581. *Studies in Nuclear Magnetic Resonance. Part II.* Application to Geometric Isomerism about the Ethylenic Double Bond.*

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A theory, based on long-range shielding effects, is developed to interpret the chemical shifts of olefinic and allylic protons in geometrically isomeric olefins. The scope of the theory is investigated by examining the specific shielding of the olefinic protons in 2-substituted propenes and the allylic protons in 1-substituted 2-methylpropenes. The results obtained indicate the types of substituent which an olefin must posses if nuclear magnetic resonance spectroscopy is to be used for the assignment of configuration to *cis*- and *trans*-isomers.

Coupling constants in 2-substituted propenes and 1-substituted 2-methylpropenes are reported.

THE theories of long-range magnetic shielding developed by Pople[1] and McConnell[2] suggest that the chemical shift of a proton in a molecule will depend significantly on the precise spatial relation between the proton and various groups of electrons in its vicinity. For this reason we may expect that nuclear magnetic resonance spectroscopy will prove of value in assigning the relative configurations of geometrical isomers. We now report chemical shifts for a number of simple olefinic compounds which establish the utility of nuclear magnetic resonance spectroscopy in the study of geometrical isomerism about carbon–carbon double bonds.

Theories of magnetic shielding are sufficiently developed to permit a qualitative understanding of proton chemical shifts. The induced magnetic fields which constitute the shielding arise from the Larmor precession of extranuclear electrons. These electron circulations or currents, as they are sometimes called, may be arbitrarily separated into three types:[1] (i) local diamagnetic circulations, (ii) paramagnetic circulations, (iii) interatomic diamagnetic circulations.

The first of these involves the circulation of the electrons surrounding the proton under investigation. This is approximately isotropic and the associated induced magnetic field is determined solely by electron density at the proton. Thus, apart from the consideration of effects such as direct electrostatic interaction and steric inhibition of mesomerism which may conceivably alter electron density, local diamagnetic circulations will not usually enter into discussions of differential shielding in stereoisomers.

Circulations of electrons about other nuclei (*e.g.*, carbon, oxygen, nitrogen, etc.) in a molecule may be restricted for certain orientations of the molecule in the applied magnetic

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* Part I, preceding paper.

[1] Pople, *Proc. Roy. Soc.*, 1957, *A*, **239**, 541, 550.

[2] McConnell, *J. Chem. Phys.*, 1957, **27**, 226.

field. The induced fields associated with these paramagnetic circulations are therefore anisotropic and may have non-zero average components at neighbouring nuclei. For example, the protons of acetylene are shielded by virtue of the anisotropic polarisability of the π-electron system of the triple bonds.[1] In certain molecules the induced circulation of electrons may, however, be facilitated by the existence of favourable paths whereby such circulations can extend over two or more atomic centres. Such induced electronic motions are referred to as interatomic diamagnetic circulations. An excellent example of this effect is provided by the benzene molecule in which the circulation occurs within the closed loop of the π-electron system, thus endowing the molecule with a large diamagnetic anisotropy which accounts for the deshielded character of aromatic protons. Less obvious, but none the less important, are the interatomic diamagnetic circulations in single bonds such as the carbon–carbon single bond. Bothner-By and Naar-Colin [3] have advanced evidence which indicates that the magnetic polarisabilities of some single bonds are appreciable and arise from interatomic circulations.

Magnetic shielding which arises from the anisotropic diamagnetic polarisability of axially symmetric groups of electrons, such as constitute single and triple bonds, has been considered by McConnell.[2] He has shown that the contribution $\sigma_{\text{av.}}$ to the shielding of a neighbouring nucleus is given approximately by equation (1):

$$\sigma_{\text{av.}} = (3 \cos^2 \theta - 1)(\chi_L - \chi_T)/3r^3 \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where r is the distance between the nucleus and the electrical centre of gravity of the group of electrons, θ is the acute angle which r makes with the symmetry axis of the group, and χ_L and χ_T are respectively the longitudinal and the transverse magnetic susceptibility which express the diamagnetic anisotropy of the group of electrons. This model involves the assumption that the induced field (averaged over all orientations) of the group of electrons can be simulated by a point dipole at the electrical centre of gravity of the group of electrons. The model is obviously unsatisfactory for molecules such as benzene, for which, however, more refined treatments are available.[4–7] A double bond in principle requires three susceptibilities to define its anisotropy [8] but, provided one of these is substantially greater than the other two, equation (1) is satisfactory for qualitative discussion. It is to be noted that, as r enters into equation (1) as the reciprocal of its cube, the magnitude of the shielding effect falls off rapidly with distance, and in fact significant long-range shielding is probably confined to distances less than 3·0 Å (except perhaps for shielding arising from aromatic rings). In this and some subsequent papers in this series which deal specifically with stereochemical problems we shall use the above ideas as a guide to the understanding of experimental results.

TABLE 1. *Differences in the chemical shifts of* cis- *and* trans-*olefinic protons in geometric isomers of the type* CHX:CHX.

X	CH_3 [b]	Cl	Br [c]	CO_2Me
$\tau_{cis} - \tau_{trans}$ (p.p.m.) [a]	−0·03	−0·08	−0·38	+0·525

[a] For the definition of τ see p. 2885. [b] Bothner-By and Naar-Colin, personal communication. [c] Tiers, personal communication.

We turn now to a consideration of the differential shielding of *cis-* and *trans-*olefinic protons by a β-substituent. Data for four stereoisomeric pairs of symmetrically substituted olefins are given in Table 1. A β-methyl group evidently produces no significant differential shielding of an olefinic proton. Bothner-By and Naar-Colin [9] have

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[3] Bothner-By and Naar-Colin, *J. Amer. Chem. Soc.*, 1958, **80**, 1728.
[4] Waugh and Fessenden, *J. Amer. Chem. Soc.*, 1957, **79**, 846.
[5] Pople, *Mol. Phys.*, 1958, **1**, 175.
[6] McWeeny, *Mol. Phys.*, 1958, **1**, 311.
[7] Johnson and Bovey, *J. Chem. Phys.*, in the press.
[8] Narasimhan and Rogers, *J. Phys. Chem.*, 1959, **63**, 1388.
[9] Bothner-By and Naar-Colin, *Ann. New York Acad. Sci.*, 1958, **70**, 833.

established that a carbon–carbon single bond has an appreciable diamagnetic anisotropy, being less readily polarised in the longitudinal than in the transverse direction. The failure of the C–CH_3 bond to produce a significant differential shielding in the but-2-enes results from the particular geometry of these systems. Thus in *cis*-but-2-ene the centre of the C–C bond is nearly 3·0 Å from the olefinic proton, which is too far for long-range shielding, and this is of course true for all other β-substituents. In the *trans*-isomer r is much shorter (2·4 Å) but the angle θ is such that the first term in equation (1) is almost zero and hence the shielding effect is very small. Bothner-By and Naar-Colin[3] have also discussed the anisotropy of carbon–halogen bonds and have concluded that the anisotropy of such bonds is determined by an interplay of electron circulations of types (ii) and (iii). Because carbon–halogen bonds are electrically dipolar, it is necessary to take r at the halogen nucleus rather than at the mid-point of the bond. This makes the term $(3 \cos^2 \theta - 1)$ small and negative. When the halogen is chlorine the paramagnetic term is probably dominant, and a small positive shielding of olefinic protons of *trans*-dichloroethylene results. With the more highly polarisable bromine atom the paramagnetic term (ii) is much larger and an even greater positive shielding of the olefinic proton in the *trans*-isomer is observed.

The appreciable deshielding of the olefinic protons in dimethyl fumarate relative to those in dimethyl maleate could be due to several causes. First, we may postulate that steric inhibition of mesomerism in the maleic ester could reduce the electron-withdrawal from the ethylenic bond which in turn could increase the electron-density and hence the local diamagnetic shielding at the olefinic protons. That this is not the sole explanation follows from the observation (Table 2) that the two olefinic protons in methyl methacrylate are unequally shielded. The most reasonable explanation is that the olefinic protons in methyl fumarate are deshielded by a long-range shielding effect of the carboxylate group. Pople[1] has pointed out that the carbonyl group is expected to have a large diamagnetic anisotropy arising from paramagnetic circulations (ii), which occur when the direction of the field is normal to the plane of the trigonal carbon atom. This anisotropy could be treated very approximately by equation (1) by assuming that the carbonyl group behaves as an axially symmetric group of electrons, the axis being some line normal to the plane of the trigonal carbon atom, and that the magnetic polarisability of this group is greatest along the axis. Equation (1) then permits the prediction that protons in the plane of the trigonal carbon atom will be deshielded.* This effect must, in part, be responsible for the deshielded character of aldehydic protons,[1] and similarly explains the deshielding of a *cis*-β-olefinic proton by a carboxyl group which will heavily populate coplanar conformations. It has been suggested[10] that weak hydrogen bonding between the carbonyl group and the β-olefinic proton might produce the observed shifts. However, it seems probable

TABLE 2. *Chemical shifts*[a] *in 2-substituted propenes* (I).

		τ (olefinic H)					τ (olefinic H)		
R	τ (Me)	*cis*[b]	*trans*[b]	$\tau_{cis} - \tau_{trans}$	R	τ (Me)	*cis*[b]	*trans*[b]	$\tau_{cis} - \tau_{trans}$
$CH_2 \cdot C(CH_3)_3$	8·22	5·37[c]	5·20[c]	0·17	COCl	7·97	3·52	3·98	−0·46
Cl	7·85	4·92	4·92	0·00	COMe	8·20	3·96	4·16	−0·20
Br	7·70	4·67	4·47	0·20	CHO	7·90	3·62	3·92	−0·30
CN	7·97	4·28[c]	4·24[c]	0·04	Ph	7·86	4·72	4·98	−0·20
CO_2Me	8·10	3·96	4·51	−0·55	OAc	8·09	5·38	5·38	0·00
$CO \cdot NH_2$	8·06	4·24	4·63	−0·39					

[a] The shifts are expressed as τ-values (see experimental). [b] *cis* and *trans* refer to the relation of R to the olefinic protons. [c] The assignment to *cis* and *trans* is uncertain.

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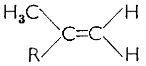
* Narasimhan and Rogers[8] have derived values for the three principle magnetic susceptibilities of the carbonyl bond from chemical-shift data in amides. Their treatment of the general problem of long-range shielding by the carbonyl group is correspondingly more refined than that given here, but the simple model based on equation (1) is quite satisfactory for the qualitative concepts which we wish to develop.

[10] Morris, Vernon, and White, *Proc. Chem. Soc.*, 1958, 303.

that long-range shielding accounts adequately for the effect without our needing to invoke a type of hydrogen bonding for which there is no other evidence.

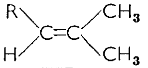
As an alternative method of evaluating the shielding of an olefinic proton by a *cis*-β-substituent, we have determined the chemical shifts of both olefinic protons in a series of 2-substituted propenes (I). The relevant data may be found in Table 2. The observed difference between the chemical shifts of the two olefinic protons provides an indication of potential usefulness of nuclear magnetic resonance for differentiating between geometric isomers of the type (II). This is shown by a comparison of the data for compounds with R = Cl, Br, and CO_2Me in Table 2 with the data for the corresponding 1,2-disubstituted ethylenes in Table 1. Derivatives of methacrylic acid, *e.g.*, the amide and acid chloride, exhibit differential shifts similar to that observed in the methyl ester. Significant differences are also observed with the aldehyde and methyl ketone, and we presume that, as in the acid derivatives, it is the protons *cis* to the carbonyl group which are deshielded although the magnitude of the effect is somewhat less than in the acid derivatives.



(I)

–CH=CR–

(II)



(III)

Two additional groups, R, produce differential shifts. These are the neopentyl and the phenyl group. It is interesting that the differential shift produced by the neopentyl group is quite large, since it confirms that carbon–carbon single bonds are magnetically anisotropic. Presumably this group spends an appreciable time in conformations in which certain of its C–C bonds are effectively oriented with respect to the *cis*-olefinic proton. The observation of differential shielding in α-methylstyrene is expected since it has been shown that the olefinic protons in *trans*-stilbene absorb at a field 0·50 p.p.m. lower than those of the *cis*-isomer,[11] and these effects are obviously associated with the interatomic diamagnetic circulations of the π-electrons of the aromatic ring.

The two remaining substituents in Table 2 which do not cause a differential shift require comment. The nitrile group, like acetylene, should give rise to paramagnetic circulations and be diamagnetically anisotropic ($\chi_L > \chi_T$). However, the electrical centre of gravity of the bond must lie close to the nitrogen nucleus and too far from either olefinic proton to make a significant shielding contribution. The failure of the acetoxy-group to effect differential shielding suggests that this substituent prefers those conformations in which the carbonyl group is well removed from *cis*-β-olefinic proton.

The conclusions drawn from the data in Table 2 have an important bearing on the theory of the shielding of *ortho*-hydrogen atoms in monosubstituted benzenes. Corio and Dailey[12] have observed that groups such as CO_2R, CHO, CO·CH_3, and NO_2 specifically deshield the *ortho*-protons and they have attributed this effect to an inductive (electrostatic) withdrawal of electrons by the substituent, which operates most strongly at the

TABLE 3. *Chemical shifts*[a] *in* 1-*substituted isobutenes* (III).

		τ (β-Me)					τ (β-Me)		
R	τ (olefinic H)	*cis*[b]	*trans*[b]	$\tau_{cis} - \tau_{trans}$	R	τ (olefinic H)	*cis*[b]	*trans*[b]	$\tau_{cis} - \tau_{trans}$
$C(CH_3)_3$ ...	4·87	8·38[c]	8·32[c]	0·06	COMe ...	4·03	7·94	8·14	−0·20
Br	4·22	8·25	8·25	0·00	CHO	4·37	7·89	8·09	−0·20
CO_2Me ...	4·38	7·88	8·16	−0·28	OAc	3·21	8·35	8·35	0·00
COCl	3·99	7·88	8·03	−0·15	C⋮CH ...	4·83	8·12[c]	8·20[c]	−0·08

[a] and [c] See corresponding footnotes to Table 2. [b] The isobutenes do not, of course, exist in separate *cis*- and *trans*-forms, but the methyl groups of $Me_2C{=}CHR$ give rise to two distinct shifts; these are labelled *cis* or *trans* according to whether they are ascribed to the methyl group *cis* or *trans* to the group R.

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[11] Curtin, Gruen, and Shoulders, *Chem. and Ind.*, 1958, 1205.

[12] Corio and Dailey, *J. Amer. Chem.*, 1956, **78**, 3043.

ortho-positions. In view of the above discussion, we believe that long-range shielding makes an important contribution to these paramagnetic shifts in the frequencies of *ortho*-protons. This conclusion is supported by the fact that the *ortho*-protons of benzonitrile are not anomalously deshielded in spite of the large $-I$ effect of the cyano-substituent. As previously noted, the nitrile group in acrylonitrile, and hence in benzonitrile, is not suitably orientated to exert a long-range shielding effect.

We have also examined the spectra of a series of compounds of the type (III), in order to evaluate the potentiality of using the chemical shifts of allylic protons to make assignments of configuration to geometric isomers. The results are given in Table 3. Because the methyl groups are freely rotating, large differential shielding effects are not expected and indeed only the highly anisotropic groups produce significant shifts. It is obvious that the presence of carbonyl substituents, R, such as CO_2Me, $CO{\cdot}CH_3$, and CHO in systems $-CMe{:}CR-$ will permit the use of nuclear magnetic resonance for configuration assignment (see Part III and ref. 10).

During this work we evaluated a number of coupling constants which are of interest. The 2-substituted propenes constitute ABX_3 spin systems. In examples in which δ_{AB} is approximately equal to the coupling constant J_{AB}, detailed analysis of the spectra is in general not feasible, for the three coupling constants J_{AB}, J_{AX}, and J_{BX} are all of the order of 1—2 c./sec. and the various lines in the spectra are difficult to resolve. In a number of examples δ_{AB} is of the order of 8—20 c./sec. and in these cases the spectra may be analysed fairly accurately as AYX_3 spin systems. The results are shown in Table 4 together with some examples of the 1-substituted isobutenes. In the 2-substituted propenes the coupling constants J_{AB} fall within the range quoted by Banwell, Cohen, Sheppard, and Turner,[13] although our analysis does not permit the evaulation of the sign relative to the other constants. In general, the values of the coupling constants J_{AX} and J_{BX} are such as to indicate that a *cis*-relation between the methyl group and the β-olefinic proton results in a coupling which is larger than for the *trans*-relation. A notable exception is provided by methacraldehyde (I; R = CHO). In contrast, the coupling constants in the isobutene series (III) show little, if any, dependence on stereochemistry, both J_{AX} and J_{BX} having values of the same order as the analogous *trans*-coupling constant in the 2-substituted propenes.

TABLE 4. *Coupling constants* (c./sec.) *in substituted propene and isobutenes.*

$R{\cdot}C(CH_3){:}CH_2$	J_{H,CH_3} (*trans*)	J_{H,CH_3} (*cis*)	$J_{H,H}$	$R{\cdot}C(CH_3){:}CH_2$	J_{H,CH_3} (*trans*)	J_{H,CH_3} (*cis*)
R = Br	0·8	1·4	1·4	R = $C(CH_3)_3$ ...	1·4	1·4
CO_3Me ...	0·9	1·45	1·8	Br	1·5	1·5
$CO{\cdot}NH_2$ ...	0·95	1·5	1·8	CO_2Me ...	1·3	1·3
COCl	0·90	1·5	0·0	COCl	1·4	1·2
COMe	0·7	1·3	0·7	OAc	1·55	1·55
CHO	1·5	1·0	1·0			

EXPERIMENTAL

Spectroscopy.—The nuclear magnetic resonance spectra were obtained with a Varian 4300 spectrometer and a 40 Mc. oscillator. The spectra were calibrated by side-band technique, a Muirhead–Wigan D-695-A audiofrequency oscillator being used. Data recorded above are the average of at least three separate determinations.

Measurements were made on *ca.* 5% solutions in carbon tetrachloride with the exception of acrylamide, which was examined in chloroform. Tetramethylsilane (1%) was used as an internal standard, and the shielding values in the Tables are expressed as τ as defined by Tiers.[14] The exact equivalence of this method of standardisation with that employing an external reference and extrapolation to infinite dilution in carbon tetrachloride was established for three of the compounds, *viz.*, α-methylstyrene, acrylonitrile, and methyl senecioate.

Materials.—The authors thank the following colleagues who supplied pure samples:

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[13] Banwell, Cohen, Sheppard, and Turner, *Proc. Chem. Soc.*, 1959, **266**,

[14] Tiers, *J. Phys. Chem.*, 1958, **62**, 1151.

Dr. J. A. Elvidge (2,4,4-trimethylpent-1-ene, 2,4,4-trimethylpent-2-ene), Dr. W. Miller (*cis-* and *trans*-dichloroethylene), Dr. P. Schwed (2-methylpent-2-en-4-yne).

Methyl senecioate, n_D^{21} 1·4388, was prepared by esterifying the acid with diazomethane and fractionating the product. Senecioyl chloride, n_D^{22} 1·4821, was prepared by the action of thionyl chloride on the acid; the crude acid chloride was fractionated.

ββ-Dimethylacraldehyde, n_D^{25} 1·4615, was prepared by the method of Young and Linder.[15]

2-Chloropropene was prepared by the action of phosphorus pentachloride on acetone.[16] The resulting mixture of the olefin, 2,2-dichloropropane, and acetone was separated by fractionation. The olefin was shown to be pure by gas–liquid chromatography.

The remaining materials were commercial samples which were purified and had the following physical constants. Dimethyl maleate (B.D.H.), m. p. 101—103°; dimethyl fumarate (B.D.H.), n_D^{23} 1·4420; methacrylonitrile, n_D^{22} 1·4011; methyl methacrylate, n_D^{22} 1·4155; methacrylamide (Lights), m. p. 105—107°; methacraldehyde (Lights), n_D^{22} 1·4215.

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[15] Young and Linder, *J. Amer. Chem. Soc.*, 1947, **69**, 2912.

[16] Henne and Renoll, *J. Amer. Chem. Soc.*, 1937, **59**, 2434.