Notes

^{13}C Chemical Shifts/λ_{max} Correlation and MNDO Calculations of the Paramagnetic Components of the Shielding Constants in *t*-Bu$_2$C=X Derivatives

G. Barbarella,*,† A. Bongini,*,‡ and S. Rossini†

Istituto dei Composti del Carbonio Contenenti Eteroatomi e loro Applicazioni, Consiglio Nazionale delle Ricerche, via Tolara di Sotto 89, 40064 Ozzano E., Bologna, Italy, and Istituto Chimico G. Ciamician, Università, via Selmi 2, 40126 Bologna, Italy

Received October 27, 1987

It is often assumed that, within a related series of compounds, the variations of $\delta(^{13}C)$ are due to changes in the electronic charge at carbon. Indeed, for groups of comparable compounds, the largest part of the differences in nuclear shielding are determined by local charge density variations. Accordingly, inductive and mesomeric effects and steric factors affecting the ^{13}C chemical shifts of most organic compounds are accounted for in terms of 2p orbital dimension changes, which are proportional to atomic charges.[1]

However, the limits within which the ^{13}C chemical shifts of a series of compounds are "comparable" are not easily defined, and the interpretation of carbon-13 chemical shift variations based exclusively on the changes of the electronic charges at carbon must be taken with caution, especially when atoms beyond the first row of the periodic system are present in the molecule. Nevertheless, the problem is relevant in relation to the large number of papers trying to interpret reactivity trends or molecular properties on the basis of the variations of the ^{13}C chemical shift of a given site.[2]

For several heteronuclei, the pattern of chemical shifts has been interpreted in terms of variations of the mean excitation energy contribution to the paramagnetic component of the shielding constant, ΔE, cf. the ^{15}N chemical shifts of azo compounds[3] or ^{33}S chemical shifts of thiomolybdates and thiotungstates[4] and that of organic sulfones.[5] In principle, ΔE should affect the chemical shifts of all nuclei of a given molecule, although to a degree that depends on the contribution of the atomic orbitals of the nucleus in question to the molecular orbital.[6] Thus, it can be argued that, in cases where ΔE changes substantially from one compound to another of a structurally correlated series, this variation affects not only the chemical shift of the heteroatom but also that of the adjacent carbons.

In an attempt to put these arguments in a more quantitative way, we have undertaken a study aimed at the identification of classes of compounds for which it can be unambiguously proved that factors different from the atomic charge dominate the variations of the ^{13}C chemical shift, and we present here our first results.

Results and Discussion

The compounds in question, **1**–**5**, are reported in Table I, which gives the ^{13}C chemical shifts of the unsaturated quaternary carbons, together with λ_{max} for UV absorptions of the C=X group, the calculated atomic charges (q), and the calculated components of the paramagnetic contribution to the shielding constants for the *C*=X carbons. The last terms were calculated on the basis of the well-known Pople expression[7] for σ_p, which for a nucleus A is given by

$$\sigma_p{}^A = -\frac{e^2\hbar^2}{8\pi m^2}\langle r^{-3}\rangle_{2p}(\Delta E)^{-1}(Q_{AA} + Q_{AB})$$

where r is the average radius of the 2p orbital of carbon (proportional to the atomic charge), ΔE is the mean value of the singlet electronic excitation energies (roughly, proportional to the lowest energy electronic transition), Q_{AA} and Q_{AB} are the elements of the charge density and bond order matrix taken for A (Q_{AA}) and over all atoms to which A is π-bonded (Q_{AB}).

According to Pople's MO theory,[7] for a second-row element the variations of the chemical shifts of a related series of compounds are dominated by the variations of the local paramagnetic term, σ_p.

The calculations of the components of σ_p given in Table I were performed on the basis of the AEE approximation[6] by MNDO[8] formalism, using density matrix elements for r^{-3}, Q_{AA} and Q_{AB}, and the configuration interaction option available with the AMPAC integrated package of the MNDO program for ΔE.

The chemical shift of thioketones has been the subject of several investigations,[9] as the carbon atom of a C=S group is deshielded by several tens of ppm compared to that of the C=O group of a keto derivative, although the dipole moments of ketones are higher than those of the corresponding thioketones (cf. the dipole moments of **3** and **4**, which are 2.53 and 2.19 D, respectively.[10] Calcd.: 2.33 and 2.17, respectively)). Even more interesting is the selenoketone, **5**, whose quaternary unsaturated carbon, as pointed out by Olah,[9a] is one of the most deshielded carbons ever observed in neutral molecules.

It is seen that the atomic charges, q, at the *C*=X carbon reflect the relative electronegativities of the X group (which

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[†] Istituto dei Composti del Carbonio Contenenti Eteroatomi e loro Applicazioni.

[‡] Istituto Chimico G. Ciamician.

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Table I. $\delta(^{13}C)$, λ_{max}, Atomic Charges (q), and Calculated[a] Paramagnetic Contributions to the Shielding Constant for the Unsaturated Quaternary Carbons (C=X) of Compounds 1–5

compound	$\delta(^{13}C)$, ppm	λ_{max}, nm	q, e^-	$1/r^3$, au	Q_{AA}	Q_{AB}	ΔE, eV
1, $t\text{-}Bu_2C{=}CH_2$	164.9	189	−0.133	1.3788	1.9994	0.3727	
2, $t\text{-}Bu_2C{=}NH$	193.5	195	+0.022	1.4406	1.9837	0.4473	4.33
3, $t\text{-}Bu_2C{=}O$	218.0	298	+0.247	1.5477	1.9504	0.4492	2.98
4, $t\text{-}Bu_2C{=}S$	278.0	540	−0.122	1.3793	1.9972	0.4568	1.11
5, $t\text{-}Bu_2C{=}Se$	292.5	706	*b*	*b*	*b*	*b*	*b*

[a] According to the AEE approximation of the paramagnetic component of the shielding constant.[6] [b] Not calculated.

increase in the order: Se < C < S < N < O[11]), as the most electropositive carbon is the one bearing the oxygen atom in **3** and the most electronegative is the one bearing the CH_2 group in **1** and that of the selenoketone **5**.

Clearly, no correlation can be found between the atomic charges and the chemical shifts; the simple rule according to which downfield shifts are associated with more electropositive and highfield shifts with more electronegative carbon atoms is not valid for **1–5**.

The comparison of the q values given in Table I with the chemical shifts suggests that the effects of the atomic charges on $\delta(^{13}C)$ are outweighed by some other factor contributing to the shielding constant.

The calculation of the components of σ for **1–5** raises a few problems. First, owing to the lack of MNDO programs parametrized for selenium, the calculations are not possible for **5**. Second, and more important, a choice must be made for the better approximation of the mean excitation energy term.[2,6] Since compounds **2–4** have in common the presence of atoms bearing lone pairs, we have taken for ΔE (see the table) the lowest calculated singlet excitation energies corresponding to $n \rightarrow \pi^*$ transitions,[12] which are known to dominate the ΔE values for atoms containing lone pairs.[2,6] However, for **1** the lowest singlet excitation energy corresponds to a $\pi \rightarrow \pi^*$ transition;[13] contrary to $n \rightarrow \pi^*$, $\pi \rightarrow \pi^*$ transitions do not contribute to ΔE.[6] Accordingly, the calculated lowest singlet excitation energy for **1**, 5.4300 eV, is not a sufficiently good approximation for ΔE and was not reported in the table. Anyway, it can be safely assumed that the mean excitation energy of **1** is significantly higher than that of **2–4**.

It is interesting to note that when the $\delta(^{13}C)$ values for **2–4** are plotted vs the corresponding calculated $(\langle r^{-3}\rangle_{2p}/\Delta E)\sum Q$ values, a straight line ($r = 0.996$) is found, indicating that the components of σ_p reported in the table are good descriptors of the experimental situation for **2–4**. Examination of the trend of the components of σ_p shows that neither $1/r^3$ nor Q_{AA} can account for the observed variations of the chemical shift. Indeed, as expected, the first term varies in the same way as the atomic charge and the second term is practically constant. On the contrary, the bond order term Q_{AB} increases on going from **2** to **4** while the mean molecular excitation energy component decreases. Thus the last two terms both contribute to the downfield shift observed for the *C*=X carbon along the series. However, while the variation of Q_{AB} is on the order of 10%, the variation of ΔE is much more important, larger than 100%. Consequently, the calculated data indicate that the chemical shifts of the *C*=X carbons are critically dependent on ΔE.

The experimental evidence showing that this is indeed the case is given in Figure 1. In fact when the chemical shifts for the *C*=X carbons of **1–5** are plotted against the wavelengths of the UV absorptions, λ_{max}, a good linear correlation is found ($r = 0.986$ for **2–5**). The plot includes the selenoketone, for which it is known that the lowest singlet transition is $n \rightarrow \pi^*$.[14] On the contrary, the pentamethylene derivative **1**, for which the lowest singlet excitation transition is not a sufficiently good approximation of ΔE, lies distinctly out of the straight line of Figure 1, emphasizing the significance of the linear correlation found for **2–5**.

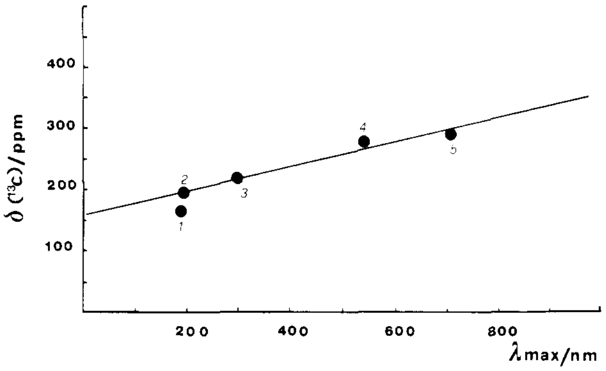

Figure 1. ^{13}C chemical shifts of compounds 1–5 against λ_{max}.

In conclusion, there is theoretical and experimental evidence showing that for the series of compounds presented here, the chemical shift variations are dominated by the energy factor.

The ΔE component of Pople equation is a ill-defined term, which is not easily calculated. However, even in cases where the calculation of ΔE is not possible, ultraviolet spectra are generally easily accessible to organic chemists and in most cases it should be possible to verify whether a correlation exists between $\delta(^{13}C)$ and λ_{max}.

Experimental Section

In order to have a set of homogeneous data, the carbon-13 chemical shifts and the λ_{max} of UV absorption spectra of **1–5** were measured and found to be in agreement with the data reported in ref 15–17.

Compounds **1**,[15] **2**,[16] **4**,[16] and **5**[17] were prepared as reported in the literature. Compound **3** is commercial and was purified by distillation before use. The ^{13}C chemical shifts were measured in $CHCl_3$ and are as follows (in ppm, downfield from TMS): 32.7, 37.8, 108.6, 164.9 (**1**); 30.4, 41.6, 193.5 (**2**); 28.5, 45.7, 218.0 (**3**); 53.5, 32.9, 278.0 (**4**); 60.3, 32.8, 292.5 (**5**).

For determination of ultraviolet absorption spectra, a Perkin-Elmer 554 UV–vis spectrophotometer was used. Solutions were prepared in cyclohexane.

For all compounds the calculations of the atomic charge and of the paramagnetic components of σ_p were performed on op-

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timized interlocked geometries with $X–C_\alpha–C_\beta–C_\gamma$ = 0°, $X-C_{\alpha'}-C_{\beta'}-C_{\gamma'}$ = 180° and 1.34 Å ($C{=}CH_2$), 1.28 Å ($C{=}NH$), 1.22 Å ($C{=}O$), 1.56 Å ($C{=}S$) bond distances.

Registry No. **1**, 5857-68-1; **2**, 29097-52-7; **3**, 815-24-7; **4**, 54396-69-9; **5**, 56956-23-1.

Preparation of Solid Thianthrene Cation Radical Tetrafluoroborate

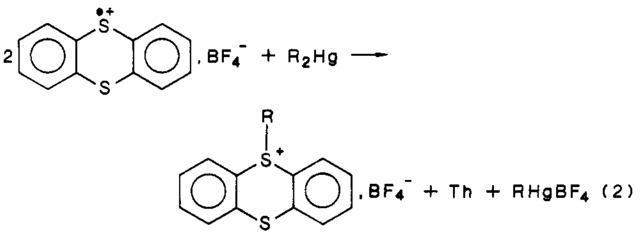
Bogdan Boduszek[1] and Henry J. Shine*

Department of Chemistry and Biochemistry, Texas Tech University, Lubbock, Texas 79409

Received February 16, 1988

For some years we have used thianthrene cation radical perchlorate ($Th^{\bullet+}ClO_4^-$) for studying the reactions of $Th^{\bullet+}$ in solution. $Th^{\bullet+}ClO_4^-$ was chosen for use because it is easily prepared in the crystalline state and its counter ion is not nucleophilic. However, use of solid $Th^{\bullet+}ClO_4^-$ can be hazardous. A warning about its use was issued in 1969 after a sample exploded when being transferred from a filter funnel.[2] Because of this hazard, $Th^{\bullet+}ClO_4^-$ should be (and has been in all of our work) made in small quantities, handled carefully, and used soon after preparation. Because of the potential for explosion, we tried on a number of occasions to prepare other isolable salts. Hexachloro- and hexafluoroantimonates can be made by reaction of Th with antimony pentachloride or pentafluoride. However, we found the use of these salts to be troublesome because of the difficulties of removing antimony compounds from products and, in the case of $Th^{\bullet+}SbCl_6^-$, because of the presence of nucleophilic chloride ion in solution. The tetrafluoroborate ($Th^{\bullet+}BF_4^-$) was an obvious, attractive alternative. Some years ago, attempts were made to prepare solid cation radical tetrafluoroborates by reactions of Th and analogues with nitrosonium tetrafluoroborate ($NOBF_4$). Success was achieved with some cation radicals, for example, those of phenothiazine and 10-methyl- and 10-phenylphenothiazine. However, we were unable to prepare solid $Th^{\bullet+}BF_4^-$. We were able to prepare solutions of $Th^{\bullet+}BF_4^-$ and to use them successfully soon after preparation, but the solutions were not stable for storage during a day or two.[3] Therefore, use of $Th^{\bullet+}BF_4^-$ solutions was discontinued. $Th^{\bullet+}BF_4^-$ had, in fact, been prepared earlier by disproportionation of Th and its 5-oxide (ThO) in fluoboric acid, but the preparation required the use of dry $HF{\cdot}BF_3$.[4] We have now found that solid $Th^{\bullet+}BF_4^-$ can be prepared in good yield and quality by a simple control of the method of reaction between Th and $NOBF_4$. The brown, solid salt can be prepared in large quantities as compared with preparations of $Th^{\bullet+}ClO_4^-$. In order to validate the usefulness of the salt, we used it quantitatively in some reactions that in the past had given excellent results with $Th^{\bullet+}ClO_4^-$, namely, reaction with water, dimethylmercury, and diphenylmercury.[5] Reaction with water gave equal and quantiative yields (by GC) of Th and ThO (eq 1). Reaction with the mercurials gave the expected 5-thianthreniumyl tetrafluoroborates (eq 2) in good yields.

$$2Th^{\bullet+} + H_2O \longrightarrow Th + ThO + 2H^+ \qquad (1)$$



We found, again,[3] that when solutions of $Th^{\bullet+}BF_4^-$ in acetonitrile were made in situ by reaction of Th with $NOBF_4$, the concentration of $Th^{\bullet+}$ diminished with time, as judged visually by the color of the solution, lasting no more than a day or two. The reason for this instability is not known, but it may be because NO from reduction of NO^+ remained in solution and, after air oxidation to NO_2, led to decomposition of $Th^{\bullet+}$. On the other hand, solutions of $Th^{\bullet+}BF_4^-$ made by dissolving the solid salt in dry acetonitrile were stable for weeks.

Thus, $Th^{\bullet+}BF_4^-$ should serve as a useful, safe substitute for $Th^{\bullet+}ClO_4^-$.

Experimental Section

Preparation of Solid $Th^{\bullet+}BF_4^-$. Thianthrene (Th, 510 mg, 2.36 mmol) and nitrosonium tetrafluoroborate (Aldrich, 290 mg, 2.48 mmol) were placed side by side in a two-necked, round-bottom 250-mL flask. The flask was kept flushed with argon while 40 mL of dry acetonitrile was added. The mixture turned dark blue very quickly and was stirred under gently flowing argon for 1 h, after which 120 mL of dry ether was added gradually with continued stirring. The dark precipitate that formed was filtered, washed with dry ether, and finally dried under vacuum for 5 h, giving 528 mg (1.74 mmol, 75.5%) of $Th^{\bullet+}BF_4^-$.

The product was assayed twice by dissolving a sample in 10 mL of acetonitrile and 10 mL of carbon tetrachloride to which was added 1 g of sodium iodide. The liberated iodine was titrated with standard sodium thiosulfate. Assays were 100.5% and 98.6% of $Th^{\bullet+}$.

Preparation was repeated on the scale of 2 g of Th (1.07 g of $NOBF_4$, 80 mL of acetonitrile, 240 mL of ether) and 5 g of Th (2.7 g of $NOBF_4$, 150 mL of acetonitrile, 550 mL of ether), giving respectively 2.0 g (73%) and 5.4 g (77%) of product. Again, assays of $Th^{\bullet+}$ content were 96.7% and 96.3%, respectively. After 3 months of storage at room temperature, the assay was 85.4%.

The isolated $Th^{\bullet+}BF_4^-$ had mp 175–180 °C, and the dark melt decomposed very quickly. Anal. Calcd for $C_{12}H_8S_2BF_4$: C, 47.5; H, 2.64; S, 21.1. Found: C, 47.7; H, 2.58; S, 21.1.[6]

Reaction of $Th^{\bullet+}BF_4^-$ with Water. A sample of 303 mg (1.0 mmol) of $Th^{\bullet+}BF_4^-$ was dissolved in 10 mL of acetonitrile. To the solution was added 1.5 mL of water, which caused the rapid disappearance of the dark blue color of $Th^{\bullet+}$. The solution was evaporated to dryness, and the residue was treated with 10 mL of water and extracted with methylene chloride. Workup gave 217 mg (96.7%) of a mixture of Th and ThO. Analysis by GC showed quantitative yields of Th and ThO. Separation by preparative-scale TLC gave 99 mg (0.46 mmol, 92%) of Th, mp 154–155.5 °C, and 83 mg (0.36 mmol, 72%) of ThO, mp 139–140 °C.

Reaction of $Th^{\bullet+}BF_4^-$ with Dimethylmercury. Dimethylmercury was added dropwise from a syringe to a stirred solution of 612 mg (2.02 mmol) of $Th^{\bullet+}BF_4^-$ in 10 mL of acetonitrile until the color of $Th^{\bullet+}$ disappeared. A small amount of solid had formed. The solvent was removed by rotary evaporation at room temperature. To the residue was added 20 mL of water, and the mixture was extracted with 2 × 30 mL of methylene chloride. The dried ($MgSO_4$) solution was evaporated to 5 mL, to which was added 40 mL of dry ether. The precipitated salt was washed several times with dry ether and dried in air to give 244 mg (0.767 mmol, 76%) of product, mp 186–191 °C. The

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