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## INDUCED CONFORMATIONAL PREFERENCE VIA METAL CARBONYL COMPLEXATION: $^1\text{H}$ NMR AND X-RAY CRYSTALLOGRAPHIC STUDIES OF 4-CHROMANONECHROMIUM(0) TRICARBONYL

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### Summary

Proton NMR studies of (4-chromanone)chromium tricarbonyl indicate that, in solution, this compound occurs with the heterocyclic ring in a sofa conformation with an O(1)–C(2)–C(3)–C(4) torsion angle of  $53^\circ$ . Single-crystal X-ray analysis of the same molecule reveals that a sofa form ( $55.6^\circ$  torsion angle) is also adopted in the solid state with the further specification that C(2) is the out-of-plane atom and is displaced in the direction proximal to the  $\text{Cr}(\text{CO})_3$  moiety.

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### Introduction

Arenechromium tricarbonyl complexes have been the subject of intensive investigations both as aids in organic synthesis [1] and as molecules of intrinsic theoretical interest [2]. Included in the latter category are studies of substituent effects on the orientation of the chromium tricarbonyl (CT) moiety with respect to the framework of the aromatic ligand. These relationships have been examined by several experimental methods and also discussed from the standpoint of molecular orbital calculations. The effect of complexation on conformational preference outside the arene-CT portion of the molecule has been studied by Mislow [3] with regard to hexaalkylbenzene-CT complexes and by Schlögl [4] with respect to mono- and di-CT complexes in the biphenyl series. The present work addresses the question of whether complexation of a benzene ring will induce a preferred conformation in a fused, partially flexible heterocyclic ring. We selected the 4-chromanone system for our initial studies.

### Results and discussion

Conversion of 4-chromanone (I) to the crystalline complex II was accomplished by standard methods [5]. The  $^1\text{H}$  NMR spectra of these two compounds were in

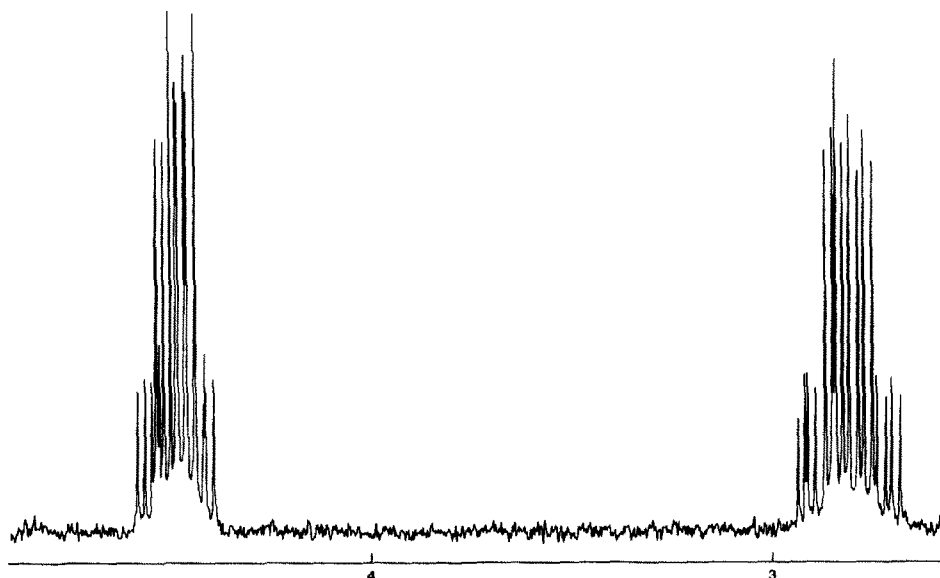


Fig. 1.  $^1\text{H}$  NMR spectrum of II at 250 MHz.

sharp contrast. In the spectrum of the former, the C(2) and C(3) methylene proton signals appeared as sharp triplets at  $\delta$  4.08 and 3.08 ppm, respectively, reflecting the rapid interconversion of out-of-plane conformers on the NMR time scale with the resulting identity of geminal protons [6]. Corresponding signals for complex II appeared as multiplets centered at  $\delta$  4.48 and 2.80 ppm. In the 250 MHz spectrum of II (Fig. 1), fifteen lines were distinguishable in the downfield pattern while sixteen lines occurred in the upfield pattern. Irradiation at the center of either multiplet caused the other to collapse to a four-line signal of the AB type, thereby allowing determination of chemical shifts for all four methylene protons as well as the geminal coupling constants. Based on these parameters, an iterative process led to a calculated spectrum which closely matched the original and thereby provided the four vicinal coupling constants. The NMR parameters are compiled in Table 1 and our proton assignments are shown in Fig. 2 on a Newman projection along the C(2)–C(3) bond. Use was then made of Lambert's *R*-value method [7] which allows

TABLE 1

CHEMICAL SHIFT VALUES AND COUPLING CONSTANTS (Hz) FOR THE TWO C(2) AND TWO C(3) METHYLENE PROTONS OF II

	Chemical shifts		Coupling constants (Hz)	
	Hz.	ppm		
H(2A)	1132.967	(4.518)	$J(2A,2B)$	–11.437
H(2B)	1112.604	(4.437)	$J(2A,3A)$	4.245 <sup>a</sup>
H(3A)	718.513	(2.865)	$J(2A,3B)$	9.357 <sup>a</sup>
H(3B)	689.325	(2.749)	$J(2B,3A)$	5.822 <sup>a</sup>
			$J(2B,3B)$	5.641 <sup>a</sup>
			$J(3A,3B)$	–17.289

<sup>a</sup> Calculated values.

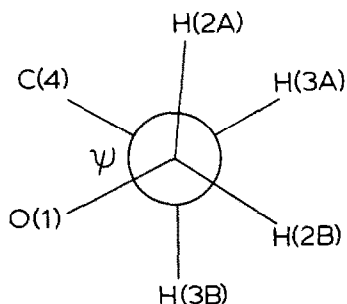
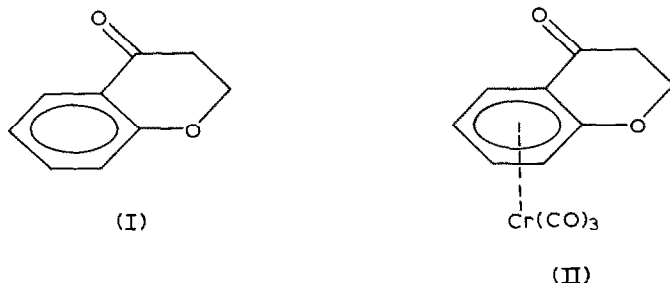


Fig. 2. Newman projection along the C(2)–C(3) bond.

calculation of the dihedral angle of any  $XCH_2CH_2Y$  moiety from the four vicinal coupling constants. The value of the O(1)–C(2)–C(3)–C(4) angle ( $\psi$ ) was determined to be  $53^\circ$  [8]. This value is close to that ( $55^\circ$ ) which is characteristic of the C(3)–C(4)–C(5)–C(6) dihedral angle of an ideal sofa form of a cyclohexene ring (C(4) or C(5) out of plane). The corresponding dihedral angle for a half-chair cyclohexene is  $62^\circ$ . The possibility that the heterocyclic ring of (4-chromanone)-CT adopts the sofa form is also consistent with the result of Philbin and Wheeler [9] who employed both angle strain calculations and special molecular models in determin-



ing that the sofa conformation is the low energy form of 4-chromanone itself. These conclusions regarding the solution conformation of (4-chromanone)-CT were strengthened by the results of a single-crystal X-ray analysis which also elucidated other important features of the geometry of (4-chromanone)-CT.

The crystal structure of II was solved by direct methods [10]. Least-squares adjustment of atomic parameters converged to  $R = 0.038$  over 1526 reflections. Final atomic positional and anisotropic thermal parameters are listed in Table 2; bond lengths and angles involving the non-hydrogen atoms in Table 3. Views of the solid-state conformation are provided in Fig. 3.

The reduced symmetry of the substituted benzene ring (C–C distances range from 1.376(6) to 1.420(6) Å, mean 1.399 Å) and the slight bowing of the ring atoms away from the  $Cr(CO)_3$  moiety (Fig. 3, Table 4) contribute to significant differences between the individual Cr–C(benzene) distances (range 2.179(4)–2.254(4) Å). In addition, however, the chromium atom is displaced slightly ( $\Delta 0.031$  Å) towards C(6) from lying directly above the centroid of the ring. Similar acentricities have been rationalized by Saillard et al. [11] for other  $Cr(CO)_3$  complexes in terms of a frontier orbital model. The mean Cr–C(benzene) distance at 2.217 Å is similar to and at the

TABLE 2

FRACTIONAL ATOMIC COORDINATES ( $\times 10^5$ ;  $\times 10^3$  FOR HYDROGENS<sup>a</sup>) AND ANISOTROPIC THERMAL PARAMETERS<sup>b</sup> IN II, WITH STANDARD DEVIATIONS IN PARENTHESES

Atom	<i>x</i>	<i>y</i>	<i>z</i>			
<i>(a) Fractional atomic coordinates</i>						
O(1)	11365(44)	53272(19)	18271(22)			
C(2)	19951(71)	58881(30)	28090(37)			
C(3)	17287(69)	54337(30)	38731(34)			
C(4)	26119(58)	44522(29)	40164(30)			
C(4a)	24523(50)	39417(24)	29369(27)			
C(5)	29405(53)	29674(27)	29182(31)			
C(6)	26054(57)	24726(27)	19196(35)			
C(7)	18809(58)	29573(30)	8954(32)			
C(8)	14529(58)	39139(29)	8776(30)			
C(8a)	16815(54)	44084(26)	19001(29)			
O(9)	32790(49)	40787(23)	49260(21)			
C(10)	70255(56)	34855(29)	29907(30)			
O(11)	85263(45)	33507(29)	36575(26)			
C(12)	56414(64)	48611(30)	16052(34)			
O(13)	62737(56)	55840(24)	14405(30)			
C(14)	59992(61)	31970(32)	8691(34)			
O(15)	68628(48)	28895(27)	2651(26)			
Cr	46480(8)	36892(4)	18758(4)			
H(2A)	360(5)	601(3)	289(3)			
H(2B)	115(8)	641(3)	259(4)			
H(3A)	237(7)	584(3)	450(4)			
H(3B)	31(6)	543(3)	397(3)			
H(5)	346(6)	269(3)	352(3)			
H(6)	297(6)	180(3)	195(3)			
H(7)	180(7)	267(3)	25(4)			
H(8)	115(6)	425(3)	25(3)			
Atom	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
<i>(b) Anisotropic thermal parameters (<math>\times 10^3</math>)</i>						
O(1)	62(2)	42(1)	40(1)	16(1)	6(1)	5(1)
C(2)	70(3)	39(2)	55(2)	9(2)	13(2)	-4(2)
C(3)	68(2)	51(2)	49(2)	4(2)	21(2)	-14(2)
C(4)	48(2)	49(2)	34(2)	-10(2)	10(1)	-4(2)
C(4a)	33(2)	37(2)	29(1)	-2(1)	5(1)	-1(1)
C(5)	37(2)	40(2)	42(2)	1(2)	10(1)	8(2)
C(6)	40(2)	34(2)	60(2)	-3(2)	13(2)	-10(2)
C(7)	39(2)	55(2)	41(2)	-2(2)	-1(2)	-17(2)
C(8)	41(2)	57(2)	30(2)	7(2)	-3(1)	O(2)
C(8a)	39(2)	38(2)	35(2)	5(2)	6(1)	1(1)
O(9)	79(2)	65(2)	31(1)	-10(2)	6(1)	3(1)
C(10)	40(2)	53(2)	31(2)	-5(2)	11(1)	O(2)
O(11)	39(1)	108(3)	44(2)	-5(2)	-3(1)	16(2)
C(12)	55(2)	41(2)	45(2)	2(2)	18(2)	2(2)
O(13)	93(2)	45(2)	86(2)	-13(2)	37(2)	8(2)
C(14)	42(2)	54(2)	42(2)	0(2)	2(2)	-9(2)
O(15)	65(2)	97(2)	67(2)	-1(2)	27(1)	-36(2)
Cr	34(0.2)	31(0.2)	27(0.2)	0(0.3)	5(0.2)	-1(0.2)

<sup>a</sup> Hydrogen atoms bear the same labels as the atoms to which they are bonded. <sup>b</sup> In the form:  $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$ .

low end of the range for those in  $\text{CH}_3\text{CO}_2\text{C}_6\text{H}_5\text{-Cr}(\text{CO})_3$ , 2.217(3) Å [12],  $\text{C}_6\text{H}_6\text{-Cr}(\text{CO})_3$ , 2.229(2) Å [13], 1,2,3-trimethoxybenzene- $\text{Cr}(\text{CO})_3$ , 2.252(2) Å [11], and  $(\text{C}_2\text{H}_5)_2\text{NC}_6\text{H}_5\text{-Cr}(\text{CO})_3$ , 2.240(3) Å [11]; conversely, the correlated mean Cr-C(carbonyl) distance at 1.848 Å lies close to the long end of the 1.813(2)–1.842(3) Å range for the corresponding bonds in these same compounds. Bond lengths in the heterocyclic ring agree well with expected values.

The orientation of the Cr-C≡O bonds with respect to the C(5), C(7), C(8a) benzene ring atoms has a mean C(carbonyl)-C(centroid)-Cr-C(carbonyl) torsion angle of 9.3° and thus is rotated away from an exactly eclipsed arrangement to a greater extent than the orientations encountered in the tricarbonylchromiumanisoletrinitrobenzene- $\text{Cr}(\text{CO})_3$  complex [14], *o*-toluidine- $\text{Cr}(\text{CO})_3$  [15],  $\text{CH}_3\text{CO}_2\text{C}_6\text{-}$

TABLE 3

INTERATOMIC DISTANCES (Å) AND ANGLES (°) IN II, WITH STANDARD DEVIATIONS IN PARENTHESES

<i>(a) Bond distances</i>					
O(1)-C(2)	1.434(5)	C(5)-C(6)	1.376(6)	Cr-C(5)	2.179(4)
O(1)-C(8a)	1.349(5)	C(6)-C(7)	1.403(6)	Cr-C(6)	2.216(4)
C(2)-C(3)	1.504(6)	C(7)-C(8)	1.384(6)	Cr-C(7)	2.205(4)
C(3)-C(4)	1.505(6)	C(8)-C(8a)	1.408(5)	Cr-C(8)	2.215(4)
C(4)-C(4a)	1.485(5)	C(10)-C(11)	1.144(5)	Cr-C(8a)	2.254(4)
C(4)-O(9)	1.211(5)	C(12)-O(13)	1.146(5)	Cr-C(10)	1.846(4)
C(4a)-C(5)	1.420(5)	C(14)-O(15)	1.138(5)	Cr-C(12)	1.851(4)
C(4a)-C(8a)	1.408(5)	Cr-C(4a)	2.234(3)	Cr-C(14)	1.846(4)
<i>(b) Bond angles</i>					
C(2)-O(1)-C(8a)	115.7(3)	C(6)-C(7)-C(8)		121.1(4)	
O(1)-C(2)-C(3)	112.1(3)	C(7)-C(8)-C(8a)		119.8(3)	
C(2)-C(3)-C(4)	111.4(4)	O(1)-C(8a)-C(4a)		123.0(3)	
C(3)-C(4)-C(4a)	114.1(3)	O(1)-C(8a)-C(8)		117.0(3)	
C(3)-C(4)-O(9)	123.7(4)	C(4a)-C(8a)-C(8)		120.0(3)	
C(4a)-C(4)-O(9)	122.1(4)	Cr-C(10)-O(11)		178.0(3)	
C(4)-C(4a)-C(5)	121.5(3)	Cr-C(12)-O(13)		179.4(4)	
C(4)-C(4a)-C(8a)	120.0(3)	Cr-C(14)-O(15)		178.7(4)	
C(5)-C(4a)-C(8a)	118.4(3)	C(10)-Cr-C(12)		89.2(2)	
C(4a)-C(5)-C(6)	121.5(3)	C(10)-Cr-C(14)		87.1(2)	
C(5)-C(6)-C(7)	119.0(4)	C(12)-Cr-C(14)		87.5(2)	
<i>(c) Torsion angles<sup>a</sup></i>					
C(8a)-O(1)-C(2)-C(3)	-49.5(4)	C(8a)-C(4a)-C(5)-C(6)		-2.4(4)	
C(2)-O(1)-C(8a)-C(4a)	20.2(4)	C(4)-C(4a)-C(8a)-O(1)		2.6(4)	
C(2)-O(1)-C(8a)-C(8)	-159.7(4)	C(4)-C(4a)-C(8a)-C(8)		-117.4(4)	
O(1)-C(2)-C(3)-C(4)	55.6(4)	C(5)-C(4a)-C(8a)-O(1)		178.7(4)	
C(2)-C(3)-C(4)-C(4a)	-32.9(4)	C(5)-C(4a)-C(8a)-C(8)		-1.4(4)	
C(2)-C(3)-C(4)-O(9)	151.7(4)	C(4a)-C(5)-C(6)-C(7)		3.9(4)	
C(3)-C(4)-C(4a)-C(5)	-171.0(4)	C(5)-C(6)-C(7)-C(8)		-1.7(4)	
C(3)-C(4)-C(4a)-C(8a)	5.0(4)	C(6)-C(7)-C(8)-C(8a)		-2.1(4)	
O(9)-C(4)-C(4a)-C(5)	4.5(4)	C(7)-C(8)-C(8a)-O(1)		-176.6(4)	
O(9)-C(4)-C(4a)-C(8a)	-179.5(4)	C(7)-C(8)-C(8a)-C(4a)		3.5(4)	
C(4)-C(4a)-C(5)-C(6)	173.6(4)				

<sup>a</sup> The torsion angle of A-B-C-D is defined as positive if, when viewed along the B-C bond, atom A must be rotated clockwise to eclipse atom D. C-H distances range from 0.84(4)–1.08(4) Å.

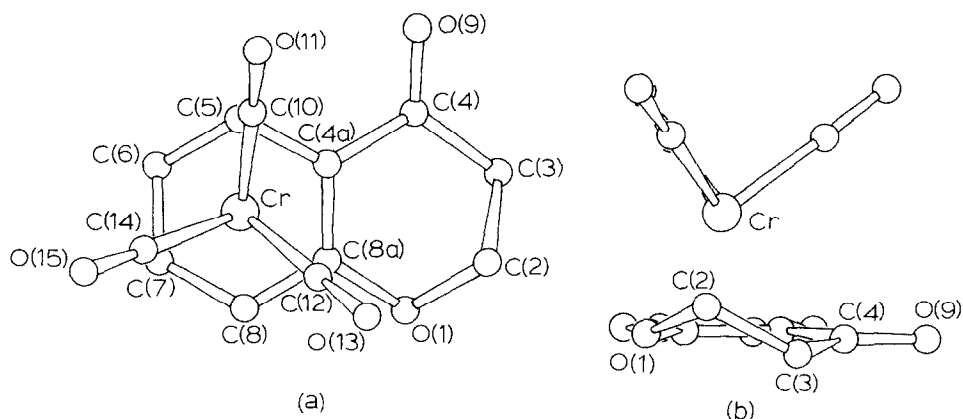


Fig. 3. Conformation of II viewed (a) perpendicular to the least-squares plane through C(4a)–C(8a) (b) along the plane through C(4a)–C(8a).

$\text{H}_5\text{-Cr}(\text{CO})_3$  [12,16], 1,2,3-trimethoxybenzene– $\text{Cr}(\text{CO})_3$  [11], and  $(\text{C}_2\text{H}_5)_2\text{-NC}_6\text{H}_5\text{-Cr}(\text{CO})_3$  [11] where the corresponding means range from 1.4–6.0°. Nevertheless, the orientation is still consistent with earlier views [17] rationalizing the

TABLE 4

EQUATIONS OF LEAST-SQUARES PLANES THROUGH GROUPS OF ATOMS, IN THE FORM  $PX + QY + RZ - S = 0^a$  WITH, IN SQUARE BRACKETS, DISPLACEMENTS (Å) OF ATOMS FROM THESE PLANES

*Plane A: C(4a)–C(8a)*

$$0.9751X + 0.2200Y - 0.0267Z - 1.862 = 0$$

[O(1)–0.066, C(2) 0.345, C(3)–0.328, C(4)–0.100, C(4a)–0.003,  
C(5) 0.021, C(6)–0.019, C(7)–0.002, C(8) 0.020, C(8a) –0.018,  
O(9) –0.082, C(10) 2.848, O(11) 3.570, C(12) 2.829, O(13) 3.525, C(14) 2.793, O(15), 3.468,  
Cr 1.719]

*Plane B: C(3), C(4), C(4a), O(9)*

$$0.9372X + 0.3489Y - 0.0058Z - 2.630 = 0$$

[O(1) 0.176, C(2) 0.703, C(3) –0.007, C(4) 0.024, C(4a) –0.007,  
C(5) –0.174, C(6) –0.333, C(7) –0.246, C(8) –0.039, C(8a) 0.045, O(9) –0.010, C(10) 2.645,  
O(11) 3.329, C(12) 2.868, O(13) 3.688, Cr 1.574]

*Plane C: C(10), C(12), C(14)*

$$0.9760X + 0.2124Y - 0.0475Z - 4.602 = 0$$

[C(4) –2.986, C(4a) –2.857, C(5) –2.821, C(6) –2.832, C(7) –2.795,  
C(8) –2.783, C(8a) –2.851, O(9) –2.986, C(10) 0.000, O(11) 0.709,  
C(12) 0.000, O(13) 0.693, C(14) 0.000, O(15) 0.694, Cr –1.105]

*Plane D: O(1), C(4), C(4a), C(8a)*

$$-0.9631X - 0.2691Y - 0.0073Z + 2.232 = 0$$

[O(1) 0.005, C(2) –0.492, C(3) 0.164, C(4) 0.005, C(4a) –0.011, C(5) 0.038,  
C(8) 0.051, C(8a) 0.011]

Dihedral angles (°) between planes: A/B 7.8; A/C 1.3; A/D 3.5; B/C 8.5; B/D 4.9; C/D 4.6.

<sup>a</sup> Cartesian coordinates ( $X, Y, Z$ ) are related to the fractional atomic coordinates ( $x, y, z$ ) listed in Table 3 by the transformations:  $X = xa + zcc\cos\beta$ ,  $Y = yb$ ,  $Z = zc\sin\beta$ .

geometrical preferences in such complexes in terms of the demands of the electron-withdrawing  $\text{Cr}(\text{CO})_3$  moiety, viz., electron-releasing substituents (here  $-\text{O}-\text{CH}_2-$ ) favor  $\text{Cr}-\text{C}\equiv\text{O}$  bond vectors directed at carbon atoms *ortho* and *para* to these groups whereas electron-withdrawing substituents (here  $-\text{CO}-\text{CH}_2-$ ) favor *meta* directed vectors.

Both of the directly bonded atoms, O(1) and C(4), are displaced significantly ( $\Delta$  0.066 and 0.100 Å, respectively) to the opposite side of the least-squares plane through the slightly bowed benzene ring carbon atoms from the  $\text{Cr}(\text{CO})_3$  moiety (Table 4). Like displacements occur at the methoxy oxygen atom ( $\Delta$  0.119 Å) in the tricarbonylchromiumanisole-1,3,5-trinitrobenzene complex [14] and at the amino nitrogen atoms in *o*-toluidine- $\text{Cr}(\text{CO})_3$  [15] and  $(\text{C}_2\text{H}_5)_2\text{NC}_6\text{H}_5-\text{Cr}(\text{CO})_3$  [11] ( $\Delta$  0.129 and 0.137 Å, respectively). The smaller value assumed by the endocyclic torsion angle about the C(4)–C(4a) bond ( $5.0^\circ$ ) compared to that of  $20.2^\circ$  about the C(8a)–O(1) bond implies that the former is more favorably oriented for delocalization with the benzene ring (the ether oxygen atom is considered to be  $sp^2$  hybridized [18]). Displacements of C(2) and C(3) from the least-squares plane through O(1), C(4), C(4a), C(8a) and analysis of deviations of the endocyclic torsion angles from symmetry-related values indicate that the heterocyclic ring approximates more closely to a sofa form with the  $C_s$  symmetry plane passing through C(2) and C(4a) than to a half-chair form with the  $C_2$  axis passing through the mid-points of the C(4a)–C(8a) and C(2)–C(3) bonds. The foregoing results indicate that preference for the observed heterocyclic ring conformation with C(2) lying on the same side of the ring plane as the  $\text{Cr}(\text{CO})_3$  moiety, rather than on the opposite side, derives from the dominating orientational demands of the  $-\text{CO}-\text{CH}_2-$  substituent for effective delocalization coupled with the syn O(1) and C(4) out-of-plane displacements accompanying complexation by  $\text{Cr}(\text{CO})_3$ . The magnitude of the O(1)–C(2)–C(3)–C(4) torsion angle at  $55.6(4)^\circ$  in the solid state is in excellent agreement with that of  $53^\circ$  predicted in solution by the  $^1\text{H}$  NMR coupling constants.

## Experimental

$^1\text{H}$  NMR spectra were recorded at 250 MHz on a Bruker WM-250 spectrometer in  $\text{CDCl}_3$ ; chemical shift values are quoted relative to  $\text{SiMe}_4$  as internal standard. Melting points were obtained on a Thomas–Hoover hot stage mounted to a Bausch–Lomb microscope.

### 4-Chromanone (I)

This compound was synthesized by the method of Loudon and Razdon [19]. Kugelrohr distillation at  $140^\circ\text{C}/20$  mmHg yielded a colorless oil with the correct spectral properties.

### 4-Chromanonechromium(0) tricarbonyl(II)

To a 2.73 g (18.45 mmol) sample of compound I placed in a 250 ml round bottomed flask with 8.12 g (2 equiv.) of chromium hexacarbonyl was added 150 ml of freshly distilled (from Na, under  $\text{N}_2$ ) dioxane. The mixture was refluxed under a dry nitrogen atmosphere on a Strohmeier apparatus for 48 h, allowed to cool to room temperature, and the solvent removed on a rotary evaporator. The crude product was dissolved in 200 ml of diethyl ether and filtered through a celite pad.

Following removal of the ether on a rotary evaporator, the product was chromatographed on a column of 130 g silica gel eluted with a solvent mixture of 10% ethyl acetate in hexane. The product fraction is preceded by a colorless fraction which is unreacted I. The product complex II elutes as a deep red solution which, after solvent removal, yielded 1.68 g (32%) of orange-red crystals, m.p. 122–124.5°C.  $^1\text{H}$  NMR:  $\delta$  6.2 (dd, 1H), 5.7 (td, 1H), 5.2 (dd, 1H), 5.0 (td, 1H), 4.4–4.6 (m, 2H), 2.7–2.9 (m, 2H) ppm. Anal. Found: C, 50.72; H, 2.86.  $\text{C}_{12}\text{H}_8\text{CrO}_5$  calcd.: C, 50.72; H, 2.84%.

### Crystal structure of II

A crystal, ca.  $0.10 \times 0.14 \times 0.56$  mm, was mounted on the end of a thin glass fiber with its long dimension approximately parallel to the fiber axis. Unit-cell dimensions, obtained initially from oscillation and Weissenberg photographs (Ni-Filtered  $\text{Cu-K}_\alpha$  radiation,  $\lambda$  1.5418 Å), were subsequently refined by least-squares treatment of the setting angles for 40 high order reflections accurately centered on an Enraf–Nonius (CAD-3 automated diffractometer; Ni-filtered  $\text{Cu-K}_\alpha$  radiation).

*Crystal Data.*  $\text{C}_{12}\text{H}_8\text{CrO}_5$ ,  $M = 284.19$ , monoclinic,  $a$  6.751(3),  $b$  14.158(7),  $c$  12.236(5) Å,  $\beta$  104.72(1)°,  $U$  1131.3 Å<sup>3</sup>,  $Z = 4$ ,  $D_{\text{calc}}$  1.669 g cm<sup>-3</sup>.  $\mu(\text{Cu-K}_\alpha)$  88.5 cm<sup>-1</sup>. Space group  $P21/c$  ( $C_{2h}^5$ ) uniquely from systematic absences.

Intensity data to  $\theta = 67^\circ$  were recorded with beam diameter 1.6 mm by procedures described in detail elsewhere [20]. Lorentz, polarization, and absorption corrections were applied to those 1526 reflections with  $I > 2.0\sigma(I)$  which were retained for use in the structure analysis.

The structure was solved by direct methods [10]. Full-matrix least-squares refinement of atomic positional and thermal parameters (anisotropic C, O, Cr; isotropic H) converged to  $R = 0.038$ . In the least-squares iterations,  $\sum w\Delta^2$  ( $\Delta = ||F_o| - |F_c||$ ) was minimized with weights being assigned according to the scheme:  $\sqrt{w} = 1$  for  $|F_o| \leq 20.0$ , and  $\sqrt{w} = 20.0/|F_o|$  for  $|F_o| > 20.0$ ; analysis of  $\langle w\Delta^2 \rangle$  values in ranges of  $|F_o|$  showed no systematic dependence. Neutral atom scattering factors for carbon, oxygen, and chromium were taken from ref. 21 and for hydrogen from ref. 22; anomalous dispersion corrections [23] for chromium were included. A list of observed and calculated structure factors is available from the authors.

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