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^{13}C NMR Chemical Shifts of Methyl Cation and Anion: A Relationship Between Chemical Shift and Charge?

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Abstract: The chemical shifts of methyl cation and anion have been calculated. The tensor components about the out-of-plane p orbitals were essentially the same, but the components about the in-plane axes differed by over 700 ppm. The experimental chemical shifts of benzene and the aromatic ions fall on the line connecting the shifts and charges of the methyl ions. These data are correlated by a simple model, that also accounts for the large downfield shifts found with carbenes. No direct connection between charge and chemical shift was found. Copyright © 1996 Elsevier Science Ltd

There has been much interest in the use of ^{13}C NMR chemical shifts to gain information about the partial charge associated with a given atom in a molecule.[1] This originated from the observation that the chemical shifts of cyclopentadienide ion (**1**), benzene (**2**) tropylium ion (**3**) and cyclooctatetraene dianion (**4**) were linearly related to the symmetry derived charges at the carbons.[2]

It is reasonable to expect a correlation between charge and chemical shift for protons since their shifts are in many cases a result of the diamagnetic component derived from the 1s electrons. However, as well recognized, with carbon (and most other nuclei), paramagnetic shielding effects typically dominate the diamagnetic terms.[3] Diamagnetic shielding leads to an upfield shift and is derived just from the ground state electron density distribution. The paramagnetic term that leads to a downfield shift results from the coupling of occupied and virtual orbitals by the perturbation of the applied magnetic field. From the form of the perturbing hamiltonian it is easily shown that only those pairs of virtual and occupied orbitals which are connected by the z angular momentum operator (z being the magnetic field direction) can contribute to this term.

In order to gain more information on these two components of the chemical shift, we have calculated[4] the shielding for methyl cation and planar methyl anion which represent a +1 and -1 charge respectively. The calculations were carried out using the GIAO[5] and IGAIM[6] methods that give the shielding of a carbon nucleus by the nearby electrons. The B3LYP theoretical model was used with the 6-311+G(3df,2p) basis. It satisfactorily reproduces the experimental data for compounds **1-4**. The calculated shieldings and chemical shifts for CH_3^+ and CH_3^- are summarized in Table 1. It should be noted that whereas the chemical shift is usually reported in ppm with respect to TMS, the chemical shielding scale is defined with respect to a bare carbon atom. On this scale, TMS has a shielding of 183.4 ppm. Thus, any carbon that is shielded by more than 183.4 ppm has an upfield chemical shift (i.e., negative) from TMS. In addition, it should be noted that the shift is in general different about the molecule's x, y and z axes, and each of these components are given. The molecules are aligned so that the unique p orbital (p_z) lies along the z molecular axis. The similarity of the z axis components, despite the difference in charge, should be noted.

Table 1. Calculated Nuclear Shielding and Chemical Shift for CH_3^+ and CH_3^-

Component	Shielding (ppm)		Chemical Shift	
	CH_3^+	CH_3^-	CH_3^+	CH_3^-
Isotropic	-221.5	258.6	404.9	-75.2
x, y	-420.0	297.6	603.4	-114.2
z	175.3	180.7	8.1	2.7

A plot of the in-plane (x,y) chemical shifts for the two ions against the charge is shown in Figure 1. The larger of the experimental in-plane tensor components (y) of benzene and the monocyclic aromatic ions[7] are included in the plot, and it can be seen that they fall on the line. Thus, the paramagnetic part of the chemical shift is linearly related to the occupancy of the out-of-plane p_z orbitals in all of these compounds. The tensor components about the z axis are also shown, and it can be seen that they are independent of the charge.

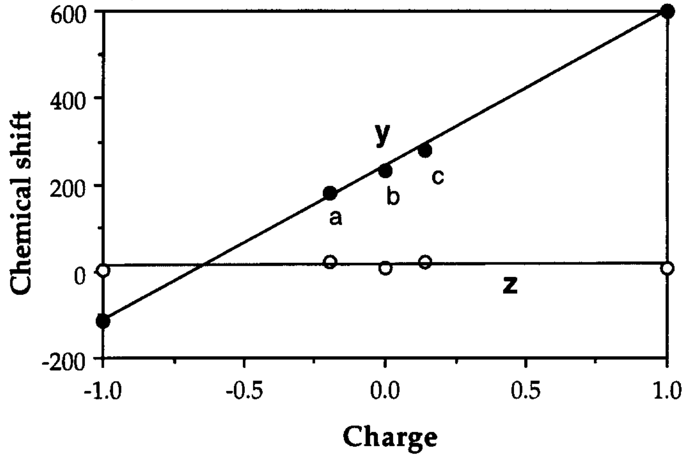

Figure 1. Correlation between the in-plane (y) and out-of-plane (z) tensor components and the symmetry determined charges. The end points are methyl cation and anion, and the experimental data are for: a. $C_5H_5^-$, b. C_6H_6, and c. $C_7H_7^+$

It is also possible to calculate the shielding at the carbon on an MO by MO basis, thus providing additional information on the origin of the chemical shifts. The results are shown in Table 2 where the MO's are labeled by the carbon atomic orbital that is involved. In common with all organic compounds, the 1s electrons give an upfield (diamagnetic) shielding of 200 ppm. Thus the 1s electrons alone would make the chemical shift upfield from TMS. The 2s electrons give a smaller shielding of 20-25 ppm because of their greater distance from the nucleus (the effect goes as $1/r^3$ where r is the distance from the nucleus). These shielding values are essentially independent of charge. With methyl anion, the six p electrons contribute an additional 61 ppm shielding about the x and y axes, leading to a total shielding of 298 ppm, or a chemical shift with respect to TMS of -114 ppm for these axes.

This appears to be about the maximum diamagnetic shift for carbon. A carbon atom with all of its 2s and 2p orbitals filled (C^{-4}) has a calculated chemical shift of -102 ppm. Similarly, the chemical shift for the long axis of acetylene, that results from the diamagnetic circulation of the π-electrons, is -95 ppm.

Table 2. Shielding Components at Carbon on an MO by MO Basis

a. CH_3^+

Component	MO					
	1s	2s	2px	2py	2pz	total
xx	200.3	27.5	12.5	-660.3		-420.0
yy	200.3	27.5	-660.3	12.5		-420.0
zz	200.3	28.2	-26.6	-26.6		175.3
Ave.	200.3	27.7	-224.8	-224.8		-221.5

b. CH_3^-

xx	200.3	22.6	13.9	-27.2	88.0	297.6
yy	200.3	22.6	-27.2	13.9	88.0	297.6
zz	200.3	24.0	-27.9	-27.9	12.4	180.9
Ave.	200.3	23.1	-13.7	-13.7	62.8	258.7

With methyl cation, the shielding about the z axis is about the same as for methyl anion, despite the difference in charge. However, about the x and y axes, there are large paramagnetic shieldings derived from coupling of the p_z orbital to either the p_x and p_y orbitals by the magnetic field. The net difference between methyl cation and methyl anion about these axes is over 700 ppm!

A qualitative explanation of the shift is as follows.[8] In methyl cation, the p_z orbital is empty, and in the presence of a magnetic field (in the xy plane), the angular momentum operator can cause an electron in a C-H bond orbital to jump into the empty p_z orbital. This creates an electron "hole" in the plane of the molecule into which the electron may then jump back to, permitting a facile circulation of electrons about the x and y axes and a paramagnetic (downfield) shift. When the out-of-plane p_z orbital is filled, as in methyl anion, it is no longer possible to move an electron from a C-H bond orbital into it, and there is no paramagnetic term. Partial occupancy then leads to a paramagnetic electron flow that decreases with increasing occupancy of this orbital.

This simple model also explains the remarkable downfield chemical shifts found with carbenes. Singlet methylene is formed by the abstraction of a proton from methyl cation. Promotion of the "lone pair" electrons to the empty p orbital in methylene costs much less energy than required for those in the C-H bond orbital in the cation. Circulation of the paramagnetic current then is much easier as creation of the electron "hole" is easier to accomplish, and should lead to a very large downfield chemical shift. In other words the magnetic field perturbation produces a stronger mixing of the virtual and occupied states because of the smaller energy difference, resulting in a larger paramagnetic current. In accord with this expectation, a very high level calculation by van Wüllen and Kutzelnigg[9] found this neutral species to have a downfield chemical shift of 2300 ppm!

The paramagnetic current should be reduced if an attached group could donate electron density into the almost empty p_z orbital. Correspondingly, difluorocarbene and diaminocarbene were found to have much smaller downfield shifts.[10] There is one known stable carbene of the latter type, the compound **5** prepared and studied by Arduengo, et. al.[10] A calculation of the chemical shift at the B3LYP/6-311+G(3df,2p) level led to values that satisfactorily agreed with the experimental values (Table 3).

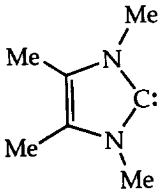

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Table 3. Chemical Shifts for Carbene 5

Component	Calc	Obs
xx	407	381±20
yy	202	188±18
zz	98	93±15
ave	236	214

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