

SEPARABLE CONTRIBUTIONS OF INDUCTION AND POLARIZATION TO THE CHEMICAL SHIFT.

I. SYMMETRICAL, SATURATED HYDROCARBONS HAVING NO INTERNAL ROTATION

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Mutual polarization of CH and CC dipoles and its effect upon ^1H and ^{13}C chemical shifts has been part of a larger and continuing study of polarization of these bonds by more polar bonds, including oxygen, nitrogen, and the halogens. Chemical shifts for cyclohexane, trans decalin, I, trans-syn-trans perhydroanthracene, II, all trans perhydrophenalene, III, adamantane, IV, and bicyclo [2.2.2]octane, V, appear in the figures and the table. With few exceptions, these data may be represented by the expression, $\delta = I + Pn$, in which δ is the observed chemical shift, I is a constant characteristic of the electron density and distribution around the carbon concerned (in the absence of polarizing dipoles β or beyond), P is the effect upon chemical shift produced by each polarizing β CH dipole, and n is the number of β CH dipoles that are nearly parallel to the CH bond whose ^{13}C and ^1H shifts are being observed.⁷

Guided by the trend in both ^{13}C and ^1H shifts seen along the vertical induction axis in Fig. 2, by the dependency of I upon the number of hydrogens on the carbon and by the opposite direction of field dependency upon bond polarization for ^{13}C and ^1H , we will suppose and eventually conclude that (1) carbon is more electronegative than hydrogen, (2) the sign of the CH dipole is $-+$ (so long as other substitutions on the carbon are either carbon or hydrogen), (3) the excess negative charge on carbon increases almost linearly with the number of hydrogens attached and is similarly (but much less) dependent upon the number of hydrogens on α carbons, (4) the $-+$ dipole of CH in $-\overset{|}{\underset{|}{\text{C}}}\text{H}$, >CH_2 , and $-\text{CH}_3$ increases in this order, (5) the $\overset{\text{H}}{\underset{|}{\text{C}}}-\bar{\text{C}}\text{H}_3$ dipole is appreciable, and the $\overset{+}{\text{C}}\text{H}-\bar{\text{C}}\text{H}_2$ dipole is not negligible, (6) shielding of the ^{13}C nucleus increases with electronic charge density and proximity--increasing as dipolar environment compresses charge toward the nucleus and decreasing as it distorts charge away, (7) shielding of the

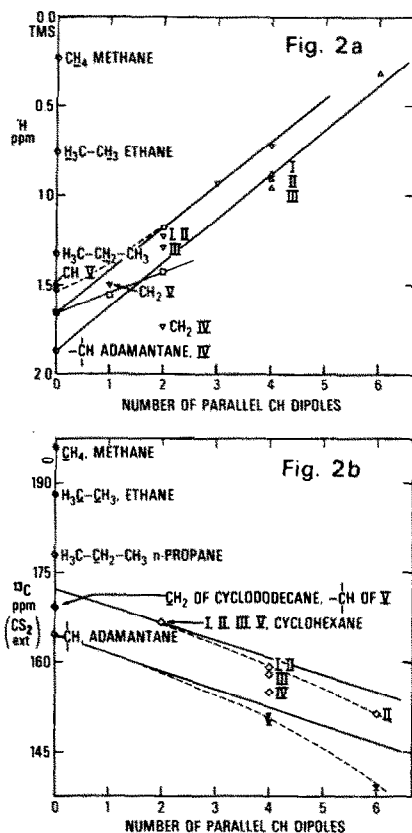
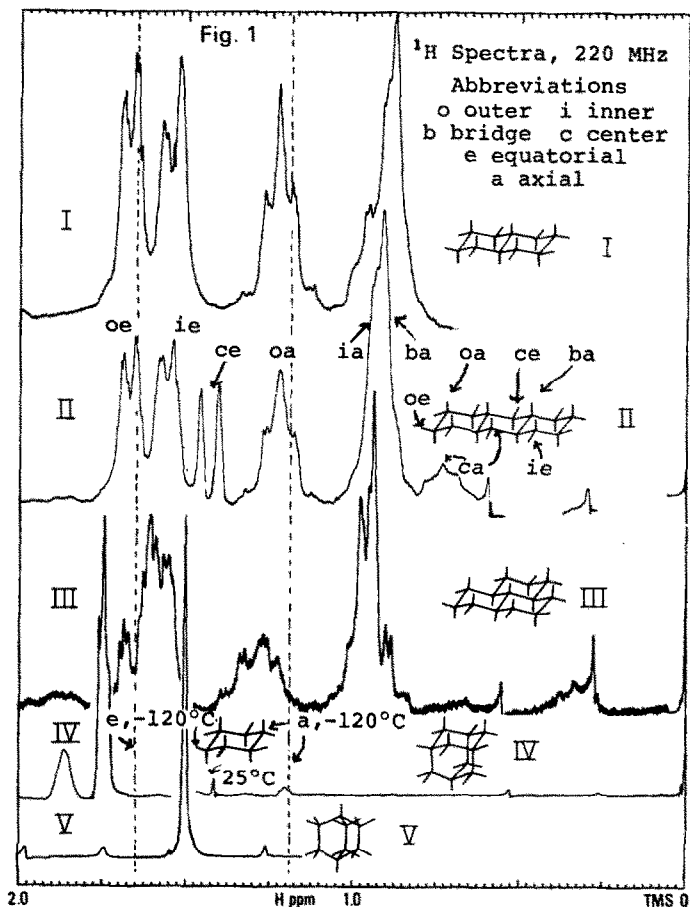


Fig. 2, Polarization curves

	Cyclohexane	I	II	III	IV	V
¹ H	oe	1.65(.00)	1.67(-.02)	1.67(-.02)	1.65(.00)	CH 1.86(.00)
	ie		1.54(.00)	1.56(-.02)	1.57(-.03)	CH ₂ 1.75(-.56)
	ce			1.43(.00)		1.50(+.36)
	oa	1.19(.00)	1.23(-.04)	1.23(-.04)	1.29(-.10)	
	ia		.95(+.01)	.95(+.01)	.95(+.01)	
	ba		.87(+.07)	.91(+.03)	.96(-.02)	
	ca			.72(+.01)	.32(+.16)	
¹³ C	o	166.2(.00)	166.6(+0.4)	166.3(+0.1)	166.6(+0.4)	CH 164.7(+1.7)
	i		159.1(-1.1)	159.2(-1.0)	158.1(-2.1)	CH ₂ 155.3(-4.9)
	b		149.7(-1.3)	149.8(-1.2)	151.1(+0.1)	169.2(+6.2)
	c			151.4(-2.8)	139.0(-6.0)	167.1(+0.9)

Chemical shift for ¹H in ppm from TMS; for ¹³C in ppm from CS₂. Deviations from $\delta = I + Pn$ are in parentheses. I for ¹H in CH₂ is 1.65 ppm; in CH, 1.86 ppm. P for ¹H is 0.23 ppm per axial CH; 0.11 ppm per equatorial CH. I for ¹³C in CH₂ is 172.2 ppm; in CH, 163.0 ppm. P for ¹³C is 3.0 ppm per CH dipole.

proton increases as charge is drawn toward it from the carbon to which it is bonded, (8) mutual polarization by bonds which are nearly parallel to each other and nearly perpendicular to their line of centers is an order of magnitude greater than by other bonds in tetrahedral array in that other bonds β and beyond are nearly perpendicular or highly skew (α bonds being included in the term I), (9) and that the contribution of magnetic anisotropy of bonds beyond α (included in I) may be considered after polarization is assessed.

The "constants" I and P in the approximate expression for δ were not chosen for best fit of the data (see table) but for the most meaningful deviations arising from the variety of substitution on the α and β carbons and for the effect of parallel $\overset{+}{\text{C}}\text{H}-\bar{\text{C}}\text{H}_2$ bonds. The lower value of P for equatorial CH than for axial probably arises from a lower dipole moment. The downfield trend in the oa proton shifts for cyclohexane, I, II, and III (see table) and the ba proton shifts for I, II, and III reflect the replacement of secondary β CH dipoles by tertiary ones. Carbon c of III is unusually low field because it is bonded to three tertiary carbons and polarized by six secondary β CH's. The latter effect is shown in a significant positive deviation for proton ca in III. Carbons i and b in I and II show deviations of about -1.0 ppm because one of the α carbons is tertiary in each case. The environment is similar for carbons i and b in III except the parallel $\overset{+}{\text{C}}\text{H}-\bar{\text{C}}\text{H}_2$ bonds withdraw electronic charge from i toward b. This effect is much greater in IV (traditionally anomalous adamantane¹) in which each $\overset{+}{\text{C}}\text{H}-\bar{\text{C}}\text{H}_2$ is parallel and similarly oriented to two others, contributing at least half to a negative deviation, -4.9 ppm, for the CH₂ carbon and +1.7 ppm for the CH carbon (the other half by α substitution). Withdrawal of charge along all four bonds of >CH_2 by two CH's parallel to each CH and two $\overset{+}{\text{C}}\text{H}-\bar{\text{C}}\text{H}_2$'s parallel to each $\overset{+}{\text{C}}\text{H}-\bar{\text{C}}\text{H}_2$ is certainly part if not most of the explanation for the unusually low field of the CH₂ protons in adamantane. In V, the bridge CH dipoles are in line but oppositely oriented, compressing electronic charge toward both carbon nuclei and hence toward the bridge protons--raising the field considerably for both ¹³C and ¹H.

Looking at these molecular systems in this way raises several questions:

(1) If mutual polarization by 1,3,5 diaxial CH's rather than magnetic anisotropy

of the β C-C bonds is the explanation for the higher field of axial protons in cyclohexane and related structures, does anisotropy of CH and CC bonds have any observable reality beyond the first or α bond?² (2) Is it safe to deduce a bond moment from a measured molecular dipole moment and transfer it to another molecular system for the purpose of calculating its contribution to chemical shift unless the polarizing systems of both the model and the molecule of interest are understood and taken into account?³ (3) Can the Buckingham⁴ expression be used more effectively in reverse, to calculate a quantity proportional to the moment of a bond from its effect upon chemical shift? (4) Who is qualified to say that induction (through bonds) has no effect upon chemical shift or that the dipolar contribution of CH and CC bonds is negligible?⁵ (5) Is hyperconjugation mutual polarization? (6) Are approximate quantum mechanical methods, e.g., CNDO, in a position to challenge or validate the observations attributed to polarization unless they give the "correct" sign and a "reasonable" magnitude for the CH dipole?⁶

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7. It was called to our attention by one referee that a similar expression was proposed by E. L. Eliel, M. H. Gianni, Th. H. Williams, and J. B. Stothers, Tetrahedron Letters, 741 (1962), but it was not discussed in terms of meaning or physical significance.