The Influence of Restricted Rotation on the Spectral Properties of Acetophenonetricarbonylchromium Complexes

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Abstract

The tricarbonylchromium complexes of the following derivatives of acetophenone have been prepared: the 2,4-, 2,5- and 3,4-dimethyl-; 2,4,5- and 2,4,6-trimethyl-; 2,3,4,5-tetramethyl-; 2,3,4,5,6-pentamethyl-; 2,6-dimethyl-4-t-butyl-; 2,4,6-triisopropyl-; 4-cyclohexyl-; 2,5-, 2,6-, 3,4- and 3,5-dimethoxy-; and 2,3,4-, 2,4,6- and 3,4,5-trimethoxyacetophenone. Preparative, analytical, IR, UV–Vis and PMR spectral data are presented. The extent to which steric hindrance influences the color and spectral properties of these complexes is discussed. Complexes containing 2,6-disubstitution are yellow whereas compounds containing other substitution patterns are orange to red. The 4-cyclohexylacetophenone complex gives an unusually simple first-order proton spectrum that allows geminal, axial and equatorial coupling constants to be determined.

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Introduction

Few derivatives of acetophenonetricarbonylchromium have been prepared and studied [1]. The parent [2], monomethyl [3] and monoethyl together with a few monoalkyl [4] derivatives are known along with several methoxy and hydroxy derivatives [4, 5]. We were interested in studying the influence of steric factors in arenetricarbonylchromium complexes and in the present paper the synthesis and spectral data for a number of new alkylated and methoxylated derivatives (Table 1) are reported.

Experimental

The syntheses of the complexes were performed using a modification of the previously reported procedure [6] which achieves high conversion in relatively short reaction times by the addition of a small percentage (5–10%) of tetrahydrofuran to the principal

TABLE 1. Reaction of arenes with 4.0 g (18.2 mmol) of $Cr(CO)_6$ to give the corresponding η^6-arenetricarbonylchromium complexes

No.	Arene in (Arene)$Cr(CO)_3$	Arene (mmol)	Reflux time (h)	Yield (g (%))	Melting point (°C)	Color
I	2,4-Dimethylacetophenone	17.24	11	0.28(6)	86–87	orange
II	2,5-Dimethylacetophenone	3.32	11	0.10(10)	47–48	orange
III	3,4-Dimethylacetophenone	16.04	11	0.14(3)	57–59	orange
IV	2,4,5-Trimethylacetophenone	4.63	12	1.30(94)	75.5–78.5	orange
V	2,4,6-Trimethylacetophenone	4.40	12	1.10(84)	130–133	yellow
VI	2,3,5,6-Tetramethylacetophenone	3.57	11	0.80(72)	89–92	yellow
VII	2,3,4,5,6-Pentamethylacetophenone	3.09	11	0.80(79)	138–140	yellow
VIII	2,4,6-Triisopropylacetophenone	2.17	12	0.60(72)	97–98	yellow
IX	4-Cyclohexylacetophenone	2.49	11	0.24(28)	105	orange
X	2,6-Dimethyl-4-t-butylacetophenone	2.60	11	0.60(68)	114–116	yellow
XI	2,5-Dimethoxyacetophenone	5.68	12	0.21(12)	101	orange
XII	2,6-Dimethoxyacetophenone	2.80	12	0.30(33)	116–118	yellow
XIII	3,4-Dimethoxyacetophenone	2.83	11	0.15(17)	122–124	orange
XIV	3,5-Dimethoxyacetophenone	5.55	11	0.22(12)	121–122	orange
XV	2,3,4-Trimethoxyacetophenone	6.44	11	0.13(6)	90–92	orange/yellow
XVI	2,4,6-Trimethoxyacetophenone	3.79	11	0.30(23)	159–160	yellow
XVII	3,4,5-Trimethoxyacetophenone	2.41	11	0.35(42)	96	orange

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solvent di-n-butyl ether rather than the previously reported 20%. This has the effect of increasing the reaction temperature, thereby lowering the reaction

$$\text{Arene} + \text{Cr(CO)}_6 \xrightarrow[(\text{n-Bu})_2\text{O}]{\text{THF}} (\text{Arene})\text{Cr(CO)}_3 + 3\text{CO}\uparrow$$

time, without significantly affecting yields. Since the THF also removes the subliming $Cr(CO)_6$ from the condenser more effectively than di-n-butyl ether, washing most of it back into the flask, if the percentage of THF drops below 5%, hexacarbonylchromium begins to accumulate excessively in the reflux condenser. In addition, the THF apparently has a catalytic effect on the reaction of this carbonyl with arenes, perhaps by forming an unstable intermediate complex $(THF)_nCr(CO)_{6-n}$.

The 2,6-, 3,4-, 3,5-dimethoxy-, 2,3,4- and 3,4,5-trimethoxyacetophenones were purchased from Aldrich Chemical Company; all other arenes were purchased from Lancaster Synthesis. Hexacarbonylchromium was purchased from Pressure Chemical Company. A typical procedure is presented below.

2,4,5-Trimethylacetophenonecarbonylchromium (IV)

Hexacarbonylchromium (4.00 g, 18.2 mmol) and 2,4,5-trimethylacetophenone (0.75 g, 4.63 mmol) were heated at reflux under nitrogen in a mixture of di-n-butyl ether (100 ml) and tetrahydrofuran (10 ml) for 12 h. The yellow/green solution was cooled on ice, filtered through Kieselguhr and the solvents evaporated under reduced pressure. The residue, an orange oil, was chromatographed on a 30 cm × 3 cm column of neutral alumina. Elution with petroleum ether (boiling point 40–60 °C) yielded some unreacted arene. Further elution with ether/petroleum ether (1:1) gave 2,4,5-trimethylacetophenonetricarbonylchromium (1.30 g, 94%). Samples for microanalysis were crystallized twice more from methylene chloride/petroleum ether.

Most of the complexes are somewhat sensitive to light, so flasks and other glassware were covered with aluminum foil during the workup procedure. As all of the complexes are stable in the workup solvents for a few minutes, there was no need to do the workup procedure under anaerobic conditions.

The other complexes listed in Table 1 were prepared and purified in a similar manner. Yields quoted are for samples after chromatography or after the final recrystallization if chromatography was not required in the workup procedure. In some cases additional solvent removal and cooling to −50 °C was necessary to aid precipitation.

Complexes containing 2,6-disubstitution were yellow in color and were generally easier to prepare, purify and gave higher yields than complexes which did not contain bis-*ortho* substitution. These latter complexes were orange or red and all required column chromatography before analytically pure samples could be obtained. The yields of these compounds were also considerably lower and crystallization significantly more difficult than in bis-*ortho*-substituted (yellow) cases.

Ultraviolet–visible spectra were obtained on a Perkin-Elmer Lambda 3B spectrometer in isopropyl alcohol ($\lambda < 270$ nm) and in chloroform ($\lambda > 270$ nm). Infrared spectra were determined in cyclohexane using a Perkin-Elmer 983 spectrometer. NMR spectra were determined in $CDCl_3$ with TMS as internal standard on either a Bruker WH400 at ambient temperature or a Varian EM360A. Analytical data are reported in Table 2 and spectral data in Tables 3–5.

TABLE 2. Microanalytical data for complexes I–XVII

No.	Calculated (%)		Found (%)	
	C	H	C	H
I	54.93	4.23	55.15	4.39
II	54.93	4.23	55.51	4.17
III	54.93	4.23	54.90	3.98
IV	56.38	4.70	56.29	4.72
V	56.38	4.70	56.52	4.61
VI	57.69	5.13	57.66	4.94
VII	58.90	5.52	59.00	5.73
VIII	62.82	6.81	62.31	6.71
IX	60.36	5.33	60.47	5.35
X	60.00	5.88	59.90	5.81
XI	49.36	3.80	49.60	4.07
XII	49.36	3.80	49.53	3.60
XIII	49.36	3.80	49.32	3.32
XIV	49.36	3.80	48.91	3.89
XV	48.55	4.05	48.58	3.81
XVI	48.55	4.05	48.51	4.25
XVII	48.55	4.05	48.68	3.85

Results and Discussion

Ultraviolet Spectra

UV–Vis spectral data are reported in Table 3. An interpretation of these spectra has been proposed [7] in which the maximum at ~210 nm is due to the arene ligand while the band at ~320 nm is assigned as a chromium to carbonyl charge transfer band (CTB) and the band at longer wavelength (~410 nm) is interpreted as a chromium to arene CTB. Their assignments as charge transfer bands were based on the relative invariance in position of the 320 nm band, while the longer wavelength band showed shifts in the absorption maximum as the substituents on the arene ring were varied. These shifts were roughly correlated with the electron-donating (or accepting) properties of the substituents.

TABLE 3. Ultraviolet–Visible and metal–carbonyl infrared spectra (with force constants) for acetophenone complexes **I–XVII**

No.	Substituent(s)	UV–Vis wavelength (nm) (ϵ_{max})	IR ν(CO) (cm^{-1})	Force constant $k \times 10^5$ (dynes/cm)
I	2,4-Me_2	210(23600), 324(10100), 404(2600)	1976, 1916, 1910	15.10
II	2,5-Me_2	210(19500), 324(10100), 407(3000)	1976, 1914, 1907	15.08
III	3,4-Me_2	212(22400), 328(9500), 417(3200)	1978, 1919, 1907	15.12
IV	2,4,5-Me_3	212(22200), 325(8900), 405(2600)	1971, 1910, 1902	15.01
V	2,4,6-Me_3	209(22000), 324(9300)	1966, 1903, 1895	14.91
VI	2,3,5,6-Me_4	212(16600), 325(8300)	1962, 1896, 1888	14.82
VII	2,3,4,5,6-Me_5	216(16300), 323(8800)	1958, 1887	14.75
VIII	2,4,6-(i-Pr)$_3$	214(20800), 320(10400)	1962, 1896, 1889	14.82
IX	4-cyclohexyl	212(17300), 318(8600), 415(2500)	1979, 1921, 1911	15.15
X	2,6-Me_2, 4-t-Bu	214(22200), 324(8900)	1963, 1895	14.85
XI	2,5-$(OMe)_2$	208(17200), 318(8500), 407(5500)	1976, 1910	15.08
XII	2,6-$(OMe)_2$	212(14800), 318(7400)	1970, 1898	14.92
XIII	3,4-$(OMe)_2$	206(27400), 326(7500), 417(2900)	1975, 1913, 1903	15.05
XIV	3,5-$(OMe)_2$	206(22000), 319(6700), 418(3900)	1976, 1912, 1904	15.06
XV	2,3,4-$(OMe)_3$	206(27900), 328(7000), 406(2500)	1977, 1917, 1904	15.09
XVI	2,4,6-$(OMe)_3$	209(22000), 318(9300)	1965, 1893, 1888	14.82
XVII	3,4,5-$(OMe)_3$	206(19500), 324(4900), 424(2600)	1968, 1897	14.90

TABLE 4. ^{1}H NMR Spectra (δ from TMS in CDCl) for alkylacetophenone complexes **I–X** and methoxyacetophenone complexes **XI–XVII** (coupling constants in Hz)

No.	(CO)*Me*	Aromatic protons	Alkyl protons
I	2.472	4.913 (3-H, d, J = 1.0) 4.982 (5-H, d of d) 5.890 (6-H, d, J = 6.3)	2.265 (2-Me, s) 2.422 (4-Me, s)
II	2.517	5.055 (3-H, d, J = 6.5) 5.455 (4-H, d of d) 5.703 (6-H, d, J = 1.3)	2.190 (2-Me, s) 2.340 (5-Me, s)
III	2.431	5.951 (2-H, d, J = 1.3) 5.171 (5-H, d, J = 6.2) 5.791 (6-H, d of d)	2.208 (3-Me, s) 2.279 (4-Me, s)
IV	2.502	5.016 (3-H, s) 5.883 (6-H, s)	2.158 (2-Me, s) 2.353 (4-Me, s) 2.265 (5-Me, s)
V	2.579	4.833 (3,5-H, s)	2.182 (2,6-di-Me, s) 2.203 (4-Me, s)
VI	2.639	5.408 (4-H, s)	2.071 (2,6-di-Me, s) 2.134 (3,5-di-Me, s)
VII	2.632		2.130 (3,5-di-Me, s) 2.153 (2,6-di-Me, s) 2.291 (4-Me, s)
VIII	2.676	5.061 (3,5-H, s)	1.199 (4-CH(CH_3)$_2$, d, J = 6.7) 1.260[a] (2,6-CH(CH_3)$_2$, d, J = 6.7) 1.361[a] (2,6-CH(CH_3)$_2$, d, J = 6.7) 2.472 (2,6-C*H*(CH_3)$_2$, m, J = 6.7) 2.691 (4-C*H*(CH_3)$_2$, m, J = 6.7)

(continued)

TABLE 4. *(continued)*

No.	(CO)*Me*	Aromatic protons	Alkyl protons
IX	2.376	5.134 (3,5-H, d) 5.96 (2,6-H, d, J = 6.9)	1.136 ($H_{4'ax}$, q of t, $J_{ax,ax}$ = 12.8, J_{gem} = 12.8, $J_{ax,eq}$ = 3.6) 1.236 ($H_{2'ax}$, q of d, $J_{ax,ax}$ = 12.8, J_{gem} = 12.3, $J_{ax,eq}$ = 3.0) 1.342 ($H_{3'ax}$, q of t, $J_{ax,ax}$ = 12.8, J_{gem} = 12.8, $J_{ax,eq}$ = 3.2) 1.699 ($H_{4'eq}$, broad d, J_{gem} = 13.1) 1.802 ($H_{3'eq}$, d of t, broadened, $J_{3',1'}$ = 2.9, J_{gem} = 13.0) 1.898 ($H_{2'eq}$, broad d, J_{gem} = 12.7) 2.250 ($H_{1'}$, t of t, $J_{1',2'ax}$ = 11.6, $J_{1',2'eq}$ = 3.1)
X	2.617	5.012 (3,5-H, s)	1.309 (4-t-Bu, s) 2.193 (2,6-di-Me, s)
			Methoxy substituents (position)
XI	2.562	5.010 (3-H, d, J = 7.0) 5.622 (4-H, d of d) 5.938 (6-H, d, J = 1.8)	3.628 (2-OMe, s) 3.818 (5-OMe, s)
XII	2.656	4.773 (3,5-H, d, J = 6.8) 5.634 (4-H, t, J = 6.8)	3.780 (2,6-di-OMe, s)
XIII	2.420	5.220 (5-H, d, J = 7.0) 5.769 (6-H, d, J = 7.0) 6.022 (2-H, s)	3.833 (4-OMe, s) 3.868 (3-OMe, s)
XIV	2.497	5.253 (2,6-H, s) 5.260 (4-H, s)	3.762 (3,5-di-OMe, s)
XV	2.567	4.911 (5-H, d, J = 7.2) 6.034 (6-H, d)	3.887 (4-OMe, s) 4.019 (3-OMe, s) 3.925 (2-OMe, s)
XVI	2.575	4.862 (3,5-H, s)	3.792 (2,6-di-OMe, s) 3.792 (4-OMe, s)
XVII	2.528	5.248 (2,6-H, s)	3.910 (3,5-di-OMe, s) 3.935 (4-OMe, s)

[a] Diastereotopic.

TABLE 5. Effects of increasing the number of *ortho*-substituents on the UV–Vis spectra of acetophenone complexes[a]

Band (nm)	No. of groups *ortho*	Substituent(s)	
		Alkyl λ_{max} (ϵ_{max})	Methoxy λ_{max} (ϵ_{max})
200	0	212(19800)	206(23000)
	1	211(21800)	207(22600)
	2	213(19600)	210(18400)
300	0	323(9000)	323(6400)
	1	324(9700)	323(7800)
	2	323(9100)	318(8400)
400	0	416(2800)	420(3100)
	1	405(2700)	406(4000)
	2	[b]	[b]

[a] Data are mean values from Table 3. [b] No band observed.

In our system, the shortest wavelength band – the arene transition – shifts from an average of 212 nm for the alkylacetophenones to 207 nm for methoxy derivatives. Although the observed shifts are small, non-2,6-disubstituted cases are almost invariant whereas the bis-*ortho*-disubstituted cases generally show shifts to longer wavelengths with more variation within each subset. The corresponding average extinction coefficients, ϵ_{max} = 20 300 for alkyl and ϵ_{max} = 20 100, for methoxy derivatives show no substituent effect.

The 320 nm band exhibits an almost invariant mean wavelength maximum relatively independent of both substituent and position – λ_{max} = 323.5 (alkyl) and 322 (alkoxy) nm – for the compounds reported, while the extinction coefficients drop from 9400 for alkyl to 7300 for methoxy derivatives on average. The low extinction coefficient for the 3,4,5-trimethoxyacetophenone isomer is attributable to

restricted rotation of the 4-OMe group as has been observed in other systems [8]. While compound **XV** should also show an analogous effect for the 3-OMe group at least, this OMe is *meta* to the acyl group and does not show the effect due to less resonance interaction of this group with the acyl group. These data are in agreement with Ellis and this transition is assigned as a Cr → CO CTB due to the minimal substituent effect.

Our data for the longer wavelength band falls into three groups: compounds with no *ortho* substituents, 1 *ortho* substituent and 2 *ortho* substituents (Table 5).

Compounds lacking an *ortho* substituent show an absorption band in the region from 415 to 424 nm, averaging 416 nm for alkyl and 420 nm for alkoxy derivatives, which gives these complexes their characteristic orange to red colors. The wavelength maxima for this group of acetophenone complexes are all at fairly low and similar energies, presumably reflecting the presence of the acyl group. Alkyl and alkoxy substituents have normal effects on the position of this maximum with alkoxy substituents causing a small bathochromic shift together with a modest hyperchromic effect for corresponding alkyl substituents.

The band maximum undergoes a hypsochromic shift of approximately 12 nm to 406 ± 2 nm upon mono-*ortho* substitution. This *ortho* effect is expected and in agreement with such effects in other systems [8]. There is no observable substituent or position effect on the wavelength maximum, but extinction coefficients for alkoxy derivatives again appear to be higher than alkyl substituents, though this assignment must be considered tentative due to the small numbers of compounds.

When a 2,6-disubstituted acetophenone is studied, the difference in spectra is very noticeable. These compounds do not even show an absorption maximum in the 400 nm region and are characteristically yellow (Table 1). The resulting inhibited conjugation due to non-coplanarity of the arene and carbonyl orbitals isolates the C(O)Me group from the ring and diminishes the effect expected from the acyl group. The CTB does not then appear in its usual low-energy position. The lack of this maximum at ~400 nm is strong evidence for assigning this band as a Cr → arene CT transition, again, in agreement with Ellis. The effect of bis-*ortho* substitution on the ^{17}O and ^{13}C NMR spectra of anisoles has been described recently. Our UV–Vis data are in agreement with their observations [9].

Infrared Spectra

The infrared spectra in the metal–carbonyl region for these complexes generally exhibit two or three bands which are reported in Table 3. Since these multiple bands are non-degenerate due to molecular symmetry, a single force constant was generated by applying the Cotton–Kraihanzel approximation [10]. These values vary from 14.75–15.15 ($\times 10^5$) dynes/cm. All 2,6-bis-*ortho*-substituted cases show a force constant lower than 14.93 while non-sterically hindered congeners generally have values greater than 15.00 ($\times 10^5$) dynes/cm. The usual explanation for a low force constant is that there is a higher electron density in the arene ring with a correspondingly higher electron density in the antibonding orbitals of the carbonyl. This weakens the bond, with the resulting low force constants [11]. The IR data thus would indicate that the –C(O)Me group in a 2,6-disubstituted compound is not exhibiting its usual electron-withdrawing effect but is showing inhibited conjugation.

NMR Spectra

NMR spectra are presented in Table 4. Analysis of the acyl methyl group signals gives results consistent with the IR and UV data. As the number of *ortho* substituents increases, the acyl signal appears at correspondingly higher frequencies, most probably due to steric effects. For acetophenones containing no *ortho* substituents, the acyl methyl signal occurs at 2.469 ± 0.059δ. The corresponding signals for mono-*ortho*- and bis-*ortho*-substituted derivatives, occur at 2.524 ± 0.052δ and at 2.628 ± 0.064δ, respectively. The effect is modest but reproducible.

Signals for aryl methyl and methoxy groups are also listed in Table 4. Methyl assignments were made in ambiguous cases by noting that *para*-methyl signal positions in a given compound occur at higher values than either the *ortho*- or *meta*-methyls and *ortho*-methyl substitution lowers a group frequency relative to TMS. A similar analysis for the methoxy compounds was made by noting that *ortho*-methoxy substituent positions occur ~0.15 upfield from non-*ortho* cases whilst *meta*-methoxy groups have little or no effect.

Assignment of ring hydrogens in cases where there could be some question was accomplished using a computer program developed to predict NMR signal position as a function of rotamer population in tricarbonylchromium complexes and will be reported separately [12]*.

Of special interest was compound **VIII** which shows diastereotopic doubling of the 2- and 6-isopropyl methyl signals ($\Delta\delta = 40.5$ Hz), while the 4-isopropyl group, due to symmetry, does not show this doubling.

The spectrum of 4-cyclohexylacetophenonetricarbonylchromium (**IX**) listed in Table 4 and shown in Fig. 1 is unique. The simple first-order spectrum observed for the cyclohexyl ring protons of this

*The use of the ^1H and ^{13}C ring positions to predict rotamer populations has been brought into question and will be discussed separately (see ref. 14).

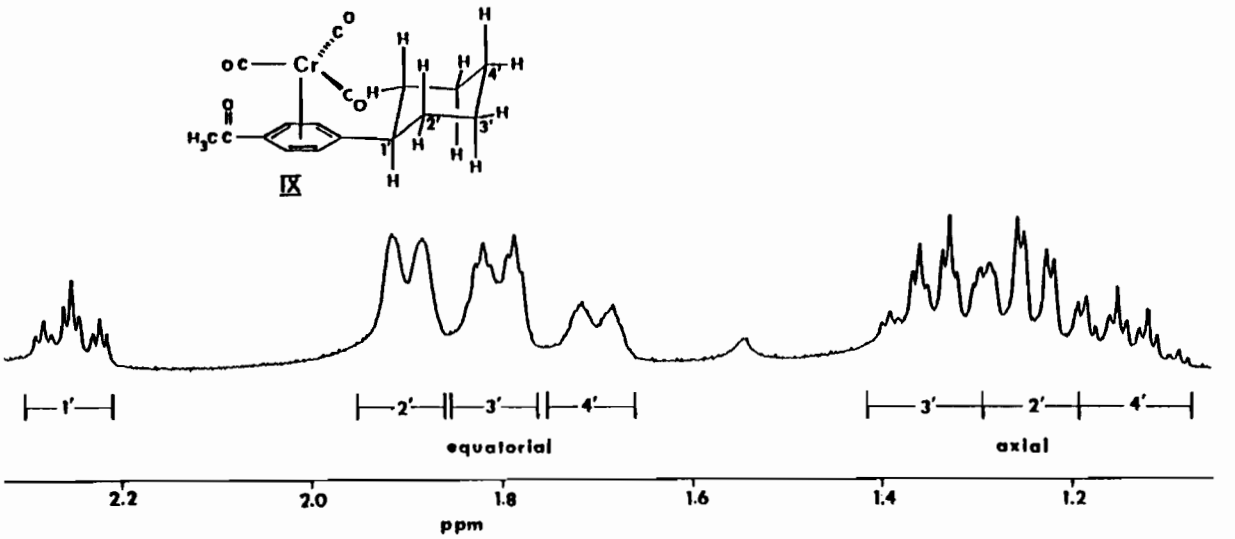

Fig. 1. The cyclohexyl region of the ^1H NMR spectrum of cyclohexylacetophenonetricarbonylchromium (IX).

compound is due to the combined steric effects of both the tricarbonylchromium and acyl group moieties on the cyclohexane ring and is not seen in the free arene itself, cyclohexylbenzene or its $Cr(CO)_3$ complex [13].

The axial and equatorial signals are well-resolved multiplets. The axial signals are observed furthest upfield at 1.136, 1.236 and 1.342δ for the 4′-, 2′- and 3′-axial protons, respectively. The 4′- and 2′-axial hydrogens are shifted more toward TMS than the 3′-axial hydrogen as they are *syn* to the arylchromium ring. J_{gem} and J_{anti} have nearly the same values (~12.5–13.0 Hz) while J_{gauche} couplings to either axial or equatorial hydrogens were ~3.0–3.6 Hz in approximate agreement with expected results. The equatorial protons are also well-resolved from each other occurring at 1.699, 1.802 and 1.898δ for the 4′-, 3′- and 2′-equatorial positions, respectively. They exist as broadened doublets, with the large splitting due to geminal coupling and the fine structure due to relatively small multiple gauche couplings by the four, four and three adjacent gauche hydrogens, respectively. The axial/equatorial frequency difference (a/e *FD*) is largest for the 2′-axial/equatorial pair (0.662δ, 264.9 Hz) as might be expected due to the proximity of the $Cr(CO)_3$ group and therefore these protons experience the largest a/e *FD*. The 4′-a/e pair shows the next largest a/e *FD* (0.563δ, 225.3 Hz), while the 3′-a/e pair has the smallest differential (0.460δ, 184.1 Hz). The uncommonly well-resolved spectrum for the cyclohexyl protons in this case ($H\text{-}1' > H_{eq} > H_{ax}$) does explain why there are three poorly resolved bands of signals normally seen in mono-substituted cyclohexane spectra.

Conclusions

The wide variety of evidence presented above leads to the conclusion that the acyl group in 2,6-disubstituted acetophenone–$Cr(CO)_3$ complexes is sterically hindered while mono-*ortho* substitution results in minor steric restriction. These effects were observed in the % yield, color, UV–Vis, IR and PMR spectra and demonstrate the remarkable utility of the tricarbonylchromium function in the study of steric phenomena.

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