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Experimental Link between the ^{13}C NMR Chemical Shift of Carbonyl Carbons and the Energy Shifts Observed in the n → 3s Optical Transition of Cyclic Ketones

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Abstract: The n → 3s transition energies of cold methylcyclopentanones and -cyclohexanones, as well as those of some branched-chain and bicyclic ketones, have been measured with 2 + 1 resonance-enhanced multiphoton ionization (REMPI). The energy shifts of the n → 3s transition origins are found to correlate in a linear fashion with reported ^{13}C NMR chemical shifts of the carbonyl carbon atoms. Several possibile explanations for the experimental connection to NMR are discussed including consideration of both the paramagnetic and diamagnetic shielding contributions to the total chemical shift.

The use of laser spectroscopy to study molecules cooled in a molecular beam allows the examination of optical transitions under high-resolution conditions. The sharp peaks of the excited-state spectrum enable precise energy measurements of electronic transitions as a function of subtle changes in molecular structure. In previous studies, using resonance-enhanced multiphoton ionization (2 + 1 REMPI), we have shown that the n → 3s electronic transitions of cyclic ketones cooled in a free jet expansion are sensitive to ring strain in unsubstituted structures[1] and to stereochemistry in their methyl-substituted isomers.[2] The results of the initial investigation relate the shift of the n → 3s transition in varying ring sizes to the carbonyl (C–CO–C) bond angle. The second study demonstrates that the transition energy shifts are additive and can be related to the relative ground-state steric energies.

This sensitivity of the electronic transition origin to molecular structure is not observed in the lower energy n → π^* transition of ketones. Cold beam fluorescence studies of the n → π^* excitation in acetone,[3a] cyclopentanone, and cyclobutanone[3b] have shown that the weak origin peaks are practically invariant (ranging over approximately 170 cm^{-1}) among these ketones, suggesting that the overall transition energy is insensitive to molecular structure. In contrast, the n → 3s transition origin energies for the same three structures are spread over a range of more than 2000 cm^{-1}. Since the electron is promoted from the same molecular orbital in both transitions, the difference in the n → 3s and n → π^* transition energies must be related to the character of the upper state. The 3s Rydberg state is atomic-like in nature and appears to exhibit little sensitivity to the molecular structure.[2] Alternatively, the valence character of the π^* state results in a higher degree of sensitivity to the structure of the molecule. It is apparent that the upper level π^* energies change similarly to the HOMO energies so that the origin bands remain constant among those ketones mentioned above.

In studying the sharp vapor-phase n → 3s spectra for a variety of cyclic ketones, it has become apparent that the transition energy shifts resulting from methyl substitution at various ring positions exhibit features commonly found in ^{13}C NMR spectroscopy. That is, the relative shifts of the n → 3s transition origins are unique for both structural isomers and stereoisomers, and these shifts are additive according to the position and orientation of the methyl substituent. It was then determined that the two types of spectroscopies are even more closely related in that there is good correlation between the relative shifts of the n → 3s transition energies and the carbonyl carbon ^{13}C chemical shift. In this paper, we will discuss this experimental correlation for a series of monocyclic, bicyclic, and small branched-chain ketones and present some possible explanations for these findings.

Experimental Section

The experimental apparatus has been described elsewhere.[1] Briefly, the resonance-enhanced MPI data were produced with the output of a Lumonics excimer pumped dye laser held at constant intensity (about 500 μJ/pulse) and focused with a 25-cm focal length lens. The molecular beam was produced with a Laser Technics 203 pulsed valve. The beam was skimmed 3 cm downstream from the 0.3-mm nozzle and intersected the laser beam 4 cm beyond the skimmer. For the experiments reported here, only the total ionization signal was desired. This was accomplished by acceleration of the electrons in a high draw-out field of 1000 V/cm and detection with a chevron microchannel plate. A gated integrator was used to collect the signal pulse followed by digital conversion and processing using an IBM PC. The laser was smoothly scanned while the computer recorded the signal in a strip-chart fashion. All samples were purchased from either Aldrich Chemical, Wiley Organic, Columbia Organic, Pfaltz and Bauer, or Alfa Chemical Co.

Results

Several examples of the 2 + 1 REMPI spectra of the n → 3s transition in cyclic ketones are shown in Figure 1. A characteristic feature of these spectra is the very sharp origin peak whose width is limited by the rotational contours. Another notable aspect is

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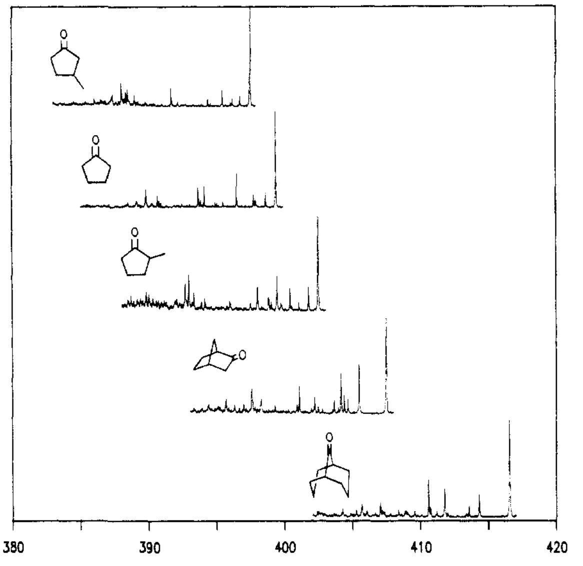

Figure 1. 2 + 1 REMPI 3s Rydberg spectra of several cyclic ketones cooled in a free jet expansion.

Table I. ^{13}C NMR Chemical Shifts and the n → 3s Transition Energies

	^{13}C chem shift, ppm (TMS)	n → 3s energy,[a] cm^{-1}
	Cyclic Ketones	
cyclohexanone	211.5[b]	50 717[c]
4-methyl-	211.4[b]	50 710[c]
3-methyl-	211.0[b]	50 826[c]
2-methyl-	212.9[b]	50 171[c]
cis-3,5-dimethyl-	210.4[b]	50 955[c]
trans-3,5-dimethyl-	211.0[b]	50 464[c]
cis-2,5-dimethyl-	213.0[b]	49 750[c]
trans-2,5-dimethyl-	211.8[b]	50 327[c]
cis-2,6-dimethyl-	213.6[b]	49 756[c]
trans-2,6-dimethyl-	216.2[b]	49 446[c]
cyclopentanone	219.4[b]	50 068[c]
3-methyl-	218.7[b]	50 308[c]
2-methyl-	220.9[b]	49 691[c]
cis-3,4-dimethyl-	218.6[b]	50 079[c]
trans-3,4-dimethyl-	217.3[b]	50 523[c]
cis-2,4-dimethyl-	220.0[b]	49 956[c]
trans-2,4-dimethyl-	221.0[b]	49 801[c]
	Branched-Chain Ketones	
acetone	204.1[d]	51 199[e]
methyl ethyl ketone	206.6[d]	50 645[e]
methyl isopropyl ketone	209.6[d]	50 303[e]
methyl *tert*-butyl ketone	210.7[d]	~50 000[e]
	Bicyclic Ketones	
norcamphor	216.9[f]	49 079[g]
bicyclo[2.2.1]heptan-7-one	216.8[h]	49 079[e]
bicyclo[3.2.1]octan-2-one	214.0[h]	49 417[e]
camphor	218.1[f]	48 911[e]
fenchone	222.0[f]	48 008[e]
bicyclo[3.3.1]nonan-9-one	221.7[i]	48 015[e]

[a] One-photon transition energies. [b] Reference 4. [c] Reference 2. [d] Reference 5. [e] Current work. [f] Reference 6. [g] Reference 1. [h] Reference 7. [i] Reference 8.

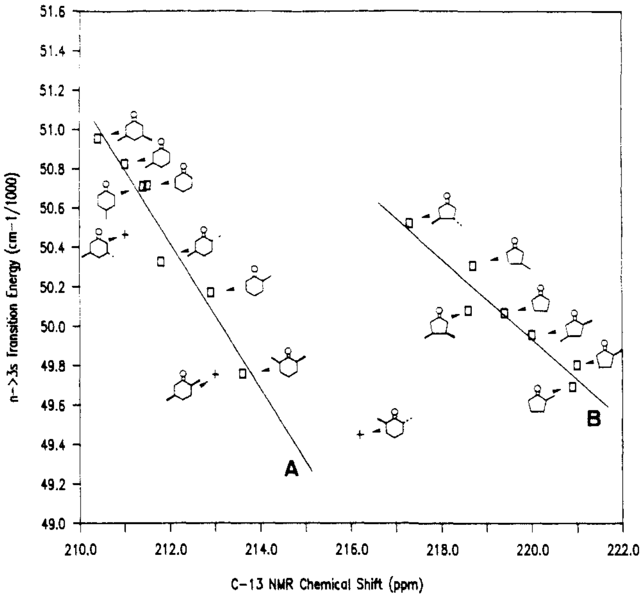

Figure 2. Correlation plot of the ^{13}C NMR chemical shifts of the carbonyl carbons vs the n → 3s optical transition energies of cyclohexanones (line A) and cyclopentanones (line B). The chemical shift values were measured in CDCl$_3$ relative to TMS. The boxes in line A represent those structures which contain only equatorial methyl groups.

the pronounced energy difference of the origin bands among these spectra. For instance, methyl substitution at the α- and β-ring positions shifts the origin peaks in opposite directions. The same effect was also observed in the α- and β-methyl isomers of cyclohexanone.[2] The n → 3s transition energies for a variety of ketones are listed in Table I. All of the values for methyl isomers of cyclohexanone and cyclopentanone were reported previously.[2] With the exception of norcamphor,[1] the 3s transition energies for the branched-chain and bicyclic ketones are new experimental values. The value for methyl *tert*-butyl ketone is approximate because of the extreme complexity of its excited-state spectrum. The acetone transition origin was determined by using a 2 + 2, rather than a 2 + 1, excitation scheme.

Dimethyl isomers of cyclic ketones exist as either cis or trans configurations, giving rise to various combinations of axial and equatorial methyl group orientations. The energies of the n → 3s origin peaks are not only sensitive to the position of methyl substitution but to its orientation as well (i.e. equatorial or axial). Configurational isomers are therefore clearly distinguishable by their n → 3s transition energy. For example, when unsubstituted cyclohexanone is used as a reference, a single equatorial 3-methyl substitution leads to a *blue* shift of 145 cm^{-1} while an axial group at the same ring position results in a *red* shift of 398 cm^{-1}. Since these shifts are found to be additive, it is possible to predict the band origin of different methyl isomers of cyclohexanone using representative shifts for equatorial and axial methyl groups at each ring position provided the backbone conformation remains essentially unchanged.[2]

Carbonyl carbon ^{13}C NMR chemical shifts for these series of compounds are also listed in Table I. These were taken from literature values, each referenced to TMS. The solvent used for the branched-chain ketones was CS$_2$, while all other samples were measured in CDCl$_3$. Values for NMR chemical shifts are known to be somewhat affected by experimental conditions. For example, an early study[9] in which the samples were dissolved in CS$_2$ reported that the difference between the carbonyl chemical shifts of cyclohexanone and cyclopentanone is 5.1 ppm while the more recent measurement using CDCl$_3$ finds the difference to be 7.9 ppm.[4] The optical measurement, however, is fixed by the energy of the molecular system, limited in precision by the reproducibility of the laser monochromator. For the laser system employed here, this variation is found to be around ±5 cm^{-1}. There are also no solvent, temperature, or dilution effects to perturb the vapor-phase energy measurement.

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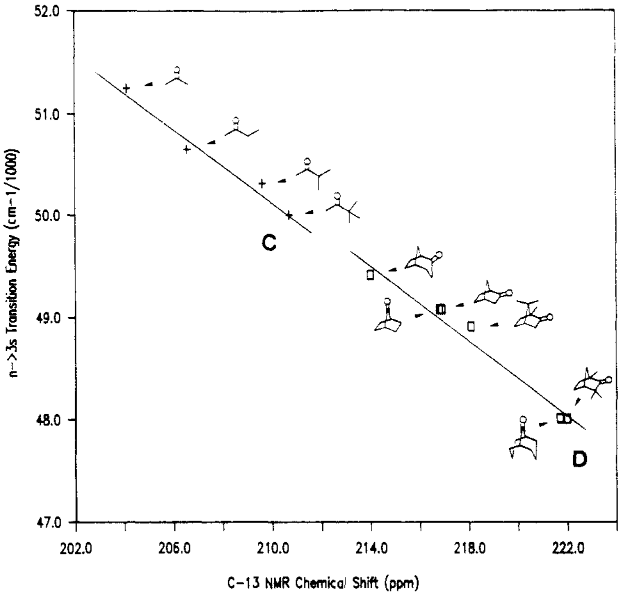

Figure 3. Correlation plot of the ^{13}C NMR chemical shifts of the carbonyl carbons vs the n → 3s transition energies of branched-chain (line C) and bicyclic ketones (line D). The NMR values for line C were measured in CS_2 while those in line D were measured in $CDCl_3$. All NMR shifts are relative to TMS.

The n → 3s transition energies are plotted against the ^{13}C NMR shifts in Figures 2 and 3. The data are divided into four groups: cyclohexanones, cyclopentanones, and branched-chain and bicyclic ketones. The points along line A in Figure 2 represent the methyl isomers of cyclohexanone. If all points are included, the correlation index is found to be 0.920 although it is evident that most of the values fall quite closely along the drawn correlation line. If the crossed points, representing those structures that contain an axial methyl group, are excluded, the correlation index is increased to 0.972 (slope −376 cm^{-1}/ppm). This prompted us to consider several possible explanations for the reduced correlation in those structures represented by the crosses.

One factor that needs to be accounted for is the significant difference in experimental conditions between the vapor-phase optical and the solution-phase NMR measurements. Ambient-temperature NMR data display an average chemical shift value if multiple conformations of a single configuration are present in solution. In contrast, cooling the sample to a few degrees kelvin in a supersonic jet will convert the entire population to the lowest energy conformation, provided the barrier of inversion is relatively low.[10] A high barrier would result in the freezing out of both conformations. The n → 3s spectra of cyclic ketones examined thus far have not indicated a mixture of conformations present in the cold jet. Therefore, attempting to compare the conformationally pure sample in the molecular beam to a ^{13}C chemical shift value representing a mixture of conformations in solution phase will almost certainly decrease the correlation.

The best fit points along line A appear to be those structures that will exist predominantly as a single conformation of the chair form in solution phase. These include the unsubstituted parent compound, its monomethyl isomers (well-known to orient the substituent in the less strained equatorial form), and those dimethyl structures in which both methyl groups are oriented equatorially. In the cases of the *cis*-2,6- and *cis*-3,5-dimethyl isomers, the diequatorial form is a substantially lower energy structure, resulting in a solution-phase equilibrium mixture that is nearly conformationally pure. However, the *cis*-2,5-dimethyl isomer forces one methyl group into the axial position in all possible conformations. Consequently, the differences in relative steric energies are not as large in magnitude, and the solution-phase samples will contain a mixture of conformations.

The points along line B represent the cyclopentanone structures (correlation index 0.956; slope −204 cm^{-1}/ppm). Each configuration of the various methyl isomers will orient itself to a minimum energy conformation, which is not necessarily the symmetric twisted form of the parent compound since the five-membered ring is a nonrigid structure. We therefore do not expect the solution-phase samples to contain a mixture of conformations. This variety of slight changes to the backbone geometry, however, may perturb the energy of the 3s state and thus reduce the overall correlation with both NMR chemical shifts and ground-state steric energy measurements. The surprisingly high correlation index for this group of structures suggests that the shifts in ring conformation of the five-membered ring structure have a minimal effect on the 3s energy.

Figure 3 plots the data representing the branched-chain and bicyclic ketones. Line C has a slope of −170 cm^{-1}/ppm (index 0.989) while that of line D is −190 cm^{-1}/ppm (index 0.985). Several observations can be made pertaining to the NMR correlation of the bicyclic ketones. First, the solution-phase NMR values correspond to a single conformation since the geometries are fixed by the bridge. This could, in part, explain the high experimental correlation observed for this collection of structures. Moreover, the correlation is high even though the geometry of the acetone chromophore varies somewhat among these bicyclic structures. The n → 3s spectra and corresponding correlation with ^{13}C NMR shifts for both groups will be discussed in detail in a future publication.[11]

Discussion

We will consider first the "chemical shift" of the n → 3s optical transition. Explanations for the alternating red and blue shifts of the 2- and 3-methyl isomers in both cyclopentanone and cyclohexanone are not obvious since methyl substitution in other ring systems, such as that observed in the n → 3s transition of methylpyridines (picolines)[12] and the $\pi \rightarrow \pi^*$ excitation of methylindoles,[13] has been found to result in red shifts, exclusively. The reduction in transition energy due to methyl substitution is generally attributed to stabilization of the excited state. In contrast, the alternating shifts of the n → 3s transitions in cyclic ketones can be correlated with the ground-state attractive and repulsive van der Waals interactions between the alkyl substituents and the carbonyl group.[2] This local steric effect, discussed in a recent series of papers by Chesnut et al.,[14] has been used to explain shielding and deshielding NMR chemical shifts, respectively, in a variety of organic compounds. The data presented earlier[2] suggest that the n → 3s transition energy measurements for a homologous series of carbonyl compounds may be useful for probing changes in the ground-state steric energies that are reflected in the highest occupied MO. A similar effect was observed in the lower Rydberg levels of ethylene[15] in which transition-energy shifts were attributed to changes in the ground-state HOMO energy as a result of alkyl substitution.

Several possible explanations for the observed optical/NMR correlation can be suggested. The important experimental information that can be derived from this relationship is that the carbonyl NMR chemical shifts are responding linearly to changes in the *energy* of the ketone's acetone chromophore. Therefore, the energy terms in the theoretical treatment of NMR shielding will be examined. While the shielding contributions discussed below are known to change simultaneously as the molecular structure near the nucleus under consideration is altered,[16] the problem to be considered is whether the contribution from a single term can dictate this very slight shift of the ^{13}C carbonyl carbon peak among structural isomers and stereoisomers of cyclic ketones.

Second-order perturbation treatment of NMR chemical shielding[17] gives rise to the local diamagnetic and paramagnetic

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contributions to the chemical shift. Other terms are also identified (distant contributions),[18] although these effects tend to cancel for nuclei other than hydrogen. Therefore, only the local terms σ_d and σ_p will be considered at this time. The expression for the paramagnetic contribution, well-known to dominate the shielding effects of carbon nuclei, contains the energy term $1/\Delta E$, which is a result of the mixing in of excited states to the ground-state wave function.[17] Karplus and Pople suggested that the transition energies of some low-lying electronic excitations may approximate the value for the $1/\Delta E$ term.[18] This term has been discussed on numerous occasions in connections between NMR chemical shifts and optical transitions including, for example, studies of excitation energies vs shielding in alkenes and various carbonyl compounds[15] as well as the shielding in ketones.[19] Variations in the $1/\Delta E$ term have been shown to contribute significantly to changes in the paramagnetic shielding.[16]

When relating the $1/\Delta E$ term to electronic transitions, one must include an analysis of the orbital symmetries involved in the transition under question. This is because only excitations in which the magnetic dipole is dominant will enter into the paramagnetic shielding contribution.[15,17] Consider acetone as the model chromophore (C_{2v}). The lowest lying $n \rightarrow \pi^*$ transition is magnetic dipole allowed (electric dipole forbidden) and therefore expected to influence σ_p. In several studies correlating the λ_{max} of the $n \rightarrow \pi^*$ transition with the carbonyl chemical shifts for a limited number of open-chain and unsubstituted cyclic ketones,[19a,b] linear relationships were indeed found, but this correlation has also been described as "too crude for general utility".[19c]

Consider next the $n \rightarrow 3s$ transition in which the n_0 (b_2) to 3s (a_1) excitation results in a B_2 excited-state symmetry. This state has a strong electric dipole component, so its magnetic component (and thus its contribution to σ_p) is likely to be small. Additionally, since the NMR data are taken in the solution phase, it is important to examine solvent effects on the $n \rightarrow 3s$ Rydberg transition. Robin[20] has reported that the characteristics of Rydberg transitions change significantly on going from the vapor to solution phases. In particular, the $n \rightarrow 3s$ excitations of ketones are transformed from the sharp vapor-phase spectra into highly diffuse bands that defy characterization. Evidently, this results from the strong interaction between the Rydberg level and the solvent. Thus, these slight $n \rightarrow 3s$ energy shifts of vapor-phase ketones, which mimic the solution-phase NMR shifts, are, in fact, not observed in the condensed-phase optical spectrum. In solvated ketones, a rather sharp peak is found at about 200 nm. However, as discussed by Robin,[21] this band can probably be attributed to either the $n \rightarrow \sigma^*$ transition or to an exciton state rather than a Rydberg level. In any event, it does not show the corresponding sensitivity to molecular structure characteristic of the vapor-phase $n \rightarrow 3s$ spectrum.

While the correlation shown in Figures 2 and 3 among similar structures is high, a comparable finding among unsubstituted cyclic ketones of various sizes is not observed (cyclobutanone to cyclooctanone). Such a correlation takes on the form of a circle rather than a line (index 0.42), serving to underscore the point made previously that the correlation betwen the $n \rightarrow 3s$ transition and the ^{13}C NMR shift applies only when slight variations in structure are involved. This situation can be contrasted with correlations previously found for the lower energy transitions (mostly $n \rightarrow \pi^*$) among a large variety of compounds containing the same chromophore. For example, the lowest lying electronic transition energies of various nitroso compounds,[22] ranging between 300 and 700 nm, were found to correlate with the paramagnetic contribution to the ^{14}N chemical shift over a shielding variation of 400 ppm. It appears that the approximate correlation of the $n \rightarrow \pi^*$ shifts with the NMR shielding in the series of unsubstituted cyclic ketones also falls into this category since variations in λ_{max} (though not the origin) of this electronic transition are significant. In contrast, within the subgroups of similar structures shown in Figures 2 and 3, the $n \rightarrow \pi^*$ λ_{max} values are found to be practically invariant. This then leaves the possibility that the 3s state is contributing to the paramagnetic shielding term. However, when both its lack of a strong magnetic component and the substantial perturbations to the excited state in solution phase are considered, this optical/NMR correlation via the $1/\Delta E$ term in the paramagnetic shielding term is somewhat less than convincing. Consequently, we have searched for other possible sources of this relationship.

As mentioned earlier, the good correlation between the $n \rightarrow 3s$ energies and the local ground-state energies[2] calculated by Chesnut et al.[14c] lends support to the contention that the observed optical shifts reflect relative ground-state steric properties. We have also performed a series of ab initio calculations in order to understand more about the lone-pair molecular orbital of the ground-state structures. These were carried out at the 6-31 G** level for cyclopentanone and its equatorially substituted 2- and 3-methyl isomers. The results show that the HOMO is extensively delocalized around much of the ring structure. In unsubstituted cyclopentanone, the significant contributions to the HOMO come from the $2p_y$ (0.455) and $3p_y$ (0.369) atomic orbitals of oxygen, the $2p_y$ (0.209) of the carbonyl carbon, and substantial contributions from the $2p_x$ (0.194), $2p_y$ (0.158), $3p_x$ (0.093), $3p_y$ (0.076), and 3s (0.159) AO"s of the α-carbon atoms. In addition, there are contributions from the $2p_x$ (0.099), $3p_x$ (0.094), and 3s (0.056) AO's of the β-ring carbons. Calculations at the 6-31 G* level for cyclohexanone show similar delocalization of the HOMO, though the γ-carbon was found to contribute negligibly to this molecular orbital. It is thus evident that the HOMO can be strongly affected by methyl substitution at the α- and β-carbon positions, but less so at the γ-carbon, consistent with the experimental shifts found in the $n \rightarrow 3s$ transition energies of cyclohexanones.[2]

If the $n \rightarrow 3s$ transition energy shifts are following relative ground-state steric energies, what other possibilities exist for explaining the experimental correlation with NMR shifts? One potential candidate is the diamagnetic contribution to the shielding in molecules. Karplus and Pople[18] have shown that the effect of this shielding term for carbon is small, contributing only a few ppm to the total shielding. This is precisely the magnitude of the shifts observed within each group of structures under consideration in the present study. It has also been pointed out by Mason[23] in interpreting ^{13}C NMR shifts of alkanes and cycloalkanes that variations in the σ_d term can be substantial and its consideration is important for the interpretation of chemical shifts in branched structures.

For the case of atoms, it was shown by Lamb[24] that the diamagnetic shielding of a nucleus is directly proportional to the electrostatic potential of the surrounding electron cloud. Ramsey's perturbation treatment of magnetic shielding in molecules[17] produces a diamagnetic term identical with that found by Lamb in the shielding of atoms. Unlike the paramagnetic contribution, determination of the diamagnetic shielding involves the ground-state wave function only. The formulas for its solution are exact, and the σ_d contributions to the total shielding are routinely calculated for small molecules.[25]

Should the potential energy contributions of the diamagnetic shielding be responsible for this experimental correlation, it would be important to establish a connection between changes in the energies of the delocalized molecular orbitals and variations in the local atomic potential at the nucleus under consideration (the carbonyl carbon) as the molecular structure is altered. Although the total energy of a molecule is often discussed in terms of the

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sum of the molecular orbital energies, Politzer and Parr[26] have shown that the total energy can also be expressed exactly as the sum of atomic-like energies in which each term is a functional of the electronic density about the corresponding nucleus. This relationship was further discussed by Politzer, Daiker, and Trefonas[27] and Politzer[28] in subsequent studies, demonstrating that the total energy of a molecule can be expressed in terms of a property evaluated at its nuclei. From the observed experimental correlation, one can speculate that, as substituents are introduced into the ring structure, the molecular and atomic contributions to the total energy change in a proportionate fashion. The molecular orbital energies would dictate the shifts in the optical spectrum while the atomic-like electrostatic potential of carbonyl carbon would determine the shifts in the NMR spectrum. It is intriguing that several groups have discussed a related correlation between the calculated diamagnetic shielding and electronic transitions through variations in the core ionization potentials of molecules (the chemical shift in ESCA).[29] This relationship is said to exist because both σ_d and core electron binding energies depend upon changes in the electrostatic potential at the nucleus due to the valence electrons.

It is well-known that there are unexplained analogies between ^{1}H and ^{13}C NMR chemical shifts for significant numbers of organic structures.[30,31] These similar trends in chemical shifts are theoretically quite puzzling since the contribution to the ^{1}H chemical shift is generally accepted to arise purely from diamagnetic contributions due to the hydrogen atom's lack of low-lying p orbitals and its high electronic excitation energies. Yet differences in ^{1}H chemical shifts of diastereotopic protons follow closely the ^{13}C shift differences in diastereotopic methyl groups, which suggests a common origin for the two as discussed by Eliel et al.[30] In light of the present results, it seems reasonable that the ^{13}C diamagnetic shielding could be responsible for this experimental connection with the ^{1}H shielding.

While the diamagnetic contribution relies upon changes in the ground-state wave functions only, perhaps accounting for the correlation's insensitivity to solvent effects on the 3s state, this explanation would also suggest that the normally dominant paramagnetic shielding term is either invariant or variant in a regular fashion. This is a possibility since the $n \rightarrow \pi^*$ transition remains practically constant for the group of structures within each ring size. There are, however, other factors involved in σ_p contribution, and it would seem an oversimplification to suggest that this was actually the case. Combinations of multiple contributions as well as long-range effects are also possible explanations but these have not yet been investigated.

Conclusions

We have demonstrated that a very subtle aspect of the ^{13}C NMR chemical shift of carbonyl compounds correlates with the high-resolution $n \rightarrow 3s$ optical transition energy. The $1/\Delta E$ term in the paramagnetic shielding contribution has been considered as the possible basis for the correlation, although the transition symmetry is not one which would be expected to contribute to the σ_p term, and significant solution-phase perturbations to the Rydberg state tend to weaken the support for this rationale. Diamagnetic shielding contributions have also been examined, and the results suggest that the basis of the optical and NMR chemical shift correlation is related to changes in the ground-state wave functions, exclusively. This rationalization is as follows: as substituents are introduced into the ring structure, the molecular and atomic contributions to the total energy change in a proportionate fashion. The diffuse molecular orbital energies would dictate the shifts in the optical spectrum while the atomic-like electrostatic potential of carbonyl carbon would determine the shifts in the NMR spectrum. It would be interesting to further investigate this possible explanation by studying the ESCA peak shifts of the carbonyl carbon in methyl isomers of cyclic ketones since the core binding energies in some type of molecules have been shown to be related to their respective diamagnetic shielding.

There are several implications of this experimental correlation. First, high-resolution optical spectroscopy may prove to be a useful technique in gaining insight into the nature of the chemical shift. Also, the possible connection between the NMR shifts and ground-state steric energies, such as the van der Waals interactions described by Chesnut, could extend the usefulness of ^{13}C shielding measurements. The application of this experimental finding to other functional groups is currently in progress.

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Combined ^{2}H and ^{18}O Isotope Effects in Support of a Concerted, Synchronous Elimination of Acetaldehyde from a Bis(benzyl ethyl ether) Radical Cation

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Abstract: No evidence has been found of "hydrogen scrambling" accompanying decomposition of the benzyl ether molecular ion at times approaching 100 μs. Isotope effects upon product ion abundances have been measured for elimination of acetaldehyde from the molecular ions of multiply labeled diethoxyxylenes and compared with the results of calculations of kinetic isotope effects using the quasi-equilibrium theory. It is concluded that this rearrangement involving a 6-membered cyclic transition state can be described as a concerted, synchronous process.

A few years ago, we reported in a preliminary communication ^{2}H and ^{18}O isotope effects manifested in the unimolecular elimination of acetaldehyde from α,α'-diethoxy-*p*-xylene (I) and proposed this decomposition to be a concerted, synchronous re-

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