J. Am. Chem. Soc. **1983**, *105*, 6423-6426

Measurements of Molecular *g* Values, Magnetic Susceptibility Anisotropies, and Quadrupole Moments for the Acetylene–HCl Complex

S. G. Kukolich,*† W. G. Read,* J. A. Shea,* and E. J. Campbell*

Contribution from Noyes Chemical Laboratory, University of Illinois,
Urbana, Illinois 61801. *Received April 11, 1983*

Abstract: Rotational transitions for acetylene–HCl were measured in magnetic fields of 28 and 30 kG using a pulsed-nozzle, Fourier transform microwave spectrometer. Measured molecular *g* values are $g_{aa} = 0.0519$ (5), $g_{bb} = -0.0006$ (2), and $g_{cc} = 0.0025$ (2). Susceptibility anisotropies are $2\chi_{aa} - \chi_{bb} - \chi_{cc} = 0.08\ (4) \times 10^{-9}$ and $2\chi_{bb} - \chi_{cc} - \chi_{aa} = -1.14\ (8) \times 10^{-9}$ MHz/G^2. Molecular quadrupole moments for the complex are $Q_{aa} = -2.6$ (3), $Q_{bb} = 6.2$ (3), and $Q_{cc} = -3.7\ (3) \times 10^{-26}$ esu cm^2. We find that the molecular *g* value for acetylene is positive, $g_\perp = 0.044$ (1). The molecular quadrupole moment of acetylene is found to be $8.0\ (16) \times 10^{-26}$ esu cm^2 in good agreement with calculated values.

I. Introduction

Microwave rotational spectra for the acetylene–HCl complex were reported by Legon, Aldrich, and Flygare.[1] This is a planar T-shaped complex with bonding of the HCl proton to the π electrons of acetylene. A series of π-bonded complexes involving acetylene, ethylene, or cyclopropane bonded to HF, HCl, or HCN have been studied using the Flygare–Balle pulsed beam spectrometer system.[2,3] The spectrometer for Zeeman measurements on complexes was described earlier.[4,5] The present Zeeman measurements on acetylene–HCl were done primarily to obtain information on the electronic structure of acetylene. It was demonstrated in other work[6] that molecular Zeeman parameters for complexes could be accurately obtained from Zeeman parameters for the substituent monomers. The Zeeman parameters of interest here are molecular *g* values, magnetic susceptibility anisotropies, and molecular quadrupole moments. Measurements of the molecular Zeeman effect for a large number of stable molecules have been reported by Flygare and co-workers and other groups. Reviews of this earlier work have been published.[7] These measurements provide data on quadrupole moments for the charge distribution in molecules and both paramagnetic and diamagnetic contributions to magnetic susceptibility tensors.

Molecular *g* values, susceptibility anisotropies, and the molecular quadrupole moments were obtained from Zeeman measurements on the acetylene–HCl complex. These values for the complex are used with previously measured parameters for HCl[8] to obtain susceptibility anisotropies and molecular quadrupole moments for acetylene.

II. Experimental Section

A sensitive high-resolution Fourier transform microwave spectrometer was developed[2,3] for the study of weakly bound complexes. A similar spectrometer[4-6] was developed for Zeeman studies using a smaller cavity placed in a superconducting solenoid magnet. This spectrometer is described in reports on ArHF[4] and ArHCl.[5] In the present experiments the magnetic field is perpendicular to the microwave electric field so $\Delta M_F = \pm 1$ transitions are observed. The total angular momentum is $F = I_{Cl} + J$. A gas mixture of 2% HCl and 2% acetylene in argon at 1.5 atm pressure was prepared in a 1-L tank. The gas was pulsed into the microwave cavity using a modified Veeco PV-10 piezoelectric valve. Following the gas pulse a microwave pulse was sent into the cavity; this produced a molecular emission signal which was detected and amplified using a gated superheterodyne receiver. The time domain molecular emission signal was digitized, averaged, and Fourier transformed to obtain the frequency spectrum. Each frequency setting of the microwave oscillator gives an effective bandwidth of about 0.5 MHz so a number of spectra were taken in the region where lines are expected. Fourier transforms are obtained using an LSI-11 computer. Magnetic fields used in these experiments were 28 113 and 30 098 G. The Zeeman splitting of the $J = 0 \rightarrow 1$ transition of OCS was used to calibrate the field. Measured spectra for $\Delta M = \pm 1$, $J = 1 \rightarrow 2$ transitions in the acetylene–HCl complex are shown in Figure 1. Results of the measurements are given in Table I.

III. Data Analysis

The Hamiltonian used to analyze the data contains terms due to the rotational energy (A, B, C are rotational constants; D_J, D_{JK} are distortion constants), the molecular *g* values (g_{gg}), the magnetic susceptibility anisotropies ($\chi_{gg} - \bar{\chi}$), nuclear quadrupole coupling of ^{35}Cl (eQq_{gg}), and magnetic moment and shielding anisotropies ($\sigma_{gg} - \bar{\sigma}$) of ^{35}Cl. The Hamiltonian, $\mathcal{H}$, is given in eq 1.

$$\begin{aligned}\mathcal{H} = {} & AJ_a^{\,2} + BJ_b^{\,2} + CJ_c^{\,2} - D_J J^2(J+1)^2 - D_{JK}J(J+1)J_a^{\,2} - \\ & \mu_N J_z H \sum_g g_{gg}\langle J_g^{\,2}\rangle/[J(J+1)] - H^2[3J_z^{\,2} - J(J+1)]\sum_g(\chi_{gg} - \\ & \bar{\chi})\langle J_g^{\,2}\rangle/[(2J-1)(2J+3)J(J+1)] + \\ & [3(\mathbf{J}\cdot\mathbf{I})^2 + 3(\mathbf{J}\cdot\mathbf{I})/2 - \mathbf{J}^2\mathbf{I}^2]\sum_g eQq_{gg}\langle J_g^{\,2}\rangle/[2J(2J-1)I(2I - \\ & 1)\,(J+1)\,(2J+3)] - g_I\mu_N(1-\bar{\sigma})I_zH + 2g_I\mu_N I_z H[3J_z^{\,2} - \\ & J(J+1)]\sum_g(\sigma_{gg} - \bar{\sigma})\langle J_g^{\,2}\rangle/[(2J-1)(2J+3)J(J+1)] \quad (1)\end{aligned}$$

The sums are *g* are taken over the principal axes, $g = a, b, c$. The components of the angular momentum vector **J** are taken in the coordinate system with *z* along the applied magnetic field. No matrix elements off-diagonal in *J* are included in this analysis. Shifts in transition frequencies due to terms off-diagonal in *J* would be a few kilohertz or less.

The valus of B, C, D_{JK}, and eQq_{gg} used in the analysis of Zeeman data are determined by fitting zero-field $J = 1 \rightarrow 2$ transitions for acetylene–HCl. A and D_J were taken from original measurements. The values obtained from the original measurements on this complex give a good fit to six rotational transitions, including $J = 1 \rightarrow 2$ and $J = 2 \rightarrow 3$ transitions, but do not give the best possible fit to $J = 1 \rightarrow 2$ transitions alone. This is most likely due to centrifugal distortion effects. Since it is important in analysis of the Zeeman data to reproduce the zero-field lines as accurately as possible, only the $1_{01} \rightarrow 2_{02}$, $1_{11} \rightarrow 2_{12}$, and 1_{10}

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† Permanent address: Department of Chemistry, University of Arizona, Tucson, Arizona 85721.

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Table I. Measured and Calculated Transition Frequencies for $J = 1 \rightarrow 2$ Transitions in Acetylene-HCl[a]

K_p	$2 \cdot F$	$2 \cdot M_F$	$2 \cdot F'$	$2 \cdot M_F'$	field	measd	calcd	Δ
1	3	1	3	3	1	9407.274 (7)	9407.284	−0.001
1	3	−1	3	1	1	9407.498 (4)	9407.490	0.008
1	5	−5	7	−7	1	9407.778 (8)	9407.785	−0.007
1	5	5	7	7	1	9408.064 (5)	9408.071	−0.007
1	3	1	3	−1	1	9408.203 (9)	9408.199	0.004
1	3	−1	3	1	1	9408.294 (3)	9308.299	−0.005
1	3	−1	3	−3	1	9408.928 (5)	9408.934	−0.006
0	5	−5	3	−3	1	9573.929 (4)	9573.918	0.011
0	1	1	3	3	1	9574.341 (2)	9574.326	0.015
0	1	1	1	−1	1	9575.318 (3)	9575.301	0.018
0	1	1	3	3	1	9576.105 (4)	9576.092	0.013
0	1	−1	1	1	1	9576.515 (4)	9576.508	0.007
0	1	−1	3	−3	1	9576.723 (4)	9576.714	0.009
0	1	−1	1	1	1	9577.864 (5)	9577.872	−0.008
0	3	3	3	5	1	9578.064 (2)	9578.062	0.003
0	1	−1	3	−3	1	9579.009 (3)	9579.003	0.006
0	5	5	7	7	1	9579.567 (3)	9579.567	0.000
0	5	−5	7	−7	1	9579.606 (3)	9579.610	−0.004
0	1	1	1	−1	1	9580.854 (1)	9580.850	0.004
0	3	3	5	5	1	9581.066 (2)	9581.073	−0.007
0	3	−3	5	−5	1	9581.156 (3)	9581.160	−0.004
0	3	3	1	1	1	9582.481 (2)	9582.482	−0.001
−1	3	−1	5	1	1	9752.374 (3)	9752.373	0.001
−1	5	−5	7	−7	1	9752.715 (1)	9752.722	−0.007
−1	5	5	7	7	1	9753.063 (3)	9753.075	−0.012
−1	3	1	3	−1	1	9753.270 (4)	9753.266	0.004
−1	3	−1	3	1	1	9753.435 (9)	9753.435	0.000
−1	3	−1	5	−3	1	9753.986 (3)	9753.992	−0.006
1	3	1	3	3	2	9407.296 (3)	9407.303	−0.007
1	3	−1	3	1	2	9407.543 (3)	9407.532	0.011
1	5	−5	7	−7	2	9407.768 (5)	9407.773	−0.005
1	5	5	7	7	2	9408.067 (6)	9408.080	−0.013
1	3	1	3	−1	2	9408.176 (1)	9408.174	0.002
1	3	−1	3	−3	2	9408.940 (4)	9408.944	−0.004
0	1	1	3	3	2	9574.208 (5)	9574.195	0.013
0	1	1	1	−1	2	9575.175 (2)	9575.160	0.016
0	1	1	3	3	2	9575.929 (2)	9575.912	0.017
0	1	−1	1	1	2	9576.447 (2)	9576.441	0.006
0	1	−1	3	−3	2	9576.714 (1)	9576.704	0.010
0	1	−1	1	1	2	9577.910 (4)	9577.916	−0.006
0	3	3	5	5	2	9578.008 (4)	9578.002	0.006
0	1	−1	3	−3	2	9578.944 (4)	9578.934	0.010
0	5	5	7	7	2	9579.571 (3)	9579.565	0.006
0	5	−5	7	−7	2	9579.604 (4)	9579.612	−0.008
0	1	1	1	−1	2	9580.828 (4)	9580.827	0.001
0	3	3	5	5	2	9581.118 (4)	9581.130	−0.012
0	3	−3	5	−5	2	9581.214 (4)	9581.222	−0.008
0	3	−3	1	−1	2	9581.577 (3)	9581.564	0.013
0	1	1	3	3	2	9581.782 (5)	9581.795	−0.013
0	3	3	1	1	2	9582.488 (2)	9582.488	0.000
−1	3	1	5	3	2	9752.372 (3)	9752.371	0.001
−1	3	−1	5	1	2	9752.429 (3)	9752.426	0.003
−1	5	−5	7	−7	2	9752.701 (6)	9752.712	−0.011
−1	5	5	7	7	2	9753.073 (6)	9753.090	−0.017
−1	3	1	3	−1	2	9753.239 (2)	9753.236	0.003
−1	3	−1	3	1	2	9753.421 (8)	9753.430	−0.009
−1	3	−1	5	−3	2	9754.005 (4)	9754.010	−0.005

[a] The $1_{11} \rightarrow 2_{12}$, $1_{01} \rightarrow 2_{02}$ and $1_{10} \rightarrow 2_{11}$ transitions are denoted by $K_p = 1, 0$, and -1, respectively. Field 1 is 28 113 G and field 2 is 30 098 G. Calculated values are obtained from a least-squares fit to the data using variable parameters listed in Table II. Frequencies are in MHz, experimental uncertainties given after measured frequencies.

$\rightarrow 2_{11}$ sets of transitions were fit to obtain rotational constants, distortion constants, and quadrupole coupling strengths which accurately give the positions of zero-field $J = 1 \rightarrow 2$ transitions. New measurements at zero field reproduced the original observed frequencies to within a few kilohertz with the exception of a typographical error on line 5 of Table I in ref 1. That observed frequency should read 9579.586 MHz. A set of parameters which give accurate values for $J = 1 \rightarrow 2$ transitions is $A = 34\,671$ MHz, $B = 2481.082$ MHz, $C = 2308.602$ MHz, $D_J = 7.9$ kHz, $D_{JK} = 501$ kHz, $eQq_{aa} = -54.34$ MHz, $eQq_{bb} - eQq_{cc} = 0.60$ MHz. These parameters are fixed at the given values for the least-squares fit to the Zeeman data. We can write the susceptibility anisotropy term in the Hamiltonian in terms of the two indepedent susceptibility anisotropies $2\chi_{aa} - \chi_{bb} - \chi_{cc}$ and $2\chi_{bb} - \chi_{aa} - \chi_{cc}$ and these are used as adjustable parameters. The other adjustable parameters are the molecular g values g_{aa}, g_{bb}, and g_{cc}. The product $g_I(1 - \bar{\sigma})$ for ^{35}Cl was fixed at 0.547 48 and the nuclear shielding anisotropy $2\sigma_{aa} - \sigma_{bb} - \sigma_{cc}$ was fixed at 600 ppm. These values were obtained from measurements on HCl.[8] No data are available for $2\sigma_{bb} - \sigma_{aa} - \sigma_{cc}$ since it is zero for HCl. We expect it to be very small in the complex, so we set it equal to zero.

The measured transition frequencies and the transition frequencies calculated using a nonlinear least-squares fitting program are given in Table I. All listed transitions are fit to within 18 kHz or better. Since the quantum numbers F and M_F are half-integer, we list $2 \cdot F$ and $2 \cdot M_F$ in the table.

The values for the adjustable parameters obtained using the fitting program are listed in Table II.

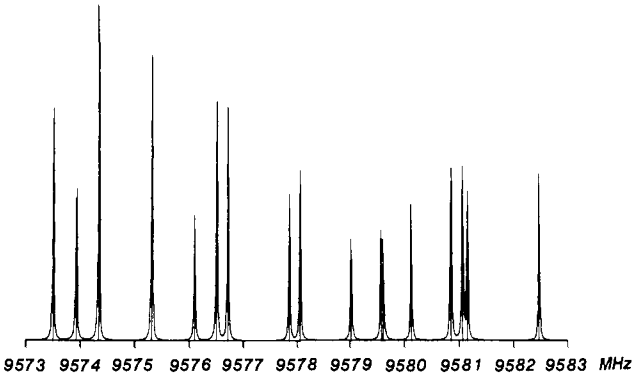

Figure 1. Plot of the measured transitions for the $1_{01} \to 2_{02}$ transition of acetylene–HCl at 28 113 G. This is a simulated spectrum constructed from measured center frequencies. Relative intensities are only approximate.

Table II. Molecular Parameters Obtained from a Least-Square Fit to the Data in Table I

parameter	value
g_{aa}	0.051 917 ± 0.000 51
g_{bb}	−0.000 55 ± 0.000 17
g_{cc}	0.002 54 ± 0.000 17
$2\chi_{aa} - \chi_{bb} - \chi_{cc}$	(0.08 ± 0.04) × 10^{-9} MHz/G^2
$2\chi_{bb} - \chi_{aa} - \chi_{cc}$	(−1.14 ± 0.08) × 10^{-9} MHz/G^2

Table III. Molecular Quadrupole Moments and Total Susceptibilities χ_{gg} for the Acetylene-HCl Complex ($\bar{\chi}$ = −4.42 (0.15) × 10^{-29} erg/G^2)

parameter	value	units
Q_{aa}	−2.58 (19)	×10^{-26} esu cm^2
Q_{bb}	6.25 (29)	
Q_{cc}	−3.67 (31)	
χ_{aa}	−4.40 (15)	×10^{-29} erg/G^2
χ_{bb}	−4,67 (15)	
χ_{cc}	−4.18 (15)	

The molecular quadrupole moments for the complex are obtained using the relation

$$Q_{zz} = -\frac{|e|\hbar}{8\pi M}\left[\frac{2g_{zz}}{G_{zz}} - \frac{g_{xx}}{G_{xx}} - \frac{g_{yy}}{G_{yy}}\right] - \frac{2mc^2}{|e|}(2\chi_{zz} - \chi_{xx} - \chi_{yy}) \tag{2}$$

where M is the atomic mass unit (1.6604 × 10^{-24} g), m is the electron mass, and G_{zz} is the z-axis rotational constant. The rotational constant used to determine quadrupole moments were from the original measurements[1] on this complex. The quadrupole moments for the complex and magnetic susceptibility tensor components are listed in Table III. The average value of the magnetic susceptibility is obtained by combining results of bulk measurements for acetylene[9] and HCl.[10] The projection equations were used successfully for susceptibility anisotropies[6] so we expect that the bulk susceptibility for the complex will be the sum of values for the individual molecules. We note that when molecular Zeeman measurements are made on a molecule with large quadrupole coupling, the signs as well as magnitudes of the molecular g values are directly obtained.

IV. Molecular *g* Values, Quadrupole Moments, and Susceptibilities for Acetylene

Previous work[6] on N_2HF, OCHF, and OCHCl has indicated that molecular g values, quadrupole moments, and susceptibility anisotropies for complexes can be reliably obtained from values for the individual molecules using projection equations. These projection equations represent a superposition of monomer values with corrections for bending vibrations and effects of translation of the center of mass.[11] Since the quadrupole moment and magnetic susceptibility anisotropy of HCl are known,[6] we can use the projection equations to obtain molecular properties for acetylene. The projection equations are given in a form suitable for asymmetric tops in a recent paper on ethylene–HCl.[12] The vibrational averaging factor $\langle 1 - 1.5 \sin^2 \theta_b \rangle$ for HCl in the complex is 0.8037 and was obtained from the measured ^{35}Cl quadrupole coupling strength. For the product $g_{bb}I_{bb}$ the appropriate vibrational averaging factor is $\langle 1 - 0.5 \sin^2 \theta_b \rangle = 0.9346$. For the dipole moment we use the factor $\cos \theta_b = 0.9323$.

Table IV. Molecular Parameters for Acetylene Obtained by Subtracting Contributions due to HCl from Values Measured for the Acetylene-HCl Complex

parameter	value	units
$g_\perp$	0.0442 (9)	
$\chi_\parallel - \chi_\perp$	−1.02 (35)	×10^{-9} MHz/G^2
$Q_\parallel$	8.0 (16)	×10^{-26} esu cm^2

Values for $g_{xx}I_{xx}$, susceptibility anisotropies, and quadrupole moments for acetylene were obtained by subtracting values for HCl from values for the complex. A value for $g_\perp$ of acetylene can be obtained using either $g_{aa}I_{aa}$ or $g_{aa}I_{cc}$ of the complex. The most precise value is obtained using $g_{aa}I_{aa}$(complex) = $g_\perp I$(acetylene) + $g_\perp I$(HCl)$\langle \sin^2 \theta_b \rangle$. This yields the value $g_\perp$(acetylene) = 0.044 (1). The g_{aa} values will also be much less dependent on the effective HCl dipole moment. The value measured by Cederberg et al.[13] is $g_\perp = -0.04903$ (4). It was noted by Hartford et. al.[14] that the negative sign for this g value leads to a serious discrepancy for the molecular quadrupole moment, but if the sign is positive, the resulting molecular quadrupole moment is in agreement with calculated values. The present measurements support a positive sign for the g value of acetylene. We believe that the magnitude given by Cederberg is probably correct but that the sign is positive with $g_\perp = 0.04903$. Parameters obtained for acetylene are given in Table IV.

The relationship of the measured values of $2\chi_{aa} - \chi_{bb} - \chi_{cc}$ and $2\chi_{bb} - \chi_{aa} - \chi_{cc}$ for the complex to the susceptibility anisotropy $\chi_\parallel - \chi_\perp$ of acetylene will depend on the vibrational angle between the acetylene axis and the a axis of the complex. If these susceptibility values for the complex were used, incomplete treatment of vibrational averaging effects would result in errors in the susceptibility for acetylene. However, the relation of the susceptibility anisotropy contribution $(2\chi_{cc} - \chi_{aa} - \chi_{bb})$ complex to $\chi_\perp - \chi_\parallel$ for acetylene will not depend on the vibrational angle, so we use this component to get $\chi_\parallel - \chi_\perp = -1.02$ (35) × 10^{-9} MHz/G^2 for acetylene. This value is in very good agreement with the theoretical value[15] of −0.89 × 10^{-9} MHz/G^2 and the value of −1.13 × 10^{-9} MHz/G^2 obtained from the local group model of Schmalz, Norris, and Flygare.[16]

The molecular quadrupole moment of acetylene can be calculated using:

$$Q = \frac{|e|\hbar}{4\pi m}\frac{g_\perp}{B} - \frac{4mc^2}{|e|}(\chi_\parallel - \chi_\perp)$$

We use the magnitude of $g_\perp$ obtained by Cederberg et al.[13] and the positive sign so $g_\perp = 0.049$. For $\chi_\parallel - \chi_\perp = -1.02$ (35) we have Q(acetylene) = 8.0 (16) × 10^{-26} esu cm^2. We can also calculate Q(acetylene) from the measured value of Q_{cc} of the complex, but this may be less reliable because the contribution

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to this quadrupole moment due to HCl depends on the effective dipole moment of HCl in the complex. The Q_{cc} components will be less dependent on the vibrational angle of acetylene. Using this second method, we get Q(acetylene) = 7.6×10^{-26} esu cm^2. These results are in reasonably good agreement with calculated values[15,17] of Q(acetylene) = 7.34 or 7.2×10^{-26} esu cm^2.

Acknowledgment. The support of the National Science Foundation and the University of Illinois School of Chemical Sciences is gratefully acknowledged. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the Americal Chemical Society, for partial support of this research. One of us (S.G.K.) thanks the University of Illinois Research Board for support. We wish to thank Peter Aldrich for the use of his computer programs for part of the data analysis.

Registry No. Acetylene-hydrochloric acid, 52218-20-9.

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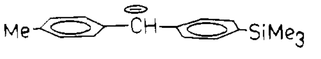
Rotational Barriers in Diphenylmethyl Anions Stabilized by Trimethylsilyl and Tricarbonylchromium(0) Moieties

Siden Top,[†] Gérard Jaouen,*[†] Brian G. Sayer,[‡] and Michael J. McGlinchey*[‡]

Contribution from the École Nationale Supérieure de Chimie, 75231 Paris Cedex 05, France, and the Department of Chemistry, McMaster University, Hamilton, Ontario, Canada L8S 4M1.
Received March 15, 1983

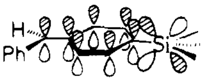
Abstract: A series of diphenylmethyl anions has been prepared in which the phenyl rings bear π-bonded $Cr(CO)_3$ groups and/or a trimethylsilyl moiety. Variable-temperature ^{13}C NMR studies on these compounds have allowed the evaluation of the barriers to phenyl rotation. It is shown that a π-bonded $Cr(CO)_3$ group stabilizes the negative charge much more efficiently than does a p-$SiMe_3$ functionality. However, when the Me_3Si substituent is bonded directly to the α-carbon atom, the charge preferentially resides on the silicon, allowing the (π-$Cr(CO)_3$–C_6H_5) groups to rotate apparently unhindered.

The delocalization of negative charge from carbanionic centers is of paramount importance in many reaction sequences.[1,2] It is well established that adjacent carbonyl functions,[3] cyano[4] or nitro[5] groups, etc., very significantly stabilize carbanions such that the carbon formally bearing the negative charge is probably best regarded as being in an sp^2-hybridized, trigonal-planar environment. In contrast, carbanions lacking neighboring groups that facilitate charge dispersal are presumably pyramidal and mimic amines in their behavior.



1

The interactions of trimethylsilyl groups with carbanions have been the subject of some debate;[6] however, it was quickly recognized that such moieties, when directly bonded to the carbanionic center, lead to marked stabilization of the anion.[7] A quantitative assessment of the stabilizing effect of a remote trimethylsilyl substituent was attempted via an ingenious NMR experiment described recently.[8] In this study, the authors used DNMR to show conclusively that in the 4-methyl-4′-(trimethylsilyl)diphenylmethyl anion, **1**, the ortho carbons (and protons) of the two phenyl rings are equilibrated via phenyl rotation at quite different rates. Indeed, the 4-methylphenyl ring is rotating faster than the 4′-(trimethylsilyl)phenyl moiety by a factor of 200 at 255 K. These data allowed the evaluation of the rotational barriers, which are ~10 kcal mol^{-1} for the methyl-substituted ring and ~12.7 kcal mol^{-1} for the silylated ring. The conclusions drawn were that the anion was essentially coplanar and that, assuming that the barrier was determined exclusively by the strength of π bonding to the benzylic carbon, the π interaction with the silylated ring was enhanced relative to that in the other ring. One possible rationale would involve pπ–dπ overlap, as in **2**, between the arene ring and a vacant d orbital on silicon.[6] Others prefer to attribute this stabilization to a polarization effect or to hyperconjugation.[7]



2

For some years now we have concerned ourselves with the capacity of the tricarbonylchromium(0) moiety to stabilize anions[9] or cations[10] at the benzylic position. Indeed, we have demonstrated the viability of a number of reactions for the (arene)$Cr(CO)_3$ complexes not readily achieved for the noncomplexed arenes.[11,12] We now report the syntheses and variable-temperature NMR spectra of diphenylmethyl anions bearing trimethylsilyl and/or tricarbonylchromium(0) substituents; this allows a direct comparison of the relative stabilizing effects of the two moieties.

[†] École Nationale Supérieure de Chimie.
[‡] McMaster University.

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