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CARBON-13 CHEMICAL SHIFTS AND ELECTRON STRUCTURE OF METHYLENE GROUPS IN HYDROCARBONS*

Introduction

Direct methods that allow to study the geometric and electronic structure of the carbon sceleton of hydrocarbons are not numerous. There are no chemical methods of general applicability for the determination and investigation of even such simple functional groups as methyl, methylene or methine carbons in saturated chains and indirect methods have to be used to study these. In addition to optical, mainly refractometric, methods molecular spectroscopy has been applied to the study of hydrocarbon structure. Infrared and ultraviolet spectra have been widely used, but the utility of the latter is confined mainly to π-electron systems in aromatic or unsaturated compounds while the former depend first of all on carbon-hydrogen, not carbon-carbon bonds. It is practically impossible to make sound conclusions about the electronic structure of saturated chains or cycles from optical spectra.

Proton magnetic resonance spectra have also been used to study the structure of hydrocarbons. Several useful relationships have been found, the spectral patterns of the methyl groups are characteristic of the chain branching and both methyl and methylene patterns are indicative of meth chain length[1], while the chemical shifts o unsaturated and α-protons are susceptible to metric isomerism[2,3]. But the shift difference erratic and small, 0.04 to 0.10 ppm only an most specific difference in spin-spin cou constants for cis and trans isomers cannot us be measured from the very complicated spe Proton spectra have proved to be especially u in the analysis of strained polycyclic hydrocarb particularly together with double resonance m ods[4]. In this particular case the spin-spin coup constants are sometimes more useful than che shifts that are often influenced by magnetic teractions in an unpredictable manner[5]. The hy carbons always contain large strongly coupled systems and the proton spectra of these molec are very complicated. It is just impossible at pre to measure the chemical shifts of all proton more complicated molecules than pentenes. E double resonance can in this case accomplish partial simplification.

The carbon-13 spectra offer in this res several important advantages. While the total ra of chemical shifts of methylene protons in uns stituted hydrocarbons does not exceed 4 ppm w well over 99 % of all shifts crowded into a sm 2 ppm range, the total span of carbon-13 chem shifts is 80 ppm for saturated methylene group hydrocarbons. This amounts to 1/3 of the t

* The lecture was delivered at the Meeting on Chemistry 1967 in Helsinki.

carbon-13 chemical shifts. The low
nce of carbon-13 nuclei (1.08 per
back as it makes the registration of
, but on the other hand it brings
portant simplification of carbon-13
tain no line splittings as a result of
ings between carbon atoms. If one
decoupling with a strong coherent
field acting on the hydrogen spins,
n-13 spectrum consists of single
for each carbon atom[6,7,8,9,10,11].
y large molecules, at present with
n atoms can be analysed and all
ical shifts measured. It would be a
to accomplish this with proton

3 chemical shifts in unsubstituted
carbons can be viewed as a con-
ty and in most cases depend on
rs only. These shifts can be calcu-
use of the empirical constitutive
avitsky[12].
the carbon-13 spectra of the satu-
rious hydrocarbons and carboxylic
ed with the object of getting some
t the electronic structure of these
ing useful analytical relationships
13 chemical shifts and molecular

k of hydrocarbon molecules has
ss attention than molecular π-elec-
e Hückel theory of π-electrons has
ssful in predicting chemical pro-
ic and unsaturated molecules and
a sort of neglect of σ-electrons and
e often been considered to be
zed[13]. In particular, the effects of
he σ—π separation in non-planar
the past been generally ignored
is known about total electronic
n atoms of saturated molecules,
play a significant role.
calculations on aliphatics[14,15,16],
steady increase of such work and
te molecular orbital (MO) theo-
ydrocarbons have appeared[17–20].
e analogous to the Hückel theory
ectrons of aromatic systems but
nd π electrons. The extended
Hoffman[21–23] is an LCAO-MO

theory with a basis set consisting of a 1s Slater orbital on each hydrogen atom in the molecule, and 2s and 2p Slater orbiltas on each carbon atom. All neighbour and non-neighbour interactions are included (non-zero differential overlap) and the complete secular determinant is treated. A somewhat different approach has been used by Whitehead. His self-consistent group orbital and bond electronegativity (SGOBE) method[23,24] and the extended Hückel theory (EHT) have both been used for charge calculations and gross atomic charge Q_k has been found to correlate successfully with the carbon chemical shifts[23], thereby providing an important link between theoretical calculations and experiment.

The total screening of a nucleus can be divided into a diamagnetic and a paramagnetic contribution from local currents associated with the given atom A, contributions from local currents on other atoms B and effects of molecular ring currents that cannot be localized[25,26]. The magnetic field at nucleus A is

$$H_A = H_o\ (1 - \sigma^A), \tag{1}$$

where σ^A is the total shielding constant of a particular nucleus.

$$\sigma^A = \sigma_p^{AA} + \sigma_d^{AA} + \sum_{B \neq A} \sigma^{AB} + \sigma^{A,\,ring} \tag{2}$$

The local paramagnetic term is given by

$$\sigma_p^{AA} = -\frac{e^2 h}{2m^2 c^2 \Delta E} \left\langle r^{-3} \right\rangle_{2p} \sum_{B} Q_{AB}, \tag{3}$$

where ΔE is the mean $\sigma \leftrightarrow \pi$ excitation energy, usually 5 to 10 eV, $\left\langle r^{-3} \right\rangle_{2p}$ is the mean inverse cube radius for carbon 2p orbitals, and Q_{AB} consists of elements of the charge density and bond order matrix $P_{\mu\nu}$ in the MO theory of the unperturbed molecule[19]. The paramagnetic terms involving Q_{AB} arise because the external magnetic field acting on atom B mixes certain excited electronic states of the molecule and thereby induces a current flow on atom A. In the approximation of localized MO wave functions used by Pople, the effect of neighbouring atoms is different from zero only if there is both σ-and π-bonding between atoms A and B, and so it is a multiple bond effect. Q_{AB} depends on orbital hybridization and accordingly $-\sigma_p^{AA}$ is equal to 207 ppm in ethane and 317 ppm in ethylene[26].

The local diamagnetic term σ_d^{AA} is given by the Lamb formula (4) and corresponds to a uniform circulation of all atomic electrons as if they were free.

$$\sigma_d^{AA} = \frac{e^2}{3mc^2} \sum_i \left\langle r_i^{-1} \right\rangle_{av}, \tag{4}$$

where $\left\langle r_i^{-1} \right\rangle_{av}$ is the mean inverse distance of electron from the nucleus A and summation is over electrons on the atom considered. Total variation of this term is much too small to account for the observed range of chemical shifts. With Slater atomic orbitals the variation of σ_d^{AA} for one added 2p or 2s electron is only 14 ppm[27] or less than 3 per cent of the total range of observed C^{13} chemical shifts.

The magnetic contributions from bond anisotropy $\sum_{B \neq A} \sigma^{AB}$ are likewise small and do not exceed a few tenth of ppm in most hydrocarbons[7], except in cyclopropane[29]. The local paramagnetic term σ_p^{AA} is dominant in determining the chemical shifts of carbon atoms and the variation of this term comes about mostly through the $\left\langle r^{-3} \right\rangle_{2p}$ term that has a strong charge dependence[26,27], although other factors, like variation of ΔE or free-valence index[27] may also contribute to a lesser extent. The atomic orbitals of an atom expand with increased negative charge due to interelectronic repulsion and $\left\langle r^{-3} \right\rangle_{2p}$ decreases. Assuming linear dependence of this term on the atomic charge[27,17], a linear charge dependence of carbon chemical shift is expected. It has been assumed and found to be consistent with experimental results for a limited class of compounds that gross atomic charges Q_K are analogous to the chemical concept of charge on an atom and should therefore correlate with chemical shifts[23].

If the electronic structure of a saturated hydrocarbon could be adequately described with completely localized molecular orbitals, then the variation of Q_{AA} and that of the paramagnetic term should be small[25,26] and the total variation of chemical shifts of saturated carbon atoms should be less than 14 ppm. Yet the reverse is true. It has been shown[9,28] that in strained unsaturated molecules a saturated methylene group can have a chemical shift as low as 117.6 ppm from carbon d
A total range of 60 ppm is possible for
groups with sp³-hybridised carbon ato
in propane the carbon chemical shift of t
is 175.9 ppm[7]. This is a clear indication
delocalization of σ-electrons and in orde
some insight into this phenomenon th
resonance spectra of hydrocarbons,
without strain, were investigated.

Experimental

Low natural abundance makes the regist
carbon-13 spectra quite difficult. The ab
signal is about four orders of magnitude
the corresponding signal from hydrogen
the same molecule. Use of adiabatic rapid
with a strong measuring *rf* field

$$\gamma H_1 \gg \frac{1}{H_1}\frac{dH_o}{dt} \gg \frac{1}{T_1},\ \frac{1}{T_2},$$

and measuring the dispersion signal ha
successful in the study of relatively simp
cules[30], but rapid sweep rates and the ne
strong measuring *rf* field γH_1 limit spectra
tion so that the saturated parts of more com
molecules give no useful spectra[9], Fig. 1;
No chemical shifts can be measured fro
featureless humps and one has either to
ceedingly strong fields and superconducti
noids to generate them or double resonanc
ods for spectrum simplification. Irradia
hydrogen atoms near their resonance freq
with a strong perturbing *rf* field H_2 decou
hydrogen and carbon-13 nuclear spins and
to get simple spectra with just one single
each carbon atom without any visible sp
splittings.

If $|\gamma|\ H_2 \gg |\Delta\omega_2|;\ 2\pi\ |J(C^{13}H^1)|$,

then the residual splitting is[32,33]:

$$J_r \cong \frac{J\ \Delta\ \omega_2}{\gamma\ H_2},$$

where $|\gamma|\ H_2$ is the amplitude of the pertur
field and $\Delta\omega_2$ deviation of the perturbi
quency from exact resonance. In our exper
a very strong *rf* field with an amplitude o
cps was used, and since

$$\Delta\omega_2 \ll \pi\ (\Delta\delta) \cdot 10^6,$$

where $\Delta\delta$ is the full range of hydrogen ch

does not exceed 1.2 ppm for the saturated
rmal alkenes and alkynes[8], the residual
bout 5 cps) is much less than linewidth
he use of a very strong decoupling *rf*
e main difference of our technique from
d of Paul and Grant[6]. No indirect meas-
of the hydrogen resonance frequencies
pted and the perturbing frequency was
nly once in each experiment and was
r optimum decoupling of either all the
or unsaturated hydrogen atoms. This
work fast and in addition some possi-
error are avoided[9].
t collapse is accompanied by a corre-
wo- or threefold increase in peak value
ditional increase in line intensity (and
alue) is possible as a result of the nuclear
r effect. Using the symbols of Abra-
we have

$$= 1 + (\sigma/\rho)\,(S_o/I_o), \qquad (9)$$

$\langle I_z \rangle$ is the steady state and I_o the equi-
agnetization of the carbon-13 nuclei.
= 1/2 for dipole-dipole relaxation and
$\gamma_H/\gamma_C \cong 4$ an up to threefold increase in
ity is possible. In benzene an increase of
up to 5.5 times has been achieved[6,9],
not always the case since other relaxation
interfere, diminishing the σ/ρ ratio.
does not depend on scalar spin-spin
nd strong enhancement is achieved for
ted sp-carbons in alkynes and carboxyl
n acids if the methyl and methylene
re saturated. For high precision it is
to use absorption spectra with a not too
rturbing field[6,9], but the sensitivity is
and the ± 0.07 ppm or even better
s of little practical use, since unsaturated
ls are susceptible to solvent effects and
n. Because of this adiabatic rapid pas-
s used in most cases and the mean shift
both sweep directions calculated. This
is simple and allows to work much
h high sensitivity. The precision is less,
5 ppm and relative line intensities are
but the mean value for both sweep
are unaffected. The spectrometer[9,36] was
l apparatus designed to allow all nuclei
ate between 1,5 and 26 Mc to be inves-
ecoupling *rf* power was available only
sonance frequency of hydrogen nuclei
(60 Mc). In all cases (monoresonance and spin decoupling, absorption signals and adiabatic rapid passage dispersion signals) time sharing was used with high pulse repetition rate[36,37]. If the pulse repetition rate is considerably higher than $1/T_2^*$, then all double resonance effects are displayed normally, but base-line stability is greatly improved[36,37]. The stability of *rf* bridges or crossed coils is not high if very strong decoupling field γH_2 is used and it would be quite difficult to register C^{13} double resonance absorption spectra without the use of pulse methods. The necessary stability of line positions was provided by spin stabilization and a sideband spin generator was used for this purpose. All spectra were registered at 15.1 Mc/sec with a 10 cps/sec frequency sweep and the line positions were measured with an electronic counter. In the case of rapid passage spectra the mean value of measured frequencies for both sweep directions was used. Standard 15 mm test tubes and 1.5 ml of sample (in some cases only 0.25 ml), mostly as neat liquid, were used. All chemical shifts were measured at room temperature from external carbon disulphide, so that

$$\delta_{CS_2} = \sigma_A - \sigma_{CS_2} \qquad (10)$$

Results

1. Alkanes.

Normal alkanes up to n-decane and several branched alkanes have been studied by Grant and Paul[7]. Selective spin decoupling was used and all carbon-13 chemical shifts assigned to particular carbon atoms. These assignments are consistent with the constitutive parameters of Savitsky[12]. The chemical shifts of saturated methylene groups in n-alkanes cover a range of 16.7 ppm. This, together with quite large vicinal spin-spin coupling constants between hydrogen atoms[38], is a clear indication that deviations from perfect pairing, or second order hyperconjugation, does occur in saturated hydrocarbon chains[9]. As a result of this there appear π-bond orders between adjacent saturated carbon atoms[20,22,23], Q_{AB} is no longer zero and gives rise to a paramagnetic shift. In addition to that there appears to be a considerable direct interaction between remote groups, particularly between the end and fourth member of a hydrocarbon chain[7]. Such interactions may play a part in Newman's »rule of six» in chemical reactivity[39].

2. Cyclic hydrocarbons.

Only very few investigations have been carried out on these compounds. Savitsky[12] notes, that even simple saturated cyclic structures, such as cyclohexane, show considerable deviations from additivity. In the case of unsaturated cyclic compounds the chemical shifts of only unsaturated $\bar{s}p^2$-carbon atoms have in a few cases been studied[12]. We measured the chemical shifts for a small representative series of cyclic compounds that allowed us to investigate the effect of strain and unsaturation on carbon chemical shifts[9,28]. The results are listed in table 1.

It is apparent that chemical shifts of saturated carbon atoms in saturated cyclic compounds are not very susceptible to strain. The carbon-13 chemical shifts of adamantane, that is completely free of strain and rigid are very similar to the chemical shifts of strained norbornane (strain energy, 18.5 kcal mole[40]), and if one uses the +6 ppm correction for every saturated 5- or 6-membered ring, then these shifts are quite comparable with chemical shifts of carbon atoms in normal and branched alkanes. However, quite unusual chemical shifts occur in unsaturated strained polycyclic compounds. The bridge methylene carbon

in both norbornene and norborna
large paramagnetic shift, as compa
bornane. Cleary, two different m
operative in determining the meth
shifts in cyclic compounds. If one
usual assumption of perfect pairi
π-bonds, then one has two kinds of
for the σ-electrons. Both act in the
and lead to a paramagnetic shift. On
hydrocarbons and is not particula
to strain while the other needs
nearby atoms and is met only in uns
cules with strain. In such molecules a
ions[22,41] a strong hyperconjugati
between π-electrons and the bridge
possible and the resulting bondings
classical. The electron structure
carbon atom may no longer be adequ
by sp^3-hybrids, this makes σ_p^{AA} larg
to a paramagnetic shift.

Since both these mechanisms ca

significant paramagnetic terms that c

a strong general charge dependen
chemical shifts is expected. Any decr
charge must lead to paramagnetic

Table 1: Chemical shifts δ_{CS_2} of some cyclic hydrocarbons.

Molecule	Carbon atom	Exptl.[a] $\delta^a_{CS_2}$	Calcd.[b] $\delta^b_{CS_2}$	Δ $\delta^a_{CS_2} - \delta^b_{CS_2}$	Calcd.[c] $\delta^c_{CS_2}$
Adamantane	CH_2	155.5	147.2	+ 8.3	159.2
	CH	165.0	145.5	+ 19.5	163.5
Norbornane	CH_2 (7)	155.0	147.2	+ 7.8	159.2
	CH (1, 4)	157.5	145.4	+ 12.1	157.4
	CH_2 (2, 3, 5, 6)	163.0	154.1	+ 8.9	166.1
Norbornene[d]	CH_2 (7)	140	147.2	— 7.2	
	CH (1, 4)	148	146.1	+ 1.9	
	CH_2 (5, 6)	160	154.1	+ 5.9	
	= CH (2, 3)	56	56.2	— 0.2	
Norbornadiene	CH_2 (7)	117.6	147.2	— 29.6	
	CH (1, 4)	142.5	146.8	— 4.3	
	= CH (2, 3, 5, 6)	49.5	56.2	— 6.7	
Quadricyclene[e]	CH (1, 4)	171.0	131.6	+ 39.4	
	CH (2, 3, 5, 6)	179.0	124.7	+ 54.3	

a) $\pm$ 1 ppm.
b) Calculated on the basis of constitutive bond parameters[25].
c) Calculated on the basis of constitutive bond parameters with a diamagnetic constitutive
+6 ppm for every independent 5- or 6-membered saturated ring structure connected w
atom under consideration. Adamantane is considered to contain 3 rings for every CH
for every CH_2 group.
d) From earlier work[17].
e) Sample was partially decomposed and impure, chemical shift of carbon-7 could not be
acceptable accuracy.

methylene and methine carbons
norbornadiene can be compared
omic charge densities Q_K of
urprisingly good linear fit is
to the dependence of carbon
net π-electron charges ρ_A in
and ions[27,42,43].

$$\omega_s = \alpha(\rho_A - 1), \qquad (11)$$

is larger than 160.

depend upon many other
arges and do not show such
, in fact in adamantane the less
carbon carries more shielded
while for methine groups the

large diamagnetic shifts are
be attributed to ring currents
red cycles that can be thought
sp²-hybridized carbon atoms
bitals in the plane of the ring[44].
n from this hybridization can
sibilities for a ring current, the
of methine carbons in highly
ene relative to cyclopropane[29]

his study show that classical
d σ-bonds are quite inadequate
chemical shifts can be used to
lectronic structure of saturated
ted hydrocarbons.

methylene groups between
omatic rings.

ive interaction between the
d double bonds in norbornadi-
liar phenomenon and it is of
, whether such interactions can
diate neighbours. Some mole-
as every reason to expect such
place were investigated and the
Table 2.

hifts δ_{CS_2} of methylene groups
pounds.

ptl.	Molecule	Exptl.
1.2	1,4-Penta-diene[a]	154
5.7	1,5-Hexa-diene[a]	158
7.0	Diphenylmeth-ane[b]	157
	Dibenzyl	154.9

I. L. Retcofsky[31].
Doran, E. B. Baker, G. A.

12, 1967

It appears that in all cases the methylene chemical shifts in these highly unsaturated compounds are comparable with chemical shifts in other alkenes and even alkanes (see Table 1.). Clearly, rigid molecules with high strain and a special geometric arrangement between the interacting groups are necessary for the special, norbornadiene kind of hyperconjugation to take place.

4. Alkynes.

Carbon-13 spectra of a few simple acetylenes have been studied by Lauterbur[46], Friedel and Retcofsky[31], and others[47,48]. Only the chemical shifts of the sp-hybridized carbon atoms were measured and found to fall into the rather narrow range 104 to 126 ppm from CS_2[49,50] that is usually free from other carbon-13 signals and can be used for the identification of triple bonds. Very little is known about the chemical shifts of saturated carbon atoms in alkynes. Methyl and methylene groups of these molecules give very complicated spectra of weak overlapping multiplets where no determination of chemical shifts is possible. We investigated some representative alkynes[10] and complete chemical shift data for these normal alkynes together with the calculated values are given in the Table 3. The values for n-octane[7] are added for comparison. The assignment of the chemical shift to a given carbon atom was made on the basis of peak intensities, additive parameters and in some cases through the use of monoresonance spectra and selective decoupling with various $\Delta\omega_2$ values.

The data for the alkynes indicate that quite regular trends exist for the chemical shift values. The chemical shifts of carbon atoms in the higher members conform very well with trends established by earlier members of the series where there is no ambiguity in spectral assignment. It is immediately apparent that the triple bond influences only the shifts of immediate neighbours, the α-carbon atoms, that show a fairly constant diamagnetic shift about 11 to 13 ppm for both methyl and methylene groups. The possible effect on β-carbon atoms is certainly less than 1 ppm if it exists at all and the shifts of β,γ and farther atoms correspond closely to the shifts in similar alkanes. The diamagnetic 11 ppm shift of α-methylene carbon atoms relative to atoms in the same position in paraffins is large. As a result of this shift, in some cases the α-methylene groups absorb in a higher field than the methyl groups of the same molecule. If this shift is caused by magnetic anisotropy of the triple bond, then this anisotropy must be even

Table 3: Carbon-13 chemical shift data for unbranched alkynes.

Carbon atom		Hexyne-1	Hexyne-2	Hexyne-3	Heptyne-1	Heptyne-2	Heptyne-3	Octyne-1	Octyne-2	Octyne-3	Octyne-4
C_1	Exptl.[1]	125.1	190.8	178.1	125.1	190.2	178.8	123.5	189.6	177.4	179.8
	Calcd.[2]	125.8	189.4	176.6	125.8	189.4	176.6	125.8	189.4	176.6	176.6
	Δ[3]	−0.7	+1.4	+1.5	−0.7	+0.8	+2.2	−2.3	+0.2	+0.8	+3.2
C_2	Exptl.	109.7	118.8	180.5	109.6	118.3	180.5	108.5	117.7	179.5	171.1
	Calcd.	110.2	118.7	182.3	110.2	118.7	182.3	110.2	118.7	182.3	169.5
	Δ	−0.5	+0.1	−1.8	−0.6	−0.4	−1.8	−1.7	−1.0	−2.8	+1.6
C_3	Exptl.	175.1	115.6	112.6	174.8	114.9	114.2	174.1	114.0	112.8	173.3
	Calcd.	173.8	110.2	110.2	173.8	110.2	110.2	173.8	110.2	110.2	173.8
	Δ	+1.3	+5.4	+2.4	+1.0	+4.7	+4.0	+0.3	+3.8	+2.6	−0.5
C_4	Exptl.	162.6	172.9	112.6	164.4	174.8	112.3	163.3	174.1	111.5	113.5
	Calcd.	161.0	173.8	110.2	161.0	173.8	110.2	161.0	173.8	110.2	110.2
	Δ	+1.6	−0.9	+2.4	+3.4	+1.0	+2.1	+2.3	+0.3	+1.3	+3.3
C_5	Exptl.	171.3	170.9	180.5	161.8	161.3	172.3	163.3	163.0	173.8	113.5
	Calcd.	169.5	169.5	182.3	161.0	161.0	173.8	161.0	161.0	173.8	110.2
	Δ	+1.8	+1.4	−1.7	+0.8	+0.3	−1.5	+2.3	+2.0	0.0	+3.3
C_6	Exptl.	179.6	180.4	178.1	170.1	170.7	170.0	160.5	161.1	160.6	173.3
	Calcd.	176.6	176.6	176.6	169.5	169.5	169.5	161.0	161.0	161.0	173.8
	Δ	+3.0	+3.8	+1.5	+0.6	+1.2	+0.5	−0.5	+0.1	−0.4	−0.5
C_7	Exptl.				178.5	179.0	179.4	169.1	169.8	169.7	171.1
	Calcd.				176.6	176.6	176.6	169.5	169.5	169.5	169.5
	Δ				+1.9	+2.4	+2.8	−0.4	+0.3	+0.2	+1.6
C_8	Exptl.							177.6	178.0	177.9	179.8
	Calcd.							176.6	176.6	176.6	176.6
	Δ							+1.0	+1.4	+1.3	+3.2

[1] ppm from external CS_2, without corrections for bulk susceptibility, $\delta_{C_6H_6} - \delta_{CS_2} = 65$ ppm.
[2] Calculated with the use of the constitutive parameters of G. B. Savitsky[12].
[3] Δ stands for the difference $\delta_{exptl.} - \delta_{calcd.}$
[4] D. M. Grant and E. G. Paul[7].

larger than the highest suggested value[51]. The difference of chemical shifts of the two sp-carbon atoms has analytical value. It is 15.2 ± 0.3 ppm in 1-alkynes, 3.4 ± 0.3 ppm in 2-alkynes and 1.6 ± 0.3 ppm in 3-alkynes. These values have significance for higher members of the series only, in the case of butynes and phenylacetylene there are large deviations from these values[47].

The differences between calculated[12] and measured chemical shifts are small and show that the Savitsky parameters can well be used in the structural analysis of aliphaties. One new constant for the -C ≡ group, +29 ppm has been added. The equality to the ≡ C- constant must be purely accidental.

The Overhauser effects provide some insight into the relaxation processes in alkynes. A large increase of line intensity of unsubstituted sp-carbon atoms was noted, even though only more distant hydrogen atoms were saturated. This is consistent with the relative insignificance of other relaxation mechanisms for these spins[35], but a very small Overhauser effect on the α-methyl group line is puzzling

since no very effective additional relaxation m
anisms for sp³-carbon atoms are known.

5. Alkenes

Carbon-13 spectra of unsaturated compounds
been actively investigated. The results of H
showed that olefinic carbon nuclei absorb i
same region as aromatic carbons. In the ab
of polar substituents the absorption falls int
very crowded region of 44 to 79 ppm from
Substituents cause additional shifts and the
range reaches from 38 to 114[50]. A systematic
of unsaturated carbon atoms of olefins has
reported by Friedel and Retcofsky[31] and
largely these results, it has been shown tha
simple hydrocarbons the chemical shift of
unsaturated sp²-carbon atoms is a constit
property that depends on the nearest neighb
only[12]. The saturated chains of alkenes
received little attention. We investigated all
metric isomers of normal octenes[11] where in
cases it was possible to separate eight distinct

s that does not exceed 1.2 ppm for the saturated of normal alkenes and alkynes[2], the residual ting (about 5 cps) is much less than linewidth T_2^*. The use of a very strong decoupling *rf* is the main difference of our technique from method of Paul and Grant[6]. No indirect measnent of the hydrogen resonance frequencies attempted and the perturbing frequency was ged only once in each experiment and was sted for optimum decoupling of either all the rated or unsaturated hydrogen atoms. This les to work fast and in addition some possiies of error are avoided[9].

ultiplet collapse is accompanied by a corrending two- or threefold increase in peak value an additional increase in line intensity (and peak value) is possible as a result of the nuclear rhauser effect. Using the symbols of Abra-[34, p. 337] we have

$$\langle I_z \rangle / I_0 = 1 + (\sigma/\rho)\,(S_0/I_0), \qquad (9)$$

re $\langle I_z \rangle$ is the steady state and I_0 the equium magnetization of the carbon-13 nuclei. e $\sigma/\rho = 1/2$ for dipole-dipole relaxation and $S_0 = \gamma_H/\gamma_C \cong 4$ an up to threefold increase in intensity is possible. In benzene an increase of value up to 5.5 times has been achieved[6,9], this is not always the case since other relaxation cesses[35] interfere, diminishing the σ/ρ ratio. effect does not depend on scalar spin-spin pling and strong enhancement is achieved for ubstituted sp-carbons in alkynes and carboxyl ons in acids if the methyl and methylene ons are saturated. For high precision it is isable to use absorption spectra with a not too ng perturbing field[6,9], but the sensitivity is h less and the ± 0.07 ppm or even better cision is of little practical use, since unsaturated npounds are susceptible to solvent effects and ciation. Because of this adiabatic rapid pas-e[7,9] was used in most cases and the mean shift ue for both sweep directions calculated. This nique is simple and allows to work much er with high sensitivity. The precision is less, y ± 0.5 ppm and relative line intensities are orted, but the mean value for both sweep ections are unaffected. The spectrometer[9,36] was niversal apparatus designed to allow all nuclei resonate between 1,5 and 26 Mc to be inves-ted. Decoupling *rf* power was available only the resonance frequency of hydrogen nuclei (60 Mc). In all cases (monoresonance and spin decoupling, absorption signals and adiabatic rapid passage dispersion signals) time sharing was used with high pulse repetition rate[36,37]. If the pulse repetition rate is considerably higher than $1/T_2^*$, then all double resonance effects are displayed normally, but base-line stability is greatly improved[36,37]. The stability of *rf* bridges or crossed coils is not high if very strong decoupling field γH_2 is used and it would be quite difficult to register C^{13} double resonance absorption spectra without the use of pulse methods. The necessary stability of line positions was provided by spin stabilization and a sideband spin generator was used for this purpose. All spectra were registered at 15.1 Mc/sec with a 10 cps/sec frequency sweep and the line positions were measured with an electronic counter. In the case of rapid passage spectra the mean value of measured frequencies for both sweep directions was used. Standard 15 mm test tubes and 1.5 ml of sample (in some cases only 0.25 ml), mostly as neat liquid, were used. All chemical shifts were measured at room temperature from external carbon disulphide, so that

$$\delta_{CS_2} = \sigma_A - \sigma_{CS_2} \qquad (10)$$

Results

1. Alkanes.

Normal alkanes up to n-decane and several branched alkanes have been studied by Grant and Paul[7]. Selective spin decoupling was used and all carbon-13 chemical shifts assigned to particular carbon atoms. These assignments are consistent with the constitutive parameters of Savitsky[12]. The chemical shifts of saturated methylene groups in n-alkanes cover a range of 16.7 ppm. This, together with quite large vicinal spin-spin coupling constants between hydrogen atoms[38], is a clear indication that deviations from perfect pairing, or second order hyperconjugation, does occur in saturated hydrocarbon chains[9]. As a result of this there appear π-bond orders between adjacent saturated carbon atoms[20,22,23], Q_{AB} is no longer zero and gives rise to a paramagnetic shift. In addition to that there appears to be a considerable direct interaction between remote groups, particularly between the end and fourth member of a hydrocarbon chain[7]. Such interactions may play a part in Newman's »rule of six» in chemical reactivity[39].

2. Cyclic hydrocarbons.

Only very few investigations have been carried out on these compounds. Savitsky[12] notes, that even simple saturated cyclic structures, such as cyclohexane, show considerable deviations from additivity. In the case of unsaturated cyclic compounds the chemical shifts of only unsaturated $\bar{S}_p^2$-carbon atoms have in a few cases been studied[12]. We measured the chemical shifts for a small representative series of cyclic compounds that allowed us to investigate the effect of strain and unsaturation on carbon chemical shifts[9,28]. The results are listed in table 1.

It is apparent that chemical shifts of saturated carbon atoms in saturated cyclic compounds are not very susceptible to strain. The carbon-13 chemical shifts of adamantane, that is completely free of strain and rigid are very similar to the chemical shifts of strained norbornane (strain energy, 18.5 kcal mole[40]), and if one uses the +6 ppm correction for every saturated 5- or 6-membered ring, then these shifts are quite comparable with chemical shifts of carbon atoms in normal and branched alkanes. However, quite unusual chemical shifts occur in unsaturated strained polycyclic compounds. The bridge methylene carbon in both norbornene and norb large paramagnetic shift, as c bornane. Cleary, two differe operative in determining the shifts in cyclic compounds. If usual assumption of perfect π-bonds, then one has two kin for the σ-electrons. Both act in and lead to a paramagnetic shif hydrocarbons and is not par to strain while the other ne nearby atoms and is met only i cules with strain. In such molec ions[22,41] a strong hypercon between π-electrons and the b possible and the resulting bon classical. The electron struc carbon atom may no longer be by sp^3-hybrids, this makes σ_p^A to a paramagnetic shift.

Since both these mechanis significant paramagnetic terms a strong general charge dep chemical shifts is expected. An charge must lead to parama

Table 1: Chemical shifts δ_{CS_2} of some cyclic hydrocarbons.

Molecule	Carbon atom	Exptl.[a] $\delta^a_{CS_2}$	Calcd.[b] $\delta^b_{CS_2}$	Δ $\delta^a_{CS_2} - \delta^b_{CS_2}$	C
Adamantane	CH_2	155.5	147.2	+ 8.3	
	CH	165.0	145.5	+ 19.5	
Norbornane	CH_2 (7)	155.0	147.2	+ 7.8	
	CH (1, 4)	157.5	145.4	+ 12.1	
	CH_2 (2, 3, 5, 6)	163.0	154.1	+ 8.9	
Norbornened[d]	CH_2 (7)	140	147.2	— 7.2	
	CH (1, 4)	148	146.1	+ 1.9	
	CH_2 (5, 6)	160	154.1	+ 5.9	
	= CH (2, 3)	56	56.2	— 0.2	
Norbornadiene	CH_2 (7)	117.6	147.2	— 29.6	
	CH (1, 4)	142.5	146.8	— 4.3	
	= CH (2, 3, 5, 6)	49.5	56.2	— 6.7	
Quadricyclene[e]	CH (1, 4)	171.0	131.6	+ 39.4	
	CH (2, 3, 5, 6)	179.0	124.7	+ 54.3	

a) $\pm$ 1 ppm.
b) Calculated on the basis of constitutive bond parameters[25].
c) Calculated on the basis of constitutive bond parameters with a diamagnetic cons +6 ppm for every independent 5- or 6-membered saturated ring structure conne atom under consideration. Adamantane is considered to contain 3 rings for e for every CH_2 group.
d) From earlier work[17].
e) Sample was partially decomposed and impure, chemical shift of carbon-7 could acceptable accuracy.

f carbon-13 chemical shifts. The low
ance of carbon-13 nuclei (1.08 per
yback as it makes the registration of
lt, but on the other hand it brings
mportant simplification of carbon-13
ntain no line splittings as a result of
olings between carbon atoms. If one
decoupling with a strong coherent
y field acting on the hydrogen spins,
on-13 spectrum consists of single
ne for each carbon atom[6,7,8,9,10,11].
ely large molecules, at present with
oon atoms can be analysed and all
mical shifts measured. It would be a
to accomplish this with proton

-13 chemical shifts in unsubstituted
lrocarbons can be viewed as a con-
erty and in most cases depend on
ours only. These shifts can be calcu-
e use of the empirical constitutive
Savitsky[12].
r the carbon-13 spectra of the satu-
various hydrocarbons and carboxylic
ssed with the object of getting some
out the electronic structure of these
nding useful analytical relationships
n-13 chemical shifts and molecular

---

ork of hydrocarbon molecules has
less attention than molecular π-elec-
The Hückel theory of π-electrons has
ccessful in predicting chemical pro-
natic and unsaturated molecules and
n a sort of neglect of σ-electrons and
ave often been considered to be
alized[13]. In particular, the effects of
f the σ—π separation in non-planar
e in the past been generally ignored
le is known about total electronic
bon atoms of saturated molecules,
ns play a significant role.
rst calculations on aliphatics[14,15,16],
a steady increase of such work and
imate molecular orbital (MO) theo-
d hydrocarbons have appeared[17–20].
are analogous to the Hückel theory
electrons of aromatic systems but
σ and π electrons. The extended
of Hoffman[21–23] is an LCAO-MO

theory with a basis set consisting of a 1s Slater orbital on each hydrogen atom in the molecule, and 2s and 2p Slater orbiltas on each carbon atom. All neighbour and non-neighbour interactions are included (non-zero differential overlap) and the complete secular determinant is treated. A somewhat different approach has been used by Whitehead. His self-consistent group orbital and bond electronegativity (SGOBE) method[23,24] and the extended Hückel theory (EHT) have both been used for charge calculations and gross atomic charge Q_k has been found to correlate successfully with the carbon chemical shifts[23], thereby providing an important link between theoretical calculations and experiment.

The total screening of a nucleus can be divided into a diamagnetic and a paramagnetic contribution from local currents associated with the given atom A, contributions from local currents on other atoms B and effects of molecular ring currents that cannot be localized[25,26]. The magnetic field at nucleus A is

$$H_A = H_o\,(1 - \sigma^A), \tag{1}$$

where σ^A is the total shielding constant of a particular nucleus.

$$\sigma^A = \sigma_p^{AA} + \sigma_d^{AA} + \sum_{B \neq A} \sigma^{AB} + \sigma^{A,\,ring} \tag{2}$$

The local paramagnetic term is given by

$$\sigma_p^{AA} = -\frac{e^2 h}{2 m^2 c^2 \Delta E} \left\langle r^{-3} \right\rangle_{2p} \sum_B Q_{AB}, \tag{3}$$

where ΔE is the mean $\sigma \leftrightarrow \pi$ excitation energy, usually 5 to 10 eV, $\left\langle r^{-3} \right\rangle_{2p}$ is the mean inverse cube radius for carbon 2p orbitals, and Q_{AB} consists of elements of the charge density and bond order matrix $P\mu_\nu$ in the MO theory of the unperturbed molecule[19]. The paramagnetic terms involving Q_{AB} arise because the external magnetic field acting on atom B mixes certain excited electronic states of the molecule and thereby induces a current flow on atom A. In the approximation of localized MO wave functions used by Pople, the effect of neighbouring atoms is different from zero only if there is both σ-and π-bonding between atoms A and B, and so it is a multiple bond effect. Q_{AB} depends on orbital hybridization and accordingly $-\sigma_p^{AA}$ is equal to 207 ppm in ethane and 317 ppm in ethylene[26].

The local diamagnetic term σ_d^{AA} is given by the Lamb formula (4) and corresponds to a uniform circulation of all atomic electrons as if they were free.

$$\sigma_d^{AA} = \frac{e^2}{3 mc^2} \sum_i \left\langle r_i^{-1} \right\rangle_{av}, \tag{4}$$

where $\left\langle r_i^{-1} \right\rangle_{av}$ is the mean inverse distance of electron from the nucleus A and summation is over electrons on the atom considered. Total variation of this term is much too small to account for the observed range of chemical shifts. With Slater atomic orbitals the variation of σ_d^{AA} for one added 2p or 2s electron is only 14 ppm[27] or less than 3 per cent of the total range of observed C^{13} chemical shifts.

The magnetic contributions from bond anisotropy $\sum_{B \neq A} \sigma^{AB}$ are likewise small and do not exceed a few tenth of ppm in most hydrocarbons[7], except in cyclopropane[29]. The local paramagnetic term σ_p^{AA} is dominant in determining the chemical shifts of carbon atoms and the variation of this term comes about mostly through the $\left\langle r^{-3} \right\rangle_{2p}$ term that has a strong charge dependence[26,27], although other factors, like variation of ΔE or free-valence index[27] may also contribute to a lesser extent. The atomic orbitals of an atom expand with increased negative charge due to interelectronic repulsion and $\left\langle r^{-3} \right\rangle_{2p}$ decreases. Assuming linear dependence of this term on the atomic charge[27,17], a linear charge dependence of carbon chemical shift is expected. It has been assumed and found to be consistent with experimental results for a limited class of compounds that gross atomic charges Q_K are analogous to the chemical concept of charge on an atom and should therefore correlate with chemical shifts[23].

If the electronic structure of a saturated hydrocarbon could be adequately described with completely localized molecular orbitals, then the variation of Q_{AA} and that of the paramagnetic term should be small[25,26] and the total variation of chemical shifts of saturated carbon atoms should be less than 14 ppm. Yet the reverse is true. It has been shown[9,28] that in strained unsaturated molecules a saturated methylene group can have a chemical shift as low as 117.6 ppm from carbon
A total range of 60 ppm is possible for
groups with sp^3-hybridised carbon at
in propane the carbon chemical shift of
is 175.9 ppm[7]. This is a clear indication
delocalization of σ-electrons and in ord
some insight into this phenomenon t
resonance spectra of hydrocarbons,
without strain, were investigated.

Experimental

Low natural abundance makes the regi
carbon-13 spectra quite difficult. The
signal is about four orders of magnitud
the corresponding signal from hydroge
the same molecule. Use of adiabatic rap
with a strong measuring *rf* field

$$\gamma H_1 \gg \frac{1}{H_1}\frac{dH_o}{dt} \gg \frac{1}{T_1}, \quad \frac{1}{T_2},$$

and measuring the dispersion signal
successful in the study of relatively sim
cules[30], but rapid sweep rates and the
strong measuring *rf* field γH_1 limit spect
tion so that the saturated parts of more co
molecules give no useful spectra[9]. Fig.
No chemical shifts can be measured f
featureless humps and one has either
ceedingly strong fields and superconduc
noids to generate them or double resona
ods for spectrum simplification. Irrad
hydrogen atoms near their resonance f
with a strong perturbing *rf* field H_2 dec
hydrogen and carbon-13 nuclear spins a
to get simple spectra with just one sing
each carbon atom without any visible
splittings.

If $|\gamma|\,H_2 \gg |\Delta\omega_2|;\ 2\pi\,|J(C^{13}H^1)|$,

then the residual splitting is[32,33]:

$$J_r \cong \frac{J\,\Delta\,\omega_2}{\gamma\,H_2},$$

where $|\gamma|\,H_2$ is the amplitude of the per
field and $\Delta\omega_2$ deviation of the pertur
quency from exact resonance. In our ex
a very strong *rf* field with an amplitud
cps was used, and since

$$\Delta\omega_2 < \pi\,(\Delta\delta)\cdot 10^6,$$

where $\Delta\delta$ is the full range of hydrogen

omplete chemical shift data for the alkenes as
as the calculated values[12] and the deviations
given in the Table 4. The assignment of carbon
mical shifts to particular carbon atoms was
le on the basis of regular deviations from the
esponding values in similar unsaturated or
rated compounds (n-octane), additive para-
ers[7,12], peak intensities and through the use of
ctive decoupling with various $\Delta\omega_2$ values.
he chemical shift data indicate that both the
nd sp^3-carbon shifts fall into the correspond-
usual ranges[50]. In the case of asymmetrically
ed double bonds in linear molecules the
rence of chemical shifts of the unsaturated
on atoms has analytical significance. It is 24
in octene-1, 7 ppm in octene-2 and 1.6 ppm
tene-3. There is every reason to expect similar
rences in higher alkenes. These differences are
ically identical in both cis and trans isomers.
he chemical shifts of saturated carbon atoms
that the double bond influences the shielding
e immediate neighbours only and there is no
tive effect on β or γ-carbon atoms. The shifts
ese and other carbon atoms are very close to the corresponding shifts in paraffins. While other carbon chemical shifts can be calculated with acceptable accuracy, the α-carbon atoms show large and significant deviations of very constant value. The chemical shifts of α-carbon atoms in all cis-trans pairs differ by 5.7 ± 1 ppm and this difference depends neither on the type of the α-carbon atom (methyl or methylene) nor on the position of the double bond in the molecule. The measured shift is larger than the calculated value in all cis-alkenes and smaller than that in all trans-alkenes. These deviations are with one exception much larger than the possible experimental error. In addition to the α-carbons all carbon atoms, both saturated and unsaturated, show in cis-alkenes a small 1 to 2 ppm diamagnetic shift relative to the corresponding atoms in trans-alkenes. This effect has also been noted for sp^2-carbon atoms in 2-butene[53] and 3-hexene[31]. The reason for this dependence of carbon chemical shifts on geometric isomerism is not clear. In the case of proton spectra of 1.2 substituted ethylenes the magnetic anisotropy of substituents has been suggested as a possible explanation[54], but this is not possible for the

e 4: Carbon-13 chemical shift data for normal alkenes.

Carbon atoms	Octene-1	cis-Octene-2	trans-Octene-2	cis-Octene-3	trans-Octene-3	cis-Octene-4	trans-Octene-4	n-Octane[4]
Exptl.[1]	78.7	180.7	174.7	179.0	179.2	179.4	178.8	179.7
Calcd.[2]	78.7	177.3	177.3	176.6	176.6	176.6	176.6	176.6
Δ[3]	0.0	+3.4	—2.6	+2.4	+2.6	+2.8	+2.2	+3.1
Exptl.	54.5	70.0	68.5	173.0	168.3	170.5	169.6	170.7
Calcd.	55.9	71.6	71.6	170.2	170.2	169.5	169.5	169.5
Δ	—1.4	—1.6	—3.1	+2.8	—1.9	+1.0	+0 1	+1.2
Exptl.	158.7	62.8	61.2	64.4	63.5	164.3	158.0	161.3
Calcd.	161.7	63.1	63.1	63.1	63.1	161.7	161.7	161.0
Δ	—3.0	—0.3	—1.9	+1.3	+0.4	+2.6	—3.7	+0.3
Exptl.	162.6	167.0	160.2	63.2	61.5	64.4	62.3	164.0
Calcd.	161.0	161.7	161.7	63.1	63.1	63.1	63.1	161.0
Δ	+1.6	+5.3	—1.5	—0.1	—1.6	+1.3	—0.8	+3.0
Exptl.	162.6	163.9	162.4	166.9	161.5	64.4	62.3	164.0
Calcd.	161.0	161.0	161.0	161.7	161.7	63.1	63.1	161.0
Δ	+1.6	+2.9	+1.4	+5.2	—0.2	+1.3	—0.8	+3.0
Exptl.	159.9	161.8	160.2	161.5	161.5	164.3	158.0	161.3
Calcd.	161.0	161.0	161.0	161.0	161.0	161.7	161.7	161.0
Δ	—1.1	+0.8	—0.8	+0.5	+0.5	+2.6	—3.7	+0.3
Exptl.	169.4	170.4	169.5	171.0	170.9	170.5	169.6	170.7
Calcd.	169.5	169.5	169.5	169.5	169.5	169.5	169.5	169.5
Δ	—0.1	+0.9	0.0	+1.5	+1.4	+1.0	+0.1	+1.2
Exptl.	178.3	179.1	178.2	179.0	179.2	179.4	178.8	179.7
Calcd.	176.6	176.6	176.6	176.6	176.6	176.6	176.6	176.6
Δ	+1.7	+2.5	+1.6	+2.4	+2.6	+2.8	+2.2	+3.1

from CS_2, without corrections for bulk susceptibility, $\delta_{C_6H_6} - \delta_{CS_2} = 65$ ppm.
ulated with the use of the constitutive parameters of G. B. Savitsky[12].
nds for the difference $\delta_{exptl.} - \delta_{calcd.}$.

symmetrically placed sp^2-carbon atoms. Magnetic effects must be very small in unsubstituted normal alkenes, since the ≲ 0.05 ppm differences of olefinic, α-methyl and α-methylene proton shifts in cis- and trans isomers are nearly two orders of magnitude smaller than in carbon spectra, with opposite signs for α-methyl and α-methylene protons[3]. Steric inhibition of conjugation, as suggested for bulky substituents[55] is quite improbable for the flexible alkyl groups where only hyperconjugation is possible, but some other forms of action through space[7,56] cannot be entirely discounted. However, since all atoms of the molecule are affected a systematic difference in ΔE suggests itself. The only strong ultraviolet absorption band of normal alkenes is for cis-2-alkenes $\lambda_{max}^{cis} = 176.5 \pm 1.5$ mμ and for trans-2-alkenes $\lambda_{max}^{trans} = 179 \pm 1$ mμ[57]. If the paramagnetic contribution to the chemical shift σ_p^{AA} has in alkenes about the same values as in ethylene[26], then a 1.8 ppm/mμ change in chemical shift values is to be expected and gives the right order of magnitude for the shift differences, although most of these are actually smaller. An analogous analysis of chemical shifts in cyclic ketones gave very similar results where the actual effect was likewise only about half of the predicted value[58].

With the exception of α-carbon atoms all calculated shifts[12] agree well with the measured values. The Savitsky parameters can be used to predict the spectra of normal alkenes and the chemical shifts of α-carbon atoms allow the geometric isomers to be recognized.

Both in alkenes and alkynes
ical shifts of methylene g
same groups in alkanes depe
on the inductive effects of
electronegativities of sp^3 and
atoms are not very different,
effect on neighbouring meth
large. The electronegativity
carbon atom is larger, but t
to divide the measured diam
the influences of magnetic an
the inductive effect of the t
alkenes and alkynes there wa
on α-methylene carbon atoms
interest to investigate the influ
larger inductive effect. As an
group was chosen, especially
this group on a saturated
irregular, so that no universa
ficient can be set up for it.

6. Carboxylic acids.

Some simple acids have been
and Lauterbur[46,60] and Savitsky
only the chemical shifts of ca
measured. We undertook to i
ical shift of all carbon atoms of
normal mono- and dicarbo
carbocylic acids were measured
carbon disulphide as interna
boxylic acids were studied as s
methanol. The results are liste

Table 5: Carbon-13 chemical shift data for carboxylic acids.

Molecule	Chemical shifts of carbon atoms							
	C_1	C_2	C_3	C_4	C_5	C_6	C_7	
Formic acid[a]	27.0							
Acetic acid[a]	15.6	174.2						
Propionic acid	12.1	166.1	184.0					
n-Butyric acid	12.5	157.1	174.6	179.1				
n-Valeric acid	12.5	159.1	165.8	170.2	179.3			
n-Caproic acid	12.7	159.2	168.5	161.1	170.0	178.9		
n-Enanthic acid	12.6	158.6	167.7	163.2	160.0	169.5	178.3	
Oxalic acid	32.8	32.8						
Malonic acid	23.3	152.3	23.3					
Succinic acid	17.3	163.7	163.7	17.3				
Glutaric acid	16.6	160.0	171.7	160.0	16.6			
Adipic acid	16.4	159.0	168.0	168.0	159.0	16.4		
Pimelic acid	16.0	158.3	167.5	163.5	167.5	158.3	16.0	
Suberic acid	16.2	158.8	167.6	163.6	163.6	167.6	158.8	1
Azelaic acid	16.0	159.2	167.9	163.7	163.7	163.7	167.9	15
Sebacic acid	16.2	158.8	167.8	163.2	163.2	163.2	163.2	16
Propane[b]	176.3	175.9	176.3					
n-Pentane[b]	180.0	171.1	159.2	171.1	180.0			
n-Decane[b]	179.6	170.7	161.3	163.8	163.4	163.4	163.8	16

[a] J. B. Stothers, P. C. Lauterbur[60].

y clear that the carboxylic group
an inductive effect that leads to a
of the neighbouring α-methylene
luence is more complicated than
lene groups do show a signi-
shift that cannot be reconciled
ductive effect. Cleary some sort
on must be invoked as well to
listic picture of the action of
on the electronic structure of a
l methylene groups. The exact
t is not at all clear, but it is quite
hat there can be no single
ion coefficients for the inductive
group. It is interesting to note
understand that the hydrogen
propionic acid do not show
the influence of the carboxylic
monotonously with distance[62].
chemical shifts of carboxylic
and dicarboxylic acids may be
t effect[63].

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s of saturated carbon atoms in
how large variations depending
ucture, that are indicative of
tions from perfect pairing and
ion. These deviations are largest
l hydrocarbons with high strain,
ent take place even in normal
n-13 chemical shifts show some
ross atomic charges in the first
h some less obvious relation-
bridization and even for ultra-
importance of magnetic inter-
e clear, these effects appear to
clopropanes and possibly in al-
ble in other compounds. In
n-13 double resonance spectra
and useful tool for the study
of hydrocarbon molecules. In
dy of electronic structure these
l unique analytical possibilities,
determination of the position
multiple bonds in alkenes and

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