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BOND ORDERS IN TRICARBONYL[η^4-CYCLOBUTADIENE]IRON COMPLEXES

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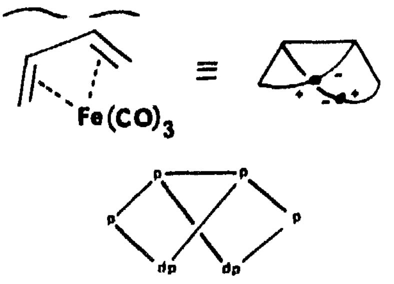
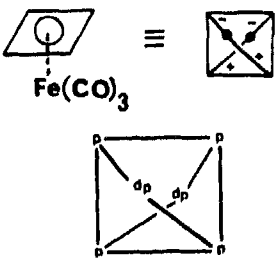
Summary

Valence bond structure-resonance theory is used to calculate bond orders in tricarbonyl cyclobutadieneiron complexes. C—Fe bond lengths show a linear correlation with the bond orders. C—Fe bond lengths in benzocyclobutadiene complexes V and VI (Table 1) which had been called "surprising", are rationalized. A graph theoretical method to calculate the bond orders is illustrated.

Introduction

A valence bond structure-resonance theory model for tricarbonyl(η^4-π-hydrocarbon)iron complexes has recently been described [1,2]. The complexes are considered to be resonance stabilized hybrids of "principal" covalent structures [3], in which two metal d—p hybrid orbitals, and four π-hydrocarbon p_z orbitals participate in three-dimensional delocalized covalent bonding [4]. The resulting orbital overlap connectivity graphs are illustrated for tricarbonyliron complexes of 1,3-butadiene and cyclobutadiene. The dots in the graphs designate the positions of metal orbitals and overlap phase discontinuities. The graphs enable one to use graph theoretical algorithms to carry out the calculations [1,2]. Using a parameterization of resonance integrals designed for π-hydro-





carbon systems [5], all known η^4-tricarbonyliron complexes are found to be substantially resonance stabilized [1,2]. In particular, association with the tricarbonyliron moiety transforms antiaromatic or non-aromatic cyclobutadienoid compounds into three-dimensional aromatic organometallic complexes [4,6—8].

This paper discusses bond orders and bond lengths in tricarbonylcyclobutadieneiron complexes within the structure-resonance theory formalism. Metal—carbon and carbon—carbon bond orders are rapidly obtained with graph theory procedures [1,2,9,10] that make use of the coefficients of nonbonding molecular orbitals (See appendix). The results are, of course, identical to Pauling bond orders [11] obtained by inspection of drawings of all covalent structures. The bonding overlap model also allows one to obtain HMO Coulson bond orders by the usual MO procedures as first demonstrated by Mingos [4]. Previously adopted [4,16,12] Coulomb and resonance integral parameters for iron orbitals are used for these latter calculations [13].

Results and discussion

Table 1 gives a listing of Pauling and Coulson bond orders, crystallographic bond lengths, and calculated bond lengths for all reported [14—24] tricarbonyliron complexes containing a cyclobutadienoid moiety. The calculated C—C bond lengths are obtained from a linear equation (eq. 1) obtained by fitting Pauling bond orders to accurately known bond lengths in standard substances

$$d(\text{C—C}) = 1.463 - 0.124\, p(P) \qquad (1)$$

(ethylene, butadiene, benzene, graphite; correlation coefficient —0.998; average deviation ±0.002 Å) [10]. The calculated C—Fe bond lengths are obtained as described below. In the table, results are only depicted for relevant delocalized portions of the complexes, lengths in symmetry related bonds have been averaged, and the position of iron is shown with a filled circle. Where pertinent bond lengths are not shown, they are not given in the cited reference.

There is a good linear correlation of Pauling bond orders with C—Fe bond lengths which is illustrated in Fig. 1. The regression line (eq. 2) has a correlation coefficient of —0.923 which is almost exactly the same as those found for

$$d(\text{C—Fe}) = 2.309 - 0.474\, p(P) \qquad (2)$$

extensive correlations of C—C bond lengths with Pauling or Coulson bond orders in π-hydrocarbons [9,10]. However, the Coulson C—Fe bond orders in Table 1 correlate less precisely with the bond lengths, correlation coefficient —0.759, a value similar to those determined in correlations of bond lengths in π-heterocyclic compounds [25]. It is possible that reparameterization might lead to improved results and this will be investigated in future work. It is noteworthy that the structure-resonance theory bond orders are obtained without parameterization.

The most significant aspect of the C—Fe bond orders is they provide a good rationalization of the rather variable positions of the iron atoms with respect to the cyclobutadiene rings. For example, the iron atom in V is "situated almost exactly above the middle of the ring", and the iron atoms in VI are "coordinated

ND BOND LENGTHS FOR TRICARBONYLCYCLOBUTADIENEIRON

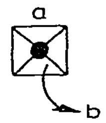
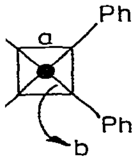
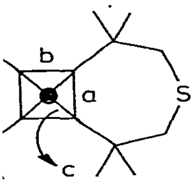
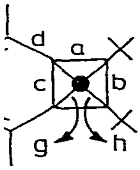
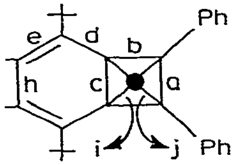
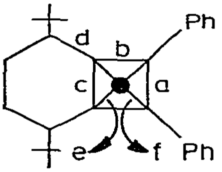
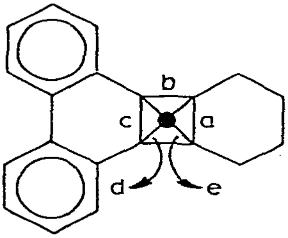
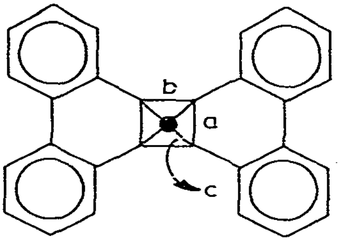
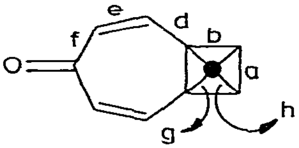
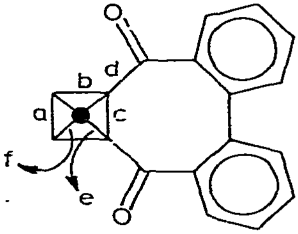
	Bond	Bond orders VB-SRT	Bond orders HMO	Bond length X-ray	Bond length calc. VB	Ref. X-ray
	a	0.250	0.500	1.456	1.432	14
	b	0.500	0.667	2.063	2.072	
	a	0.250	0.454	1.459	1.432	15
	b	0.500	0.611	2.068	2.072	
	a	0.250	0.454	1.479	1.432	16
	b	0.250	0.454	1.470	1.432	
	c	0.500	0.611	2.069	2.072	
	a	0.200	0.460	1.478	1.438	17,18
	b	0.200	0.487	1.495	1.438	
	c	0.200	0.416	1.431	1.438	
	d	0.200	0.459	1.432	1.438	
	e	0.800	0.775	1.371	1.364	
	f	0.200	0.550	1.434	1.438	
	g	0.400	0.579	2.144	2.119	
	h	0.600	0.684	2.027	2.025	
	a	0.250	0.516	1.458	1.432	20,21
	b	0.250	0.466	1.461	1.432	
	c	0.250	0.425	1.468	1.432	
	d	0.0	0.413	1.466	1.463	
	e	1.0	0.793	1.354	1.339	
	f	0.0	0.338	1.499	1.463	
	g	1.0	0.809	1.369	1.339	
	h	0.0	0.389	1.491	1.463	
	i	0.500	0.600	2.090	2.072	
	j	0.500	0.652	2.074	2.072	
	a	0.125	0.469	1.48	1.448	20,21
	b	0.125	0.445	1.475	1.448	
	c	0.125	0.391	1.48	1.448	
	d	0.500	0.532	1.41	1.401	
	e	0.250	0.549	2.21	2.191	
	f	0.750	0.701	1.985	1.954	

TABLE 1 (continued)

BOND ORDERS AND BOND LENGTHS FOR TRICARBONYLCYCLOBUTADIENEIRON

	Structure[a]	Bond	Bond orders VB-SRT	Bond orders HMO	Bond length X-ray	Bond length calc. VB	Ref. X-ray
VII		a	0.235	0.504		1.434	22
		b	0.235	0.473		1.434	
		c	0.235	0.438		1.434	
		d	0.471	0.611	2.103	2.086	
		e	0.529	0.664	2.048	2.058	
VIII		a	0.222	0.441		1.435	22
		b	0.222	0.445		1.435	
		c	0.500	0.608	2.076	2.072	
IX		a	0.250	0.517	1.444	1.432	23
		b	0.250	0.471	1.454	1.432	
		c	0.250	0.401	1.437	1.432	
		d	0.0	0.446	1.435	1.463	
		e	1.0	0.793	1.339	1.339	
		f	0.0	0.464	1.472	1.463	
		g	0.500	0.582	2.057	2.072	
		h	0.500	0.652	2.054	2.074	
X		a	0.250	0.538	1.41	1.432	24
		b	0.250	0.478	1.44	1.432	
		c	0.250	0.422	1.46	1.432	
		d	0.0	0.374	1.468	1.463	
		e	0.5	0.607	2.027	2.072	
		f	0.5	0.632	2.053	2.072	

[a] The position of the iron atom is indicated by  .

more strongly to the outer double bonds”. These facts have been called “surprising” by Butters, Toda, and Wiener [20]. Considering the equivalent C—Fe bond orders calculated for V, and the large bond order difference between the two kinds of C—Fe bonds in VI, it is felt that the observed experimental results are rather to be expected.

Excluding the C—C bonds where both carbon atoms are coordinated to iron, the qualitative agreement of C—C bond lengths with both types of calculated

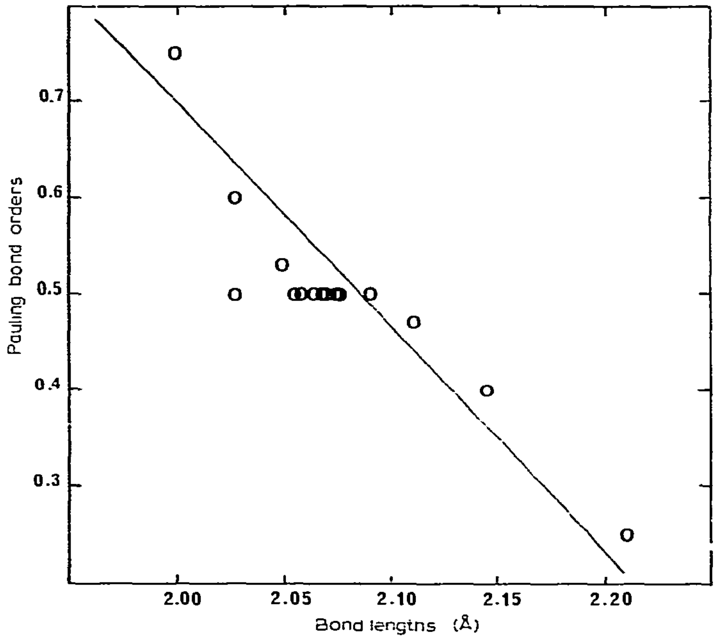


Fig. 1. C—Fe bond orders vs. bond lengths for cyclobutadieneiron tricarbonyl complexes.

bond orders is reasonably good. High and low bond orders generally correlate with short and long bond lengths respectively, and the structures in the table are drawn with double and single C—C bonds to reflect the X-ray data and these relationships. However the iron-coordinated bonds are consistently (one exception) 0.02 to 0.05 Å longer than would be expected from the Pauling bond order values which cover the small range 0.125 to 0.250. One possible interpretation is that there is a deficit of π-bonding electrons associated with the complexed cyclobutadiene moiety, consistent with designating the hydrocarbon as an electron donor in the complex-forming reaction. This description is not consistent with the results of an ab initio molecular orbital calculation [26], where the population analysis places a negative charge of ca. —0.8 on the complexed cyclobutadiene fragment. One expects that Fenske—Hall [27] non-empirical calculations will lead to a lower charge-distribution asymmetry, but the population analysis for tricarbonylcyclobutadieneiron has not been reported [7].

A final interesting result is that the cyclobutadienoid rings are always calculated to have equal Pauling bond orders for all C—C bonds, even in the presence of highly asymmetric calculated C—Fe bond orders. All complexed cyclobutadiene rings are therefore inferred to be squares, even though the C—Fe bond lengths may vary. The bond lengths in V and VI are in very good agreement with these conjectures, but those in IV and X are not. Substituent electronic and steric effects are obviously important and must be considered in a more complete theory. It should be noted that experimental data and recent ab initio π-CI-calculations* [28] for substituted cyclobutadienes have established profound substituent steric effects upon bond lengths.

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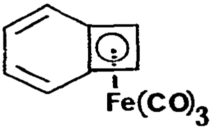
* CI = configuration interaction.

Conclusions

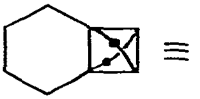
The results given here and the previous calculations [1,2] on relative stabilities and reactivities of tricarbonyliron complexes show that structure-resonance theory provides a simple, workable model for some aspects of bonding in these organometallic compounds. The most useful characteristics of the theory are that the numerical results are quickly obtainable by hand, and that the calculations can actually be carried out by anyone who can draw valence bond structures. Finally, the characterizations of these complexes as aromatic compounds, and in particular the description by Schleyer of VI as an organometallic anthracene [29], are supported by the results delineated in this work.

Appendix

Obtaining valence bond structure-resonance theory bond orders is best illustrated with an example, and the tricarbonyliron complex of benzocyclobutadiene will therefore be used for this purpose. The connectivity graph for the three-dimensional C(2*p*)—Fe(*d*—*p* hybrid) orbital network is shown below [1,2,4]. The graph has 10 vertices representing the eight C(2*p*) orbitals from the hydrocarbon ligand and the two *d*—*p* hybrid orbitals arising from iron. The vertices (dots) in the graph that represent the orthogonal iron *d*—*p* hybrids can be separated for clarity of presentation. The carbon framework and the iron atom contribute eight and two electrons respectively towards covalent bonding. The theoretical and experimental evidence justifying this model have been previously summarized [1,2,4,6,7].



1



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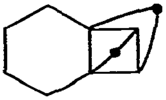
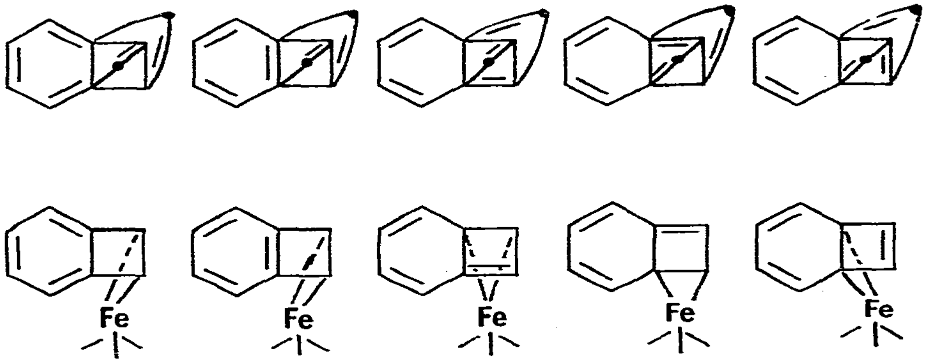


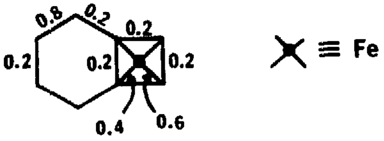
3

A valence bond structure-graph is a diagram in which five double lines (five pairs of electrons) have been inserted into the overlap connectivity graph so that double and single lines alternate. Each structure-graph corresponds to a covalent structure. The valence bond structures are written below the structure-graphs in 4, and the one-to-one correspondence is apparent. It is also apparent



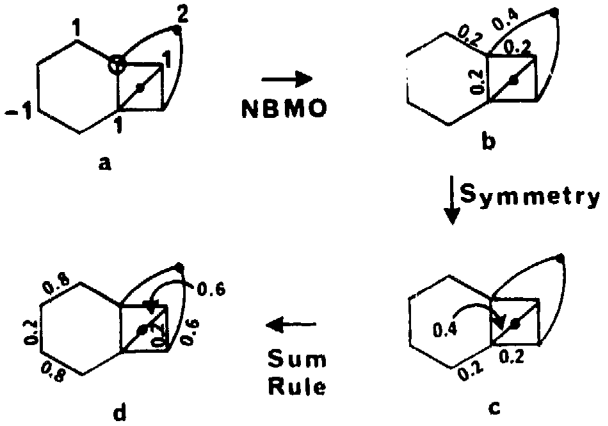
4

that the total structure-count (SC) is five, and that the Pauling bond orders (defined as the number of structures in which a line is the structural-graph is double divided by the total number of structures) are given as shown in 5.



5

Several simple methods using graph theoretical procedures have been previously described that can be used to find bond orders [9,10]. The types of compounds considered in this paper are most easily treated by using the mathematical properties of diagrams obtained by deletion of any vertex from the orbital connectivity diagram. It is convenient to delete a vertex with high connectivity as depicted in 6.



6

Deletion of the circled vertex gives an odd alternant graph which possesses a non-bonding molecular orbital (NBMO). The unnormalized coefficients of the NBMO can be written by inspection using the fact that the coefficients sum to zero around each vertex position in the odd alternant diagram [4,18]. Since the overlap at the iron orbital position changes sign (phase inversion), NBMO coefficients do not change sign when related by the iron orbital positions (heavy dots in 6a).

The total SC is given by the sum of the absolute values of the numbers adjacent to the deleted vertex, SC = 5 in 6. Each coefficient in turn denotes the number of structure-graphs that can be drawn with a double line (bond) to the coefficient position. This allows the assignment of bond orders shown in 6b. The symmetry of the orbital network can be used to assign additional bond orders, 6c, and all remaining bond orders follow because the sum of the Pauling bond orders around any vertex position in the orbital connectivity diagram must be unity, **6d**. Of course the operations outlined in **6** would normally be carried out on a single molecular diagram of the orbital overlap network.

Acknowledgement

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