interaction matrix element and $\delta\epsilon_{ij}$ is the energy difference between orbitals. The relative importance of sulfur and oxygen π-bonding is then given by eq 3. Some estimates[7a] of the various parameters

$$\frac{\mathrm{SE(S)}}{\mathrm{SE(O)}} = \frac{(H_{ij}^2)^{(S)}}{(H_{ij}^2)^{(O)}} \frac{\delta\epsilon_{ij}^{(O)}}{\delta\epsilon_{ij}^{(S)}} \qquad (3)$$

for $^{+}CH_2$ and phenyl as π-acceptors are given in Table I. With a good π-acceptor such as $^{+}CH_2$, sulfur is predicted to be the better π-donor, due to control of eq 3 by the energy gap ratio, $\delta\epsilon_{ij}^{(O)}/\delta\epsilon_{ij}^{(S)}$. This ratio will be close to unity for a poor π-acceptor such as phenyl, and oxygen will be the better π-donor due to domination of eq 3 by the term involving the interaction matrix elements.[23] If the energy of π^* for the formyl group is taken as 4.35 eV,[24,25] then $\delta\epsilon_{ij}^{(O)}/\delta\epsilon_{ij}^{(S)}$ for **3** and **4** can be estimated as 1.14. This ratio is only slightly larger than the value for phenyl as π-acceptor, and a ratio of $(H_{ij}^2)^{(S)}/(H_{ij}^2)^{(O)}$ close to the values in Table I would lead to the prediction that conjugation should be more important for **4** than for **3**, as observed experimentally in this work.

Registry No. **3**, 32779-88-7; $^{+}CH_2SH$, 54043-03-7; $^{+}CH_2OH$, 18682-95-6; C_6H_5SH, 108-98-5; C_6H_5OH, 108-95-2.

---

[23] The ratio of the $\sigma_R°$ values for thioanisole (−0.25) and anisole (−0.43) is 0.58, in agreement with the conclusion from the theoretical studies that oxygen is the better π-donor in these systems.

[24] Reference 7c, p 11.

[25] The uncertainties in this energy and those of Table I are probably large. The LUMO energy of ethylene,[24] calculated by the same method as for formaldehyde (CNDO/2), is 5.43 ile the electron affinity of ethylene is given[24] as −2.8 eV.

Isotopic Perturbation of Reso in Benzylic Cations

David A. Forsyth* and Matthew M. MacConnell

Department of Chemistry, Northeastern University
Boston, Massachusetts 02115

Received April 8, 1983

Deuterium substitution in the methyl groups of the phenyldimethylcarbenium ion (**1**) induces downfield shifts of the ^{13}C NMR signals of the ortho and para carbons.[1,2] These long-range isotope shifts apparently arise from isotopic perturbation of hyperconjugation, with the CH_3 group behaving as a better electron donor than the CD_3 group.[1-4] Other recent studies indicate a hyperconjugative contribution to isotope shifts in neutral, allylically or benzylically deuterated compounds.[5-7]

In this paper, we investigate the possibility that isotope shifts in arylcarbenium ions could serve as a probe of π charge distribution and also provide evidence for the origin of long-range isotope shifts. The premises are that isotopic perturbation of hyperconjugation will reduce slightly the supply of electrons to the carbenium center and that this additional electron deficiency will be distributed among the aryl positions in a pattern reflecting the existing charge distribution. The isotope shift at each position would then indicate the amount of charge, assuming a direct relationship between the change in chemical shifts and change in charge density. We expected that the isotope shifts would be a better probe of charge than shifts induced by other substituents,[8] because of the very minor structural perturbation involved. However, this expectation is only partially borne out in the results described below.

Table I. ^{13}C Chemical Shifts, Deuterium Isotope Effects, and π Charge Densities for Aryldimethylcarbenium Ions

compd	carbon	δ_C[a]	$\Delta\delta_C$[b]	q_π[c]
1	C-2,6	142.4	0.170	0.147
1	C-3,5	133.3	0.031	0.042
1	C-4	155.9	0.222	0.200
2	C-2	150.6	0.191	0.184
2	C-4	159.2	0.241	0.225
2	C-4a	135.0	−0.036	−0.017
2	C-5	134.4	0.070	0.084
2	C-7	136.8	0.084	0.107
2	C-8	127.5	0.042	0.010
3	C-1	153.2	0.205	0.210
3	C-3	128.4	0.064	0.050
3	C-4a	145.5	0.093	0.074
3	C-6	142.8	0.111	0.116
3	C-8	137.8	0.061	0.067
4	C-2,6	142.4	0.03, 0.11	
4	C-4	155.9	0.11	

[a] ^{13}C chemical shifts in ppm for the unlabeled ions, measured relative to external (capillary) Me_4Si (from ref 8 and new measurements at 15.0 and 125.8 MHz). [b] Deuterium-induced isotope shift at aryl carbons in ppm; positive sign indicates downfield shift in the deuterated compound. Measured at 125.8 MHz on mixtures of deuterated and unlabeled ions. Error estimate ±0.012 ppm, digital resolution better than 0.007 ppm. [c] SCF-π MO charge in $ArCH_2^+$ (ref 8).

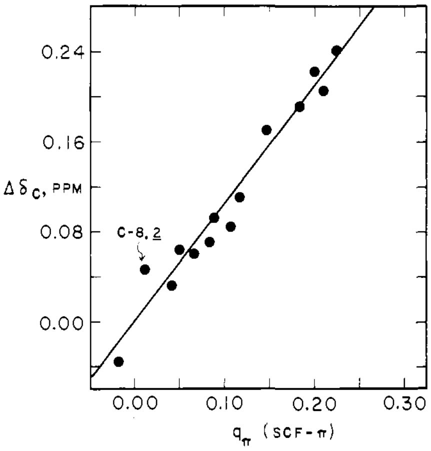
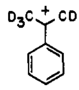
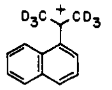


Figure 1. Plot of isotope shifts vs. π-charge densities.

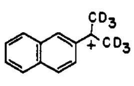
Isotope shifts observed at aryl carbons of ions **1**–**4** are listed



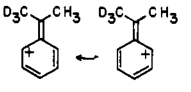
1



2



3



4a 4b

in Table I, along with the ^{13}C chemical shifts for the unlabeled ions. Not all carbons displayed measurable isotope shifts. The smallest resolved peak separation was 0.031 ppm; smaller isotope shifts may be unresolved due to the broadened resonances typical of cations (3–5-Hz line widths). Also listed in Table I are values of q_π, the π charge at each position, from SCF-π MO calculations

---

[1] Servis, K. L.; Shue, F.-F. *J. Am. Chem. Soc.* **1980**, *102*, 7233–7240.

[2] Forsyth, D. A.; Lucas, P.; Burk, R. M. *J. Am. Chem. Soc.* **1982**, *104*, 240–245.

[3] Timberlake, J. W.; Thompson, J. A.; Taft, R. W. *J. Am. Chem. Soc.* **1971**, *93*, 274–276.

[4] For a review of isotope effects on ^{13}C spectra, see: Forsyth, D. A. In "Isotopes in Organic Chemistry"; Lee, C. C., Buncel, E., Eds.; Elsevier: Amsterdam; Vol. 6, in press.

[5] Ernst, L.; Eltamany, S.; Hopf, H. *J. Am. Chem. Soc.* **1982**, *104*, 299–300.

[6] Hansen, P. E.; Led, J. J. *Org. Magn. Reson.* **1981**, *15*, 288–293.

[7] Wisener, J. R.; Günther, H. *Tetrahedron Lett.* **1982**, *223*, 2845–2848.

[8] (a) Forsyth, D. A.; Spear, R. J.; Olah, G. A. *J. Am. Chem. Soc.* **1976**, *98*, 2512–2518. (b) New values for chemical shifts of **2** are reported here, but the assignments remain the same as in the above paper.

0002-7863/83/1505-5920$01.50/0

on the arylcarbenium ions, $ArCH_2^+$.[8]

It is evident from Table I and consideration of the ion structures that the largest isotope shifts are observed at positions to which substantial charge is delocalized. Isotope shifts for **1**–**3** are plotted vs. q_π in Figure 1. A very good correlation is obtained ($\Delta\delta_c = 1.052q_\pi - 0.002$; correlation coeff = 0.976) including even the ortho- and peri-type positions. It is interesting to note that an upfield shift is observed at C-4a in **2** where a negative charge is predicted. The simple correlation of ^{13}C chemical shifts vs. charge for the same set of carbons is considerably worse: $\delta_c = 118.1q_\pi + 129.0$; correlation coeff = 0.888. The δ_c vs. charge correlation is poor primarily because of the substantial upfield shifts displayed by the ortho- and peri-type carbons due to the steric proximity of the methyl groups.[8]

The quality of the correlation in Figure 1 for hydrocarbon arylcarbenium ions is sufficiently good to view the isotope shift as a probe of charge distribution in such systems and to suggest that perturbation of hyperconjugation is the principal source of the long-range isotope shifts. However, the results for ion **4** indicate an intriguing nonequivalence of shifts for the ortho carbons. The ortho positions in **4** differ by 0.081 ppm,[9] with $\Delta\delta_c$ of 0.11 ppm for one position and 0.03 ppm for the other. If the isotope shifts were purely hyperconjugative in origin, transmitted through the π-system by a simple reduction in electron supply to the carbenium center, the ortho isotope shifts would be identical, and exactly half the magnitude of the shifts for **1**. Instead, one ortho carbon resonance in **4** is more deshielded and the other is less deshielded than by the expected 0.085 ppm.

The chemical shift nonequivalence in **4** raises the possibility of a *through-space* isotopic perturbation of resonance,[10] which shifts charge from one ortho position to the other. We make a tentative assignment of the more deshielded ortho carbon as being syn to the deuterated methyl,[11] on the presumption that deuteration diminishes through-space orbital interactions, similar to hyperconjugation, that have been postulated to account for part of the shielding by syn methyl groups.[12] In resonance terms, canonical form **4a** is suggested to contribute more than **4b**. The alternative origin for the effects in **4** of a stereochemically dependent effect operating through σ bonds seems less likely, because isotope shifts through more than three bonds are usually very small. Similarly, an isotope shift arising from perturbation of a steric interaction with the ortho C–H bond seems unlikely because no such isotope shift was found in even more crowded saturated systems.[13] In neutral systems related to **1** and **4**, we find no detectable (<0.008 ppm) isotope shift at ortho carbons in 2-chloro-2-phenylpropane-*1,1,1,3,3,3*-d_6 and small $\Delta\delta_c$ of 0.025 and 0.010 ppm at ortho and para carbons, respectively, in 2-phenylpropene-*1,1,3,3,3*-d_5. It is clear that further experimental and theoretical study will be required to establish the precise origin of the unusual ortho effects in **4**.[14]

An additional indication of a through-space effect may be the isotope shift for the peri carbon, C-8, in the 1-naphthyl system, **2**. The data point for this position deviates most from the correlation line in Figure 1, and the deviation is in the direction of a larger downfield shift than predicted. A small downfield isotope shift of apparent through-space origin has also been reported in deuterated methylcyclophanes.[5]

In conclusion, long-range shifts induced by isotopic perturbation of hyperconjugation can serve as a probe of π charge distribution. However, such shifts must be significantly larger than those produced by through-bond or other effects.[3,7,15] Effects through three bonds are well-known,[3,13] and in the cations described here, positions near the site of substitution may experience isotope shifts that are not due to a simple perturbation of electron supply to the π-system. Thus, the NMR isotope shifts may reliably reflect charge effects only at sterically remote positions.

Acknowledgment. This work was supported by the National Science Foundation (CHE-8211125). NMR spectra were obtained at the Northeast Regional NSF-NMR Facility at Yale University.

Registry No. 1, 75296-07-0; **2**, 86688-67-7; **3**, 86688-68-8; **4**, 86688-69-9.

---

[9] The peak separation was obtained from an independent measurement with only the labeled ion present.

[10] The concept of isotopic perturbation of resonance was introduced by: Saunders, M.; Kates, M. R. *J. Am. Chem. Soc.* **1977**, *99*, 8071–8072.

[11] This assignment is supported by our unpublished observations of isotope shifts at C-3 in (2-thienyl)methylcarbenium ion, for which *E* and *Z* isomers are known: Forsyth, D. A.; Olah, G. A. *J. Am. Chem. Soc.* **1979**, *101*, 5309–5316.

[12] Forsyth, D. A.; Vogel, D. E.; Stanke, S. J. *J. Am. Chem. Soc.* **1978**, *100*, 5215–5216.

[13] Anet, F. A. L.; Dekmezian, A. H. *J. Am. Chem. Soc.* **1979**, *101*, 5499–5451.

[14] One referee suggests a steric origin and a second referee suggests a through-bond perturbation of resonance.

[15] Berger, S.; Künzer, H. *Tetrahedron* **1983**, *39*, 1327–1329.

Metallacumulenes: A Diruthenium Vinylidene–Alkylidene Complex from the Apparent Dimerization of $[Ru(C{=}C{=}CMe_2)(PPh_3)_2(Cp)][PF_6]$

John P. Selegue

Department of Chemistry, University of Kentucky
Lexington, Kentucky 40506-0055

Received January 31, 1983
Revised Manuscript Received July 11, 1983

Only recently have reliable methods for the preparation of metal allenylidene complexes ($M{=}C{=}C{=}CR_2$) been developed,[1] and their chemistry remains largely unexplored.[1b,e] We previously reported that diphenylallenylidene complex Ia resulted from reaction 1.[1a] This reaction takes a different course when 2-methyl-3-butyn-2-ol is the substrate.

$$[\mathrm{RuClL_2(Cp)}] + \mathrm{HC{\equiv}CC(OH)R_2} + \mathrm{NH_4PF_6} \rightarrow [\mathrm{Ru(C{=}C{=}CR_2)L_2(Cp)}][\mathrm{PF_6}] \quad (1)$$

Ia, L = PMe_3; R = Ph
Ib, L = PPh_3; R = Me

A mixture of 1.0 g (1.4 mmol) of $[RuCl(PPh_3)_2(Cp)]$, 0.67 g (4.1 mmol) of NH_4PF_6, and 0.35 mL (5.2 mmol) of $HC{\equiv}CC(OH)Me_2$ in dry methanol (50 mL) was stirred for 21 h at room temperature, during which time the color changed from orange to deep purple. The volatile components were removed in vacuo, and the residue was recrystallized from dichloromethane/ethyl ether to give 1.2 g (97%) of a microcrystalline, red-purple solid (II).[2] Slow recrystallization from dichloromethane/ethyl ether produced crystals suitable for X-ray diffraction. Crystal structure analysis[4] revealed that product II is a *dimer* of the expected

---

[1] (a) Selegue, J. P. *Organometallics* **1982**, *1*, 217–218. (b) Berke, H.; Huttner, G.; von Seyerl, J. *Z. Naturforsch., B* **1981**, *36B*, 1277–1288. (c) Berke, H.; Harter, P.; Huttner, G.; von Seyerl, J. *J. Organomet. Chem.* **1981**, *219*, 317–327. (d) Berke, H. *Chem. Ber.* **1980**, *113*, 1370–1376. (e) Berke, H. *J. Organomet. Chem.* **1980**, *185*, 75–78. (f) Fischer, E. O.; Kalder, H.-J.; Frank, A.; Köhler, F. H; Huttner, G. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 623. (g) Berke, H. *Ibid.* **1976**, *15*, 624.

[2] ^1H NMR (90 MHz, $(CD_3)_2CO$ δ 7.7–7.0 (ca. 61 H, m, aromatic and vinyl), 6.24 (1 H, s, C=CH), 5.63 (5 H, s, Cp), 5.07 (5 H, s, Cp′), 3.67 (2 H, s, CH_2), 1.50 (2 H, s, CH_2'); IR (mull) 1565 (m, C=C)[3], 835 (vs, $[PF_6]^-$) cm^{-1}. Anal. ($C_{92}H_{82}F_{12}P_6Ru_2$) C, H, P.

[3] (a) Davison, A.; Selegue, J. P. *J. Am. Chem. Soc.* **1978**, *100*, 7763–7765. (b) Bruce, M. I.; Wallis, R. C. *Aust. J. Chem.* **1979**, *32*, 1471. (c) Berke, H. *Z. Naturforsch., B* **1980**, *35B*, 86–90. (d) Berke, H.; Huttner, G.; von Seyerl, J. *J. Organomet. Chem.* **1981**, *218*, 193–200.

[4] Crystal data for compound II: space group $P\bar{1}$, a = 13.172 (4) Å, b = 15.344 (3) Å, c = 22.026 (5) Å, α = 71.68 (3)°, β = 75.72 (3)°, γ = 85.93 (2)°, V = 4095.41 Å^3, Z = 2, ρ_{calcd} = 1.463 g·cm^{-3}, μ = 5.86 cm^{-1}. The structure was solved using MULTAN 77 to locate the two ruthenium atoms and two of the phosphorus atoms by direct methods, and the remaining atoms were found from subsequent difference Fourier maps. The 72 carbon atoms belonging to the 12 phenyl rings were treated as rigid groups. Hydrogen atoms were placed in idealized positions and were not refined. All other atoms were refined using anisotropic thermal parameters. Refinement by full-matrix least-squares procedures led to R = 7.9%, R_w = 9.6% using 5203 reflections with $F^2 \geq 3\sigma(F^2)$.

0002-7863/83/1505-5921$01.50/0