Bond length and bond multiplicity: σ-bond prevents short π-bonds†

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Analysis of model compounds such as $Fe_2(CO)_6$, C_2 and HBBH shows that π-bonds left to themselves are shorter than σ-bonds; in many ways σ-bonds prevent π-bonds from adopting their optimal shorter distances.
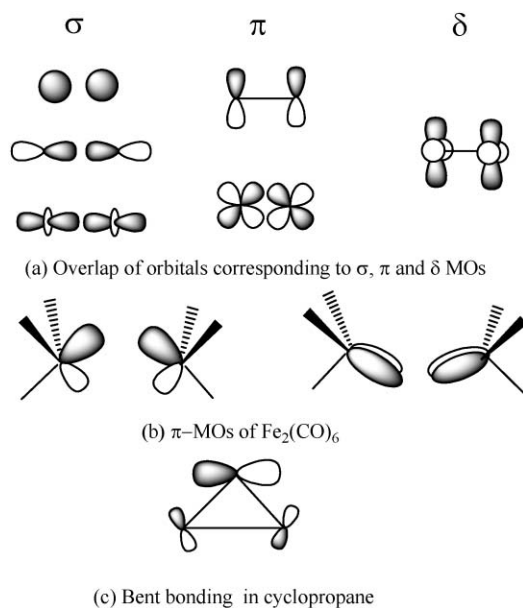
The concept of σ-, π- and δ-bonds is ingrained into the thought process of chemists. The cylindrically symmetrical σ-bond is traditionally estimated to be stronger than the π-bond, which in turn is stronger than the δ-bond. The linear overlap of orbitals in the σ-bond is supposed to be more effective than the sideways overlap available in the π- and δ-bonds (Scheme 1a). Closely related to the discussion of σ-, π- and δ-bonds and their bond strengths is the issue of bond length. The decrease of bond length in going from a single σ-bond to multiple bonds involving σ and π components are exemplified by $H_3C–CH_3$, $H_2C=CH_2$, and $HC≡CH$ with C–C bond lengths of 1.538 Å, 1.338 Å and 1.203 Å, respectively.[1] In transition metal chemistry there are the familiar

examples of short M–M quadruple bonds constituted from one σ-, two π-, and one δ-bonds as in $Re_2Cl_8^{-2}$ with an Re–Re bond length of 2.240 Å.[2] In these discussions the σ-bond is considered to be the strongest and the bond strength is thought to be inversely proportional to the bond length.

However the variation of orbital overlap as a function of internuclear distance (Fig. 1) shows that maximum overlap occurs at shorter distances for π- and δ-bonds. It is therefore logical to anticipate that π-bonds (unsupported by an underlying σ-bond) could be shorter than σ-bonds. We present here several such examples and conclude that σ-bonds prevent π-bonds from getting to their natural, shorter interatomic distances.[3a]

The difficulty in designing structures with π-alone-bonds is the following. The σ-levels (sp^x hybrid orbitals) of common main group fragments such as –BH, –CH and –CH_2 are lower in energy than the p orbitals that form the π-bonds. As a result π-bonds always come with the underlying σ-bond (Scheme 2a). Transition metal fragments provide an opportunity to reverse this situation. For example the degenerate π-type frontier orbitals of the $Fe(CO)_3$ fragment are lower in energy than the symmetric σ-orbital (Scheme 2b).[3b] It is therefore logical to anticipate shorter than usual M–M bond lengths in dimers of such fragments.

$Fe_2(CO)_6$ itself is a case in point. This is calculated to be a minimum in its potential energy surface,[4,5] with a relatively short predicted metal–metal distance of 2.002 Å. Compared with

(a) Overlap of orbitals corresponding to σ, π and δ MOs

(b) π–MOs of $Fe_2(CO)_6$

(c) Bent bonding in cyclopropane

Scheme 1 Overlapping orbitals.

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† Electronic supplementary information (ESI) available: Wiberg bond index, Mulliken population (Table 1) and electron densities at bond critical point (Table 2). See DOI: 10.1039/b602116f
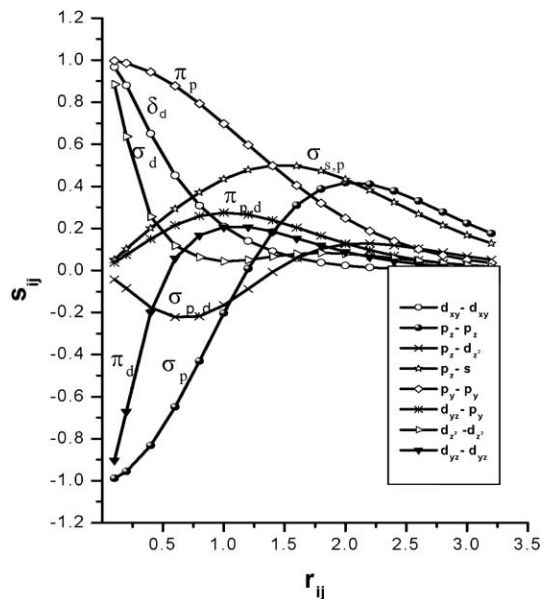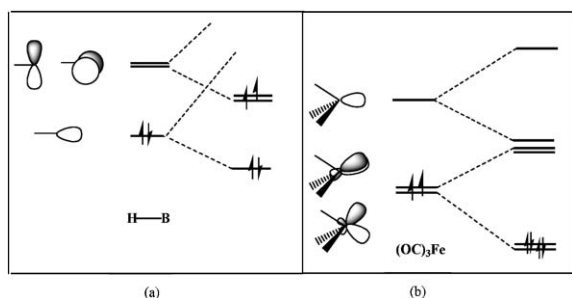

Fig. 1 Variation of orbital overlap (s_{ij}) as a function of internuclear distance (r_{ij}) using contracted Gaussian orbitals corresponding to a minimal basis of Fe.

Scheme 2 Interaction diagram for the formation of H_2B_2 (a) and of $Fe_2(CO)_6$ (b).

experimentally known compounds such as $Mn_2(CO)_{10}$ (Mn–Mn = 2.904 Å) or $M_2(Cp)_2(CO)_6$ (M = Cr, Mo and W), which have only M–M single bonds in the range 3.221–3.228 Å, the metal–metal bond length in $Fe_2(CO)_6$ is very short indeed.[6–8] The short bond length and a simple-minded application of the 18-electron rule would suggest an Fe–Fe quadruple bond.[5] A detailed interaction diagram (Fig. 2) provides an occupancy of $1a_1'$, $1e'$, $1e''$, $1a_2''$ and $2e'$ levels (counting from HOMO-7, as $1a_1'$) for the 16 valence electrons, corresponding to σ-, π/δ-, π*/δ*-, σ*- and two π-levels. Thus the formal net M–M bonding is provided by two π-type molecular orbitals, (Scheme 1b). At the long distances direct CO···CO interactions in $(OC)_3Fe–Fe(CO)_3$ are minimal, so that the eclipsed conformation with better overlap is favored. This is to be contrasted with the rotational preferences of ethane.[9] Independent of the conformation, the bond multiplicity must be only two. It is possible to see the influence of π-bonds in reducing bond lengths in more familiar examples. The C–C bond in cyclopropane is anticipated to be weak owing to strain. However,

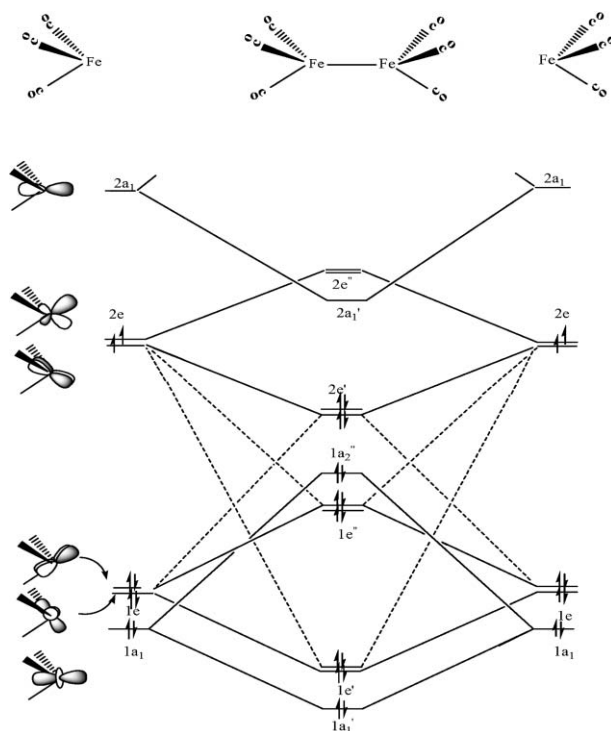the C–C distance is shown to be shorter (1.510 Å)[10] than is the case for regular C–C bonds (1.538 Å). Optimum overlap for the orbitals, overlapping in a sideways manner in the bent bonds (Scheme 1c), occurs at shorter distances than for a conventional σ-bond, explaining the short distance of a strained bond. The overlap of orbitals in π-bonds in $Fe_2(CO)_6$ (Scheme 1b) is similar to the bent bonds of cyclopropane (Scheme 1c). The shorter distances necessary to obtain optimum overlap for these π-type MOs result in shorter than expected bond lengths. If the shorter distances are a requirement for optimum overlap for π-MOs, these requirements must also exist in multiple bonds involving σ- and π-bonds. The π- bonds, however, are forced by the overwhelming δ-bonds to be at non-optimal overlapping distances. While there are many factors that contribute to the observed bond lengths in a binuclear transition metal complex, shorter distances would be mandated by π- and δ-MOs for optimum overlap. The π-alone-bonding proposed for $Fe_2(CO)_6$ allows π-bonds to attain their natural shorter distances.

The influence of σ-bonds in bond lengthening is seen in $L_3M–ML_3$ complexes with six valence electrons. According to the ordering of MO energy levels (Fig. 2), such compounds should be triply bonded with one σ-bond and two π-bonds ($1a_1'$, $1e'$). The bond is expected to be longer due to its σ-component. There are four examples from literature, namely $Mo_2(CH_2Ph)_2(NMe_2)_4$ 2.20 Å, $Mo_2(O^iPr)_2(SC_6H_2Me_3)_4$ 2.23 Å, $Mo_2(OC(CF_3)_2CH_3)_6$ 2.23 Å and $W_2Br_2(NEt_2)_4$ 2.30 Å.[11] While these distances are not directly comparable, the M–M bond distances are much longer than that calculated for $Fe_2(CO)_6$.

First row diatomics provide other examples where π-orbitals are filled before σ. The diatomic C_2 has a ground state $^1\Sigma_g^+$ with a double bond,[12] both components of which are π-bonds (Scheme 3a). Relative to the standard triple bond in N_2, the $3\sigma_g$ molecular orbital in C_2 is unoccupied. The bond distance in C_2, of 1.240 Å, is shorter than any σ + π carbon–carbon double bond by a large margin. Another example is B_2.[13] With two electrons less than C_2, B_2 has two half π-bonds (Scheme 3d). The distance of 1.590 Å in B_2 is shorter than any B–B single σ-bond. Among the heavier main group elements with weak σ-bonds, there are examples of distorted structures with short π distances,[14] arising from dative interactions.

The preference of π-bonds for short distances is further supported by the study of the excited states of C_2.[12] A triplet state obtained by shifting (Scheme 3b) one of the electrons from the π-bonding MO of C_2 to the vacant σ-bonding MO should increase the C–C distance. This is indeed found to be the case.

Fig. 2 Interaction diagram between two $Fe(CO)_3$ fragments to give $(OC)_3Fe–Fe(CO)_3$.

	$^1\Sigma_g^+$	$^3\Pi_u$	$^3\Sigma_g^+$	$^3\Sigma_g^-$
$3\sigma_g$	—	↿	↿⇂	—
$1\pi_u$	⇅ ⇅	⇅ ↿	⇅ ↿	⇅ ↿
$2\sigma_u^*$	⇅	⇅	⇅	⇅
$2\sigma_g$	⇅	⇅	⇅	⇅
Bond length	1.240 Å	1.313 Å	1.370 Å	1.590 Å
	(a)	(b)	(c)	(d)

Scheme 3 Experimental bond lengths of C_2 $^1\Sigma_g^+$ (a), $^3\Pi_u$ (b), and of B_2 $^3\Sigma_g^-$ (d). Bond length of C_2 $^3\Sigma_g^+$ (c) is obtained from calculations at the B3LYP/6-311+G* level.

Thus the $^3\Pi_u$ state of C_2 has a bond length of 1.313 Å. Another triplet state ($^3\Sigma_g^+$) obtained by shifting another electron from a π- to σ-level elongates the bond to 1.370 Å (Scheme 3c). It could be argued that the LUMO of C_2 is nearly nonbonding and hence the elongation of C_2 in the excited state may be more due to the bonding lost in vacating the π-bond rather than the new σ-bonding added. However recent experimental evidence indicates that the HOMO of N_2 has substantial bonding character.[12] The effect of bond length shortening on the formation of a π-bond is more directly shown in the linear HB–BH. The B–B bond length in the ground state ($^3\Sigma_g^-$) where there are two electrons in the degenerate π-MO is 1.511 Å. An excited state ($^1\Sigma_g^+$) where the two σ-electrons are placed in the π-levels, must have a shorter B–B bond, if the arguments are correct. The distance calculated is 1.469 Å which is shorter than that in the ground state. π-Bonds, in the absence of σ-bond are definitely shorter. While it is tempting to assume exact cancellation of a bond when both the bonding and the corresponding antibonding orbitals are occupied, this is never the case. We have analyzed the nature and the extent of bonding in these molecules by overlap populations and electron density analysis. Any method of estimating the bond strength based on an overlap population has limitations. Similarly quantitative comparisons of bond order indices of different pairs of atoms are also difficult. Despite these limitations, we have found it useful to compare the Mulliken overlap populations[15] using wavefunctions obtained at the HF/6-31G level.[16] The overlap population calculated for C_2 (0.652) is between those of C_2H_4 (0.593) and C_2H_2 (1.067). Comparisons of overlap populations are even more difficult in transition metal complexes and yet these are used to find the contribution of the HOMO (2e′, Fig. 2) to the total Fe–Fe overlap population in $Fe_2(CO)_6$. The total Fe–Fe overlap population is 0.235 at this level. The degenerate HOMO which constitutes the maximum to the binding contributes 0.162 to this, clearly signifying the importance of this pair of π-orbitals in the Fe–Fe bonding. The contributions from the σ- and σ*- (1a′ and 1a″, Fig. 2) levels nearly cancel each other. Similar conclusions are obtained using the Wiberg bond index of natural bond orbitals except for C_2.[17] The variation of the electron density[18] calculated at the center of the C–C bond in C_2, C_2H_2, C_2H_4 and C_2H_6 (0.2690, 0.3741, 0.3064 and 0.2198 a. u. respectively) indicates that in the absence of a fully fledged σ-bond the electron density in the middle of C_2 is lower as anticipated. This work suggests that absence of σ-bonds may play a role in producing short bond distances.

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