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Note

Characterization of electronic properties of the $Cr(CO)_3$ group in chromium, tricarbonyl [3-[(η^6-aryl)methylene]-*Z*-1(3*H*)-isobenzofuranones] using spectral and theoretical methods

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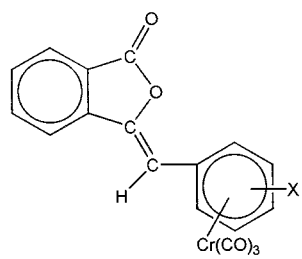
Abstract

The IR, ^{13}C- and ^{17}O-NMR spectral characteristics of the $Cr(CO)_3$ group in a series of eight chromium, tricarbonyl[3-[(η^6-aryl)methylene]-*Z*-1(3*H*)-isobenzofuranones] were correlated mutually as well as with theoretical data obtained by optimized MMX force-field and EHT calculations. The net charges on the carbon and oxygen atoms of the C=O group and their differences were found as the most appropriate quantitative characteristics for the electronic properties of the $Cr(CO)_3$ group. Using the results of the previously reported linear correlations, the electron-withdrawing effect of the $PhCr(CO)_3$ moiety, weakened by the back-donation effect, was estimated as $\sigma_\alpha \cong 0.45$ on the scale of Hammett substituent constants. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Chromium, tricarbonyl; Isobenzofuranone; ^{13}C- and ^{17}O-NMR spectroscopy; IR spectroscopy; EHT calculation

1. Introduction

Recently the IR and ^{13}C-NMR spectra and the kinetics of base-catalyzed ring fission of chromium, tricarbonyl [3-[(η^6-aryl)methylene]-*Z*-1(3*H*)-isobenzofuranones] were studied [1]. Using correlations between the spectral and kinetic data and empirical substituent constants the transmission of the electronic effect from the substituted benzene ring to the C=O group of the isobenzofuranone moiety has been investigated. Since the electronic properties of the $Cr(CO)_3$ group in chromium, tricarbonyl complexes of 3-arylmethylene-1(3*H*)-isobenzofuranones have not been reported so far, the aim of the present work is to correlate the IR, ^{13}C- and ^{17}O-NMR characteristics for a series of compounds **I**–**VIII** (Scheme 1) mutually and with theoretical data obtained by the EHT quantum chemical method. This paper also deals with the use of previously reported relationships for a quantitative estimation of the electronic effect of the $PhCr(CO)_3$ group.



X: I - 3,4-$(OCH_3)_2$
II - 4-OCH_3
III - 4-CH_3
IV - 2-CH_3
V - H
VI - 4-F
VII - 3-F
VIII - 3-CF_3

Scheme 1.

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Table 1
The ^{17}O-NMR chemical shifts (in CD_3CN) and EHT theoretical data for the $Cr(CO)_3$ group of compounds **I–VIII** [a]

Compound	$\delta(^{17}O)$ [b]	$Q(C^1)$	$Q(C^2)$	$Q(C^3)$	$-Q(O^1)$	$-Q(O^2)$	$-Q(O^3)$
I	375.7	0.042	0.544	0.227	0.834	0.499	0.738
II	374.3	0.144	0.138	0.163	0.743	0.760	0.754
III	372.4	0.141	0.222	0.141	0.745	0.772	0.753
IV	372.3	0.145	0.133	0.157	0.748	0.755	0.742
V	372.7	0.183	0.125	0.151	0.735	0.751	0.754
VI	376.4	0.207	0.121	0.572	0.730	0.800	0.557
VII	375.7	0.121	0.565	0.348	0.811	0.493	0.723
VIII	376.4	0.164	0.571	0.367	0.848	0.493	0.727

[a] For the numbering of the carbon and oxygen atoms see Scheme 1 for **V**.
[b] Given in ppm.

2. Results and discussion

The ^{17}O-NMR chemical shifts of the $Cr(CO)_3$ group together with the theoretical data, i.e. the net charges on the carbon (Q(C)) and oxygen atoms (Q(O)) of the C≡O groups, obtained by the EHT method for compounds **I–VIII** are listed in Table 1. It is known that the uncomplexed 3-arylmethylene-*Z*-1(3*H*) isobenzofuranones in CD_3CN at 75°C exhibit well-resolved ^{17}O-NMR signals belonging to the C=O group of the isobenzofuranone moiety [2]. Since the compounds **I–VIII** were thermally unstable at elevated temperatures, their ^{17}O-NMR spectra were measured at 30°C in CD_3CN solutions. At this temperature the only reliable ^{17}O-NMR signal observed originated from the $Cr(CO)_3$ group. The sharpness of this signal (i.e. the high signal/noise ratio) was caused by the fact that the rotational correlation time and relaxation characteristics of these carbonyls are not bound to the overall molecular motion and all three carbonyls gave a single time-averaged signal on the NMR-time scale [3].

The ^{13}C-NMR chemical shifts of the $Cr(CO)_3$ group of compounds **I–VIII** treated in later correlations were measured previously in $CDCl_3$ and taken from Ref. [1]. They vary in the range of $\delta = 231–235$ ppm, which is similar to that for the previously studied chromium, tricarbonyl complexes of aromatic hydrocarbons [3].

The arithmetic means of the symmetric and asymmetric IR stretching vibration wave numbers of the chromium, tricarbonyl moiety for derivatives **I–VIII** ($\nu(C{\equiv}O)_{av} = [\nu(C{\equiv}O)_s + \nu(C{\equiv}O)_{as}]/2$) measured in $CHCl_3$ and CCl_4 and taken from [1] were used in correlations with ^{17}O-NMR and theoretical data.

The statistical treatment of selected correlations is given in Table 2. From the investigated spectral characteristics of the $Cr(CO)_3$ moiety only the $\nu(C{\equiv}O)_{av}$ values exhibited reasonable correlations with empirical Hammett σ substituent constants [1]. The $\delta(^{17}O)$ chemical shifts showed very poor linear dependencies on σ (or σ^+) values. A possible explanation why the ^{17}O-NMR chemical shift of the $Cr(CO)_3$ moiety is not directly correlated with the nature of the substituent is that the observed signal is a time average of the chemical shifts of three carbonyls under fast exchange. If the substituent effects on these three carbonyls are opposite when their positions are different with respect to the substituent, the average substituent effect can be vanish. It follows from Table 2 that the ^{17}O-NMR chemical shifts show satisfactory correlation with the $\nu(C{\equiv}O)_{av}$ values measured in both $CHCl_3$ and CCl_4 solutions. The inverted proportionality of the $\delta(^{13}C)$- and $\delta(^{17}O)$-NMR values [4] seems to suggest a back-donation effect by the chromium d-orbital to the π*-orbitals of the C≡O groups. Investigating the correlations of the $\delta(^{17}O)$ and $\nu(C{\equiv}O)_{av}$ values with the EHT theoretical data the statistically significant results were obtained for the $C^1{\equiv}O^1$ group, which has a steric orientation pointing to the position of the aryl group C^2 atom adjacent to the hydrogen atom of the methylene bridge (see Scheme 2). In the correlation of $\nu(C{\equiv}O)_{av}$ values the measure of the electronic nature of the C≡O bond was characterized by the difference between the EHT net charges on the carbon and oxygen atoms (ΔQ), which is similar to the approach used previously for the Nb=O group [5]. The $\delta(^{17}O)$ data show a correlation with $Q(O^1)$ net charges, while the $\delta(^{13}C)$ chemical shifts correlate most significantly with the differences between the net charges $\Delta Q(1)$. This phenomenon is probably again caused by a strong back-donation effect existing between the Cr atom and the C≡O groups, which more readily influences the electronic properties of the carbon atom than those of the oxygen one.

Using the statistical results for the ν(C=O) versus σ correlations for the 3-arylmethy-lene-*Z*-1(3*H*)-isobenzofuranone series and the log k versus σ correlations of the base-catalyzed ring fission for the same compounds [1], as well as the spectral and kinetic data of the parent compound **V,** it was possible to estimate the Hammett substituent constant for the chromium, tricarbonyl phenyl moiety $\sigma_\alpha[PhCr(CO)_3] \cong 0.45$. This value shows that the electron-withdrawing effect of the $PhCr(CO)_3$ group is approximately three times weaker than that of

Table 2
Correlation analysis of selected spectral and theoretical data of compounds **I–VIII** ($y = ax + b$)

y	x	n [a]	r [b]	a	b	s [c]	F [d]
$\delta(^{17}O)$	$Q(O^1)$	6 [e]	0.975	-37.65 ± 4.29	344.6	0.48	77
$\delta(^{17}O)$	$\nu(C{\equiv}O)_{av}$ ($CHCl_3$)	6 [e]	0.902	0.14 ± 0.03	101.7	0.93	17
$\delta(^{17}O)$	$\nu(C{\equiv}O)_{av}$ (CCl_4)	6 [e]	0.889	0.19 ± 0.05	0.8	1.00	15
$\delta(^{13}C)$	$\delta(^{17}O)$	6 [f]	0.971	-0.33 ± 0.04	356.5	0.16	66
$\delta(^{13}C)$	$\Delta Q(1)$ [g]	6 [e]	0.969	-23.70 ± 3.03	255.2	0.34	61
$\nu(C{\equiv}O)_{av}$ ($CHCl_3$)	$\Delta Q(1)$ [g]	7 [h]	0.974	195.25 ± 20.28	1761.9	2.20	93
$\nu(C{\equiv}O)_{av}$ (CCl_4)	$\Delta Q(1)$ [g]	7 [h]	0.954	193.69 ± 27.22	1771.4	2.95	51

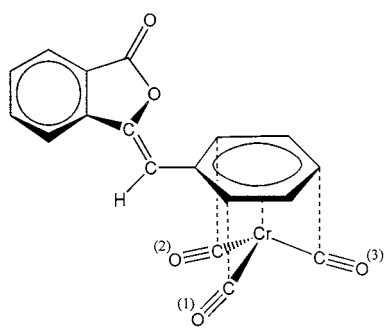
[a] Number of compounds used in the correlation.
[b] Correlation coefficient.
[c] Standard deviation.
[d] F-ratio of the correlation.
[e] Data for compounds **II** and **VI** were rejected as outliers.
[f] Data for compounds **I** and **VIII** were rejected as outliers.
[g] $\Delta Q(1) = Q(C^1) - Q(O^1)$.
[h] Data for compound **I** were rejected as outliers.

the ferrocene moiety ($\sigma_\alpha(Fc) = 1.55$) [9,10]. It can be finally concluded that the $Cr(CO)_3$ moiety complexed with the phenyl group of 3-phenylmethylene-*Z*-1(3*H*)-isobenzofuranone has a medium electron-withdrawing effect, which is, however, significantly weakened by the back-donation effect between chromium central atom and the C≡O groups.

3. Experimental

The preparation, IR and ^{13}C-NMR spectral properties of compounds **I–VIII** were described previously [1,6].

The ^{17}O-NMR spectra of chromium, tricarbonyl derivatives **I–VIII** have been measured for saturated CD_3CN solutions at 30°C by using a Bruker Avance DRX500 spectrometer working at 67.82 MHz and equipped with a 5 mm diameter direct observation multinuclear probe-head. An *aring* pulse sequence was used to remove baseline artefacts caused due to acoustic ringing. The spectral width was 610 ppm and the number of data points in the time domain was 8000, which was zero filled to 16 000 and exponentially windowed by 50 Hz prior to Fourier transformation. The acquisition time was 100 ms and a pulse delay of 100 ms was also included in the pulse sequence. The number of scans was typically 430 000, corresponding to a total measuring time of 24 h. A 1 mm diameter capillary tube of H_2O inserted coaxially inside the NMR tube was used as a reference signal ($\delta = 0.0$ ppm).



Geometrical structure of the parent compound **V**

Scheme 2.

4. Computational details

The theoretical calculations have been realized using molecular mechanics and quantum chemical methods. The force-field optimization of the geometric parameters was performed by the molecular mechanics MMX method using PCMODEL program [7]. Net charges have been obtained by the quantum chemical EHT method with standard parametrization [8].

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