

RESULTS OF CARBON-13 NMR SPECTROSCOPY IN THE FIELD OF CYCLIC CONJUGATED π -ELECTRON SYSTEMS

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ABSTRACT

The theoretical basis for the interpretation of ^{13}C chemical shifts is reviewed briefly. Possible ring current contributions to the shielding of the ^{13}C nucleus are discussed in detail with examples from the field of polycyclic nonbenzenoid π -systems and bridged annulenes. The fingerprint nature of ^{13}C n.m.r. data is stressed and the significance of σ -bond structure is demonstrated for bridged [14]annulenes and related compounds. Pyrene and the two isopyrenes dicyclopenta[ef,kl]heptalene and dicyclohepta[cd,gh]pentalene serve to illustrate typical features of ^{13}C n.m.r. spectra of alternating and non-alternating π -systems. Finally, the sensitivity of ^{13}C n.m.r. for the detection of valence isomerizations is exemplified with results obtained for 11,11-disubstituted 1,6-methano-[10]annulenes.

INTRODUCTION

The most important developments that have occurred in the field of nuclear magnetic resonance (n.m.r.) spectroscopy since the first ISNA was held in Japan in 1970 certainly resulted from the invention of the pulse Fourier transform (PFT) method. This powerful experimental technique, brought to the n.m.r. laboratory by Ernst and Anderson¹ in their famous paper published in 1966, revolutionized n.m.r. spectroscopy as a whole and in particular that of less abundant nuclei. Thus, very soon the dominating rôle played nearly 25 years by proton n.m.r.² was challenged and, as a consequence, the number of papers dealing with heavier nuclei has increased enormously during the last few years. In fact, both from the theoretical as well as from the empirical point of view high resolution proton n.m.r. is now a well established tool for solving chemical problems of all kinds and the spectroscopist eagerly turns his efforts to more virginal grounds if he has not already done so.

From those nuclei that gained most in popularity the leading one undoubtedly is carbon-13, whose spectroscopy by definition must be regarded as *the* spectroscopy of organic molecules. Indeed, carbon-13 n.m.r. was bound to make large progress due to the new experimental technique, since its development had been severely hampered both by low sensitivity and low natural abundance. Since most chemical laboratories have acquired PFT facilities by now, many important results obtained by this method must be expected for the near future and the lectures presented at this symposium

are believed to demonstrate this. Today I will try to outline the potential behind carbon-13 n.m.r. spectroscopy and its application in the field of cyclic conjugated π -electron systems.

THE CHEMICAL SHIFT OF CARBON-13

From the three parameters obtained by carbon-13 n.m.r.—chemical shifts, coupling constants, and spin lattice relaxation times (T_1)—the chemical shifts are by far the most important for two reasons: (1) chemical shift data are most easily measured since routine carbon-13 n.m.r. spectra are recorded with proton decoupling and the resonance frequencies of the singlets are read off by the computer, and (2) the sensitivity of chemical shifts to chemical environment directly yields n.m.r.-structure relationships that are most illustrative to the chemist. In many instances ^{13}C , ^1H - and ^{13}C , ^{13}C -coupling constants will be undoubtedly of great value, as are the T_1 -data for our understanding of the dynamic behaviour of molecules in the liquid phase; however, the leading role played by the chemical shift information suggests that I concentrate on this parameter exclusively.

Following Saika and Slichter³, the shielding constant σ for a nucleus in the magnetic field may be broken up into three parts

$$\sigma = \sigma_d + \sigma_p + \sigma' \quad (1)$$

where σ_d stands for the local diamagnetic contribution produced by the surrounding electrons, σ_p stands for the local paramagnetic contribution, and σ' is a collection of long range shielding effects arising from neighbouring atoms and groups and originating mainly from magnetic anisotropy and electric field effects. Theory tells us that, contrary to the situation met with the proton, the shielding of heavier nuclei is determined mainly by the paramagnetic term in equation 1. For sp^2 carbons, according to Karplus and Pople⁴, whose theoretical approach is probably still best suited for chemical interpretation at least in a qualitative sense, this term is proportional to the inverse electronic excitation energy ΔE , to the inverse cube of the radius r of the carbon $2p$ orbitals, and to the sum of charge density and bond order terms Q_{AB} involving next neighbours:

$$\sigma_p \propto -\Delta E^{-1} \langle r^{-3} \rangle_{2p} \sum_B Q_{AB} \quad (2)$$

This equation explains the well known dependence of carbon chemical shifts on π -charge density⁵, where positive charge leads to orbital contraction and to an increase of σ_p , thus producing a downfield shift, and negative charge has the opposite effect. It also explains the unexpected upfield shift observed for the α -carbons in pyridine and other nitrogen heterocycles upon protonation, since the ΔE term increases in the ions, thereby producing a decrease of σ_p and a highfield shift⁶.

THE RING CURRENT EFFECT

For annulene chemists, the most interesting contribution to the shielding constant of the proton has turned out to be the neighbouring anisotropy effect of cyclic conjugated π -electron systems that is well known as the so-

called ring current effect⁷⁻⁹. I believe one can easily imagine that annulene chemistry would lose much of its glamour if the record-breaking reports on upfield and downfield shifts were missing. It may be disappointing at first, therefore, if we realize that ring current effects range among the least important contributions to the shielding of the carbon nucleus. They are part of the σ' -term in equation 1 that as a whole is believed to constitute approximately only ten per cent of the total screening. Indeed, despite a number of investigations undertaken to uncover ring current effects in carbon-13 n.m.r., up to now only a few examples are known that may convince this audience that at least a diamagnetic ring current effect exists.

To begin with, there is of course the fact that aromatic carbon resonances do not fall into a separate shift range. Instead, all sp^2 carbons have absorptions in the same area of the carbon chemical shift scale. This observation is easily rationalized with the familiar picture of the current loop, where the ring carbons are now located in the zero field region as shown in *Figure 1*.

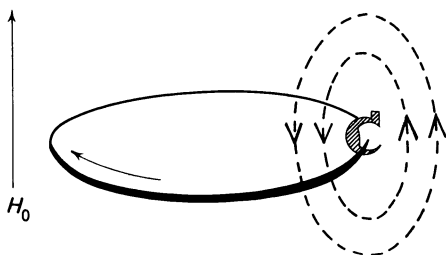


Figure 1. Diamagnetic ring current model for carbon-13

As for protons, in order to feel the ring current effect the carbon nucleus must be located in the shielding or deshielding region of the π -system. Furthermore, since the induced secondary field at a certain position is determined by the properties of the annulene and the spatial factor alone, the shifts expected are of the same order of magnitude as the shifts observed for protons. A 3 to 4 p.p.m. shift, already fairly large for proton n.m.r., is, however, a small quantity for carbon-13, where normal shifts caused by changes in the local paramagnetic term are an order of magnitude larger. It is immediately clear then that the naïve approach completely fails to give conclusive results. This is shown in *Figure 2*, where a number of methyl carbon resonances are compared. The results given in the second row clearly render any conclusion drawn from the relative upfield and downfield shifts noted in the [14]annulene and in toluene, respectively, premature†.

Turning to a more attractive set of model compounds, the data reported by Jones *et al.*¹⁰ for acepleiadiene (1) and acepleiadylene (2) may be cited. Also in the light of results recently reported for pleiadiene (3)¹¹ they give rise to a rather convincing argument in favour of a diamagnetic ring current

† All carbon chemical shift data in this article are given in p.p.m. on the δ -scale with tetramethylsilane as internal reference. Contributions to the shielding constant are denoted as $\Delta\sigma$, where positive sign indicates shielding and negative sign deshielding.

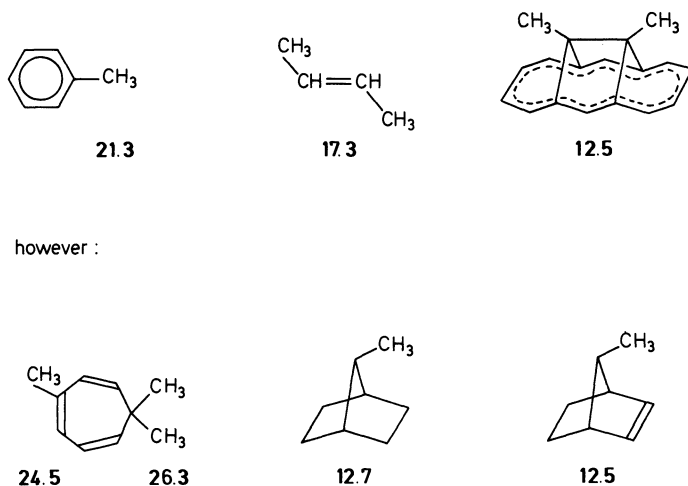
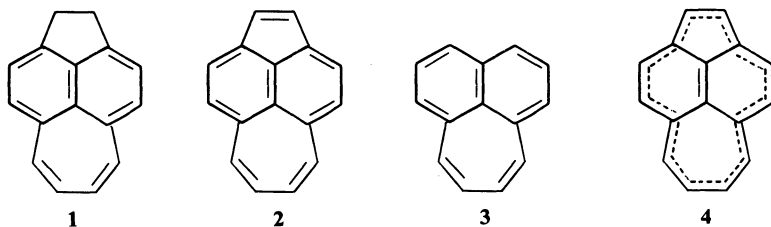
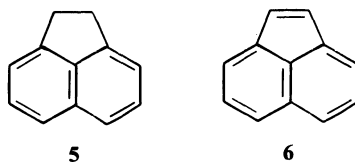


Figure 2. Carbon-13 resonance frequencies of selected methyl groups

contribution to the carbon-13 chemical shift. Upfield shifts of 15.7 and 9.9 p.p.m. are observed¹⁰ for the central carbons when the 14 π -electron system of **1** is transformed into the 16 π -electron system of **2** that may be regarded as



composed of an outer 14 π -electron loop and an isolated double bond in the centre (**4**). In order to determine how much of these upfield shifts can be attributed to ring current shielding, the structural features of **2** are added stepwise to naphthalene. From the resulting increments $\Delta\delta$ shifts for **2** are predicted that turn out to be larger by 6.5 and 7.1 p.p.m. than the observed δ -values (Figure 3). Similar unexpected upfield shifts result when acenaphthene (**5**) and acenaphthylene (**6**)¹² are used as model compounds (Figure 4). A shielding of 5 p.p.m. for the central carbons of **2** due to a peripheral diamagnetic ring current seems, therefore, well established.



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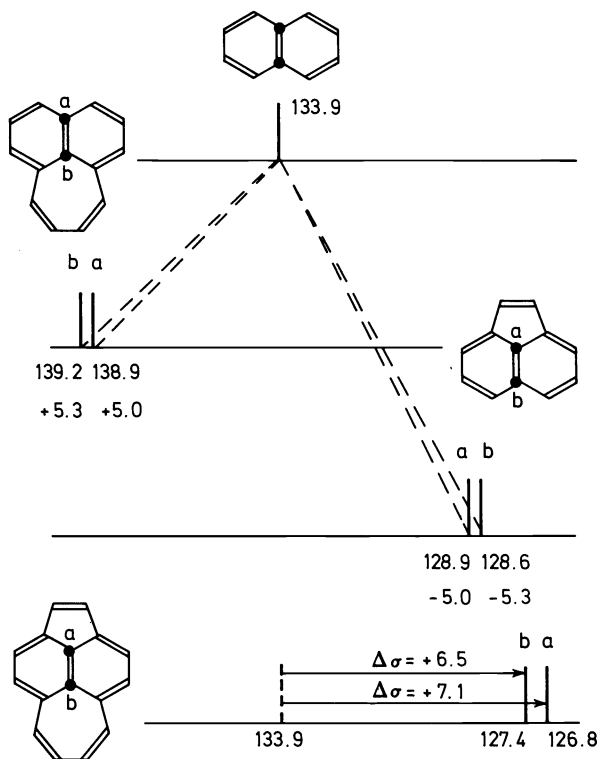


Figure 3. Ring current contribution $\Delta\sigma$ (p.p.m.) to the shielding of the central carbons in acepleiadylene using naphthalene, pleiadiene and acenaphthylene as model compounds

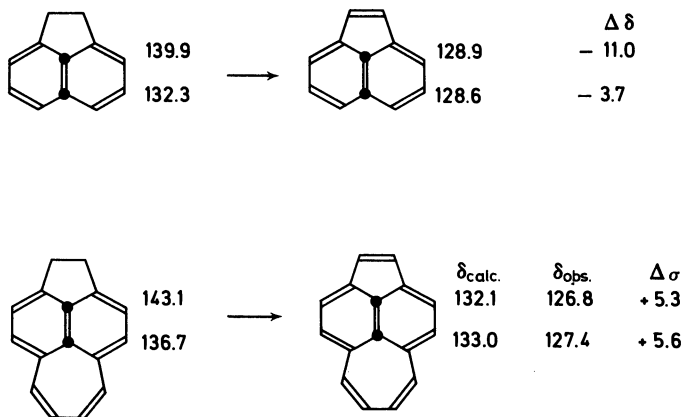
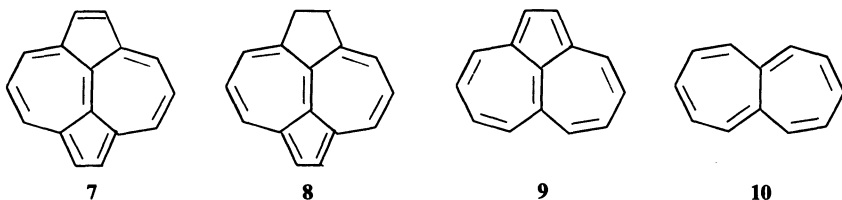


Figure 4. Ring current contribution $\Delta\sigma$ (p.p.m.) to the shielding of the central carbons in acepleiadylene using acenaphthene, acepleiadiene and acenaphthylene as model compounds



This interpretation is supported by results found in our laboratory for a very similar pair of compounds: dicyclopenta[ef,kl]heptalene (**7**)^{13,14} and its dihydro-predecessor **8**, kindly provided by Prof. Jutz. Both systems are identified by their proton n.m.r. spectra (*Figure 5*) as diatropic and paratropic, respectively, in accord with theoretical calculations¹⁵ and earlier findings for

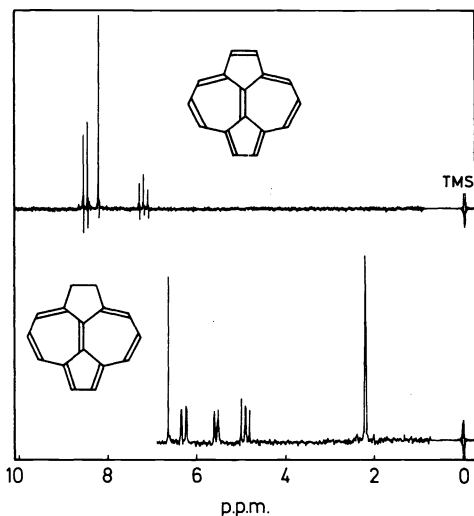


Figure 5. ¹H-n.m.r. spectra of dicyclopenta[ef,kl]heptalene (above) and dihydro-dicyclopenta[ef,kl]heptalene (below)

aceheptylene (**9**)¹⁶. Again, we might expect that **7** sustains a peripheral diamagnetic ring current leading to additional shielding for the central carbons. Analysing the carbon n.m.r. data, we start with heptalene (**10**), where $\delta = 140.9$ p.p.m. was reported recently for the quaternary carbons by Oth *et al.*¹⁷. Shift increments for the introduction of the dimethylene bridge are found from the model pairs naphthalene/**5** and **3/1** as +5 and -2 p.p.m. for the next and for the remote carbon, respectively. The double bond effect is then calculated from the data found for **8** as +6 and +1 p.p.m. Again, the δ -values calculated on this basis for **7** are too large by 10 p.p.m., indicating a considerable ring current contribution to the chemical shift of the central carbons in this compound (*Figure 6*).

An even more convincing analysis is made possible through data determined

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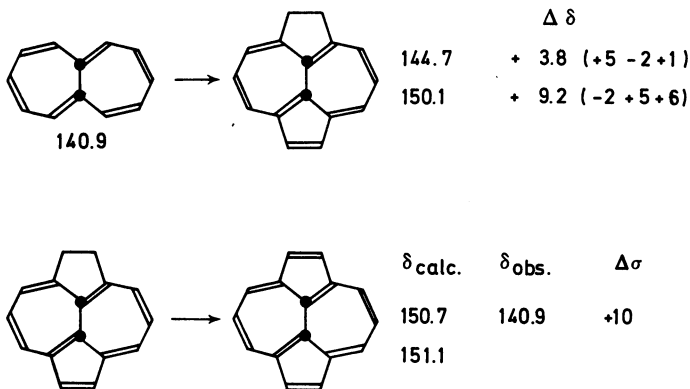


Figure 6. Ring current contribution $\Delta\sigma$ (p.p.m.) to the shielding of the central carbons in dicyclopenta[ef,kl]heptalene using heptalene and dihydro-dicyclopenta[ef,kl]heptalene as model compounds

by Braun¹⁸ for aceheptylene (9) (Figure 7). Starting again with heptalene, the central carbons of 7 turn out to be nearly 30 p.p.m. more shielded than predicted†!

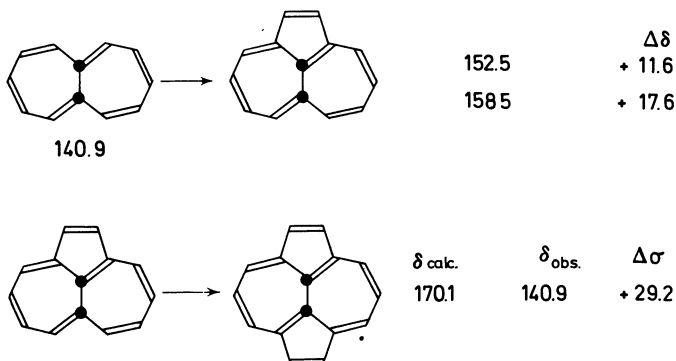


Figure 7. Ring current contribution $\Delta\sigma$ (p.p.m.) to the shielding of the central carbons in dicyclopenta[ef,kl]heptalene using heptalene and aceheptylene as model compounds

Further information about ring current effects are expected from bridged annulenes of the Vogel-type which we investigated in collaboration with the Cologne group¹⁹, since appreciable shielding and deshielding effects were observed for these compounds in proton n.m.r.^{9, 20-22}. The special

† It must be emphasized that the analysis of the carbon-13 n.m.r. data presented here for 2 and 7 implies additivity of substituent effects and disregards any additional shielding or deshielding in the model compounds originating from charge density changes. A quantitative detection of the ring current contribution is, therefore, not possible. In the present case, calculations for 1-10 show that charge densities are fairly constant in the two series.

geometry met here proved, however, to be far more important for carbon chemical shifts than the diatropic nature of these systems. As is seen in *Figure 8*, only a small upfield shift is found for the methylene carbon in 1,6-methano-[10]annulene (**11**) when compared with the olefinic systems **12** and **13**. Going from **14** to **15** and **16**, even a downfield shift is found as was also noted by Masamune *et al.*²³ As the pair **14/15** clearly demonstrates, the introduction of sp^2 carbons in α position to the bridge is already sufficient to produce the

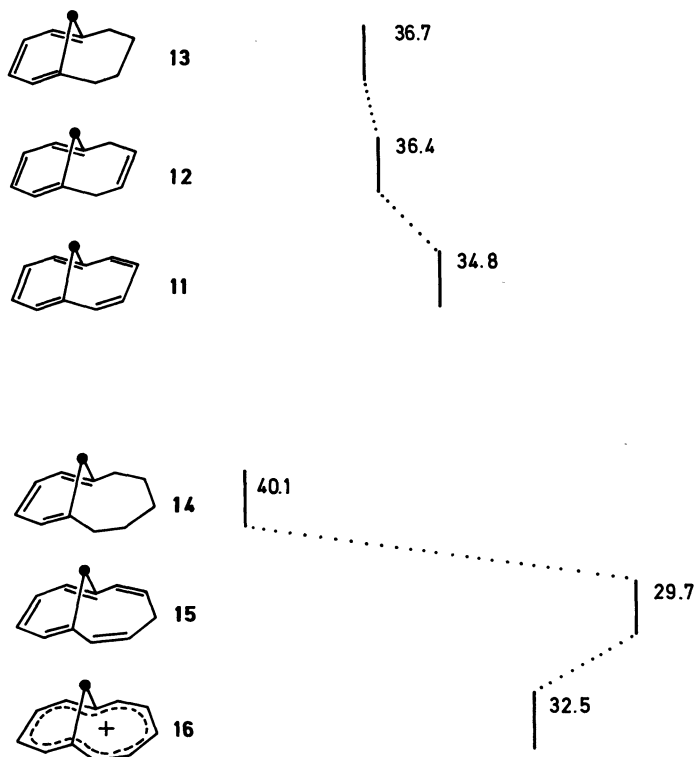


Figure 8. Carbon-13 resonance frequencies of the methylene carbons in 1,6-methano-[10]-annulene (**11**) and related compounds

observed shielding of the bridge carbon. It follows also that the shift found for the methylene resonance in **11** is most probably of different origin. Further examples for the marked effect of sp^2 carbons are collected in *Figure 9*, where one must remember that the anti-1,6,8,13-bismethano-[14]annulene was shown by us to exist as an olefinic system without a ring current²⁴.

In the light of these findings the upfield shifts observed for the bridge carbon resonances in the pair **17/18** (*Figure 9*) lose their ring current supporting aspect, with the exception perhaps of the change found for the carbonyl carbon resonance. This carbon occupies the γ -position with respect to the structural

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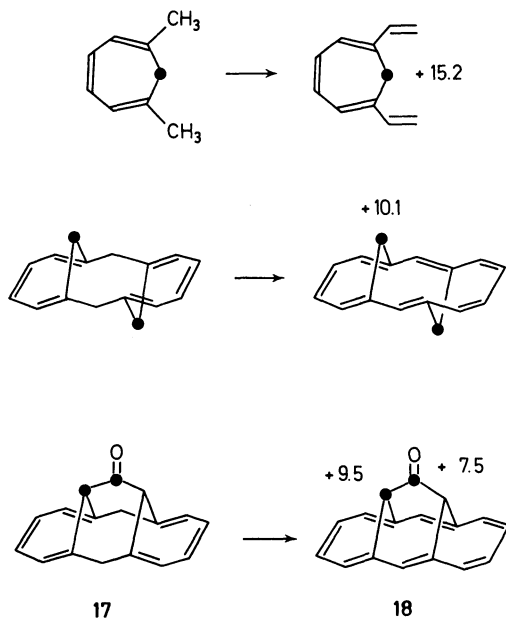


Figure 9. The influence of sp^2 carbons on the shielding of the methylene carbon in cycloheptatriene and some bridged [14]annulenes

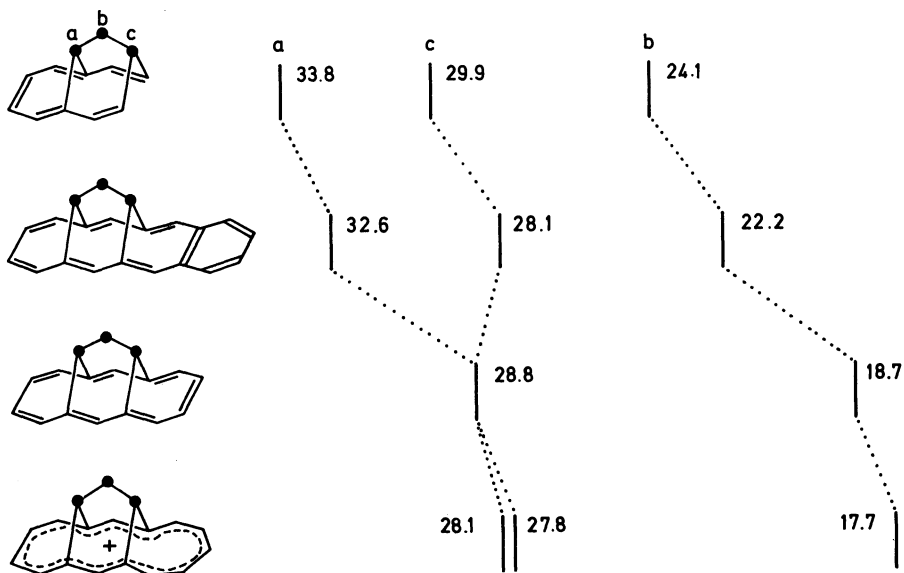
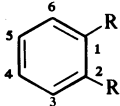
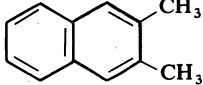
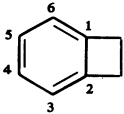
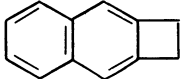
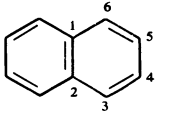
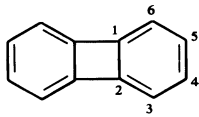


Figure 10. The influence of increasing diatropism on the shielding of bridge carbons in selected compounds

Table I. Effect of four-membered ring formation on the chemical shifts of aromatic ^{13}C nuclei (δ -values in p.p.m. are referred to internal TMS)²⁷

	$\delta(1,2)$	$\delta(3,6)$	$\delta(4,5)$	$\delta(\text{benzyl.})$
R = R' = $-\text{CH}_2\text{Br}$ $= -\text{CHBr}_2$ $= -\text{CHO}$ $= -\text{CH}_3$	136.5 137.6 136.3 135.8	130.8 129.2 130.8 129.4	129.0 130.0 133.4 125.6	29.2 35.6 191.6 19.6
	134.8	127.3 [126.7]	132.0	20.0
				
R-R = <i>trans</i> - $\text{CHBr}-\text{CHBr}$ $= -\text{CBr}_2-\text{CBr}_2$ $= -\text{CO}-\text{CO}-$ $= -\text{CH}_2-\text{CH}_2-$	142.2 143.0 173.4 145.2	122.8 121.5 122.4 122.1	131.0 133.2 135.5 126.5	49.2 65.0 194.3 29.5
	144.2	120.1	133.7	29.2
	133.9	128.3	126.1	—
	151.9	118.0	128.8	—

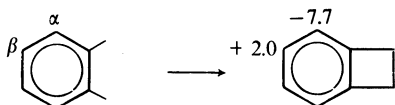
change occurring in the perimeter and in analogy to other findings one might expect a sign reversal for the shift increment if no ring current contribution were present.

If the mere introduction of double bonds already yields highfield shifts one has to choose model compounds where the double bonds are present from the beginning. This is done in *Figure 10*, where the compounds are arranged in order of increasing diatropism, as well documented by their proton n.m.r. spectra. Starting with the atropic system at the top a gradual shielding is observed for carbon a that is the most remote from the structural changes that are inevitably necessary in order to bring about the desired change of electronic properties. These data are then presented in a final attempt to convince you that a diamagnetic ring current effect for carbon-13 indeed exists. Its magnitude, or—better—its very smallness is in agreement with shifts observed by others in a few different cases²⁵.

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If the situation must be regarded as difficult already for diamagnetic ring currents it is even worse for paramagnetic ring currents, where so far no convincing example has been found. This is, of course, also a consequence of the fact that paratropic species are far less abundant than diatropic ones.

The early report on a paramagnetic ring current effect for the α -carbon resonance in biphenylene²⁶ today can hardly be regarded as valid in the light of the extended range of model compounds available. Comparing a number of *o*-disubstituted benzenes and naphthalenes with the corresponding compounds that contain a four-membered ring with the same substituents (Table 1) one is able to show that the fusion of a four-membered ring causes an α -effect of -7.7 and a β -effect of $+2.0$ p.p.m. for the carbon-13 δ -values²⁷:



Compared to naphthalene, the shifts of biphenylene are then quite normal and can be understood without the need to invoke a paramagnetic ring current contribution. Similar conclusions were reached recently by Jones *et al.*²⁸.

Turning once again to bridged annulenes, the comparison of the shift data for **11** and 1,7-methano-[12]annulene, a paratropic molecule by proton n.m.r.^{17, 19}, speaks for itself (Figure 11).

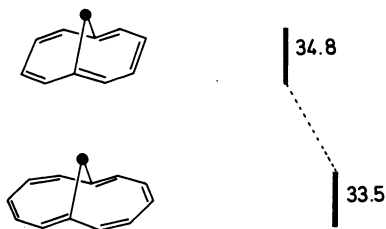


Figure 11. Carbon-13 resonances of the methylene carbon in 1,6-methano-[10]annulene and 1,7-methano-[12]annulene

To summarize then, it can safely be concluded from the experimental evidence available that only in a few cases is an unequivocal isolation of ring current effects on carbon-13 shielding to be expected and that normally ring current contributions will be overshadowed by other factors of stronger influence. It follows also that in the future ring current effects will be the domain of proton n.m.r. and their detection for carbon-13 may be regarded as of mere academic importance.

THE DOMINATING ROLE OF σ -BOND STRUCTURE

On the other hand, the investigations cited have clearly demonstrated the fingerprint nature of carbon chemical shift data with regard to chemical structure in a more general sense. A particularly nice example in this respect

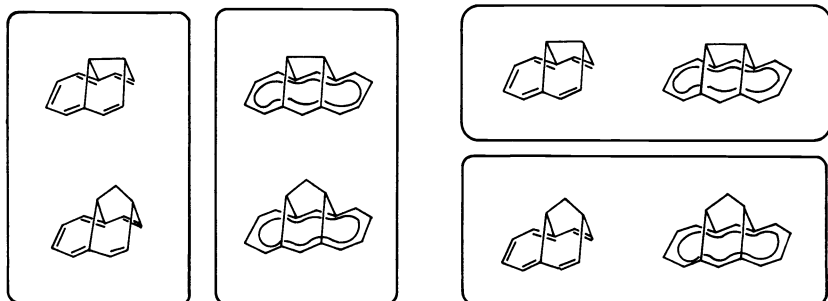
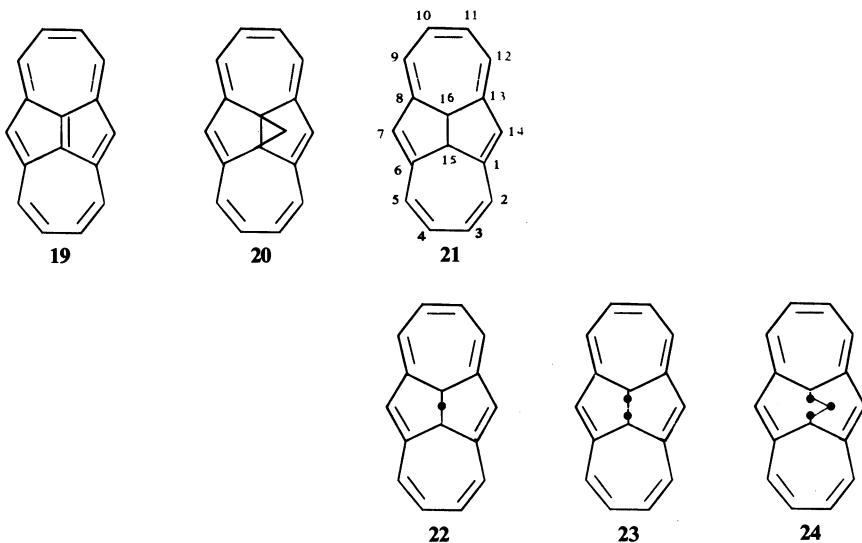
^1H
 ^{13}C


Figure 12. Structural relationships within a set of four selected compounds as derived from proton and carbon-13 n.m.r.

that illuminates the typical features of proton and carbon n.m.r. was found with two pairs of compounds from the Cologne school (Figure 12), where proton n.m.r. clearly distinguishes between the olefinic and aromatic, or, to be more precise, between the atropic and the diatropic sets²⁹, whereas carbon-13 n.m.r. connects the systems with the same geometry of the bridge, thereby emphasizing the significance of stereochemical factors for carbon chemical shifts³⁰.



A similar dominating role of the σ -skeleton is met in the series of bridged [14]annulenes **19–24** synthesized by Vogel *et al.* in recent years^{31, 32}. As the diagram of our results (Figure 13, Table 2) shows, starting with the cyclopropano-bridged compound **20**, the first two members of the family which

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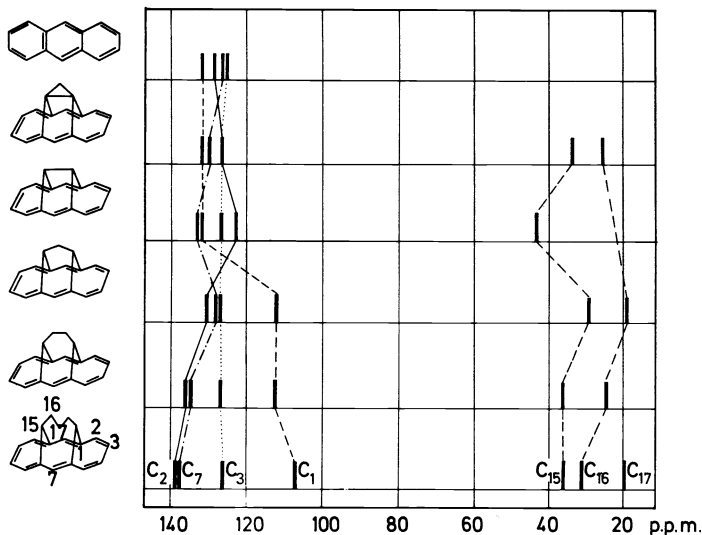


Figure 13. Carbon-13 n.m.r. spectra of bridged [14]annulenes with anthracene perimeter

have a direct link between the two methine carbons possess a shift range for the perimeter resonances that is very similar to that of the carbon resonances in anthracene³³ (**25**). The introduction of one additional methylene group then causes a large upfield shift of 20 p.p.m. for the quaternary carbon (C-1), whose resonance stays at highest field also in the remaining systems. This must clearly be seen as the consequence of a reverse β -effect, i.e. the introduction of an additional hydrogen in the β -position.

The effect of the structural change occurring in **22** for the resonance of C-2 and C-7 that are in the γ -position is not unexpectedly of different sign and these signals gradually move to lower field. The most remote carbon, C-3, shows no significant change of its resonance frequency in the whole series.

Table 2. ¹³C chemical shifts (δ -values in p.p.m. referred to internal TMS) of anthracene (**25**) and bridged [14]annulenes with anthracene perimeter

	C-1	C-2	C-3	C-7	C-15	C-16	C-17	$\Delta\delta^c$
19	143.6	129.7	128.6	114.7	123.6	—	—	28.9
25	131.6	128.1	125.3	126.1	—	—	—	6.3
20	131.7	126.2	126.2	129.4	33.1	25.1	—	5.4
21	131.4	122.8	126.5	132.4	42.8	—	—	9.7
22	111.9	130.0	127.0	127.7	28.8	18.7	—	18.2
23	111.9	135.5	126.3	134.6	35.3	24.0	—	23.7
24^a	106.2	138.1	125.8	137.1	35.2	30.6	19.7	31.9
24^b	{ 107.2 103.4	{ 138.4 137.6	{ 125.9 125.2	{ 138.9 135.4	{ 34.5	{ 30.1	{ 19.3	{ 35.5

^a at 50°C.

^b at -30°C; due to an inversion of the bridge all perimeter carbon resonances are split in the slow exchange limit (see ref. 32).

^c range of perimeter carbon resonances in p.p.m.

This indicates that its local electronic environment is very little affected by structural changes introduced into the bridging unit.

The findings discussed may also be interpreted, at least in part, as a documentation of the change in ring size that takes place for the structural fragment in the centre of these compounds, in particular, when also the resonance of the methine carbon C-15 is considered. Except for one case a close correspondence for the sign and the magnitude of the chemical shifts is indeed observed when data of cycloalkenes³⁴ are used for comparison (*Figure 14*).

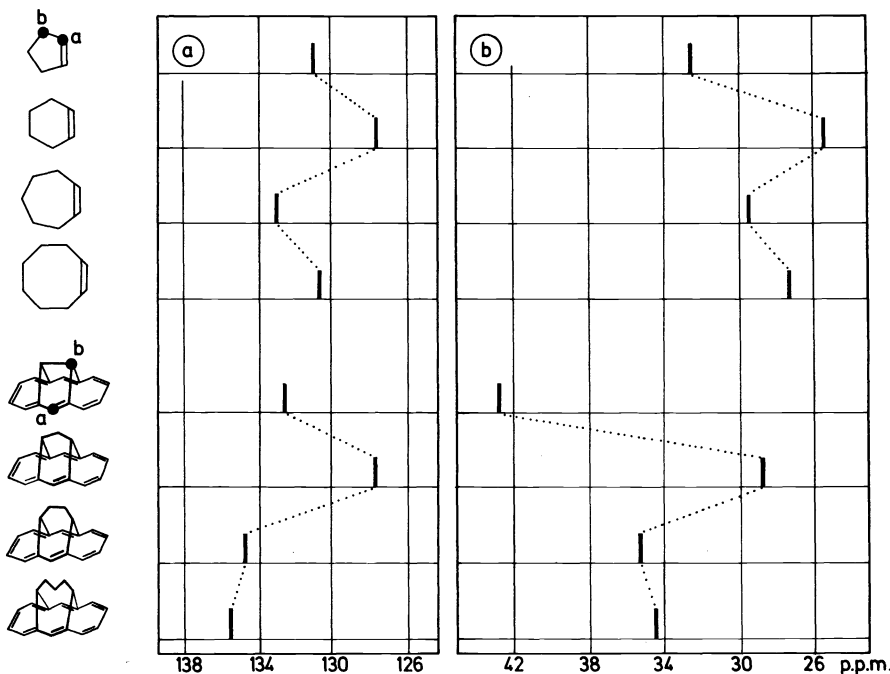


Figure 14. The influence of ring size on the chemical shifts of C-7 and C-15 in bridged [14]-annulenes

THE CHARGE DENSITY EFFECT—ALTERNATING AND NON-ALTERNATING SYSTEMS

Looking again at the carbon-13 n.m.r. data for those bridged [14]annulenes that presumably possess the most planar perimeter, namely **19**, **20** and **21**, the dicyclohepta[cd,gh]pentalene (**19**) clearly stands out (*Figure 15*). The shift range is five to six times larger than that for anthracene or the other two systems and the obvious reason for this observation is the non-alternating nature of **19**. Lauterbur has already shown³⁵ that non-alternating hydrocarbons display a much larger carbon-13 chemical shift range than alternating hydrocarbons, attributing this fact to the non-uniform charge distribution in

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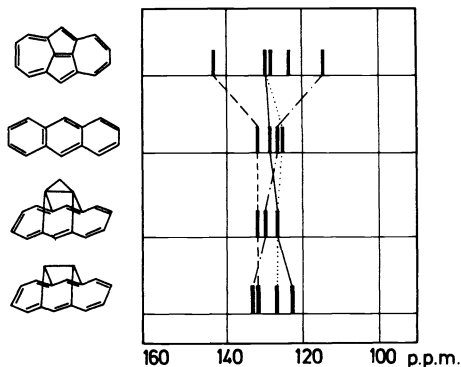


Figure 15. Carbon-13 n.m.r. spectrum of the non-alternating dicyclohepta[cd,gh]pentalene (19) in comparison with the spectra of alternating hydrocarbons

the former class. This leads to a further interesting aspect of carbon-13 n.m.r., mentioned briefly at the beginning: its dependence on local charge density.

To look into this with some detail, we have a nice trio of compounds at hand: pyrene and the two isopyrenes 7 and 19 from Munich and Cologne, respectively, that are both non-alternating π -systems. Clearly, as Figure 16

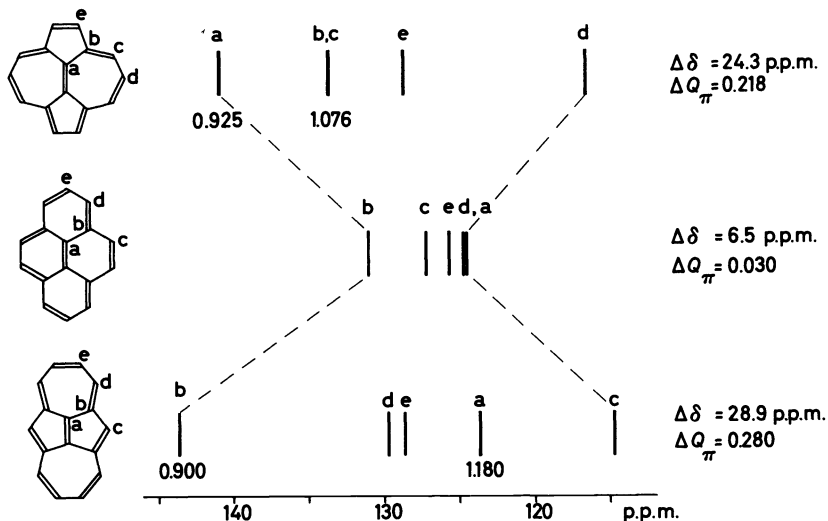
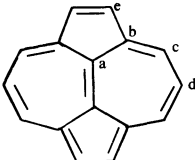
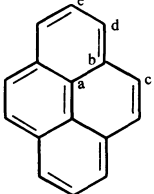
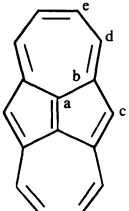


Figure 16. Carbon-13 n.m.r. data and π -charge density in pyrene and the two isopyrenes 7 and 19

demonstrates, the shift range observation is confirmed and in agreement with the range of π -charge densities which were calculated by the INDO method (Hückel data will do as well). Also the relative positions of the carbon resonances in the two isopyrenes correspond to the respective charge density, increasing charge causing highfield shifts and vice versa, as long as carbons

of the same structural type, e.g. C_a or C_b , are compared. Any attempt, however, to fit the data of *Table 3* by a simple linear charge density-chemical shift relation similar to the one set up by Spiesscke and Schneider⁵ for monocyclic ions, fails completely. This is not so surprising if we remember equation 2 for the local paramagnetic contribution to the chemical shift of carbon-13,

Table 3. ^{13}C chemical shifts (δ -values in p.p.m. referred to internal TMS) and π -charge densities of dicyclopenta[ef,kl]heptalene, pyrene and dicyclohepta[cd,gh]pentalene

	Position	$\delta(^{13}C)$	$Q_\pi(\text{INDO})$	$Q_\pi(\text{HMO})$
	a	140.9	0.925	0.936
	b	133.7	1.076	1.066
	c	133.7	0.869	0.865
	d	116.6	1.087	1.035
	e	128.7	1.049	1.083
	a	124.5	1.006	1.000
	b	131.0	0.984	1.000
	c	[127.2]	1.004	1.000
	d	[124.7]	1.013	1.000
	e	125.6	0.993	1.000
	a	123.6	1.180	1.130
	b	143.6	0.900	0.968
	c	114.7	1.146	1.167
	d	129.7	0.969	0.936
	e	128.6	0.968	0.948

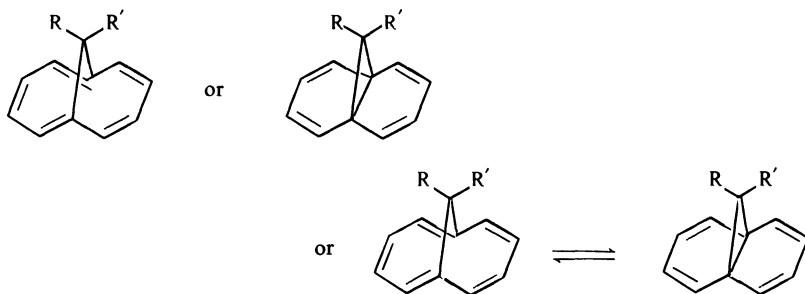
where also the ΔE -term and bond order terms are present. This multiparameter dependence jeopardizes the success of any linear regression analysis. Attempts to determine charge densities from carbon chemical shift data must, therefore, be met with caution.

DYNAMIC PHENOMENA

The sensitivity of carbon-13 n.m.r. for changes of σ -bond structure discussed in the preceding section suggests that this method is of great value for the detection of valence tautomers, bond shifts and other dynamic phenomena. This has indeed been demonstrated in several cases, most impressively for the first time by the work of Masamune on [10]annulenes³⁶. Without doubt, carbon-13 n.m.r. has several attractive features in this respect if compared with proton n.m.r. The larger chemical shifts are helpful for the detection of low energy processes and the routinely employed proton decoupling renders the spectra simpler, reduces line overlap and very often provides several exchange systems suitable for line shape calculations³⁷.

RESULTS OF CARBON-13 NMR SPECTROSCOPY

In our laboratory we employed carbon-13 n.m.r. to tackle the long standing question about the structure of bridge-substituted 1,6-methano-[10]-annulenes, where a number of observations³⁸ suggested the possibility that these compounds exist as 'double-' or 'bisnorcaradiene' or as fluxional systems:



Earlier we had shown³⁹⁻⁴¹ that carbon-13 n.m.r. is an especially powerful technique for the uncovering of norcaradiene or cycloheptatriene valence tautomers, since the carbons in 1,6-position undergo a 80-100 p.p.m. change for their resonance frequency as a consequence of their different bonding.

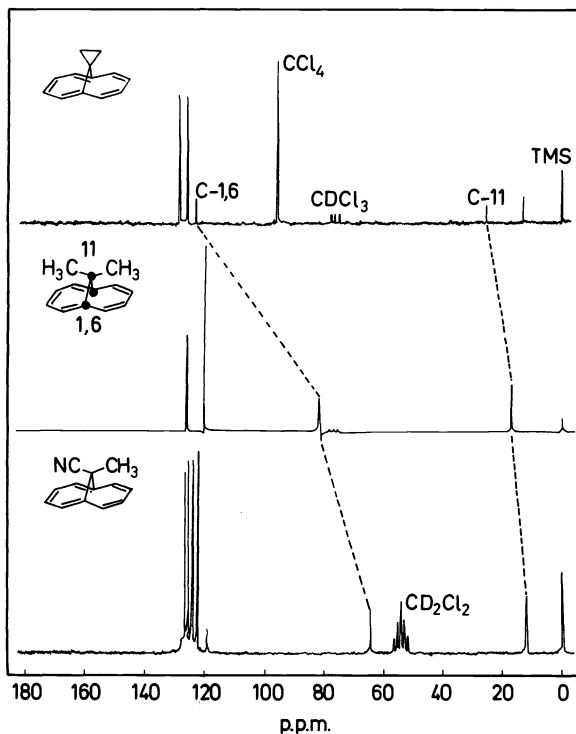


Figure 17. Carbon-13 n.m.r. spectra of 11,11-dimethylene-, 11,11-dimethyl- and 11-cyano-11-methyl-1,6-methano-[10]annulene at room temperature

From the large number of bridge substituted systems investigated so far, *Figure 17* shows three typical examples. The dramatic variation in shielding observed for the bridgehead carbon and for the carbons in 1,6-position clearly overrides any 'normal' substituent effect and indicates that profound structural transformations must occur.

That indeed a valence tautomerism between the [10]annulene and the bisnorcaradiene structure exists is then most convincingly demonstrated by the temperature dependence of the spectra, shown in *Figure 18* for 11,11-dimethyl- and 11-cyano-11-methyl-1,6-methano-[10]annulene⁴². From this

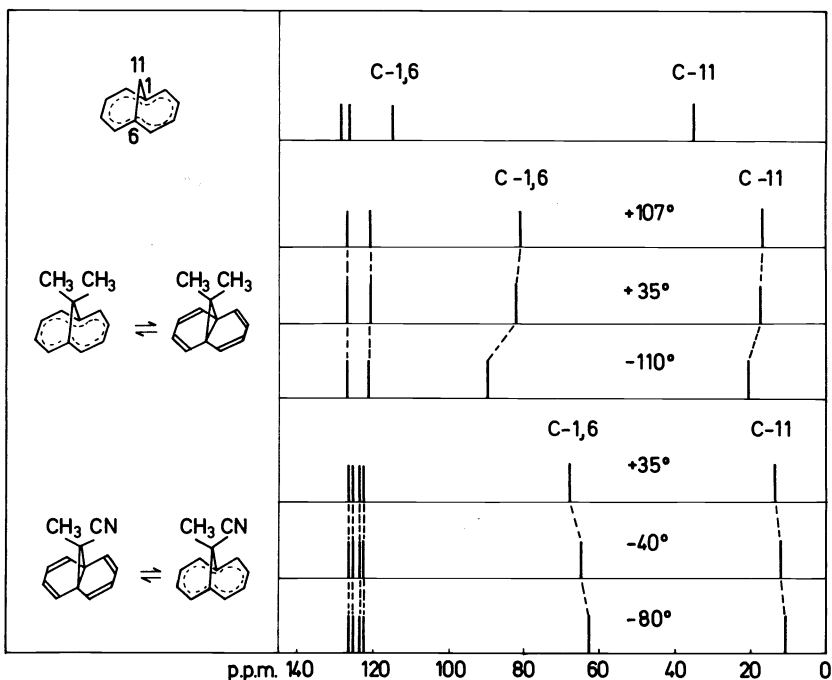


Figure 18. Temperature dependence of the carbon-13 n.m.r. spectra of 11,11-dimethyl- and 11-cyano-11-methyl-1,6-methano-[10]annulene

observation two important facts emerge immediately: (1) the position of the average signal indicates that both valence tautomers are of comparable energy, and (2) their relative stability may vary with either one as the more stable component, since downfield or upfield shifts are observed.

Looking at results obtained for a variety of substituents (*Figure 19*), the C-1,6 resonance covers the whole range from 123.2 p.p.m. observed for the cyclopropano-compound to 55.0 p.p.m. for the dicyano-compound, a value that still awaits confirmation since the instability of the material rendered the measurements difficult. Two categories may be distinguished: compounds with temperature independent and compounds with temperature dependent chemical shifts. The latter group is further subdivided into systems

RESULTS OF CARBON-13 NMR SPECTROSCOPY

displaying lowfield shifts and those displaying highfield shifts with decreasing temperature. In structural terms that means that we have molecules existing exclusively—within the limits of detection—as [10]annulenes, and we have fluxional systems with either the [10]annulene or the tetraene as the more stable isomer.

No systematic quantitative study of the substituent effects has been made so

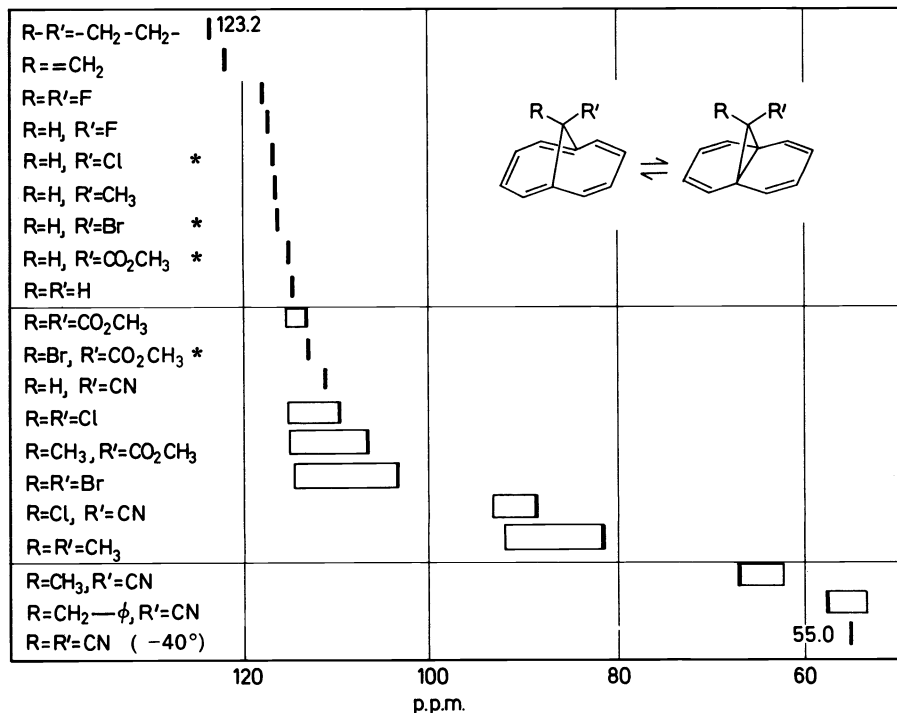


Figure 19. The C-13 resonance in 11,11-disubstituted 1,6-methano-[10]annulenes and their temperature dependence. Compounds marked * have been measured only at room temperature

far but from the results it can be concluded that bulky groups as well as electron-withdrawing groups— π -acceptors—stabilize the tetraene. Similar effects are operating in the norcaradiene-cycloheptatriene system^{43,44}, where cyclopropane stabilization is important. Estimating the chemical shifts for both isomers from data obtained for model compounds, their energy difference can be calculated for the fluxional systems from the observed shifts as in the order of a few hundreds cal/mole. Since no line broadening could be observed in the carbon-13 spectrum even at -130°C , the energy barrier for the valence tautomerism must be lower than *ca.* 6 kcal/mole. This is not surprising, however, in view of the particular geometry of the system that favours bond formation between the 1- and 6-position. A variety of sources (ultra-violet⁴⁵ and photoelectron⁴⁶ spectroscopy as well as calculations³²)

have already indicated that an appreciable 1,6-overlap is present in the parent compound.

In order to get more information about the structural principles and the energetic relationships behind this first valence tautomerism between an olefinic and an aromatic system— if you allow me this familiar terminology—the temperature dependence of the carbon-13 n.m.r. spectra of several molecules with closely related structure was tested⁴⁷ (Figure 20). The two

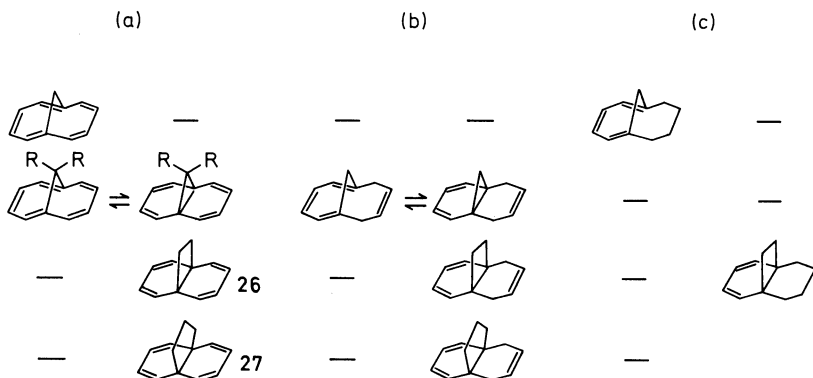


Figure 20. Dominating structures of various propellanes

propellanes **26** and **27** show no fluxional behaviour and exist as tetraenes, a fact that emerged earlier from their proton n.m.r. spectra^{48,49}. It is then interesting to note that also in the two other series investigated (b and c in Figure 20) the tendency to open the 1,6-bond appears to be a unique feature of the methano-bridged compounds. In the other systems strong σ -bond compression is expected if the 1,6-distance increases and this is certainly the prohibitive factor for bond cleavage. In the methano-bridged compounds no such σ -bond compression occurs. On the contrary, the system profits from the partial release of the strain energy associated with the three-membered ring. Since the open form also exists in cases where pure olefinic systems are involved, the driving force behind the formation of the [10]-annulene must be to a considerable extent of steric origin.

CONCLUSION

Using examples from the literature and from our own research I have tried to outline the scope of useful applications of carbon-13 n.m.r. spectroscopy in the field of cyclic conjugated π -electron systems, emphasizing also the limitations of this tool. It is evident that the dominance of local atomic contributions to the shielding constant prevents the carbon nucleus from being a probe for ring current effects. This is, however, no disadvantage, since proton n.m.r. will take care of ring currents and there is no need to duplicate these results. On the other side, the large chemical shifts and the sensitive response to even minor structural variations make carbon-13 an extremely valuable

nucleus for chemical studies even on a purely empirical basis. It is also clear that the understanding of carbon chemical shifts still needs some good thinking from the theoretical side and progress here will then pave the way for a better interpretation of carbon resonance frequencies in terms of chemical significance. The amount of carbon n.m.r. data that evolve from the chemical laboratories will certainly stimulate work in this direction.

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