staggered, because of the greater steric crowding of the latter structure, as shown earlier in **8**.

Summary and Conclusions

The ground states, triplet states, cations, and anions of propene, acetaldehyde imine, acetaldehyde, biacetyl, and dimethylbutadiene and the singlet excited states of acetaldehyde and biacetyl have been investigated by ab initio molecular orbital theory. The calculations are in good agreement with the experimental results, where known. In a large number of cases, the preference for one conformation over the other can be explained in terms of simple perturbation theory arguments.

Calculations on the ground states indicate that the rotational barrier is mainly governed by the repulsion between the filled π_{CX} and π_{CH_3} orbitals, but other effects can contribute significantly

in specific cases. Our calculations confirm that in the first excited triplet states the staggered or distaggered conformations are generally more stable. This reversal of the ground-state preference is mainly due to the more favorable overlap of the $\pi^*_{C=X}$ orbital with the $\pi^*_{CH_3}$ orbital in the staggered conformation. In agreement with this conclusion, the radical anions of most species show a preference for the staggered conformation, while the cations are always more stable in the eclipsed conformation, but have relatively low barriers.

The experimental study of cases for which predictions have been made is eagerly awaited.

YCoC: A Simple Organometallic Polymer in the Solid State with Strong Co–C π Bonding

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Abstract: Gerss and Jeitschko recently synthesized YCoC, which contains well-isolated infinite linear CoC^{3-} chains, marked by a short Co–C distance. We have examined the bonding in this polymer. It has substantial π character, and that bonding could be strengthened by decreasing the electron count or oxidation. We think the chains should be magnetic.

Gerss and Jeitschko recently synthesized a series of ternary lanthanide carbides, LnCoC, with a new, simple structure.[1] These molecules contain an extraordinary organometallic chain, whose electronic structure is the subject of this paper.

Two views of the $P4_2/mmc$ structure of YCoC are shown in **1** and **2**. Note the striking (–Co–C–Co–C–) infinite linear chains, well separated from each other. The Co–C distance in one of
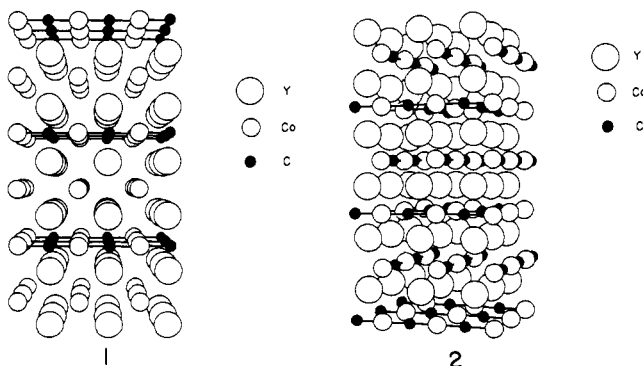
these chains is a short 1.825 Å. That is a little shorter than typical metal–carbon distances in bulk transition-metal carbides (1.871 Å in Co_2C),[2] discrete cluster carbides (≥ 1.90 Å in $[Co_8C(CO)_{18}]^{2-}$ and $[Co_6C(CO)_{14}]^-$),[3] or even Co–carbene (1.905 Å in CpCo(SPh)CR$_2$)[4] complexes. Transitional-metal carbonyls have com-

parable distances (1.82 Å in $Co(CO)_4^-$),[5] shorter in other carbonyls. The extended structure before us clearly has well-defined organometallic chains characterized by some metal–carbon multiple bonding. If yttrium is taken as 3+, then formally we have CoC^{3-}. There are interesting conducting and magnetic possibilities for this chain.

Figure 1 shows an extended Hückel band structure of a one-dimensional CoC chain. The computational details are in the Appendix. This is a textbook example of orbital interaction in an extended material, and indeed it has been analyzed in detail by Burdett[6] and by Whangbo.[7] But it has one surprise.

Symmetry-adapted linear combinations of the four carbon valence orbitals and the metal d block are shown in **3** at Γ (same sign in each unit cell) and X (change sign between unit cells). It is clear that the δ $M(x^2 - y^2, xy)$ set does not interact with any C orbitals and will by itself form a narrow band. Metal (xz,yz) does not mix with $C(x,y)$ at Γ, but it does so at X. This π bonding will push up $M(xz,yz)$ toward X and push $C(x,y)$ down. That is what the band structure shows.

Metal z^2 carries a surprise. At Γ it mixes with C s, at X with C z. Since C z is much closer in energy to M z^2 than C s, we would expect the z^2 band to rise in energy as one goes from Γ to X. But as the figure shows, z^2 is remarkably flat. It goes up from Γ to X, but imperceptibly so.

Why this unusual behavior? Certainly the mixing with C s and z analyzed above is there—see for instance the mirror image trend

(1) Gerss, M. H.; Jeitschko, W. *Z. Naturforsch.* **1986**, *41b*, 946.

(2) Clarke, J.; Jack, K. H. *Chem. Ind. (London)* **1951**, *46*, 1004.

(3) Albano, V. G.; Chini, P.; Ciani, G.; Martinengo, S.; Sansoni, M. *J. Chem. Soc., Dalton Trans.* **1978**, 463. Albano, V. G.; Chini, P.; Ciani, G.; Sansoni, M.; Strumolo, D.; Heaton, B. T. Martinengo, S. *J. Am. Chem. Soc.* **1976**, *98*, 5027.

(4) Macomber, D. W.; Rogers, R. D. *Organometallics* **1985**, *4*, 1485.

(5) Schussler, D. P.; Robinson, W. R.; Edgell, W. F. *Inorg. Chem.* **1974**, *13*, 153. McNeill, E. A.; Scholer, F. R. *J. Am. Chem. Soc.* **1977**, *99*, 6243.

(6) Burdett, J. K. *Prog. Solid State Chem.* **1984**, *15*, 173.

(7) Whangbo, M.-H. In *Crystal Chemistry and Properties of Materials with Quasi one Dimensional Structures*; Rouxel, J., Ed.; Reidel: Dordrecht, 1986, p 27.
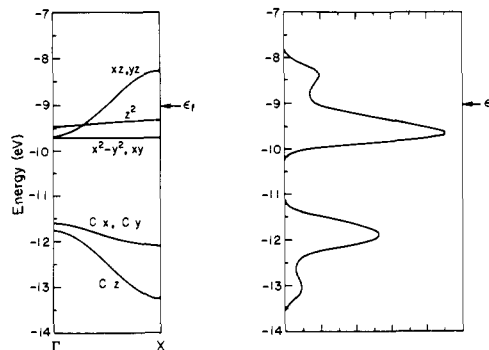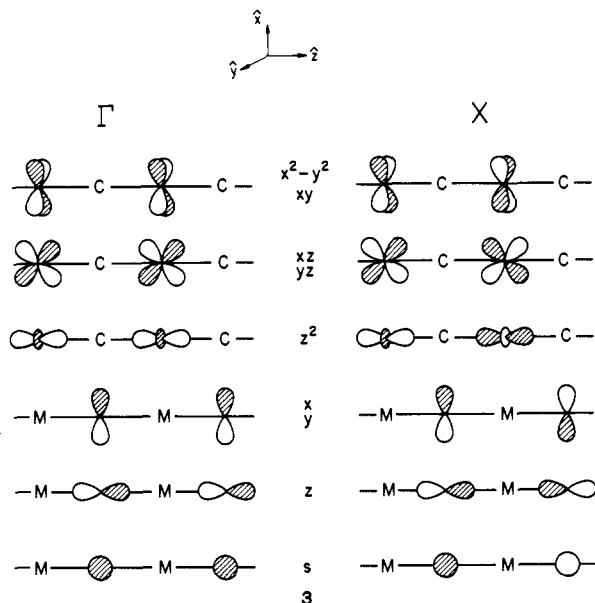
Figure 1. Band structure and density of states curves of the one-dimensional CoC^{3-} chain. On the left is the band structure. Orbitals that have a large contribution to a band are indicated along with that band. On the right is the total DOS projection of the system. Fermi level is indicated with an arrow.
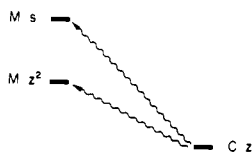

Figure 2. DOS and COOP projections of the CoC^{3-} 1D chain. On the left is the density of states curve. The shaded area is the C contribution and the dashed line the total DOS. The Co–C crystal orbital overlap population curve is shown at the right.

in C z. What happens is that metal 4s mixes in (see **4**). It does so moderately strongly, to an extent that varies with k, and increases toward the zone edge X.
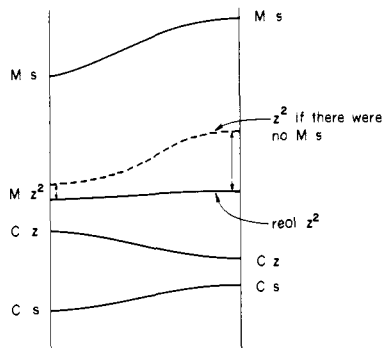
There are three ways at least to explain this mixing.

(1) The first is second-order perturbation theory.[8] M s mixes into z^2 only through the C z contribution into M z^2 (see **5**). That admixture of z^2 and z increases with k.

(2) Let us set up the complete matrix for a three-orbital interaction, as in eq i below. The k dependence is in the off-diagonal

$$
\begin{matrix}
s \\
z^2 \\
z
\end{matrix}
\begin{pmatrix}
H_{ss} - E & 0 & H_{sz} - ES_{sz} \\
0 & H_{z^2z^2} - E & H_{z^2z} - ES_{z^2z} \\
& & H_{zz} - E
\end{pmatrix} \quad (i)
$$

matrix elements. If some simplifying approximations are made (neglect overlaps, moving into the Hückel model, and set $H_{z^2z^2}$
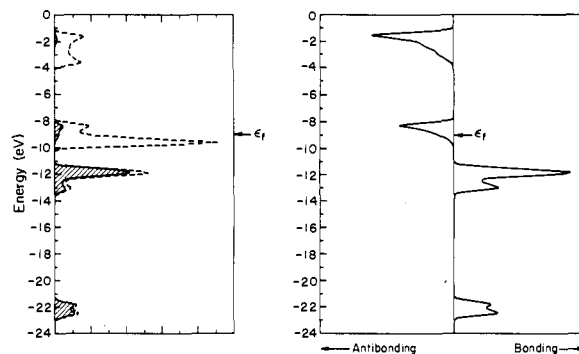
$= H_{ss}$) then it can be shown[9] that one of the roots of the secular determinant is k independent.

(3) The mathematics behind (2) above is essentially that it is possible to take linear combinations of M s and M z^2 such that one of those combinations has a minimal overlap with C z and the other has a large overlap. If the 4s metal orbital were $Ar^2e^{-\zeta r}$ (it is not quite, given the Slater orbitals we use in extended Hückel calculations) with the same exponent ζ as the z^2 orbital, which is $B(3z^2 - r^2)e^{-\zeta r}$, then one could form linear combinations

$$(2z^2 - x^2 - y^2) + \lambda(x^2 + y^2 + z^2) =$$
$$(2 + \lambda)z^2 + (-1 + \lambda)(x^2 + y^2) \quad (ii)$$

$$\lambda(2z^2 - x^2 - y^2) - (x^2 + y^2 + z^2) =$$
$$(2\lambda - 1)z^2 + (-\lambda - 1)(x^2 + y^2) \quad (iii)$$

One of these would be mainly z^2 and the other mainly $x^2 + y^2$. The first, roughly symbolized by **6**, would have an effective overlap with C z, the other, **7**, would have poor overlap.
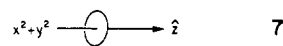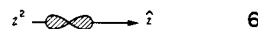
A way to probe this mode of reasoning is to change the energy of the metal 4s orbital relative to 3d. Indeed, if the metal 4s H_{ii} is raised the z^2 band becomes less flat.

Let us return now to a general analysis of the electronic structure of this interesting polymer. Figure 2 shows the total density of states again (dashed line) and the contribution to that DOS of carbon levels. What is not on carbon is on cobalt. The

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(8) See: Libit, L.; Hoffmann, R. *J. Am. Chem. Soc.* **1974**, *96*, 1370 and references therein.

(9) Reference 6, p 241.

Table I. Parameters for C and Co Atoms

atom	orbital	H_{ii} (eV)	ζ_1	ζ_2	$C_1{}^a$	$C_2{}^a$
C	2s	−21.4	1.62			
	2p	−11.4	1.62			
Co	4s	−7.8	2.00			
	4p	−3.8	2.00			
	3d	−9.7	5.55	2.10	0.5680	0.6060

^{a} Coefficients used in the double-ζ expansion of the 3d orbitals.

energy window is now a little larger than in Figure 1, so as to include the C 2s band. This decomposition confirms the characterization of the bands of Figure 1 as mainly carbon or cobalt. The Co δ level of course is all metal; the σz^2 band also has very little carbon mixing (see above). The only significant carbon mixing in the metal d band is π-type, with xz, yz.

There is substantial π bonding in these chains. The right-hand side of Figure 2 shows the crystal orbital overlap population (COOP) curve[10] for the system. Note the large peak near −12 eV. That is the contribution of the in-phase Co–C π bonding combinations, exemplified by the representative orbital **8** at X. The corresponding antibonding combinations (near −8 to −9 eV) are only half-filled. The net result is strong π bonding. Of the 0.777 Co–C total overlap population, 0.560 is σ and 0.217 is π.
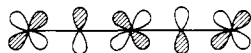
8

One interesting consequence of this picture is that the CoC^{3-} electron count does not correspond to maximal π bonding. Greater π bonding could be achieved, and with it a still shorter metal–carbon distance, if the polymer could be oxidized, or made with Fe or Mn instead of Co.

In the CoC^{3-} chain we have a half-filled (xz,yz) band. Little is as yet known about the conducting or magnetic properties of this material.[1] Two extreme possibilities are that the material is non-magnetic and the lower half of the xz,yz band is doubly filled, **9**. Or the electrons could unpair, **10**, resulting in a ferromagnetic or high-spin system.

(10) See, for example: Wijeyesekera, S. D.; Hoffmann, R. *Organometallics* **1984**, *3*, 949. Kertesz, M.;Hoffmann, R. *J. Am. Chem. Soc.* **1984**, *106*, 3453. Saillard, J.-Y.; Hoffmann, R. *Ibid.* **1984**, *106*, 2006.

9   **I0**
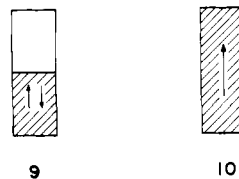
Whangbo has discussed the physical factors guiding this choice;[7] extended Hückel calculations are not capable of deciding which (**9** or **10**) will be the ground state of the system.

But if the polymer is low spin, **9**, then the half-filled band raises the possibility of a Peierls distortion.[6,7] This is the solid-state analogue of a Jahn–Teller effect, the stabilization of a polymer by deformation along a lattice vibration which opens up a band gap just at the Fermi level.

We have examined two such possible distortions, shown in **11**. Both open up substantial gaps of $\sim$1 eV at the Fermi level and stabilize the system significantly. There are still other distortions
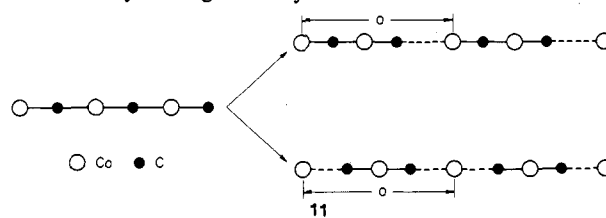
11

that will accomplish the same thing. Since the observed crystal structure of YCoC shows no unit cell doubling distortion,[1] we think the material is likely to be magnetic, of type **10**.

Further studies of the properties of this fascinating organometallic material and the synthesis of related polymers should be encouraged.

Appendix

Calculations are performed with the extended Hückel tight-binding method. Atomic parameters for Co and C are listed in Table I. A 50 k-point set is chosen in calculating the average properties of the CoC^{3-} chain system. The geometry is taken from the experimental data.

Nature of Carbon–Lithium Bonding in Dilithiated Polynuclear Aromatics: An MNDO Study

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Abstract: An MNDO study shows that the nonsymmetric crystal structures of dilithionaphthalene and dilithioanthracene are not the result of crystal-packing forces, but rather reflect the internal minimum energy arrangement of the molecules considered. On the other hand, the optimal structures of the complexes of the respective dianions with two positive charges are symmetrical. This difference suggests that partial covalency of the carbon–lithium bonding may be responsible for the nonsymmetric arrangement becoming the most stable in the crystal state.

The metal–ammonia reduction of polynuclear aromatics provides an intriguing array of intermediates during the course of reaction.[1] The most interesting and least explored of these intermediates are the dianions. These species, albeit antiaromatic, are nonetheless quite stable.[2] The nature of metal bonding in these anions, especially with lithium, is perplexing. The dianions

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(1) (a) Harvery, R. G. *Synthesis* **1970**, *4*, 161. (b) See also: Rabideau, P. W. In *Chemistry of Polynuclear Aromatics*; Ebert, L. B., Ed.; ACS Symposium Series 217; American Chemical Society: Washington, DC, 1987.