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The crystal structure of the bis-tricarbonylchromium complex of dibenzo[*a,e*]cyclooctatetraene: Cr(CO)₃ orientation controlled by short C–H···O hydrogen bonding

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Abstract

The structure of the title compound, **1**, was determined by X-ray crystallography. One tricarbonylchromium [*syn*-Cr(CO)₃] moiety is bound to the concave side of the dibenzo[*a,e*]cyclooctatetraene ligand while the other metal is bound to the convex side yielding an *anti*-Cr(CO)₃. There are four independent molecules in the crystal with the main difference between them being the orientation of the *anti*-Cr(CO)₃. Analysis of intermolecular interactions in the solid state confirms that the variable tripodal rotations are the result of short C–H···O(carbonyl) hydrogen bonds. In **1**, the organic framework has flattened slightly relative to uncoordinated dibenzo[*a,e*]cyclooctatetraene. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Arenetricarbonylchromium complexes; Hydrogen bonding; Crystal structures; Dibenzo[*a,e*]cyclooctatetraene

1. Introduction

Interesting reduction chemistry is observed for bis-tricarbonylchromium complexes of conjugated diarenes bridged by (HC=CH)ₓ groups (x = 0, 1, 2) [1–8]. A closely related complex is η⁶,η⁶-dibenzo[*a,e*]cyclo-octatetraenebis(tricarbonylchromium) (**1**) reported by Müller et al. [9]. Dibenzo[*a,e*]cyclooctatetraene (**2**) can be envisioned as a conjugated diarene with two *ortho* bridging HC=CH groups. Further reason to study the reduction chemistry of this complex is to determine whether it exhibits enhanced stabilization of the arenetricarbonylchromium anion as is observed for naphthalenetricarbonylchromium [10–12].

In the reference describing the synthesis of **1**, no conclusive evidence was provided as to whether the chromium atoms were coordinated to the same side of the organic or to opposite sides [9]. To determine unequivocally whether the two Cr(CO)₃ groups were bound in a *syn,anti* or *anti,anti* conformation, the crystal structure of **1** was determined by X-ray crystallography. The effect of the coordination of the two Cr(CO)₃ groups on the geometry of the organic backbone is facilitated because the structure of **2** has been reported [13].

anti,anti   *syn,anti*
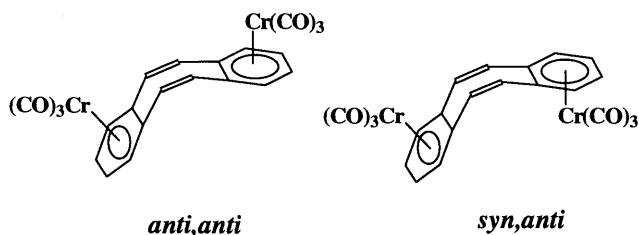
In addition, it was of interest to determine the tripod orientation of the Cr(CO)₃ groups in **1** as this structural feature is of interest in arenetricarbonylchromium chemistry [14]. For arenes fused to another ring, there are usually three limiting situations considered [14–17]. These are the eclipsed, *exo* staggered, and *endo* staggered isomers. A theoretical discussion of the conformational preferences in complexes of this type has been made [15].

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Table 1
Crystal data and structure refinement for **1**

Empirical formula	$C_{22}H_{12}Cr_2O_6$
Formula weight	476.32
Temperature (K)	292(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2(1)$ (# 4)
Unit cell dimensions	
a (Å)	7.089(3)
b (Å)	20.164(7)
c (Å)	27.173(9)
α (°)	90
β (°)	90.96(3)
γ (°)	90
Volume (Å^3)	3884(3)
Z	8
Absorption coefficient (mm^{-1})	1.157
Crystal color	Orange
Crystal size (mm)	$0.50 \times 0.40 \times 0.15$
θ range for data collection (°)	1.81–27.50
Index ranges	$0 \leq h \leq 9$, $0 \leq k \leq 26$, $-35 \leq l \leq 35$
Reflections collected	9851
Independent reflections	9155 [$R_{int} = 0.0261$]
Structure solution	Direct methods (SHELXS-86 [19])
Refinement method	Full-matrix least-squares on F^2 (SHELXL-93 [20])
Data/restraints/parameters	9155/1/1081
Goodness-of-fit on F^2	0.735
Final R indices [$I > 2\sigma(I)$] [a]	$R_1 = 0.0435$, $wR_2 = 0.0934$
R indices (all data)	$R_1 = 0.0847$, $wR_2 = 0.1009$
Extinction coefficient	0.02(2)
Largest difference peak and hole (e Å^{-3})	0.726 and -0.411

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4]^{1/2}$.

eclipsed **exo staggered** **endo staggered**
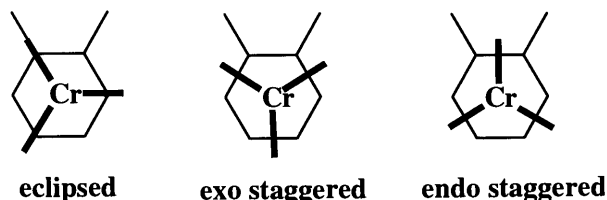
2. Results and discussion

Complex **1** was synthesized as described in the literature [9]. ^{1}H-NMR and IR for the compound obtained agree with those reported. **2** was likewise synthesized as previously reported [18].

2.1. Crystal structure determination of **1**

To obtain crystals suitable for X-ray crystallography, slow vapor diffusion of hexanes into a concentrated dichloromethane solution of **1** was utilized. Data for compound **1** were collected on a Siemens R3m/V automated diffractometer fitted with a molybdenum source and a graphite monochromator (K_α radiation; wavelength 0.71073 Å). The structure was discovered with application of program SHELXS-86 [19] and refined with SHELXL-93 [20]. Hydrogen atom positions were calculated and their contribution was included although their positions were not refined. The final R value was 0.0435. Relevant crystallographic data and structure refinement information for **1** are summarized in Table 1.

2.2. Structure of **1**

There are four independent molecules of **1** in the solid state (labeled A through D). Fig. 1 contains a drawing of the four molecules showing the relative orientation of them in the crystal, while Fig. 2 provides a side view of the four molecules. From Fig. 2 it is clear that **1** adopts the *syn,anti* configuration where the *syn*-Cr(CO)$_3$ group is on the concave face of the dibenzocyclooctatetraene ligand. This *trans* configuration of the two Cr(CO)$_3$ moieties agrees with previous results for tricarbonylchromium complexes of bent diarene ligands [21–23].

Tables 2 and 3 give listings for selected bond lengths and bond angles for **1**. While the gross geometry of the ligand has not changed significantly upon coordination of the two tricarbonylchromium moieties, some subtle differences do exist. As is common when a Cr(CO)$_3$ group coordinates to an arene, there is an increase in the arene C–C bond lengths [14]. The greatest differences in the organic backbone between **1** and **2** can be found by analyzing the angles between planes of carbon atoms (Table 4). Apparently, the occupation of the interior of the dibenzocyclooctatetraene by the *syn*-
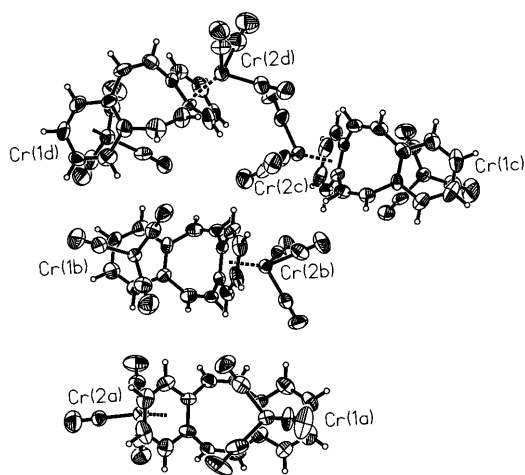

Fig. 1. The crystal structure of **1** showing the relative positions of the four independent molecules, A, B, C, and D (bottom to top). Thermal ellipsoids are shown at 50% probability.
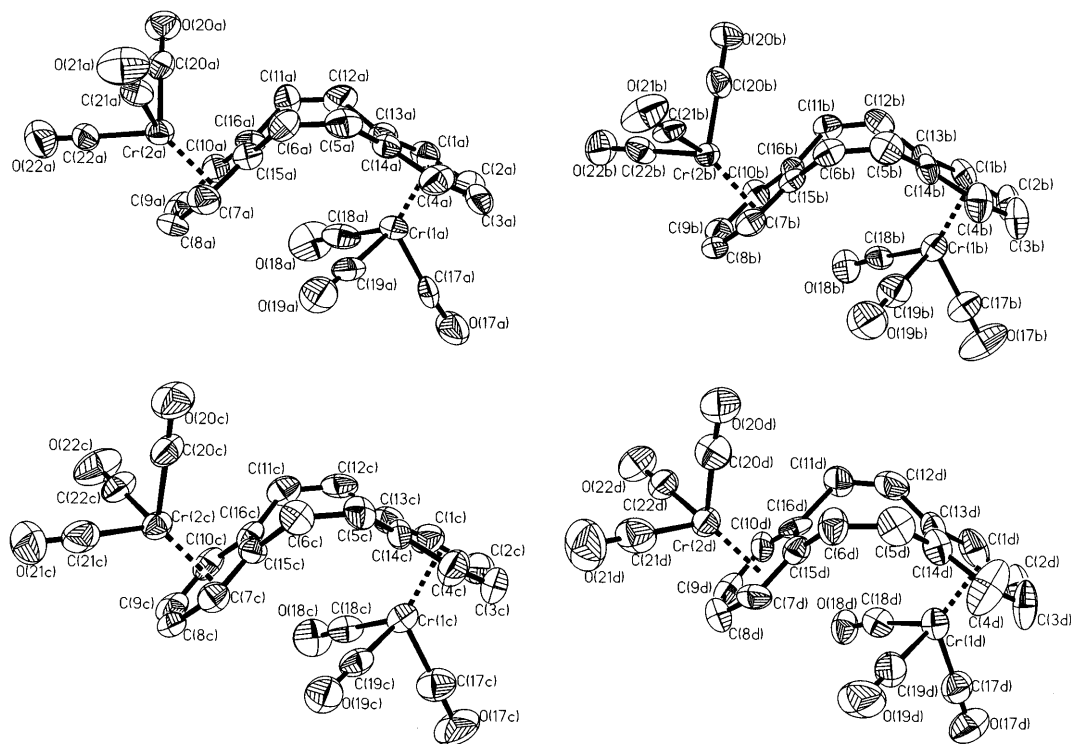
Fig. 2. The molecular structures of the four molecules of **1** showing the *syn,anti* conformation of the $Cr(CO)_3$ groups (A, upper left; B, upper right; C, lower left; D, lower right). Thermal ellipsoids are shown at 50% probability.

$Cr(CO)_3$ has the effect of flattening the organic. This is most obvious when a comparison between the arene ring planes for **1** (average of 73.3°) and **2** (81.3°) is performed. Thus, the angle between the arene rings has decreased by an average of 8.0° upon coordination of the metal. Most of this is accounted for by the decrease of the angle at the C(5) and C(12) hinge by an average of 5.5°.

The primary difference between the four molecules of **1** is that the *anti*-$Cr(CO)_3$ group adopts different rotational orientations in the crystal structure. Molecule A is *exo* staggered in contrast to molecule D which is approximately *endo* staggered. Molecule B can be considered as eclipsed while molecule C is intermediate between *endo* staggered and eclipsed. Thus, the angles away from perfectly *endo* staggered (0° *endo* staggered; 30° eclipsed; 60° *exo* staggered) for the four isomers are: A, 53.8°; B, 29.2°; C, 21.0°; D, 9.5°. The closely related η^6-benzocyclooctatetraenetricarbonylchromium has the *anti*-$Cr(CO)_3$ conformation with the tripod about 20° from a perfectly *endo* staggered configuration, similar to what is observed for molecule C [24]. While it is unusual for there to be different $Cr(CO)_3$ orientations in the solid state for arenetricarbonylchromium complexes, examples exist where equivalent tricarbonylchromium moieties on the same molecule adopt different orientations [25,26] and two examples exist where there are two independent

molecules in the crystal with different tripod conformations [27,28]. All of the *syn*-$Cr(CO)_3$ groups in **1** are oriented in an *exo* staggered configuration due to steric restrictions associated with the concave side of the dibenzocyclooctatetraene fragment.

To find an explanation for the existence of the four different tripod arrangements, intermolecular distances were investigated. It was found that 24 intermolecular O···H distances less than the sum of the van der Waals radii (2.7 Å [29]) are present in the structure of **1** when the C–H bond distances are normalized to 1.08 Å [30]. These interactions, with the associated geometric parameters, are listed in Table 5. Clearly, there is a large variation of interactions present with the shortest O···H being 2.29 Å and the distance increasing to the cutoff value of 2.7 Å. The presence of these interactions in the crystal structure of **1** requires the determination as to whether some or all of these interactions should be considered C–H···O hydrogen bonds.

While the existence of C–H···O hydrogen bonds was suggested many years ago [31–34], acceptance that cohesive C–H···O interactions can be classified as hydrogen bonds has been relatively recent [35,36]. However, there is some disagreement concerning the criteria that should be applied when assigning a C–H···O (C–H···X) interaction as a weak hydrogen bond or van der Waals interaction. It has been suggested that no arbitrary H···X distance cutoff for C–H···X hydrogen bonds is appropriate and that even interactions greater

than the sum of the van der Waals radii still constitute hydrogen bonds [37,38]. This concept has been challenged with the suggestion that only H···X contacts significantly shorter than the sum of the van der Waals radii be considered hydrogen bonds [39]. Indeed, C–H···O hydrogen bonds have been the subject of theoretical studies [40–42] and much information concerning their importance has been obtained by intense analysis of the Cambridge Structural Database (CSD) [35–38,43–62].

For the present study, it is assumed that C–H···O hydrogen bonds have H···O distances less than the sum of the van der Waals radii and the angle at hydrogen is greater than 110°. Using this definition, all intermolecular interactions for **1** in Table 5 are determined to be C–H···O hydrogen bonds. A search of the 1993 CSD yielded 474 structures in which a terminal chromium carbonyl oxygen acted as a hydrogen bond acceptor for a hydrogen bound to carbon (C–H normalized to 1.08 Å; O···H distances < 2.8 Å) [63]. The following mean values were reported: C···O distance 3.51 Å; H···O distance 2.64 Å; C–H···O angle 140.1°; C–O···H angle 124.9°. A comparison of these with the values in Table

Table 2
Selected bond lengths (Å) for **1**

	A	B	C	D
C(1)–C(2)	1.359(11)	1.364(12)	1.372(12)	1.400(12)
C(1)–C(13)	1.369(10)	1.452(10)	1.373(11)	1.444(11)
C(2)–C(3)	1.426(11)	1.406(11)	1.422(12)	1.392(11)
C(3)–C(4)	1.382(11)	1.333(11)	1.424(13)	1.328(11)
C(4)–C(14)	1.417(10)	1.454(11)	1.389(10)	1.447(12)
C(5)–C(14)	1.488(10)	1.477(10)	1.483(10)	1.465(10)
C(5)–C(6)	1.311(10)	1.306(10)	1.315(10)	1.351(10)
C(6)–C(15)	1.491(10)	1.457(10)	1.502(9)	1.423(10)
C(7)–C(8)	1.321(11)	1.403(11)	1.388(10)	1.399(11)
C(7)–C(15)	1.446(10)	1.436(10)	1.392(10)	1.420(10)
C(8)–C(9)	1.423(11)	1.369(11)	1.413(12)	1.429(12)
C(9)–C(10)	1.379(11)	1.384(10)	1.376(12)	1.338(11)
C(10)–C(16)	1.413(10)	1.430(10)	1.390(10)	1.283(10)
C(11)–C(12)	1.305(11)	1.302(10)	1.301(11)	1.274(11)
C(11)–C(16)	1.454(10)	1.484(9)	1.446(10)	1.557(11)
C(12)–C(13)	1.502(11)	1.474(11)	1.463(11)	1.490(12)
C(13)–C(14)	1.458(9)	1.399(10)	1.449(10)	1.410(10)
C(15)–C(16)	1.410(9)	1.418(9)	1.431(9)	1.420(9)
Cr(1)–C(1)	2.191(8)	2.217(8)	2.195(9)	2.206(9)
Cr(1)–C(2)	2.183(8)	2.208(9)	2.222(9)	2.218(8)
Cr(1)–C(3)	2.210(8)	2.197(9)	2.227(9)	2.204(8)
Cr(1)–C(4)	2.205(8)	2.220(8)	2.209(9)	2.221(9)
Cr(1)–C(13)	2.215(8)	2.257(8)	2.260(8)	2.253(9)
Cr(1)–C(14)	2.234(7)	2.261(8)	2.261(7)	2.260(8)
Cr(2)–C(7)	2.171(8)	2.191(7)	2.219(7)	2.201(8)
Cr(2)–C(8)	2.197(8)	2.235(8)	2.195(8)	2.170(10)
Cr(2)–C(9)	2.201(7)	2.210(8)	2.221(8)	2.210(8)
Cr(2)–C(10)	2.193(8)	2.218(7)	2.157(7)	2.106(9)
Cr(2)–C(15)	2.247(8)	2.217(7)	2.204(7)	2.254(7)
Cr(2)–C(16)	2.236(8)	2.211(7)	2.249(7)	2.170(8)

Table 3
Selected bond angles (°) for **1**

	A	B	C	D
C(2)–C(1)–C(13)	124.0(8)	121.3(7)	124.5(9)	122.2(8)
C(3)–C(2)–C(1)	120.5(8)	119.3(8)	119.5(9)	117.1(8)
C(2)–C(3)–C(4)	117.7(8)	121.7(9)	117.1(9)	122.5(10)
C(3)–C(4)–C(14)	122.2(8)	121.1(8)	122.9(9)	123.1(9)
C(6)–C(5)–C(14)	132.1(8)	129.4(7)	130.0(7)	127.1(7)
C(5)–C(6)–C(15)	125.8(8)	130.2(7)	128.7(7)	129.1(7)
C(8)–C(7)–C(15)	122.4(7)	122.2(7)	119.6(7)	121.5(7)
C(9)–C(8)–C(7)	120.8(8)	119.0(8)	120.6(8)	118.0(8)
C(8)–C(9)–C(10)	118.4(8)	121.8(8)	117.4(8)	116.9(8)
C(9)–C(10)–C(16)	122.1(8)	120.3(8)	125.4(8)	126.3(9)
C(12)–C(11)–C(16)	131.1(8)	130.4(7)	128.3(7)	127.0(8)
C(11)–C(12)–C(13)	127.3(7)	129.4(7)	132.1(8)	132.1(8)
C(1)–C(13)–C(14)	117.1(7)	118.2(7)	117.7(8)	118.6(8)
C(1)–C(13)–C(12)	119.8(7)	116.6(7)	119.9(8)	117.5(8)
C(14)–C(13)–C(12)	122.3(7)	125.0(7)	122.3(7)	123.6(8)
C(13)–C(14)–C(4)	118.5(7)	118.4(7)	118.3(7)	116.4(8)
C(13)–C(14)–C(5)	125.8(7)	124.1(7)	125.3(7)	124.6(8)
C(4)–C(14)–C(5)	115.7(6)	117.3(7)	116.3(7)	118.9(7)
C(16)–C(15)–C(7)	117.5(7)	117.0(7)	116.3(7)	115.4(7)
C(16)–C(15)–C(6)	123.0(7)	125.1(7)	122.4(7)	124.5(7)
C(7)–C(15)–C(6)	119.3(6)	117.8(6)	115.6(6)	119.8(7)
C(15)–C(16)–C(10)	118.7(7)	119.7(7)	114.9(7)	121.1(8)
C(15)–C(16)–C(11)	123.1(7)	122.6(7)	124.9(7)	118.5(7)
C(10)–C(16)–C(11)	118.1(7)	117.7(6)	119.9(7)	120.3(7)

5 indicates that most distances found for **1** are less than the mean values reported and the angles are in the range expected. From the above survey, it can be deduced that the crystal structure of **1** contains a number of strong C–H···O hydrogen bonds represented by the short H···O distances in Table 5. Other crystallographic studies have found hydrogen bonding in (arene)tricarbonylchromium complexes [28,57,64–70], although there are few reports of C–H···O(carbonyl) interactions [65,70]. In addition, it has recently been reported that an intermolecular interaction between carbonyl oxygen atoms and the π electron density of the coordinated arene is observed in the crystal structure of some (arene)tricarbonylchromium complexes [71]. It should be mentioned that there is also spectroscopic evidence for the involvement of (arene)tricarbonylchromium complexes in hydrogen bonding [72–77].

In view of the structural results, the question arises as to whether the C–H···O hydrogen bonds involving the *anti*-Cr(CO)$_3$ groups in **1** should be strong enough to overcome the barrier to rotation found in arenetricarbonylchromium compounds. It has been reported that the strongest hydrogen bonds of this type are approximately 5 kcal mol^{-1} [63]. The barrier to rotation in benzenetricarbonylchromium has been assigned a value of circa 0.5 kcal mol^{-1} experimentally [78] and 0.3 kcal mol^{-1} based on theoretical calculations [17,79]. A better value to use would be the calculated one reported

Table 4
Angles (°) between planes for **2** and **1**

Plane	Plane	**2** [a]	**1**			
			A	B	C	D
C(1)C(2)C(3)C(4)	C(5)C(14)C(13)C(12)	2.3 [b]	5.4(8)	4.7(1)	4.8(1)	4.1(5)
C(7)C(8)C(9)C(10)	C(6)C(15)C(16)C(11)	2.3 [b]	1.3(9)	3.3(5)	2.9(5)	1.8(7)
C(1)C(2)C(3)C(4)	C(1)C(13)C(14)C(4)	1.4 [b]	1.1(7)	0.1(1)	1.3(1)	1.0(5)
C(7)C(8)C(9)C(10)	C(7)C(15)C(16)C(10)	1.4 [b]	2.3(9)	0.4(5)	1.3(5)	2.6(7)
C(5)C(14)C(13)C(12)	C(1)–C(4)C(14)C(13)	2.9 [b]	6.0(6)	4.8(1)	4.1(1)	4.6(4)
C(6)C(15)C(16)C(11)	C(7)–C(10)C(16)C(15)	2.9 [b]	2.5(7)	3.1(4)	3.5(4)	1.5(6)
C(5)C(6)C(11)C(12)	C(5)C(14)C(13)C(12)	43.2 [b]	36.7(4)	39.1(4)	37.2(4)	37.7(4)
C(5)C(6)C(11)C(12)	C(6)C(15)C(16)C(11)	43.2 [b]	44.3(5)	39.3(5)	42.0(5)	44.8(6)
C(5)C(6)C(11)C(12)	C(1)–C(4)C(14)C(13)	40.7 [b]	30.8(3)	34.4(3)	33.1(3)	33.4(3)
C(5)C(6)C(11)C(12)	C(7)–C(10)C(16)C(15)	40.7 [b]	41.9(4)	36.1(4)	38.5(4)	45.0(4)
C(1)–C(4)C(14)C(13)	C(7)–C(10)C(16)C(15)	81.3	72.6(2)	70.5(3)	71.6(3)	78.4(3)

[a] Calculated from atomic positions given in ref. [13].
[b] Average of two equivalent angles.

for naphthalenetricarbonylchromium (2.5 kcal mol^{-1}) [15]. Clearly, if these values are correct, a strong C–H···O hydrogen bond is strong enough to overcome the barrier to rotation in **1**. This agrees with the suggestion that the conformational preference of arenetricarbonylchromium complexes in the solid state may be determined by factors other than internal electronic effects [80].

An analysis of the hydrogen bonding contacts for the *anti*-Cr(CO)$_3$ groups provides evidence for the ability of strong C–H···O hydrogen bonds to control the orientation of the tripod. Notice that the oxygen atoms on *anti*-Cr(CO)$_3$ groups for molecules A [O(21A)···H(8A) 2.45 Å; O(20A)···H(9A) 2.51 Å; O(21A)···H(4B) 2.51 Å], B [O(21B)···H(4A) 2.38 Å; O(20B)···H(7C) 2.47 Å], and D [O(20D)···H(8D) 2.36 Å; O(20D)···H(3D) 2.53 Å; O(22D)···H(9C) 2.55 Å] participate in significant hydrogen bond interactions, suggesting that their orientations are determined by these interactions. However, only one oxygen atom of the *anti*-Cr(CO)$_3$ group of molecule C participates in an intermolecular interaction and that one is long [O(20C)···H(10D) 2.65 Å]. This agrees with the similarity in orientation between the *anti*-Cr(CO)$_3$ group of molecule C and that found for η^6-benzocyclooctatetraenetricarbonylchromium [24] because the weak C–H···O interaction involved is not strong enough to overcome the internal electronic preference in this molecule.

With the identification of the intermolecular interactions in **1** and the determination that they have affected the *anti*-Cr(CO)$_3$ group orientations, it is of interest to determine whether they likewise have an affect on the dibenzocyclooctatetraene ligand. Two of the three strongest C–H···O hydrogen bonds are between carbonyl oxygen atoms and H(4C) and H(4A). The hydrogen bond donors for these interactions are C(4C) and C(4A). A comparison of the carbon–carbon bonds

Table 5
Distances (Å) and angles (°) for C–H···O intermolecular interactions (hydrogen bonds) <2.7 Å in **1**

H	O	O···H	O···C	C–O···H	C–H···O
H(4C)	O(18A) [a]	2.29	3.232(8)	148	145
H(8D)	O(20D) [b]	2.36	3.404(8)	109	162
H(4A)	O(21B) [c]	2.38	3.285(8)	109	141
H(8A)	O(21A) [d]	2.45	3.327(10)	120	138
H(7C)	O(20B) [c]	2.47	3.366(7)	136	139
H(6B)	O(19A) [b]	2.49	3.366(7)	140	137
H(7A)	O(19B) [c]	2.50	3.550(8)	149	164
H(9A)	O(20A) [d]	2.51	3.377(10)	107	137
H(4B)	O(21A) [c]	2.51	3.552(8)	153	162
H(2C)	O(17D) [e]	2.51	3.446(9)	93	144
H(2B)	O(17D) [c]	2.52	3.364(8)	127	134
H(12D)	O(18D) [d]	2.52	3.551(8)	112	160
H(3D)	O(20D) [f]	2.53	3.467(9)	101	144
H(9C)	O(22D) [b]	2.55	3.365(8)	152	132
H(6D)	O(18C) [g]	2.57	3.504(6)	156	145
H(3B)	O(17A) [h]	2.59	3.359(9)	124	128
H(1B)	O(18D) [c]	2.59	3.416(8)	102	133
H(1C)	O(20D) [i]	2.60	3.492(8)	153	140
H(10A)	O(19C) [j]	2.61	3.571(9)	146	147
H(9B)	O(20B) [d]	2.63	3.460(10)	119	134
H(5C)	O(22B) [c]	2.63	3.485(7)	131	135
H(1D)	O(18B) [c]	2.63	3.491(5)	108	137
H(10D)	O(20C) [c]	2.65	3.496(6)	120	135
H(2D)	O(17B) [c]	2.68	3.575(7)	119	141

[a] $1-x$, $0.5+y$, $1-z$.
[b] $-1+x$, y, z.
[c] x, y, z.
[d] $1+x$, y, z.
[e] x, $1+y$, z.
[f] $1-x$, $-0.5+y$, $2-z$.
[g] $-x$, $-0.5+y$, $2-z$.
[h] $1-x$, $-0.5+y$, $1-z$.
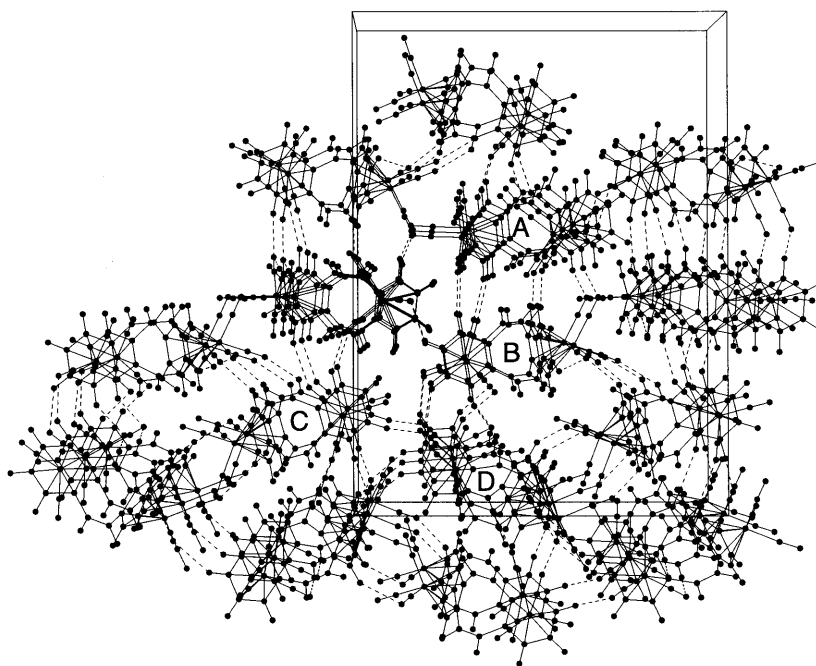[i] $1-x$, $0.5+y$, $2-z$.
[j] $-x$, $-0.5+y$, $1-z$.

Fig. 3. Crystal packing diagram of **1** showing C–H⋯O hydrogen bonds. View is perpendicular to the *bc* plane.

involving C(4) in Table 2 suggests that the hydrogen bonding has affected the geometry of the organic fragment. Notice that the two carbon donors with the strongest C–H⋯O hydrogen bonds participate in bonds with lengths significantly different than the other carbon atoms [i.e. C(3A)–C(4A) 1.382 Å and C(3C)–C(4C) 1.424 Å compared with C(3B)–C(4B) 1.333 Å and C(3D)–C(4D) 1.328 Å]. Likewise, from Table 3, it is observed that one of the angles with C(4) as a terminal atom [C(2)–C(3)–C(4)] varies significantly between the four molecules with the angles in molecules A and C smaller than in the other molecules.

Fig. 3 contains a crystal packing diagram showing the hydrogen bonding network in the structure. In the crystal, the molecules form stacks parallel to the crystallographic *a* axis (Fig. 3). These stacks are interconnected by C–H⋯O hydrogen bonds. The A, B, and D molecules are connected to the ones above and below by hydrogen bonds.

It is well documented that the oxygen atom of a metal carbonyl can act as a hydrogen bond acceptor for a hydrogen bound to carbon [52–54,57,72,81–84]. Likewise, coordinated arenes can serve as C–H hydrogen bond donors [83–86]. Even with these precedents, the C–H⋯O hydrogen bonding in **1** is more extensive and comprises more strong interactions than is found in most organometallic compounds that form C–H⋯O hydrogen bonds. A possible explanation for the strength of the hydrogen bonds in **1** involves the increased acidity that coordination of a Cr(CO)$_3$ group

imparts upon arene hydrogen atoms and hydrogen atoms α and β to the coordinated arene [86]. In fact, it has been reported that the coordination of a second Cr(CO)$_3$ group to stilbene greatly enhances the acidity of both the arene and olefinic hydrogen atoms [87]. It is known that the strength of a C–H⋯O hydrogen bond increases with the acidity of the hydrogen atoms [48,50,51]. In **1**, the combined effect of two Cr(CO)$_3$ groups accepting electron density from the dibenzocyclooctatetraene increases the acidity of all hydrogen atoms resulting in increased propensity for strong C–H⋯O hydrogen bond formation.

A comparison of the bond lengths, bond angles, and angles between planes (Tables 2–4) indicates significant differences between the different molecules of **1**, some of which have already been mentioned. An analysis of the distances between the Cr atoms and the arene centroids yields a somewhat surprising result. For the four *anti*-Cr(CO)$_3$ groups, the distances from the metal to the centroid of the coordinated arene are 1.708, 1.709, 1.709, and 1.695 Å for molecules A through D, respectively. However, for the *syn*-Cr(CO)$_3$ groups, the distances are 1.704, 1.731, 1.731, and 1.729 Å. While all of these values are within the range expected for arenetricarbonylchromium complexes [14], the difference between the value for the *syn*-Cr(CO)$_3$ of molecule A and the other molecules is perplexing. Clearly, there is a complex interplay between intermolecular and intramolecular forces which controls the geometries of the four molecules in **1**.

3. Conclusions

The tricarbonylchromium groups in **1** coordinate to opposite sides of the dibenzocyclooctatetraene fragment resulting in *syn*- and *anti*-Cr(CO)$_3$ moieties. **1** contains four independent molecules in the crystal. A three-dimensional array of C–H···O hydrogen bonds exists in the crystal structure of **1**. These intermolecular interactions control the orientation of the *anti*-Cr(CO)$_3$ groups. The main difference between the organic backbone in **1** and the structure of **2** is that the presence of the *syn*-Cr(CO)$_3$ has the effect of flattening the boat conformation slightly.

The structural results reported here have two profound implications. First, this research clearly indicates that arenetricarbonylchromium complexes are another class of compounds that can serve as organometallic synthons in supramolecular chemistry [59,88–90]. In addition, the control of the carbonyl orientation by intermolecular interactions supports previous indications that this may be the situation for a number of arenetricarbonylchromium complexes [80].

4. Supplementary material

Crystallographic data for the structural analysis of compound **1** have been deposited with the Cambridge Crystallographic Data Center (CCDC no. 138097). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

References

[1] R.D. Rieke, K.P. Daruwala, J. Org. Chem. 53 (1988) 2073.
[2] R.D. Rieke, K.P. Daruwala, M.W. Forkner, Organometallics 10 (1991) 2946.
[3] R.D. Rieke, K.P. Daruwala, L.D. Schulte, S.M. Pankas, Organometallics 11 (1992) 284.
[4] S.N. Milligan, R.D. Rieke, Organometallics 2 (1983) 171.
[5] L.D. Schulte, R.D. Rieke, J. Org. Chem. 52 (1987) 4827.
[6] L.D. Schulte, R.D. Rieke, Tetrahedron Lett. 29 (1988) 5483.
[7] R.D. Rieke, K.P. Daruwala, M.W. Forkner, J. Org. Chem. 54 (1989) 21.
[8] R.D. Rieke, L.D. Schulte, B.T. Dawson, S.S. Yang, J. Am. Chem. Soc. 112 (1990) 8388.
[9] J. Müller, P. Göser, M. Elian, Angew. Chem. Int. Ed. Engl. 8 (1969) 374.
[10] R.D. Rieke, J.S. Arney, W.E. Rich, B.R. Willeford, B.S. Poliner, J. Am. Chem. Soc. 97 (1975) 5951.
[11] W.P. Henry, R.D. Rieke, J. Am. Chem. Soc. 105 (1983) 6314.
[12] R.D. Rieke, W.P. Henry, J.S. Arney, Inorg. Chem. 26 (1987) 420.
[13] H. Irngartinger, W.R.K. Reibel, Acta Crystallogr. Sect. B 37 (1981) 1724.
[14] E.L. Muetterties, J.R. Bleeke, E.J. Wucherer, T.A. Albright, Chem. Rev. 82 (1982) 499.
[15] R.D. Rogers, J.L. Atwood, T.A. Albright, W.A. Lee, M.D. Rausch, Organometallics 3 (1984) 263.
[16] T.A. Albright, P. Hofmann, R. Hoffmann, C.P. Lillya, P.A. Dobosh, J. Am. Chem. Soc. 105 (1983) 3396.
[17] T.A. Albright, Acc. Chem. Res. 15 (1982) 149.
[18] M. Avram, I.G. Dinulescu, D. Dinu, G. Mateescu, C.D. Nenitzescu, Tetrahedron 19 (1963) 309.
[19] G.M. Sheldrick, Acta Crystallogr. Sect. A 46 (1990) 467.
[20] G.M. Sheldrick, SHELXL-93, Program for the Refinement of Crystal Structures, University of Göttingen, Germany, 1993.
[21] T.E. Bitterwolf, R. Herzog, P.D. Rockswold, J. Organomet. Chem. 320 (1987) 197.
[22] T.E. Bitterwolf, A. Ceccon, A. Gambaro, P. Ganis, D. Kuck, F. Manoli, A.L. Rheingold, G. Valle, A. Venzo, J. Chem. Soc. Perkin Trans. 2 (1997) 735.
[23] A. Ceccon, A. Gambaro, F. Manoli, A. Venzo, D. Kuck, T.E. Bitterwolf, P. Ganis, G. Valle, J. Chem. Soc. Perkin Trans. 2 (1991) 233.
[24] P. Berno, A. Ceccon, A. Gambaro, A. Venzo, P. Ganis, G. Valle, J. Chem. Soc. Perkin Trans. 2 (1987) 935.
[25] S.J. Hughes, J.R. Moss, K.J. Naidoo, J.F. Kelly, A.S. Batsanov, J. Organomet. Chem. 588 (1999) 176.
[26] D.J. Peitz, R.T. Palmer, L.J. Radonovich, N.F. Woolsley, Organometallics 12 (1993) 4580.
[27] T.G. Traylor, M.J. Goldberg, A.R. Miksztal, C.E. Strouse, Organometallics 8 (1989) 1101.
[28] N. Sardone, P. Seresini, G. Zecchi, Acta Crystallogr. Sect. C 52 (1996) 613.
[29] A. Bondi, J. Phys. Chem. 68 (1964) 441.
[30] H.-B. Burgi, J.D. Dunitz, Structure Correlation, vol. 2, VCH, New York, 1994, p. 773.
[31] D.J. Sutor, J. Chem. Soc. (1963) 1105.
[32] G. Ferguson, K.M.S. Islam, J. Chem. Soc. B (1966) 593.
[33] D.J. Sutor, Nature 195 (1962) 68.
[34] G. Ferguson, J. Tyrrell, Chem. Commun. (1965) 195.
[35] R. Taylor, O. Kennard, J. Am. Chem. Soc. 104 (1982) 5063.
[36] G.A. Jeffrey, W. Saenger, Hydrogen Bonding in Biological Structures, Springer-Verlag, Berlin, 1991.
[37] T. Steiner, Chem. Commun. (1997) 727.
[38] T. Steiner, G.R. Desiraju, Chem. Commun. (1998) 891.
[39] F.A. Cotton, L.M. Daniels, G.T.I. Jordan, C.A. Murillo, Chem. Commun. (1997) 1673.
[40] Y. Gu, T. Kar, S. Scheiner, J. Am. Chem. Soc. 121 (1999) 9411.
[41] K.N. Houk, S. Menzer, S.P. Newton, F.M. Raymo, J.F. Stoddart, D.J. Williams, J. Am. Chem. Soc. 121 (1999) 1479.
[42] S. Scheiner, Hydrogen Bonding: A Theoretical Approach, Oxford University Press, New York, 1997.
[43] G.R. Desiraju, Acc. Chem. Res. 29 (1996) 441.

[44] G.R. Desiraju, S. Kashino, M.M. Coombs, J.P. Glusker, Acta Crystallogr. Sect. B 49 (1993) 880.

[45] J.D. Chaney, C.R. Goss, K. Folting, B.D. Santarsiero, M.D. Hollingsworth, J. Am. Chem. Soc. 118 (1996) 9432.

[46] T. Steiner, W. Saenger, J. Am. Chem. Soc. 115 (1993) 4540.

[47] T. Steiner, J. Chem. Soc. Chem. Commun. (1994) 101.

[48] V.R. Pedireddi, G.R. Desiraju, J. Chem. Soc. Chem. Commun. (1992) 988.

[49] T. Steiner, J. Chem. Soc. Chem. Commun. (1994) 2341.

[50] G.R. Desiraju, J. Chem. Soc. Chem. Commun. (1989) 179.

[51] G.R. Desiraju, J. Chem. Soc. Chem. Commun. (1990) 454.

[52] D. Braga, F. Grepioni, H. Wadepohl, S. Gebert, M.J. Calhorda, L.F. Veiros, Organometallics 14 (1995) 5350.

[53] K. Biradha, G.R. Desiraju, D. Braga, F. Grepioni, Organometallics 15 (1996) 1284.

[54] D. Braga, F. Grepioni, E. Tedesco, K. Biradha, G.R. Desiraju, Organometallics 15 (1996) 2692.

[55] T. Steiner, W. Saenger, J. Am. Chem. Soc. 114 (1992) 10146.

[56] K.C.V. Sharma, G.R. Desiraju, J. Chem. Soc. Perkin Trans. 2 (1994) 2345.

[57] D. Braga, F. Grepioni, Acc. Chem. Res. 30 (1997) 81.

[58] D. Braga, F. Grepioni, E. Tedesco, H. Wadepohl, S. Gebert, J. Chem. Soc. Dalton Trans. (1997) 1727.

[59] D. Braga, F. Grepioni, G.R. Desiraju, J. Organomet. Chem. 548 (1997) 33.

[60] T. Steiner, Chem. Commun. (1999) 313.

[61] T. Steiner, J.A. Kanters, J. Kroon, Chem. Commun. (1996) 1277.

[62] R. Taylor, O. Kennard, Acc. Chem. Res. 17 (1984) 320.

[63] D. Braga, F. Grepioni, K. Biradha, V.R. Pedireddi, G.R. Desiraju, J. Am. Chem. Soc. 117 (1995) 3156.

[64] O.L. Carter, A.T. McPhail, G.A. Sim, J. Chem. Soc. A (1967) 228.

[65] C. Bonifaci, A. Ceccon, A. Gambaro, P. Ganis, S. Santi, G. Valle, A. Venzo, J. Organomet. Chem. 492 (1995) 35.

[66] M.M. Kubicki, P. Richard, B. Gautheron, M. Viotte, S. Toma, M. Hudecek, V. Gajda, J. Organomet. Chem. 476 (1994) 55.

[67] D. Braga, F. Grepioni, P. Sabatino, G.R. Desiraju, Organometallics 13 (1994) 3532.

[68] P.J. Dickens, A.M.Z. Slawin, D.A. Widdowson, D.J. Williams, Tetrahedron Lett. 29 (1988) 103.

[69] J. Lamiot, F. Baert, J. Brocard, S. Goetgheluck, Acta Crystallogr. Sect. C 52 (1996) 595.

[70] S. Camiolo, S.J. Coles, P.A. Gale, M.B. Hursthouse, T.A. Mayer, M.A. Paver, Chem. Commun. (2000) 275.

[71] A. Gambaro, P. Ganis, F. Manoli, A. Polimeno, S. Santi, A. Venzo, J. Organomet. Chem. 583 (1999) 126.

[72] A. Perjessy, P. Hrnciar, Z. Sustekova, K. Bowden, R.J. Ranson, O. Hritzova, N. Pronayova, J. Organomet. Chem. 552 (1998) 1.

[73] G. Hunter, C. Rochester, A.G. Wilkinson, J. Mol. Catal. A: Chem. 121 (1997) 81.

[74] G. Hunter, C.H. Rochester, A.J. Wilkinson, J. Paton, J. Chem. Soc. Faraday Trans. 92 (1996) 4763.

[75] G. Hunter, C.H. Rochester, A.G. Wilkinson, J. Paton, J. Chem. Soc. Faraday Trans. 93 (1997) 1205.

[76] G. Hunter, C.H. Rochester, A.G. Wilkinson, J. Paton, J. Chem. Soc. Faraday Trans. 92 (1996) 5093.

[77] B.V. Lokshin, S.G. Kazaryan, A.G. Ginzburg, J. Mol. Struct. 174 (1988) 29.

[78] N.-S. Chiu, L. Schafer, R. Seip, J. Organomet. Chem. 101 (1975) 331.

[79] T.A. Albright, P. Hofmann, R. Hoffmann, J. Am. Chem. Soc. 99 (1977) 7546.

[80] T.M. Gilbert, A.H. Bond, R.D. Rogers, J. Organomet. Chem. 479 (1994) 73.

[81] D. Braga, J.J. Byrne, F. Grepioni, E. Parisini, P.J. Dyson, P.E. Gaede, B.F.G. Johnson, D. Reed, Organometallics 14 (1995) 4892.

[82] H. Wadepohl, D. Braga, F. Grepioni, Organometallics 14 (1995) 24.

[83] D. Braga, F. Grepioni, M.J. Calhorda, L.F. Veiros, Organometallics 14 (1995) 1992.

[84] D. Braga, P.J. Dyson, F. Grepioni, B.F.G. Johnson, M.J. Calhorda, Inorg. Chem. 33 (1994) 3218.

[85] F. Grepioni, D. Braga, P.J. Dyson, B.F.G. Johnson, F.M. Sanderson, M.J. Calhorda, L.F. Veiros, Organometallics 14 (1995) 121.

[86] M.F. Semmelhack, G.R. Clark, J.L. Garcia, J.J. Harrison, Y. Thebtaranonth, W. Wulff, A. Yamashita, Tetrahedron 37 (1981) 3957.

[87] Z.V. Todres, E.A. Ionina, J. Organomet. Chem. 453 (1993) 197.

[88] D. Braga, F. Grepioni, Chem. Commun. (1996) 571.

[89] D. Braga, F. Grepioni, G.R. Desiraju, Chem. Rev. 98 (1998) 1375.

[90] D. Braga, F. Grepioni, J. Chem. Soc. Dalton Trans. (1999) 1.