measured for toluene,[5] 1-methylnaphthalene,[6] 2-methylnaphthalene,[6] 2-methylanthracene,[6] 3-methylfuran,[6] acetone oxime,[10] methyl acetate,[3] acetic anhydride,[3] and the *tert*-butyl, *tert*-amyl, and 1-methylcyclopentyl carbocations.[8,11] The isotope effects on the neutral substrates of this additional group fit in well with the present data, but those on the carbocations do not. This may be because the carbocation spectra were recorded in SbF_5 or SbF_5/FSO_3H solution at -70 to -80 °C, whereas the present measurements were made for the most part in C_6D_6 solution at 20 °C.

It is interesting that the present correlation shows a smooth progression of isotope effects from large negative values for substances containing strongly electronegative groups and a strong need for hyperconjugative stabilization, through zero, to moderately positive values for substances in which hyperconjugation is expected to be weak. This requires the simultaneous operation of two different mechanisms by which isotopic substitution affects the chemical shift: one that moves it downfield and another that moves it upfield. Upfield isotope effects are commonly attributed to the anharmonic nature of carbon–hydrogen bond stretching vibrations and the lower zero-point energy and consequent smaller vibrational amplitude of the heavier system; this makes the time-average length of a C–D bond shorter than that of a C–H bond, which makes the C-D bond more shielding.[1,12]

Bond shortening is also believed to account for downfield hyperconjugative isotope effects.[13] Recent calculations in which isotopic bond shortening was simulated artificially showed that, whereas shortening increases electron density at the position α to the "isotopic substitution", it *lowers* electron density at the β-position in systems where (positive) hyperconjugation can operate. This would, of course, deshield a β-carbon atom and lead to a downfield isotope effect at this position. It is not clear, however, just how this phenomenon operates nor whether it can account for hyperconjugative isotope effects completely, i.e., whether or not other mechanisms of isotope effect generation are operative. It is possible, for example, to visualize another mechanism in which bending vibrations are involved. Bending vibrations of carbon–hydrogen bonds adjacent to trigonal, electron-deficient carbon atoms should be anharmonic in the sense that motion toward the electron-deficient carbon (closing the angle θ shown in **3**) will be less constrained than motion in the opposite direction. The greater vibrational amplitude of a C–H over a C–D bond will then place the C–H bond in an average position more nearly parallel to the adjacent p-orbital and thus better able to interact with it hyperconjugatively; this will make the C–H bond effectively more shielding than the C–D bond, and that will produce a downfield isotope effect.



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Experimental Section

NMR Spectra. Proton-decoupled NMR spectra were recorded at 50.3 MHz with a Varian XL-200 NMR spectrometer. Spectral widths of 14000–10000 Hz were used with 32K data points and zero-filling to 64K before transformation; in some cases resolution was improved with a resolution-enhancement weighting function. Samples were 12–15 vol % solutions of 3:1 mixtures of deuterated to undeuterated substrates. Unless otherwise indicated, probe temperatures were ambient (20 °C) and C_6D_6 was the solvent; the latter also served as both lock signal and internal reference (δ 128.0).

Preparation of Materials. Acetone 2,4-dinitrophenylhydrazone was prepared from acetone-d_6 (Aldrich, 99+ atom % D) by a standard procedure and was recrystallized from ethanol, mp 125–126 °C. 2-(Methyl-d_3)-2-butene-*1,1,1*-d_3 and 2-(methyl-d_3)-3-methyl-2-butene-*1,1,1*-d_3 were made from the corresponding alcohols by dehydration in 30% H_2SO_4, and the alcohols were prepared by treating acetone-d_6 with the appropriate Grignard reagent.

Acetic acid-d_4 (Aldrich, 99+ atom % D) was allowed to stand in methanol overnight and was then distilled to give acetic-d_3 acid. Acetyl-d_3 chloride was made from acetic acid-d_4 and thionyl chloride. Phenyl acetate-d_3 was prepared by acid-catalyzed esterification of acetic acid-d_4 in benzene solution.

Acetaldehyde-*2,2,2*-d_3 diethyl acetal was synthesized from methyl-d_3 iodide (MSD Isotopes, 9919 atom % D) and triethyl orthoformate.[14] The acetal was hydrolyzed in a 4% aqueous HCl solution to give acetaldehyde-*2,2,2*-d_3.

Acetophenone-α,α,α-d_3 and 2,4,6-trimethylacetophenone-α,α,α-d_3 were prepared by base-catalyzed exchange of the appropriate protio compound in a solvent consisting of D_2O and a minimum amount of THF containing ca. 0.01 M NaOD. This solution was heated under reflux for 24 h; the THF was then removed by distillation, the residue was extracted with pentanes, the pentanes were evaporated off, and the product was distilled. Proton NMR showed complete deuteration of the α-carbon.

trans-β-(Methyl-d_3)styrene was prepared as follows: methyl iodide-d_3 was added to an equimolar mixture of phenylacetylene and *n*-butyllithium in dry THF at -20 °C. The mixture was then quenched with ice and extracted with ether. Distillation gave 1-phenyl-1-propyne-*3,3,3*-d_3, which was reduced with $LiAlH_4$[15] to give the *trans*-alkene.

These substances were purified either by distillation or by gas chromatography. All other materials were best available commercial grades and were used as received.

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Acknowledgment. We are grateful to Professor Andrew Streitwieser for helping us generate our bending vibration explanation of hyperconjugative isotope effects, and we also thank the Natural Sciences and Engineering Research Council of Canada and donors of the Petroleum Research Fund, administered by the American Chemical Society, for financial support of this work.

Registry No. $(CH_3)_2COH^+$, 43022-03-3; 2,4,6-$(CH_3)_3C_6H_2COCH_3$, 1667-01-2; $(CH_3)_2CO$, 67-64-1; $(CH_3)_3CCOCH_3$, 75-97-8; CH_3CHO, 75-07-0; C_6H_5-$COCH_3$, 98-86-2; $CH_3CO_2H_2^+$, 18639-92-4; CH_3CO_2H, 64-19-7; $CH_3COOC_6H_5$, 122-79-2; CH_3COCl, 75-36-5; 2,4-$(NO_2)_2C_6H_3NHN{=}C(CH_3)_2$, 1567-89-1; $(CH_3)_2C{=}CHCH_3$, 513-35-9; $CH_3CH{=}CHC_6H_5$, 637-50-3; $(CH_3)_2C{=}C(CH_3)_2$, 563-79-1; 2,4-$(NO_2)_2C_6H_3NHN{=}C(CD_3)_2$, 92350-12-4; $(CD_3)_2C{=}CHCH_3$, 1787-45-7; $(CD_3)_2C{=}C(CH_3)_2$, 38132-23-9; $(CD_3)_2C(OH)CH_2CH_3$, 75295-95-3; $(CD_3)_2C(OH)CH(CH_3)_2$, 104977-32-4; $C_6H_5COCD_3$, 17537-31-4; C_6H_5OH, 108-95-2; $(C_2H_5O)_2CHCD_3$, 92144-49-5; CD_3CHO, 19901-15-6; $C_6H_5COCD_3$, 17537-31-4; 2,4,6-$(CH_3)_3C_6H_2COCl_3$, 59660-67-2; (*E*)-$C_6H_5CH{=}CHCD_3$, 104977-33-5; $C_6H_5C{\equiv}CCD_3$, 71257-77-7; CD_3COOD, 1186-52-3; CD_3CO_2H, 1112-02-3; CD_3COCl, 19259-90-6; D_2, 7782-39-0; acetone-d_6, 666-52-4; methyl-d_3 iodide, 865-50-9; triethyl orthoformate, 122-51-0; phenylacetylene, 536-74-3.

Supplementary Material Available: Table of NMR data (1 page). Ordering information is given on any current masthead page.

The Radical Anion of Homoazulene and Its Rearrangement Products. An ESR and ENDOR Study

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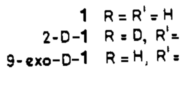
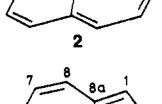
Abstract: The radical anions of homoazulene (1,5-methano[10]annulene, **1**) and two of its deuterio derivatives have been studied by ESR and, in part, by ENDOR spectroscopy. The compound **1** is reduced to the radical anion at less negative potential ($E_{1/2} = -1.94$ V) than the isomeric 1,6-methano[10]annulene (**2**) (−2.21 V), but $\mathbf{1}^{\bullet-}$ is markedly less persistent than $\mathbf{2}^{\bullet-}$. The most prominent hyperfine feature of $\mathbf{1}^{\bullet-}$ is the very large splitting (1.342 mT) from the exo proton in the methano bridging group. The next largest coupling constants (0.685 and 0.432 mT) are due to the protons at the π-centers situated in the mirror plane (m) of **1**. Both the $E_{1/2}$ value of **1** and the hyperfine data for $\mathbf{1}^{\bullet-}$ indicate that the SOMO in $\mathbf{1}^{\bullet-}$ correlates with one of the lowest antibonding perimeter MO's (ψ_S) which is symmetric with respect to the plane m. The decrease in energy of ψ_S relative to its antisymmetric counterpart (ψ_A) is attributed to homoconjugation which should be particularly favored in **1** by deviations of the perimeter from planarity. The dominant role of homoconjugation in removing the degeneracies of the perimeter MO's accounts for the similarities in the coupling constants of the protons which are attached to the corresponding π-centers in $\mathbf{1}^{\bullet-}$ and in the radical anion of azulene (**3**). Nonplanarity of the π-system seems to have a less profound effect on the coupling constants of these protons in $\mathbf{1}^{\bullet-}$ than it has on the analogous values for the isomeric $\mathbf{2}^{\bullet-}$. The different nodal properties of the SOMO's, a ψ_S-like MO in $\mathbf{1}^{\bullet-}$ and a ψ_A-like one in $\mathbf{2}^{\bullet-}$, are invoked to provide a rationalization of this finding. The primary radical anion $\mathbf{1}^{\bullet-}$ readily rearranges into secondary reduction products having the carbon frameworks of bicyclo[5.4.0]undeca-1,3,5,7,9-pentaenyl (benzotropyl, **4**) or bicyclo[6.3.0]undeca-1,3,5,7,9-pentaenyl (**5**), so that the corresponding radical dianions, $\mathbf{4}^{\bullet2-}$ or $\mathbf{5}^{\bullet2-}$, are obtained as the final paramagnetic species. Whereas $\mathbf{4}^{\bullet2-}$ has been known from previous studies, characterization of $\mathbf{5}^{\bullet2-}$ by ESR and ENDOR spectroscopy is reported only in the present work. A reaction mechanism is suggested for the conversion of $\mathbf{1}^{\bullet-}$ into each of the two radical dianions.

Homoazulene (1,5-methano[10]annulene or bicyclo[5.3.1]undeca-1,3,5,7,9-pentaene, **1**) was synthesized a few years ago by two research groups.[2] It is an isomer of 1,6-methano[10]annulene (bicyclo[4.4.1]undeca-1,3,5,7,9-pentaene, **2**) which has been known since 1964.[3] Although **1**, like its isomer **2**, exhibits properties attributable to cyclic conjugation, such as an induced diamagnetic ring current,[4] it strongly differs from **2** in its physical and chemical properties. Deviations of the ten-membered π-perimeter from planarity should be much more pronounced in **1** than in **2**. Particularly, the largest dihedral angle between the 2p axes at the consecutive carbon π-centers in **1** is predicted to be 54° by molecular mechanics,[5] whereas the analogous angle in a derivative of **2** is 34°, as determined by an X-ray crystallographic structure analysis.[6] The substantially lower resonance energy of **1** relative to **2** (27 vs. 72 kJ/mol)[7] is reflected by a higher



1 R = R' = H
2-D-**1** R = D, R' = H
9-exo-D-**1** R = H, R' = D



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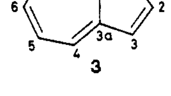

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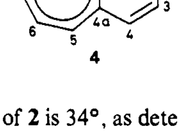

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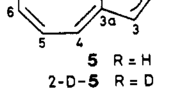

5 R = H
2-D-**5** R = D

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