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STERIC DESHIELDING BY ALKYL GROUPS IN CONJUGATED ALKADIENES: A PMR METHOD FOR DETERMINING CIS-TRANS ISOMERISM

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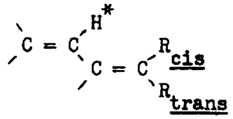
We have found that the chemical shift of the internal protons in substituted butadienes is greatly affected by the geometry of the adjacent double bond. Thus, H^* in I is strongly deshielded when $R_{\underline{cis}}$ = alkyl. The table cites a list of compounds which exemplify this effect.



R = alkyl, H.

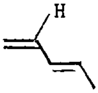
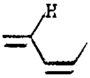
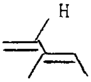
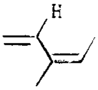
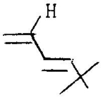
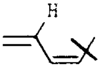
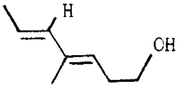
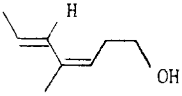
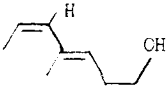
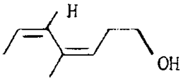
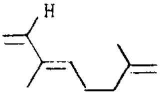
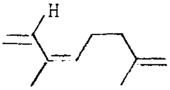
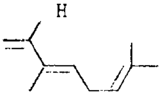
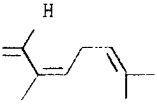
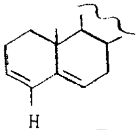
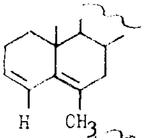
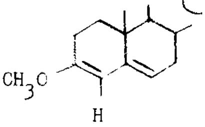
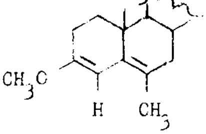
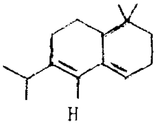
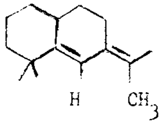
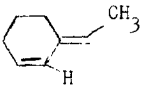
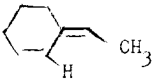
I

The observed shift (20-40 Hz) is general and is diminished only in X by the influence of the methoxy substituent. The one exception (VI) which shows negligible deshielding will be discussed below.

This correlation finds its utility where other methods fail. For example, $III_{\underline{cis}}$ and $III_{\underline{trans}}$ are indistinguishable by infrared (1) and the chemical shift of the methyl singlet, although apparently deshielded by 3 Hz (2) in $III_{\underline{cis}}$, is partially obscured by overlap with the doublet of the terminal methyl. The proton at C-2, however, appears clearly as the A portion (3) of an ABC system ($J_{\underline{cis}}$ = 10.5 and $J_{\underline{trans}}$ = 17.3 Hz) and is deshielded 26 Hz in the *cis* isomer. Mixtures are also discernable: examination of the spectrum of 1,3,7-octatriene published by Smutny and Chung (4) shows an approximately equimolar ratio of isomers (a doublet of triplets representing the proton at C-2 in the *cis* isomer is centered at 3.32τ; $J_{\underline{cis}} = J_{\underline{vic}}$ = 10.0 and $J_{\underline{trans}}$ = 16.5 Hz).

Greatest applicability is found in dienes where the internal substituent is other than methyl and which are incapable of undergoing the Diels-Alder reaction, such as the 3-ethylidenecyclohexene pair (XII). This pair of isomers has been prepared and separated by Bank, Rowe, Naslund and Schriesheim and the isomers have been shown to have properties so similar as to preclude unequivocal identification (5). These authors tentatively assigned the *cis* structure to the isomer having the lower extinction coefficient in the ultraviolet absorption (15,600 and 15,100

CHEMICAL SHIFT OF THE INDICATED PROTON IN REPRESENTATIVE CONJUGATED ALKADIENES[a]

Compound	trans	τ	cis	τ	Δ, Hz	ϵ max. of cis isomer
II		3.9-4.0		3.42[b]	~ 30	22,600[c]
III		3.70		3.27	26	21,900
IV		~ 3.8		3.09	~ 40	21,600
V		3.98[d]		3.60[d]	23	15,000[d]
VI		4.12[d]		4.11[d]	~ 1	5,850[d]
VII		3.69[e]		3.35[e]	20	21,600[e]
VIII		3.70[e]		3.27[e]	20	21,000[e]
IX		4.22[f]		3.58[g]	38	19,800[g]
X		4.87[f]		4.73[f]	9	24,800[f]
XI		4.28[h]		3.83[h]	27	17,000[h]
XII		4.00		3.63	22	17,400[i]

(a) Data obtained from the literature or by inspection of spectra obtained on a Varian A-60 spectrometer.

(b) D. F. Koster and A. Dante, J. Phys. Chem. 69, 486 (1965).

(c) E. A. Braude and J. A. Coles, J. Chem. Soc., 2085 (1951).

(d) See reference 7.

(e) G. Ohloff, J. Seibl and E. sz. Kovats, Ann., 675, 83 (1964); these authors note the chemical shift differences in the VII and VIII pairs without further comment.

(f) C. C. Leznoff and G. Just, Can. J. Chem., 42, 2919 (1964).

(g) G. Just and H. Lee-Ruff, ibid., 44, 2587 (1966).

(h) D. G. Farnum and G. Mehta, Chem. Commun., 1643 (1968).

(i) See reference 5.

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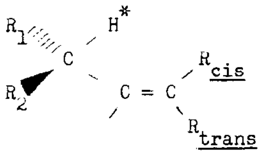
vs. 17,400). We make the reverse assignment based on a difference of 22 Hz in the chemical shift of the proton at C-2 (doublet, J = 10 Hz).

There are many well documented examples of proton deshielding in cyclic hydrocarbons due to intramolecular steric interaction with nearby hydrogen atoms (6). The effect operates through space and is dependent upon the degree of interaction. In conjugated alkadienes, the effect is, therefore, dependent upon the planarity of the transoid system. Because of the non-rigidity of the system reported herein, the calculation of the expected steric shift becomes highly complex. Examination of the table, however, shows that the cis compounds do achieve planarity as evidenced by their normal extinction coefficients. The one exception is VI_{cis} which exhibits no deshielding and which has an extinction coefficient of 5,850 (7). Braude's approximation (8) for the relationship between extinction coefficient and dihedral angle gives a mean dihedral angle approaching 60°. Thus, R_{cis} in this case is not in a deshielding position and no effect is expected.

A steric effect may also be invoked in explaining the deshielding of allylic methine protons in cis mono-alkenes as reported by Stehling and Bartz (9) and more recently by Frost and Ward (10) and by Bates et al (11). The latter authors ascribe the shift to a deshielding effect of the double bond on H^* in rotamer XIII. This rotamer would be expected (11) to be more predominant in cis (R_{cis} = alkyl) than in trans olefins (R_{cis} = H). Our data on rigid cyclic systems (IX, X, XI



XIII

and XII), where the position of the proton relative to the double bond remains unchanged, favor a steric rather than an anisotropic effect. The rotamer population is important, however, in maintaining the proximity of the proton to R_{cis}. As R_1 and R_2 are replaced by hydrogens the rotamer distribution changes and the degree of deshielding should decrease until other effects predominate. Stehling and Bartz (9) report that $\tau_{trans} - \tau_{cis}$ is ~0.5 ppm for methines, ~0.1 ppm for methylenes, and ~-0.1 ppm for methyls (12).

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12. The author is grateful to Dr. D. S. Weinberg for helpful discussions.