J. Am. Chem. Soc. 1984, 106, 4297-4299

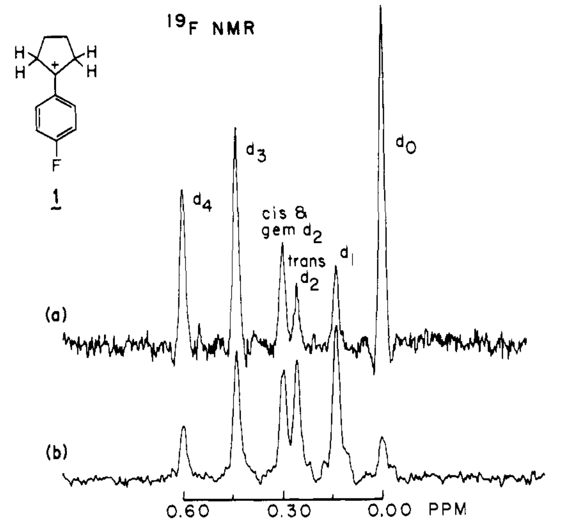

Figure 1. Proton-decoupled 56.2-MHz ^{19}F NMR spectra, at about −75 °C, of the 1-(*p*-fluorophenyl)cyclopentyl cation as mixtures of isotopomers due to deuteration at C_2 and C_5 in the cyclopentyl ring. Spectrum a is of a mixture of the unlabeled ion and a randomly labeled (~70% deuteration) ion sample; spectrum b is of another mixture enriched in the trans-2,5-d_2 isotopomer. Spectra were obtained on a JEOL FX-60Q spectrometer in 30 pulses or fewer, with an 8.3-s pulse repetition rate, and either 500-Hz width with 8192 data points (a), or 1000-Hz width and 16384 data points (b).

isotope shifts almost precisely half that of the tetradeuterated isotopomer. If the cation had assumed the envelope shape, *cis*-**1**-*2,5-d*$_2$ would have preferred the envelope conformation which places both deuterium atoms in quasi-equatorial rather than quasi-axial positions, because a C–H bond is a better hyperconjugative electron donor than a C–D bond[2-5] and an axial position is better aligned for overlap with the p-orbital (Scheme I). The trans labeled cation, *trans*-**1**-*2,5-d*$_2$, would not have perturbed the equilibrium between envelope conformations, because in either envelope conformation one C–D bond is in and one is out of alignment with the p-orbital. However, since it is the trans labeled cation that exhibits the nonadditive isotope shift, it must be this isotopomer that perturbs the conformational equilibrium to favor the diequatorial placement of the deuterium atoms, which can only occur if the cyclopentyl cation has the twist shape (Scheme II). The cis dideuterated isotopomer leaves the equilibrium between twist conformers unperturbed (Scheme II) and therefore exhibits an additive isotope shift. Geminal dideuteration does not perturb the equilibrium for the twist form and would not for the envelope form either. Only when the equilibrium is perturbed is a reduced, nonadditive, NMR isotope shift observed for ^{19}F in the *p*-fluorophenyl group, because then the C–H(D) bonds are preferentially placed in equatorial positions where they are less strongly involved in hyperconjugation and can have less influence on the charge distribution in the π system.

The cyclopentyl cation examined here adopts the twist conformation, as does cyclopentanone.[6,10] Djerassi et al. have recently demonstrated a conformational isotope effect in cyclopentanone from variable-temperature circular dichroism spectra.[11] They estimate that the deuterium in twist cyclopentanone-*2-d* prefers the quasi-equatorial position by about 10 cal/mol. We anticipate at least an order of magnitude larger energetic effects in cations, based on the greater importance of hyperconjugative interactions. We are now investigating the temperature dependence of the nonadditivity of NMR isotope shifts, as well as further applications of the magnitude and additivity of isotope shifts as probes of conformation in carbocations and carbanions.

Acknowledgment. This work was supported by the National Science Foundation (CHE-8211125).

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Radical Anion of Bis(η^6-benzene)chromium[1]

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The orbitally degenerate benzene radical anion[2] has played a central role in the development of ESR of π-perimeter radicals,[3] and subtle details pertaining to the deviation of the *g* factor from the free-spin value,[4] the line widths in fluid solution,[5] and the related topic of Jahn–Teller instability remain a subject of investigation.[6] In the light of recent interest in the ESR of orbitally degenerate sandwich complexes,[7] the preparation of the unperturbed prototype bis(η^6-benzene)chromium radical anion appeared desirable. We now wish to report the characterization by ESR of a species obtained via reduction of $(\eta^6\text{-}C_6H_6)_2Cr$ (**1**) with potassium in dimethoxyethane (DME) in the presence of dicyclohexyl-18-crown-6, which we believe is the radical anion $\mathbf{1}^{-}\cdot$. During the course of the reduction of **1**, as evident from the appearance of ^{53}Cr satellite spectra, three different organochromium radicals were observed: initially the spectrum of $\mathbf{1}^{+}\cdot$, adventitiously present, prevails; upon contact with the potassium mirror it is replaced by the spectrum of the deprotonated species $(\eta^6\text{-}C_6H_6)(\eta^6\text{-}C_6H_5^-)Cr^+\cdot$ (**2**), which undergoes intramolecular interannular proton exchange.[8] Further contact with potassium and maintenance at ambient temperature yields $\mathbf{1}^{-}\cdot$. Contrary to binary sandwich complexes of anellated[9] and trimethylsilyl-substituted[10a] arenes, attempts to generate $\mathbf{1}^{-}\cdot$ electrochemically failed down to a potential of −3.3 V (vs. SCE; $n\text{-}Bu_4NClO_4$, DME).[10b] The ESR spectra recorded in fluid and rigid solutions are depicted in Figure 1, the parameters are collected in Table I.

Whereas in the case of $\mathbf{1}^{+}\cdot$ hyperfine splitting caused by 12 equivalent protons reflects a sixfold symmetry axis, the more complicated hyperfine pattern of $\mathbf{1}^{-}\cdot$ signalizes a reduction of symmetry. Analysis of this spectrum in terms of four sets of inequivalent protons led to a simulated trace which is in satisfactory agreement with the experimental spectrum. The line width of 0.7 G (minimum at −55 °C), which most likely contains contributions from the *g* and hyperfine anisotropies, precludes a more stringent dissection of the hyperfine pattern and its behavior under

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Table I. ESR Parameters for $(C_6H_6)_2Cr^{+\cdot}$ ($\mathbf{1}^{+\cdot}$), $(C_6H_6)_2Cr^{-\cdot}$ ($\mathbf{1}^{-\cdot}$), $(C_6H_6)(C_6H_5^-)Cr^{+\cdot}$ ($\mathbf{2}\cdot$), and Their Perdeuterated Derivatives

	fluid solution[a]			rigid solution[a]			
	$\langle g\rangle$	$a(^{53}Cr)$, G	$a(^1H,^2D)$, G	$g_\parallel$	$g_\perp$	$A_\parallel(^{53}Cr)$, G	$A_\perp(^{53}Cr)$, G
$\mathbf{1}^{+\cdot}$	1.9859[b]	18.0	3.48 (12 H)	2.0026[c]	1.9757	*d*	26.9
$\mathbf{1}^{+\cdot}$-d_{12}	1.9856[b]	17.9	0.55 (12 D)	2.0026[e]	1.9770	*d*	25.7
$\mathbf{1}^{-\cdot}$	1.9956[f]	14.5	7.75 (2 H) 4.65 (6 H) 1.57 (2 H) 1.00 (2 H)	1.9811[g]	2.0040	*d*	*d*
$\mathbf{1}^{-\cdot}$-d_{12}	1.9957[h]	14.63	*d*	1.9816[i]	2.0036	8.3	18.7
$\mathbf{2}\cdot$	1.9911[h]	17.65	*j*	1.9727[e]	2.0026	*d*	*d*
$\mathbf{2}\cdot$-d_{11}	1.9910[f]	17.67	*d*	1.9734[e]	2.0018	*d*	*d*

[a] Solvent, dimethoxyethane. [b] −30 °C. [c] −150 °C. [d] Not resolved. [e] −119 °C. [f] −57 °C. [g] −131 °C. [h] −47 °C. [i] −143 °C. [j] Reference 8.

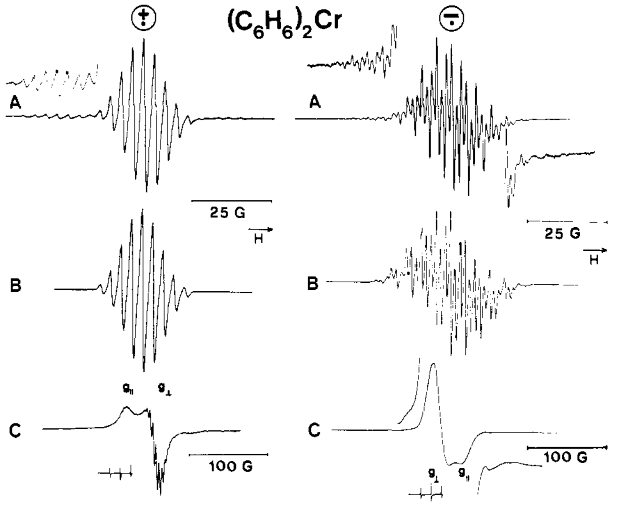
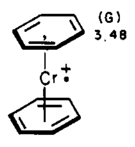


Figure 1. ESR spectra of the radical cation $\mathbf{1}^{+\cdot}$ and the radical anion $\mathbf{1}^{-\cdot}$ of bis(benzene)chromium in dimethoxyethane; counterion, K^+ [dicyclohexyl-18-crown-6]. (A) Liquid solution, 218 K. (B) Computer simulation, parameters see Table I. (C) Rigid solution, 138 K. External standard: Fremy salt $\langle g\rangle$ = 2.00565.

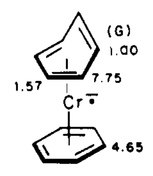
temperature variations. A second conspicuous feature of the spectra of $\mathbf{1}^{+\cdot}$ and $\mathbf{1}^{-\cdot}$ is the inverted relative magnitude of the g tensor components $g_\parallel$ and $g_\perp$ ($\mathbf{1}^{+\cdot}$, 2.0023 $\approx g_\parallel > g_\perp$; $\mathbf{1}^{-\cdot}$, 2.0023 $\approx g_\perp > g_\parallel$).

In the following, the g and hyperfine data for $\mathbf{1}^{-\cdot}$ will be rationalized on the basis of the electronic structure of **1** and put into perspective. The electronic configuration of **1** in the frontier orbital region is believed to be ...$(e_{2g},Md\delta)^4(a_{1g},Md\sigma)^2(e_{1g},Md\pi)^0(e_{2u},L\pi)^0$...[11a,14] ESR of $\mathbf{1}^{+\cdot}$, a Cr(d^5) complex with an orbitally nondegenerate ground state $^2A_{1g}$, was observed[12] shortly after the first preparation of the parent compound **1** and its features are well understood.[13,14] As to $\mathbf{1}^{-\cdot}$, classification either as a Cr(d^7) species or a Cr(d^6) complex with single occupancy of a ligand orbital depends on the energetic sequence of the orbitals e_{1g} (≈75% Cr $d_{xz,yz}$) and e_{2u} (ligand pπ). Whereas for $\mathbf{1}^{+\cdot}$ according to MS Xα calculations[11a] e_{1g} lies below e_{2u}, a reverse ordering of these levels is predicted for **1** and $\mathbf{1}^{-\cdot}$.[11b,15] Since the ground state $^2E_{2u}$ to the configuration $(e_{2g},Md\delta)^4(a_{1g},Md\sigma)^2(e_{2u},L\pi)^1$ is orbitally degenerate, Jahn–Teller activity is expected for $\mathbf{1}^{-\cdot}$.

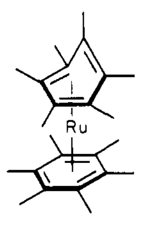
Contrary to orbitally degenerate or near degenerate d^7 metallocenes, which do not exhibit ESR signals in fluid solution and for which the Jahn–Teller distortion in the C_5H_5 rings is thought to remain dynamic,[7] in the present 19-VE bis(arene) chromium radical anion (VE = valence electron), the distortion appears to be static—at least on the ESR time scale in the accessible temperature range. In this context it is notable that static deviations from axial symmetry upon exceeding the 18-VE configuration have previously been observed for bis(arene)metal complexes in 19-VE as well as in 20-VE cases. Examples include [bis(hexamethylbenzene)iron(I)]$^{+\cdot}$, $\mathbf{3}^{+\cdot}$ (rhombic distortion, ESR evidence[16]), bis(hexamethylbenzene)ruthenium(0), **4** (η^6, η^4 coordination, η^4-arene nonplanar, X-ray crystallography[17]), and [bis(hexamethylbenzene)cobalt(I)]$^+$, **5** (slipped sandwich, X-ray crystallography[18]). In the present case of $\mathbf{1}^{-\cdot}$, the ESR results apart from pointing out loss of axial symmetry do not furnish unequivocal evidence for the geometric nature of the distortion. However, the hyperfine pattern for $\mathbf{1}^{-\cdot}$ would conform with a structure analogous to **4**. In this description of $\mathbf{1}^{-\cdot}$, the appearance of six equivalent protons would result from rapid rotation of the planar η^6-arene.[19] Fluxionality of the nonplanar η^4-arene, on the other hand, is likely to be a process of higher activation energy[20] such that coalescence cannot be reached on the ESR time scale and three pairs of inequivalent protons are observed for this ring. The large spread in the magnitudes of the respective hyperfine coupling constants is concordant with the single occupancy of a π-ligand orbital belonging to a formerly degenerate set. The ratio 7.75/1.57 for the coupling constants in the η^4-arene suggests that the symmetric rather than the antisymmetric component of the e_{2u} precursor set contributes to the singly occupied MO in $\mathbf{1}^{-\cdot}$. The large spectral width of 48.5 G is not necessarily in conflict with a π-radical description for $\mathbf{1}^{-\cdot}$ since widths of ≈25 G are characteristic for planar π-radicals only. In the case of $\mathbf{1}^{-\cdot}$, on the other hand, the parallel disposition of two π-perimeters allows for more extensive C(p$_\pi$)–H spin polarization leading to a greater span of the proton hyperfine pattern.[21] To explain the isotropic



$\mathbf{1}^{+\cdot}$



$\mathbf{1}^{-\cdot}$



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(21) Total width of the ESR spectrum of $(\eta\text{-}C_5H_5)Cr(\eta\text{-}C_7H_7)^{-\cdot}$, which is an isomer of $(\eta\text{-}C_6H_6)_2Cr^{-\cdot}$, amounts to 39.4 G: Elschenbroich, Ch.; Gerson, F.; Stohler, F. *J. Am. Chem. Soc.* **1973**, *95*, 6956–6961.

coupling to ^{53}Cr, which we observe for $\mathbf{1}^{-}\cdot$, $C(p_\pi)$–Cr(ns) spin polarization is to be inferred.

Turning to the g factors, it is noted that, as in the case of aromatic radicals,[22] for $\mathbf{1}^{-}\cdot$ the relation $g_\perp > g_\parallel$ applies. However, contrary to aromatic radicals, for the complex radical anion $\mathbf{1}^{-}\cdot$ $g_\perp$ rather than $g_\parallel$ approaches the free-spin value. Furthermore, $\Delta g = |g_\parallel - g_\perp|$ is considerably larger for $\mathbf{1}^{-}\cdot$ ($\Delta g = 0.022$) as compared to aromatic radicals ($\Delta g = 0.0005$). The larger g anisotropy Δg does not contradict the proposed π-ligand character of the singly occupied MO of $\mathbf{1}^{-}\cdot$ since it is via the contribution of the central metal atom to other MO's, which are connected to the singly occupied MO via spin orbit coupling and which may contain a higher metal contribution, that chromium can influence the magnitude of Δg. In view of the uncertainty about the nature of the distortion and the lack of a quantitative energy level scheme, attempts to interpret the numerical values of $g_\parallel$ and $g_\perp$ would be premature. However, a comparison of $\mathbf{1}^{-}\cdot$ with the isoelectronic iron complex $\mathbf{3}^{+}\cdot$ ($g_x = 2.086$, $g_y = 1.996$, $g_z = 1.865$[16]) seems appropriate. For both species, the g values display the same trend,[23] yet Δg is larger for $\mathbf{3}^{+}\cdot$ than for $\mathbf{1}^{-}\cdot$. This may be traced to larger metal contribution to the MO's of $\mathbf{3}^{+}\cdot$[24] as compared to corresponding orbitals of $\mathbf{1}^{-}\cdot$.

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Simple Method for Determination of Spin Coupling Networks in NMR Spectroscopy

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Investigations of molecules in liquids by NMR have relied to a considerable extent on the information present in spin–spin couplings. The couplings can contain information that is useful for conformational and structural analysis. To be able to utilize the information present in the couplings, the relevant signals must be observable and a determination of the coupling network—which nuclei are coupled to which—be made. While in some favorable cases the coupling network can be determined by inspection of the NMR data, in many instances there is either insufficient resolution or the connectivities are not obvious.

When the NMR spectrum is at least partially resolved assignments of which nuclei are coupled to which, neighbor spins, can be determined via selective decoupling or chemical shift correlation experiments.[1] Correlations between nuclei that are not coupled to one another but do share a common coupling partner, remote spins, can be performed via relay transfer[2] or multiple-quantum experiments.[3] For AX spin systems a procedure based on double-quantum filtering can be useful in the absence of resolution of either signal.[4] Each of these experimental approaches has distinct advantages and disadvantages and will not be discussed further.

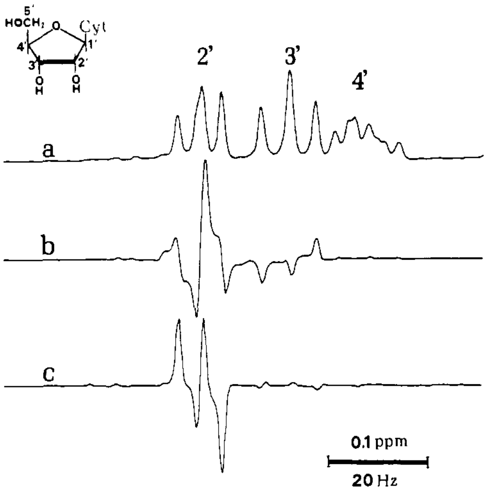

Figure 1. Normal proton spectrum of the 2′-, 3′-, and 4′-protons of cytidine (a), whose structure is also given. Fourier transform of the difference between the free induction decays obtained with and without selective decoupling of the 1′-proton during t_m followed by double-quantum filtering (b).[9] Fourier transform of the difference between the free induction decays obtained with and without selective saturation of the 1′-proton prior to double-quantum filtering.[9]

Multiple-quantum filters have been shown to be a useful technique for selective detection of nuclei with a particular number of coupling partners.[5] For example, experiments have been performed to detect only those protons coupled to two other protons.[5] Selective multiple-quantum filtering is also possible and allows determination of coupling networks in one-dimensional NMR experiments. The fundamental idea is to alter the generation of multiple-quantum coherence by means of selective irradiation of a single spin. The difference spectrum constructed by subtracting the spectrum obtained with selective irradiation from that obtained without allows direct identification of the coupling network to which the irradiated spin belongs.

One form of this technique is the identification of all of the neighbors of a particular spin. To obtain this information selective saturation of spin A is performed prior to double-quantum filtering. The saturation of A decreases the net generation of double-quantum coherence between A and each of its neighbors. The difference spectrum constructed between the spectrum obtained with and without saturation of A will contain signals only from spin A and its neighbors.[6] The multiplet patterns of the neighbor spins will correspond to the difference between the subspectra associated with the two polarizations of spin A.[7] The procedure for simulating such difference spectra has been discussed previously in the context of heteronuclear two-dimensional spectroscopy.[8]

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(7) The multiplet pattern that will be observed when degenerate nuclei are irradiated can be predicted in the limit of weak coupling by treating the system as AA′X. Selective saturation of the A and A′ spins leads to a difference spectrum corresponding to the difference between the subspectra associated with A and A′ being $\alpha\alpha$ and $\beta\beta$. Similar rules can be developed for other spin systems.

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