

# Alternating C–C Bond Lengths in Gas-Phase (Benzene)chromium Tricarbonyl

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**Abstract:** The microwave rotational spectrum of ([1,2-D<sub>2</sub>]benzene)chromium tricarbonyl was measured in the 4–12 GHz range using a Flygare–Balle-type spectrometer. This spectrum contains transitions due to two different structural isomers of this complex. These results are interpreted in terms of a reduction of the symmetry of benzene to C<sub>3v</sub> due to interactions with the Cr(CO)<sub>3</sub> moiety. One structural isomer (isomer *E*) occurs when the deuterium atoms are at the ends of a “long” C–C bond, the other (isomer *S*), when the deuterium atoms are at the ends of a “short” C–C bond. The data indicate a difference of 0.016 Å in adjacent benzene C–C bond lengths in this complex.

## Introduction

Interactions of arenes with transition metal complexes have been shown to significantly modify the structure and the reactivity of the complexed arene. Reactions useful in organic synthesis<sup>1</sup> are facilitated by the activation of arenes toward nucleophilic attack by complexation with Cr(CO)<sub>3</sub>. More recently,<sup>2</sup> chiral (arene)chromium tricarbonyl complexes have been used in stereospecific syntheses with high enantioselectivity.

The lowering of the benzene symmetry to C<sub>3v</sub> in crystals of the (benzene)chromium tricarbonyl complex was observed in neutron diffraction studies<sup>3</sup> over 20 years ago. Similar effects were observed more recently using diffraction methods for other arene complexes, (C<sub>6</sub>(CH<sub>3</sub>)<sub>6</sub>) Cr(CO)<sub>3</sub><sup>4</sup> and (C<sub>6</sub>(CH<sub>3</sub>)<sub>6</sub>) Mo(CO)<sub>3</sub>.<sup>5</sup> These results were supported by theoretical and photoelectron studies<sup>6</sup> of the bonding in these complexes. There was some controversy over these results since earlier measurements<sup>7</sup> indicated D<sub>6h</sub> symmetry for the complexed benzene and there was also the possibility that the benzene structure was deformed by crystal packing forces.

## Experimental Section

Microwave spectra were measured in the 4–12 GHz range in order to determine rotational constants of [1,2-D<sub>2</sub>](η<sup>6</sup>-C<sub>6</sub>H<sub>4</sub>D<sub>2</sub>)Cr(CO)<sub>3</sub>. The structure of this complex is shown in Figure 1. If the structure of the benzene moiety were D<sub>6h</sub> or C<sub>6v</sub> in the complex, and the Cr(CO)<sub>3</sub> group C<sub>3v</sub> symmetry, the rotational constants of the complex would be the same for all relative orientations of the benzene and Cr(CO)<sub>3</sub> groups. If, on the other hand, the Cr(CO)<sub>3</sub> group induces a lowering of the benzene symmetry to C<sub>3v</sub>, then there will be structural isomers with different rotational constants, depending on whether the C–C bond with two D substitutions eclipses a Cr–CO group (isomer *E*) or is staggered with respect to two Cr–CO groups (isomer *S*). Axial views of these two isomers are shown in Figure 2.

The sample was synthesized by refluxing 2 mL of [1,2-D<sub>2</sub>]benzene (C/D/N Isotopes, D-1133) and 2 g of Cr(CO)<sub>6</sub> in 40 mL of solvent

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(1) Pearson, A. J. *Metallo-Organic Chemistry*; John Wiley & Sons: New York, 1985; Chapter 9.

(2) Jones, G. B.; Heaton, S. B. *Tetrahedron: Asymmetry* **1993**, *4*, 261.

Jones, G. B.; Heaton, S. B. *Tetrahedron Lett.* **1992**, *33*, 1693.

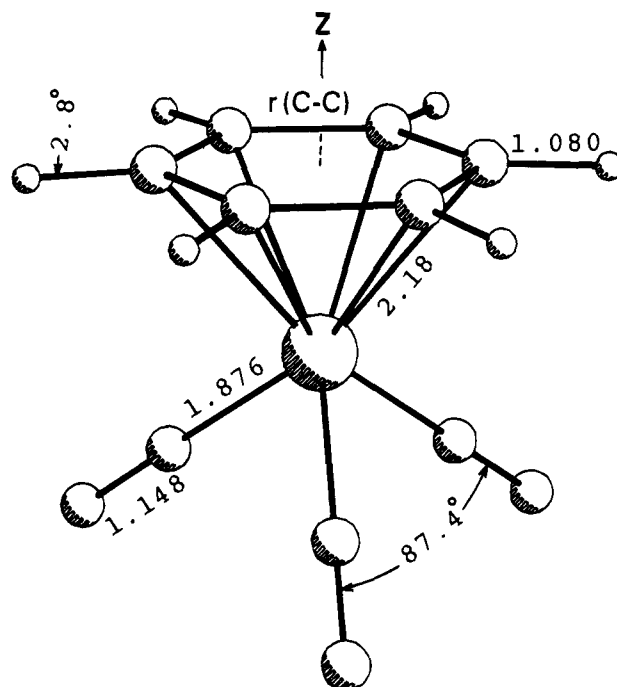
(3) Rees, B.; Coppens, P. *Acta Crystallogr., Sect. B* **1973**, *29*, 2515.

(4) Byers, B. P.; Hall, M. B. *Inorg. Chem.* **1987**, *26*, 2186.

(5) Chesick, J. P.; Koshland, D. E.; Myers, S. E. *Acta Crystallogr., Sect. B* **1977**, *33*, 2013.

(6) Byers, B. P.; Hall, M. B. *Organometallics* **1987**, *6*, 2319.

(7) Bailey, M. F.; Dahl, L. F. *Inorg. Chem.* **1965**, *4*, 1314–1319, 1298–1306.



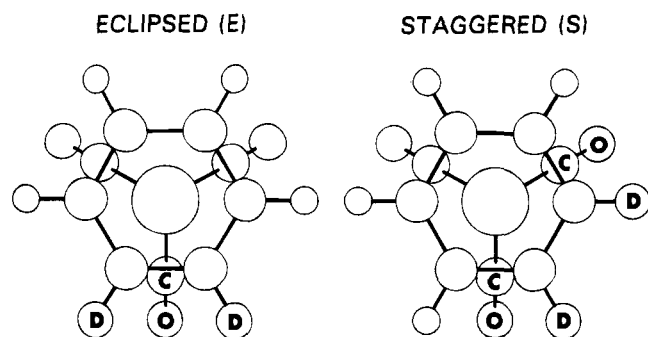
**Figure 1.** Structure of the (benzene)chromium tricarbonyl complex determined from microwave spectroscopy measurements. The C–C bond lengths ( $r(\text{C}-\text{C})$ ) alternate between 1.406 and 1.422 Å. The H atoms are displaced out of the plane of the benzene carbon atoms, toward the Cr atom by the angle  $\gamma = 2.8^\circ$ .

(90% diglyme, 10% butyl acetate) under a nitrogen atmosphere. In testing many solvent combinations, we found better efficiency, when using a minimal amount of benzene, with this combination of diglyme<sup>8</sup> and butyl acetate catalyst.<sup>9</sup> The efforts to improve yields, with the condition of using small proportional amounts of benzene, were prompted by the high cost and limited availability of [1,2-D<sub>2</sub>]benzene. The sample was purified by vacuum sublimation and maintained at 100 °C in neon buffer gas for injection into the spectrometer.

The predicted differences in rotational constants for the D atoms being at the ends of a “short” C–C bond compared with those for the D atoms at the ends of a “long” C–C bond were only 0.01%, based on the crystal diffraction results.<sup>3</sup> Since these small differences in rotational constants would only result in shifts of approximately 100 kHz in observed transitions, high-resolution was required to observe these differences. The Flygare–Balle-type spectrometer system<sup>10</sup>

(8) Nicholls, B.; Whiting, M. C. *J. Chem. Soc.* **1959**, 551.

(9) Hudeček, M.; Toma, S. *J. Organomet. Chem.* **1991**, *406*, 147.



**Figure 2.** Axial views down the  $z$ -axis (which nearly coincides with the  $a$ -axis) of the two structural isomers of (benzene)chromium tricarbonyl. The eclipsed  $E$  isomer occurs when the two deuterium substitutions are at the ends of a "longer" C–C bond, which eclipses the CO group below. For the staggered  $S$  isomer, the "shorter" bond has a deuterium atom at each end and is believed to occur when this bond is staggered with respect to two CO groups below.

**Table 1.** Measured Transition Frequencies for the Two Structural Isomers of ([1,2- $D_2$ ])benzene)chromium Tricarbonyl<sup>a</sup>

$J_{K_p K_o}$	$J'_{K'_p K'_o}$	$E$ isomer	$S$ isomer
2 <sub>12</sub>	3 <sub>13</sub>	4316.145	4316.357
2 <sub>02</sub>	3 <sub>03</sub>	4324.709	4324.733
2 <sub>11</sub>	3 <sub>12</sub>	4334.317	4334.091
3 <sub>13</sub>	4 <sub>14</sub>	5764.683	5754.969
3 <sub>03</sub>	4 <sub>04</sub>	5765.564	5765.620
3 <sub>22</sub>	4 <sub>23</sub>		5766.966
3 <sub>30</sub>	4 <sub>31</sub>		5767.389
3 <sub>12</sub>	4 <sub>13</sub>	5778.895	5778.605
4 <sub>14</sub>	5 <sub>15</sub>	7193.070	7193.444
4 <sub>04</sub>	5 <sub>04</sub>	7205.818	7205.940
4 <sub>23</sub>	5 <sub>24</sub>	7208.520	
4 <sub>22</sub>	5 <sub>23</sub>	7211.563	7211.417
4 <sub>13</sub>	5 <sub>14</sub>	7223.308	7222.956
5 <sub>15</sub>	6 <sub>16</sub>	8631.291	8631.754
5 <sub>05</sub>	6 <sub>06</sub>	8645.351	8645.571
5 <sub>24</sub>	6 <sub>25</sub>	8649.936	
5 <sub>23</sub>	6 <sub>24</sub>	8655.200	8654.966
5 <sub>14</sub>	6 <sub>15</sub>	8667.493	8667.096
6 <sub>16</sub>	7 <sub>17</sub>	10069.308	10069.872
6 <sub>06</sub>	7 <sub>07</sub>	10084.082	10084.431
6 <sub>24</sub>	7 <sub>25</sub>	10099.473	10099.123
6 <sub>15</sub>	7 <sub>16</sub>	10111.401	10110.972
7 <sub>17</sub>	8 <sub>18</sub>	11507.117	11507.789
7 <sub>07</sub>	8 <sub>08</sub>	11521.977	11522.485
7 <sub>26</sub>	8 <sub>27</sub>	11532.252	11532.304
7 <sub>25</sub>	8 <sub>26</sub>	11544.385	11543.899
7 <sub>16</sub>	8 <sub>17</sub>	11554.962	11554.519

<sup>a</sup> Experimental uncertainties for the measured lines ranged from 1 to 6 kHz. The listed values are in MHz.

provides excellent sensitivity along with sufficient resolution to accurately measure these small differences in line positions and rotational constants.

Rotational constants for six isotopomers of (benzene)chromium tricarbonyl had been measured previously<sup>11,12</sup> and used to obtain an accurate, gas-phase structure for this complex. This structure was used to determine the changes in rotational constants with the C–C bond length alternation and to predict rotational constants for the [1,2- $D_2$ ]-benzene isotopomer. The experimental parameter ( $B - C$ ), the difference between  $B$  and  $C$  rotational constants, is the parameter most directly correlated with differences in alternate C–C bond lengths.

The measured transition frequencies are listed in Table 1. Listed are 25 measured  $a$ -dipole transitions each for the  $E$  and the  $S$  isomers.

(10) Balle, T. J.; Flygare, W. H. *Rev. Sci. Instrum.* **1981**, *52*, 33. Bumgarner, R. E.; Kukolich, S. G. *J. Chem. Phys.* **1987**, *86*, 1083.

(11) Sickafoose, S. M.; Breckenridge, S. M.; Kukolich, S. G. *Inorg. Chem.* **1994**, *33*, 5176.

(12) Kukolich, S. G.; Sickafoose, S. M.; Flores, L. D.; Breckenridge, S. M. *J. Chem. Phys.* **1994**, *100*, 6125.

**Table 2.** Rotational and Distortion Constants Obtained using a Least-Squares Fit to Measured Lines in Table 1 for the  $E$  and  $S$  Structural Isomers<sup>a</sup>

parameter	$E$ isomer	$S$ isomer
$A$ (MHz)	900.05(5)	900.02(5)
$B$ (MHz)	723.9167(2)	723.8423(2)
$C$ (MHz)	717.8598(2)	717.9305(2)
$\Delta_J$ (kHz)	0.046(2)	0.048(2)
$\Delta_{JK}$ (kHz)	-0.10(6)	-0.11(5)
$\sigma_{\text{fit}}$ (kHz)	1.8	1.8

<sup>a</sup> Listed uncertainties are  $2\sigma$ .  $\sigma_{\text{fit}}$  denotes the standard deviation for the fit.

**Table 3.** Cartesian Atomic Coordinates for (Benzene)chromium Tricarbonyl (in Å) Obtained by Fitting the Microwave Data<sup>a</sup>

atom	$x$	$y$	$z$
C1	1.227	0.703	-1.654
C2	1.227	-0.703	-1.654
C3	-0.005	-1.414	-1.654
C4	-1.222	-0.711	-1.654
C5	-1.222	0.711	-1.654
C6	-0.005	1.414	-1.654
H1	2.162	1.239	-1.602
H2	2.162	-1.239	-1.602
H3	-0.008	-2.492	-1.602
H4	-2.154	-1.253	-1.602
H5	-2.154	1.253	-1.602
H6	-0.008	2.492	-1.602
Cr	0.000	0.000	0.004
C7	1.496	0.000	1.135
C8	-0.748	-1.296	1.135
C9	-0.748	1.296	1.135
O1	2.412	0.000	1.827
O2	-1.206	-2.088	1.827
O3	-1.206	2.088	1.827

<sup>a</sup> The Origin is the Center-of-Mass for the Common Isotopomer.

The measured transition frequencies were within a few tenths of 1 MHz of the predicted values. The predicted values for transition frequencies were obtained using the previous microwave structure<sup>11</sup> and including the C–C bond length alternation data from the diffraction work.<sup>3</sup> Rotational and centrifugal distortion constants obtained by fitting the measured lines are listed in Table 2. The observed rotational transitions were fit using a Watson-type  $A$ -reduced Hamiltonian.<sup>13</sup> The rotational constants are in excellent agreement with those predicted using structural parameters obtained from the previous work.<sup>11,12</sup> The distortion constants are also in agreement with values for the other isotopomers.<sup>11,12</sup>

The measured differences in values for  $B - C$  for the two isomers may be used to obtain differences in the distances between adjacent hydrogen atoms. If we assume that hydrogen and carbon atom coordinates, relative to the center of the benzene ring are proportional, then we can obtain the differences in C–C bond lengths. Fitting the measured differences in ( $B - C$ ) gives directly a difference in distances between adjacent H atoms of  $\Delta_{\text{HH}} = 0.0288$  Å. With the assumption of proportional C and H atom coordinates for the benzene moiety, we get a difference in C–C bond lengths of  $\Delta_{\text{CC}} = 0.0163$  Å. The propagated errors from the rotational constant measurements are less than 1%. We would estimate additional model errors due to vibrational averaging effects to be 2–5%.

Cartesian coordinates for the basic structure of the complex are given in Table 3, with the origin at the center-of-mass of the common isotopomer. These coordinates were obtained from an improved fit to the earlier rotational constants<sup>11,12</sup> and also include the current results on the C–C bond length alternation. In this coordinate system, the Cr atom  $z$ -coordinate will have the greatest uncertainty, since that atom is so close to the center-of-mass of the complex. The revised bond lengths and interbond angles are listed in Table 4.

(13) Watson, J. K. G. In *Vibrational Spectra and Structure*; Durig, J. R., Ed.; Elsevier: New York, 1977; Vol. 6, p 1.

**Table 4.** Bond Lengths and Interbond Angles for (Benzene)chromium Tricarbonyl<sup>a</sup>

bond length (Å)		interbond angle	
$r(\text{C}-\text{C})(E)$	1.422(4)	$\angle\text{OC}-\text{Cr}-\text{CO}$	87.4(7)°
$r(\text{C}-\text{C})(S)$	1.406(4)		
$r(\text{C}-\text{H})$	1.08(1)		
$r(\text{Cr}-\text{C})(\text{Bz})$	2.179(18)	$\angle\text{H}-\text{C}_1-\text{C}_4$	2.8(2)°
$r(\text{Cr}-\text{CO})$	1.876(7)		
$r(\text{C}-\text{O})$	1.148(7)		

<sup>a</sup> Rotational constants for six isotopomers were given in refs 10 and 11. Bz refers to benzene.

## Discussion

The microwave data clearly indicate that the spectrum assigned to the *E* isomer is due to the isomer with D atom substitutions at the ends of the "long" C–C bonds, and the *S* isomer spectrum, for the D atoms at the ends of the "short" C–C bonds. Since <sup>13</sup>C spectra were not analyzed in the present work, we must use the diffraction results<sup>3</sup> to locate the long C–C bonds eclipsing the CO groups and the short C–C bonds as "staggered", or lying between CO groups.

Higher order isotope effects resulting from shorter C–D bonds compared with C–H bonds could, in principle, distort the *C*<sub>3v</sub> symmetry of the Cr(CO)<sub>3</sub> moiety and cause differences in rotational constants for the "eclipsed" and "staggered" conformations discussed above. We believe, however, that these higher order effects would be much too small to account for the observed differences in rotational constants between the *E* and *S* isomers.

A comparison of observed C–C bond length differences for (arene)metal tricarbonyl complexes is shown in Table 5. We note that the present, gas-phase result is in excellent agreement with the solid-state, neutron diffraction result of Rees and Coppens. The resonance stabilization of benzene is an important part of basic chemistry, so it was perhaps surprising to observe

**Table 5.** Comparison of Observed Arene C–C Bond Length Differences ( $\Delta_{\text{CC}}$ ) for (Arene)metal Tricarbonyl Complexes

complex	$\Delta_{\text{CC}}$	ref
(C <sub>6</sub> H <sub>4</sub> D <sub>2</sub> )Cr(CO) <sub>3</sub>	0.016	present work
(C <sub>6</sub> H <sub>6</sub> )Cr(CO) <sub>3</sub>	0.017	Rees and Coppens <sup>1</sup>
(C <sub>6</sub> (CH <sub>3</sub> ) <sub>6</sub> )Cr(CO) <sub>3</sub>	0.021	Byers and Hall <sup>2</sup>
(C <sub>6</sub> (CH <sub>3</sub> ) <sub>6</sub> )Mo(CO) <sub>3</sub>	0.036	Chesick, Koshland, and Myers <sup>3</sup>

a reduction of the benzene symmetry and interruption of the aromaticity in stable arene–metal complexes. Bond angles of carbonyl groups, on the other hand, are more easily distorted by interactions involving other ligands. The approximate *C*<sub>3v</sub> symmetry of Fe(CO)<sub>3</sub> in (butadiene)iron tricarbonyl<sup>14</sup> is reduced to *C*<sub>2v</sub> by interactions involving the *cis*-butadiene.

The usefulness of (arene)chromium tricarbonyl complexes in organic synthesis<sup>1,2</sup> apparently results from a reduction in the stability of the complexed arene, making it more susceptible to nucleophilic attack. Since the aromaticity is often associated with increased stability, it may not be too surprising that complexation with Cr(CO)<sub>3</sub> reduces the aromaticity. Another indication of the reduced stability of benzene in this complex is the increased average C–C bond length<sup>11</sup> of 1.414(4) Å in the complex compared with 1.397(1) Å for free benzene.<sup>15</sup>

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(14) Kukolich, S. G.; Roehrig, M. A.; Wallace, D. W.; Henderson, G. L. *J. Am. Chem. Soc.* **1993**, *115*, 2021.

(15) Pliva, J.; Johns, J. W. C.; Goodman, L. *J. Mol. Spectrosc.* **1990**, *140*, 214.