

Accepted Manuscript

Isolation and structure of the *anti,anti* isomer and a DFT study of it and the *syn,anti* isomer of bis(tricarbonylchromium)dibenzo[*a,e*]-cyclooctatetraene. Evidence for an attractive electrostatic interaction between carbonyl oxygen atoms and Cr(CO)₃-coordinated arene carbon atoms



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PII: S0022-328X(13)00477-4

DOI: [10.1016/j.jorganchem.2013.06.029](https://doi.org/10.1016/j.jorganchem.2013.06.029)

Reference: JOM 18102

To appear in: *Journal of Organometallic Chemistry*

Received Date: 25 August 2012

Revised Date: 5 June 2013

Accepted Date: 22 June 2013

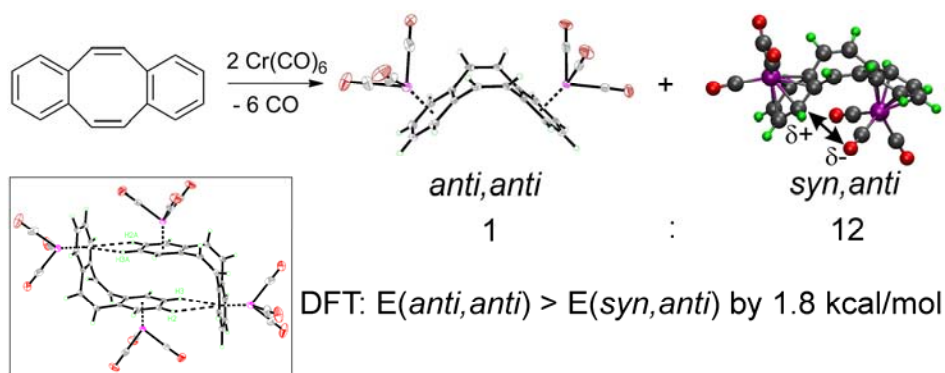
Please cite this article as: N. Bandara, C.N. Ratnaweera, S.R. Gwaltney, W.P. Henry, Isolation and structure of the *anti,anti* isomer and a DFT study of it and the *syn,anti* isomer of bis(tricarbonylchromium)dibenzo[*a,e*]-cyclooctatetraene. Evidence for an attractive electrostatic interaction between carbonyl oxygen atoms and Cr(CO)₃-coordinated arene carbon atoms, *Journal of Organometallic Chemistry* (2013), doi: 10.1016/j.jorganchem.2013.06.029.

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Graphical Abstract: Synopsis

Synthesis, crystal structure and theoretical calculations on *anti,anti*-dibenzo[*a,e*]cyclooctatetraene[Cr(CO)₃]₂ are reported. Comparison of DFT results with those for the *syn,anti* isomer suggest the latter is more stable by 1.8 kcal/mol because of an electrostatic interaction between carbonyl oxygen atom and coordinated arene.

ACCEPTED MANUSCRIPT



Isolation and structure of the *anti,anti* isomer and a DFT study of it and the *syn,anti* isomer of bis(tricarbonylchromium)dibenzo[*a,e*]-cyclooctatetraene. Evidence for an attractive electrostatic interaction between carbonyl oxygen atoms and Cr(CO)₃-coordinated arene carbon atoms

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ABSTRACT

When dibenzo[*a,e*]cyclooctatetraene and hexacarbonylchromium are refluxed in di-*n*-butyl ether/THF for an extended period, both the *syn,anti* and *anti,anti* isomers of the bis-tricarbonylchromium complex are obtained. After separation by column chromatography, the *syn,anti:anti,anti* isomer ratio is approximately 12:1. The *anti,anti* arrangement of the Cr(CO)₃ groups was verified by X-ray crystallographic structure determination. The orientations of the two tricarbonylchromium tripods relative to the 1,2-disubstituted arene rings differ. One is *exo* staggered while the other is eclipsed. Intermolecular C-H...O hydrogen bonding is prevalent in the crystal and is reminiscent of the *syn,anti* isomer. A dimeric motif in the solid resulting from C-H... π interactions is observed. DFT calculations on both isomers confirms that the *syn,anti* isomer is favored. The preferred orientation for the *anti* Cr(CO)₃ groups in both cases is *exo* staggered. However, the barrier to rotation is low, allowing hydrogen bonding to readily overcome this barrier and control the orientation of the tripod. While thermodynamic consideration support the preference for the *syn,anti* isomer, kinetic factors may also be important as this isomer would be formed preferentially due to steric inhibition of the diene coordination site by the mononuclear *anti* isomer. The stabilization of the *syn,anti* isomer occurs by an electrostatic attraction of the *syn* carbonyl groups with the *anti* Cr(CO)₃-coordinated arene carbon atoms. A reexamination of the structural parameters verifies nonbonded carbon-oxygen distances less than the sum of the van der Waals radii in the *syn,anti* isomer. A search of the

Cambridge Structural Database results in a significant number of interactions of this nature for arenetricarbonylchromium complexes.

Keywords:

Arenetricarbonylchromium
Dibenzo[*a,e*]cyclooctatetraene
DFT calculations
Crystal structure
Hydrogen bonding
Electrostatic interaction

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