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CARBON-13 DOUBLE RESONANCE ABSORPTION SPECTRA OF STRAINED MOLECULES

I Introduction

The σ -framework of hydrocarbon molecules has received much less attention than molecular π -electron systems. The Hückel theory of π -electrons has been quite successful in predicting chemical properties of aromatic and unsaturated molecules and it has resulted in a sort of neglect of σ -electrons and bonds that have often been considered to be completely localized [1]. In particular, the effects of the violation of the σ - π separation in non-planar molecules have in the past been generally ignored and as yet little is known about total electronic charges on carbon atoms of saturated molecules, where σ -electrons play a significant role.

After the first calculations on aliphatics [2-4], there has been a steady increase of such work and several approximate molecular orbital (MO) theories of saturated hydrocarbons have appeared [5-8]. These methods are analogous to the Hückel theory for the mobile electrons of aromatic systems but include both σ and π electrons. The extended Hückel theory of Hoffman [9-11] 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 orbitals 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 [11, 12] 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 [11], 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 [12, 14]. The magnetic field at nucleus A is

$$H_A = H_0(1 - \sigma^A), \quad (1)$$

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

$$\sigma^A = \sigma_p^{AA} + \sigma_d^{AA} + \sum_{B \neq A} \sigma_{AB} + \sigma^{A, \text{ring}}, \quad (2)$$

The local paramagnetic term is given by

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

where ΔE is the mean $\sigma \leftrightarrow \pi$ excitation energy, $\langle r^{-3} \rangle_{2p}$ 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 [7]. 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.

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.

$$\sigma_d^{AA} = \frac{e^2}{3mc^2} \sum_i \langle r_i^{-1} \rangle_{av.} \quad (4)$$

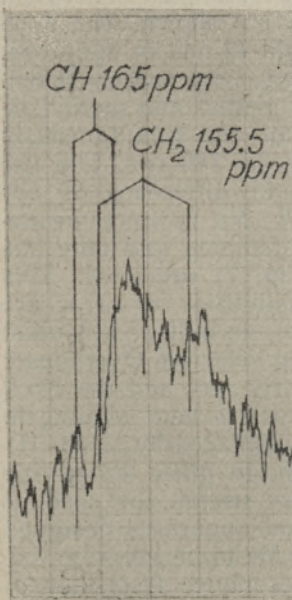
where $\langle r_i^{-1} \rangle_{av.}$ is the mean inverse distance of electron i from the nucleus A and summation is over electrons on the atom considered. Total variation of this term is much too small to account for the observed range of chemical shifts. With Slater atomic orbitals the variation of σ_d^{AA} for one added $2p$ or $2s$ electron is only 14 ppm [15] 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 tenths of ppm in hydrocarbons [16]. 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 $\langle r^{-3} \rangle_{2p}$ term that has a strong charge dependence [14, 15], although other factors, like variation of ΔE or free-valence index [15] may also contribute to a much lesser extent. The atomic orbitals of an atom expand with increased negative charge due to interelectronic repulsion and $\langle r^{-3} \rangle_{2p}$ decreases. Assuming linear dependence of this term on the atomic charge [14, 15], 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 [11].

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 [13, 14] 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 in our first paper [17] that in strained unsaturated molecules a saturated methylene group can have a chemical shift as low as 117.6 ppm from carbon disulphide. Accordingly, a total range of 60 ppm is possible for methylene groups with sp^3 -hybridized carbon atoms since in propane the carbon chemical shift of this group is 177.6 ppm [16]. This is a clear indication of strong delocalization of σ -electrons in strained cyclic hydrocarbons and in order to gain some insight into this phenomenon the spectra of cyclic model compounds, with and without strain, were investigated and the shifts compared with computed EHT gross atomic charges.

II Experimental

Low natural abundance combined with the low inherent sensitivity and quite long (5 to 50 sec) relaxation time T_1 of carbon-13 make the registration of its magnetic resonance spectra very difficult. The signal is about four orders of magnitude less than the corresponding signal from hydrogen nuclei of the same molecule. Use of adiabatic rapid passage technique in the dispersion mode has been quite successful in the study of relatively simple molecules, but the sensitivity is inadequate and the rapid sweep rates and strong measuring rf field limit the spectral resolution so that more complicated molecules with superimposed multiplets do not give useful spectra. The rapid passage dispersion mode spectrum of adamantane (0.33 g in 2 ml of supersaturated benzene solution) is shown in Fig. 1. No chemical shifts can be measured from such spectra and one has either to use exceedingly strong fields H_0 and superconducting solenoids to generate them or double resonance methods for spectrum simplification. Strong irradiation of hydrogen atoms decouples the hydrogen and carbon-13 nuclear spins and allows to get simple spectra without spin-spin splittings. At the same time as a result of the nuclear Overhauser effect [18, 19] the line intensities are strongly enhanced, so that the peak value rises more than 5 times, as shown in Fig. 2. The decoupled line has



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Fig. 1. Adiabatic rapid passage carbon-13 spectrum of adamantane (0.33 g in 2 ml of benzene solution).

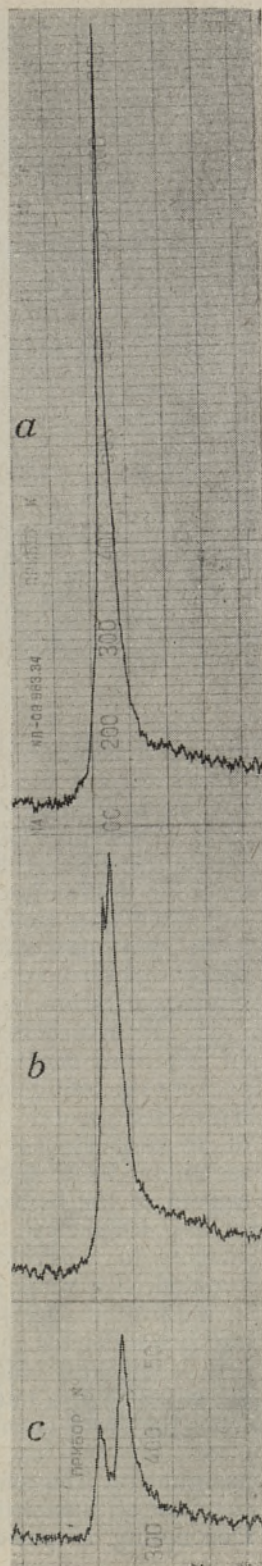


Fig. 2. C^{13} rapid passage (sweep rate 6.25 cps/sec) dispersion signals of benzene (1 ml): a collapse; b partial collapse; c monoresonance.



a peculiar shape with a very sharp peak. This is useful, since it practically enhances spectral resolution. If even better resolution and unperturbed line intensities are needed, the absorption signal has to be used. As shown in Fig. 3, the absorption signal is much weaker than the rapid passage signal, but symmetrical. In the case of spin decoupling the intensity of the absorption signal likewise rises about 5 times, so that in the case of not too complicated molecules the use of absorption spectra of carbon-13 is quite practical.

Strong irradiation of both methylene and methine protons of adamantane with small proton chemical shift difference (only 0.1 ppm) is very simple and good decoupled rapid passage spectra can be obtained (Fig. 4a). These spectra can be used for chemical shift determination, but the dispersion signals are

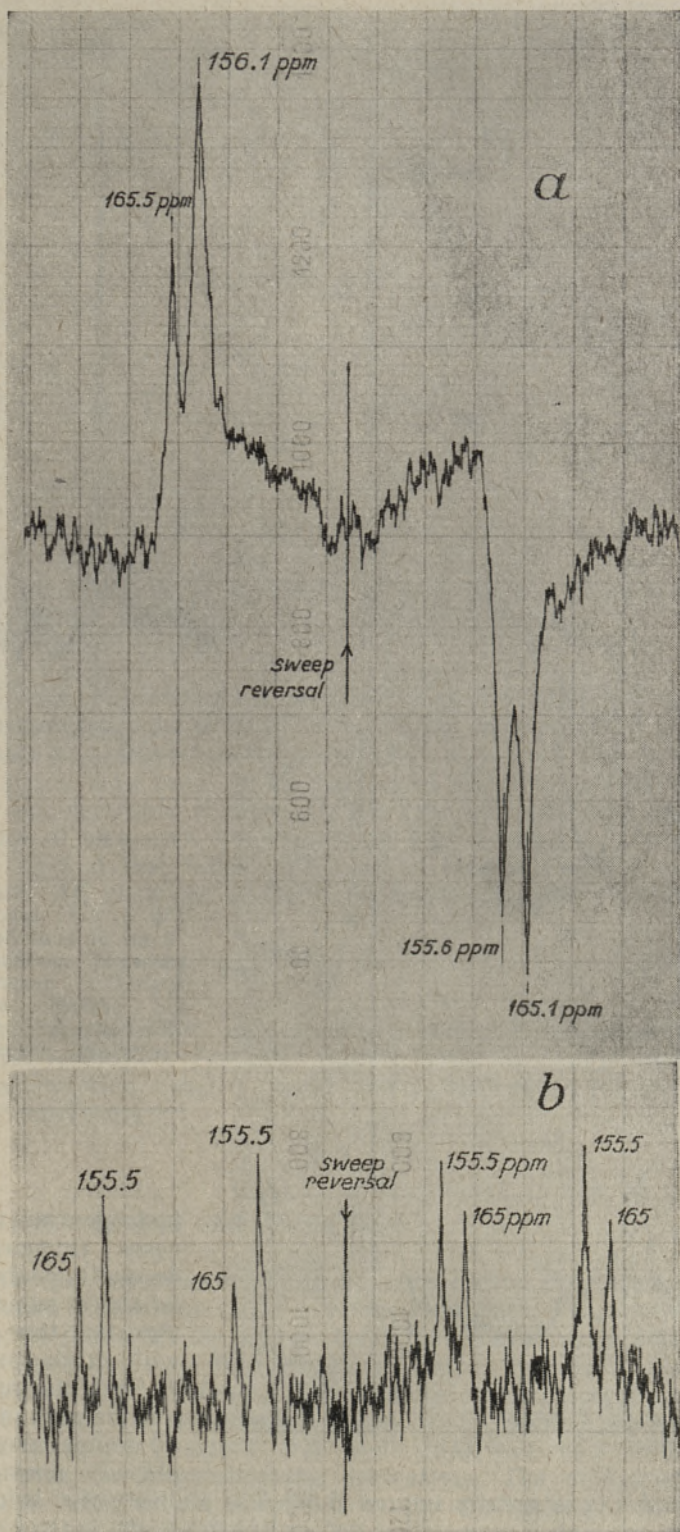
Fig. 3. C^{13} absorption spectrum of benzene (2 ml). Sweep rate 6.25 cps/sec.

always somewhat distorted and accompanied by small base-line shift in the vicinity of the line, so that the relative intensities are distorted. The spectra in Fig. 4a cannot be used to assign the chemical shifts to the two sorts of carbon atoms in the very symmetrical adamantane molecule. The decoupled absorption spectra, though with low signal/noise ratio can be used for this assignment, since the 4:6 ratio is well borne out. The same technique was used with all the molecules investigated and in Fig. 5a, b, c the monoresonance, decoupled rapid passage and decoupled absorption spectra of norbornadiene ([2.2.1] bicycloheptadiene) are shown. The good signal/noise ratio is the result of the use of neat liquid (2 ml) in the probe.

It is not necessary to have the strong decoupling field exactly tuned. In fact good decoupling could be achieved for both methyl and methylene carbons in ethyl alcohol, where the total span of the simultaneously irradiated proton spectrum of these groups exceeds 180 cps. The use of a very strong decoupling rf field is the main difference of our technique from the method of Paul and Grant^[20]. No indirect measurement of the hydrogen resonance frequencies is attempted and only one or two frequency settings of this synthesizer (Fig. 7) are used. This enables to work fast and in addition some possibilities of error are avoided. If a weak decoupling field is tuned just to one half of a doublet in the proton spectrum (one satellite), a very strong selective Overhauser effect results, the intensity of $\Lambda=0$ line being nearly zero and the $\Lambda=2$ line is strongly enhanced^[21]. The resulting spectrum is very similar to the collapse of a multiplet, yet the enhanced line is displaced by $1/2 J(\text{CH})$ from the true chemical shift of this carbon atom. In other cases this effect, as well as selective collapse, can be very useful for spectral assignment. The spectrometer (Fig. 7) is a universal apparatus designed to allow all nuclei that resonate between 1.5 and 26 Mc to be investigated.

Decoupling rf power is available only at the resonance frequency of

Fig. 4. C^{13} double resonance spectra of adamantane (0.33g in 2 ml of benzene solution); *a* rapid passage dispersion signal; *b* absorption signal. The spectra have been registered with both increasing and decreasing measuring frequency and in addition the absorption spectra with a low signal to noise ratio are registered twice for both sweep directions.



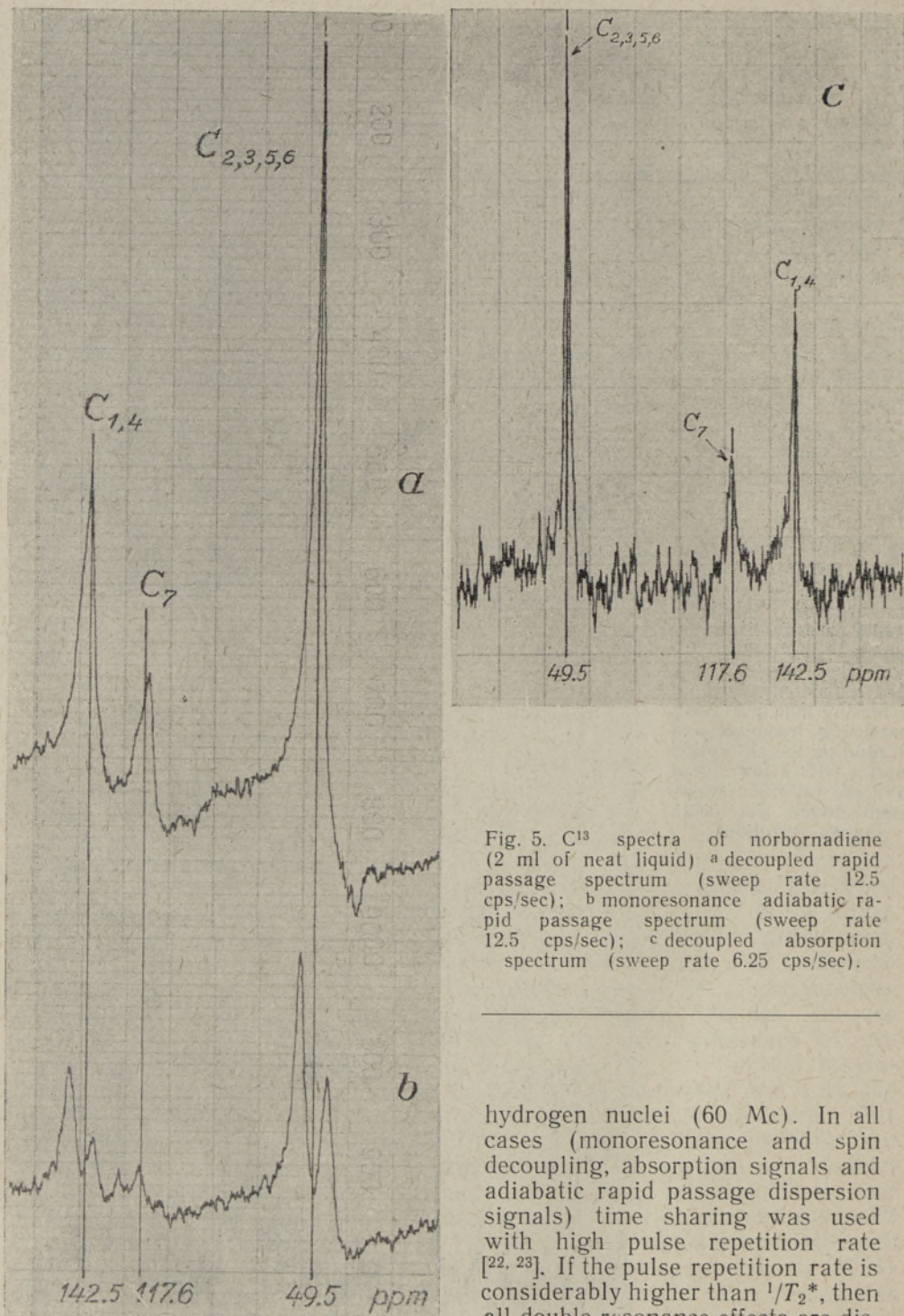


Fig. 5. ^{13}C spectra of norbornadiene (2 ml of neat liquid) a decoupled rapid passage spectrum (sweep rate 12.5 cps/sec); b monoresonance adiabatic rapid passage spectrum (sweep rate 12.5 cps/sec); c decoupled absorption spectrum (sweep rate 6.25 cps/sec).

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 [22, 23]. 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 [22]. 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

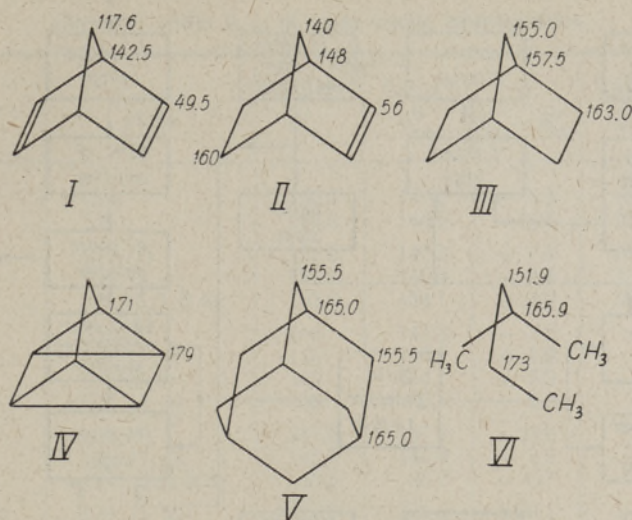


Fig. 6. Structures and carbon-13 chemical shifts of hydrocarbons investigated. The shift values of II are cited from [17] and VI from [16].

difficult to register C¹³ 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. Frequency sweep was used in all cases 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 2 ml of sample, mostly as neat liquid, were used. All chemical shifts were measured from carbon disulphide, so that

$$\delta_{\text{CS}_2} = \sigma_A - \sigma_{\text{CS}_2} \quad (5)$$

The measuring rf field strength γH_1 was always a compromise between sensitivity and spectral resolution. The absorption spectra were registered with low rf power (attenuation about 8 times) and at half speed relative to the rapid passage conditions.

III Results and discussion

The molecules that were investigated (Fig. 6) were chosen for various characteristics, particularly norbornadiene (I) has both high strain and two double bonds to interact with the bridge methylene, norbornene (II) has only one double bond but also high strain, in norbornane (III) the strain is less and it contains no double bonds. Quadricyclene (IV) is highly strained, but does not contain π -bonds in the usual sense. Adamantane (V) is completely strain free and rigid, but has some structural similarity with the bicycloheptane derivatives. The measured chemical shifts together with values estimated by the application of the constitutive rule of Savitsky [25] are listed in Table 1.

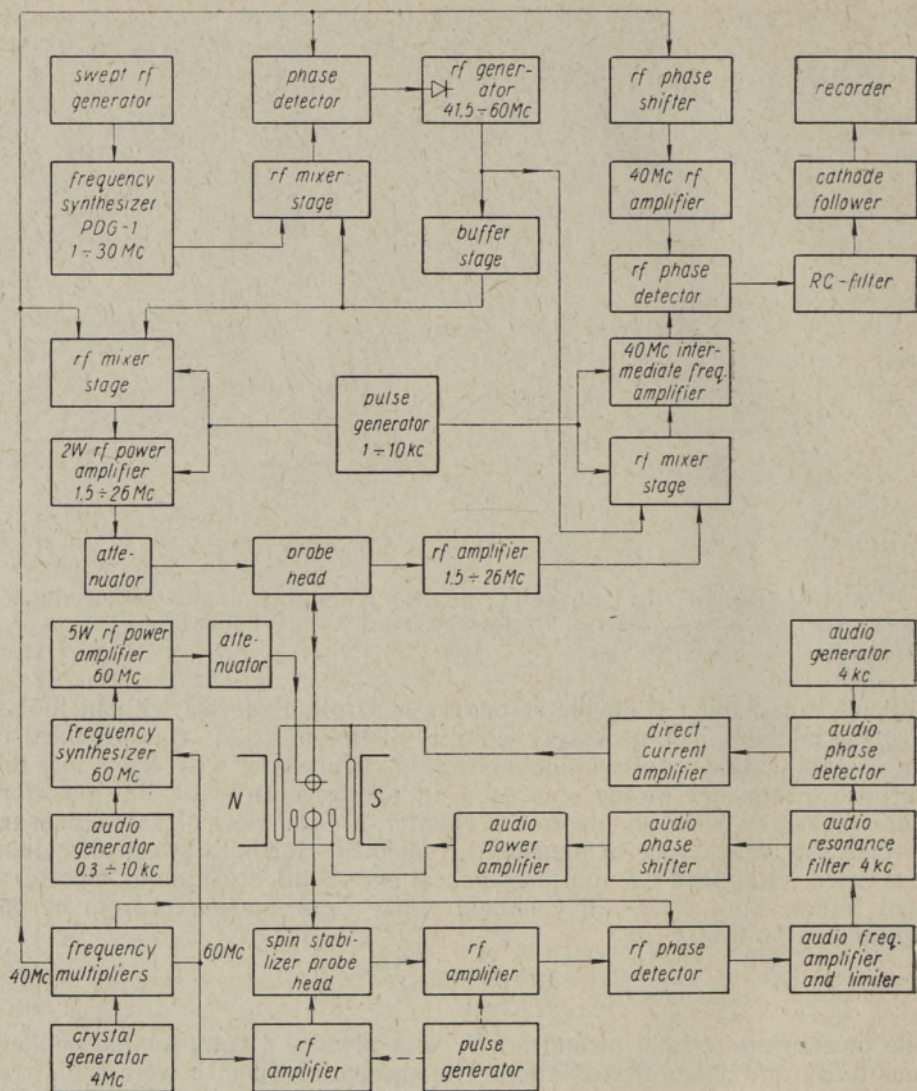


Fig. 7. Block diagram of the spectrometer.

It is apparent that chemical shifts of saturated carbon atoms in cyclic compounds are different from those of aliphatics. Chemical shift values for alkanes and alkenes can be described with a linear equation and depend mainly on the extent of branching^[16, 25]. This linear relationship shows that in many cases the influence of the next neighbour atoms can be ignored. Yet cyclic alkanes show consistently positive deviations and cyclic polyenes negative deviations from this additive scheme^[25]. If +6 ppm is added for each 5- or 6-membered ring, a quite good fit with experimental data is achieved. With such corrections the predicted values for saturates do not differ for more than ± 4 ppm from experimental values, the maximum allowed deviation in the Savitsky calculations. This

Table 1

Chemical shifts δ_{cs_2} of some cyclic hydrocarbons

Molecule	Carbon atom	Exptl. ^a $\delta_{cs_2}^a$	Calcd. ^b $\delta_{cs_2}^b$	Δ	Calcd. ^c $\delta_{cs_2}^c$	Δ'
				$\delta_{cc_2}^a - \delta_{cs_2}^b$		$\delta_{cs_2}^a - \delta_{cs_2}^c$
Adamantane	CH ₂	155.5	147.2	+ 8.3	159.2	-3.7
	CH	165.0	145.5	+19.5	163.5	+1.5
Norbornane	CH ₂ (7)	155.0	147.2	+ 7.8	159.2	-4.2
	CH (1, 4)	157.5	145.4	+12.1	157.4	+0.1
	CH ₂ (2, 3, 5, 6)	163.0	154.1	+ 8.9	166.1	-3.1
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 ± 1 ppm. ^bCalculated on the basis of constitutive bond parameters [25]. ^cCalculated on the basis of constitutive bond parameters with a diamagnetic constitutive correction of +6 ppm for every independent 5- or 6-membered saturated ring structure connected with the carbon atom under consideration. Adamantane is considered to contain 3 rings for every CH group and 2 for every CH₂ group. ^dFrom earlier work [17]. ^eSample was partially decomposed and impure, chemical shift of carbon-7 could not be measured with acceptable accuracy.

constitutive correction is more than somewhat similar with the constitutive correction $\lambda = -3$ for alicyclic 6-membered saturated ring in the Pascal scheme for diamagnetic susceptibilities [24]. Here, too, unsaturation and saturated rings do need constitutive corrections of different sign.

The data of Table 1 show that two different mechanisms are operative in determining the methylene chemical shifts in cyclic compounds. If one adheres to the usual sp^2 -, sp^3 -hybridization of $2s$ -, $2p$ -orbitals and σ - and π -bonds, then we have two kinds of delocalization for σ -electrons. Both act in the same direction and lead to a paramagnetic shift. One is active in all compounds and is not particularly susceptible to strain, the other needs π -electrons on nearby atoms and is met only in unsaturated molecules with strain.

The first kind of delocalization is well illustrated by the results of various LCAO-MO calculations [8, 10, 11]. There appear π -bond orders between adjacent carbon atoms even in ethane and of course Q_{AB} is in this case no longer zero. This corresponds to second order hyperconjugation of Mulliken [26] and gives rise to a paramagnetic shift. Similar EHT calculations show that considerable and unevenly distributed gross atomic charges appear in saturated norbornane [10]. This is qualitatively consistent with the very high dipole moment 1.63 D of this molecule [27]. Grant and Paul [16] admit that the correlation of chemical shifts with structure for aliphatics could be explained in terms of direct interactions between remote groups. Such interactions play a part in Newman's "rule of six" in chemical reactivity [28]. Various indirect evidence make delocalization in saturated cycles quite probable. Particularly in

adamantane the overlap of the rear lobes of bridgehead sp^3 CH-bond orbitals inside the cage could account for long-range inductive effects^[29, 30, 31] and the fact that in adamantane radical anion, the added electron resides in the central cavity and couples with the four bridgehead hydrogens^[32]. Deviations from tetrahedral symmetry as a result of steric strain may also change the hybridization of the carbon atom and in general a low-field paramagnetic proton shift is observed^[35], but in the case of carbon chemical shifts such additional effects appear to be small. There is no big difference between chemical shifts in norbornane, adamantane and 2-methylpentane^[16], though norbornane has a strain energy of 18.5 kcal/mole^[33] and adamantane is completely free of strain. The second mechanism in σ -electron delocalization is clearly different from the first. Large paramagnetic shifts of carbon atoms in methylene groups appear as soon as double bonds are introduced into the molecule. In such molecules and particularly ions^[10, 34] a strong hyperconjugative interaction between π -electrons and 7-carbon atom is possible and the resulting bondings are rather non-classical. The electron structure of the 7-carbon atom may no longer be adequately described by sp^3 -hybrids and this would make σ_p^{AA} significant.

Since both mechanisms can give rise to significant paramagnetic terms that contain $\langle r^{-3} \rangle$, a strong general charge dependence of carbon chemical shifts is expected. Any decrease of atomic charge must lead to paramagnetic shifts^[15]. The chemical shifts of methylene and methine carbons in norbornane, norbornene and norbornadiene are compared with the gross atomic charge densities Q_k of Hoffman in Fig. 8. A surprisingly good linear fit is achieved, similar to the dependence of carbon chemical shifts on net π -electron charges q_A in aromatic molecules and ions^[15].

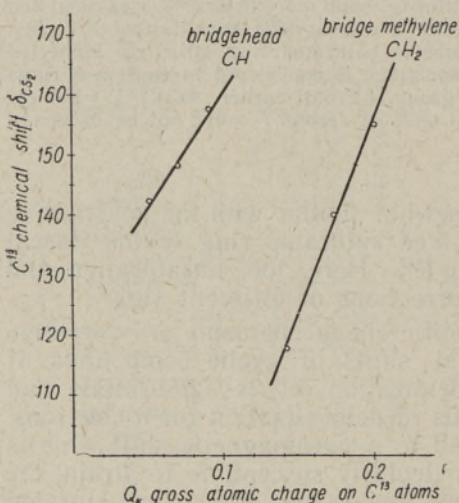


Fig. 8. Correlation of EHT gross atomic charge densities Q_k with sp^3 -carbon-13 chemical shifts of norbornane, norbornene and norbornadiene.

$$\Delta\delta_{CS_2} = \alpha(Q_A - 1), \quad (6)$$

Hydrogen shifts depend upon many other factors besides charges and do not show such useful relationships, in fact in adamantane the less shielded methylene carbon carries more shielded hydrogen atoms, while for methine groups the reverse is true.

In quadricyclene large diamagnetic shifts are observed and can be attributed to ring currents in the three-membered cycles that can be thought of as consisting of sp^2 -hybridized carbon atoms with the pure p-orbitals in the plane of the ring^[37]. Since any deviation from this hybridization can only lessen the possibilities for a ring current, the paramagnetic shifts of methine carbons in highly strained quadricyclene relative to cyclopropane^[38] are understandable.

The results of this study show that classical models with localized σ -bonds are quite inadequate and that carbon-13 chemical shifts can be

used to investigate the real electronic structure of saturated as well as unsaturated hydrocarbons. The saturated methylene groups show a very wide range of chemical shifts, more than 80 ppm. This shift is very sensitive to all changes of molecular structure and can be correlated with the results of molecular orbital calculations. Spin decoupling and in some cases absorption spectra must be used to obtain and assign the chemical shifts. A spin-stabilized double resonance spectrometer using frequency sweep and time sharing to eliminate base-line drift is described.

IV Appendix

Norbornane (bicyclo [2.2.1] heptane).

Bicycloheptadiene (3g) was dissolved in 50 ml ethyl ether and hydrogenated for 2.5 h at 25°C in the presence of Adams catalyst (0.2g). Retention volumes relative to bicycloheptadiene in squalane column at 90°C were: Norbornane 1.62, norbornene 1.24.

Quadricyclene (tetracyclo [2.2.1.0^{2,6}.0^{3,5}] heptane)

Bicycloheptadiene (5 g), dissolved in 11 of ethyl ether was photoisomerized with UV-radiation from a PRK-2 mercury lamp^[39]. Acetophenone (3 g) was added for energy transfer and the isomerization process was followed by VPC analysis. Quadricyclene was isolated with vacuum distillation in 80 per cent purity. Retention volume relative to bicycloheptadiene in squalane column at 60°C was 1.15. An attempt to use preparative gas chromatography for further purification of this compound proved unsuccessful.

Adamantane (tricyclo [3.3.1.1^{3,7}] decane).

Dicyclopentadiene (75 g) was hydrogenated at 25°C in ether solution in the presence of Adams catalyst (0.4 g), yielding endo-trimethylene-norbornane, which was refluxed for 15 h with AlBr₃ (10 g), the product distilled, crystallized and sublimed. Overall yield 5 g^[40]

Acknowledgment

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SISEPINGEGA MOLEKULIDE SÜSINIK-13 TOPELTRESONANTS- ABSORPTSIOONSPEKTRID

Klassikalised struktuurid lokaliseeritud σ -sidemetega on süsivesinike elektronstruktuuri kirjeldamiseks ebapiisavad. Küllastatud metüleenrühmade süsinik-13 keemiliste nihete ulatus on väga lai: enam kui $80 \cdot 10^{-6}$. Selle rühma keemiline nihe sõltub väga tugevasti molekuli struktuurist ja σ -elektronide delokalisatsioonist ning korreleerub arvatud summaarsete laengutega vastavil aatomeil. Nende keemiliste nihete mõetmisel on topeltresonantsi kasutamine C^{13} tuumade lahtisidestuseks mõõdapäasmatu ja paljudel juhtudel tuleb mõõta väga nõrku C^{13} absorptsioonspektreid. Kirjeldatakse vastavat spektromeetrit.

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АБСОРБЦИОННЫЕ СПЕКТРЫ ДВОЙНОГО МАГНИТНОГО РЕЗОНАНСА ЯДЕР УГЛЕРОДА-13 В НАПРЯЖЕННЫХ СОЕДИНЕНИЯХ

Классические структуры с локализованными σ -связями недостаточно точно отражают действительную электронную структуру углеводородов. Химические сдвиги углеродных атомов насыщенных метиленовых групп занимают очень широкий диапазон — более 80 м.д. — и очень чувствительны к изменениям структуры молекулы. Этот химический сдвиг зависит от делокализации σ -электронов и может быть коррелирован с полным зарядом на соответствующих углеродных атомах. Для измерения этих химических сдвигов необходимо применение двойного резонанса для развязки спинов C^{13} и регистрация абсорбционных спектров углеродных атомов этих соединений. Приводится описание соответствующего спектрометра.