Is a C≡C Quadruple Bond Possible?

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Summary: *Ab initio computations predict a minimum for a carbon-carbon quadruple bond in C_2. While the computed C-C separation, 1.128 Å, fits Pauling's bond order-bond length relationship well, this result is an artifact of the restricted Hartree Fock theory.*

Can all eight valence electrons in diatomic C_2 be involved in covalent bonding? This would result in a quadruple C≡C bond, and might be represented by **1** in a bent-bond formulation. This idea is not completely far-fetched, even though C_2 is known to have $^1\Sigma_g^+$ ground state ($R_e = 1.2425$ Å) and no higher lying "quadruple" bound state has been detected experimentally.[2] The five valence molecular orbitals of C_2 are shown in Figure 1. Four of these are bonding, but one MO ($2\sigma_u$) is an *antibonding* combination largely comprised of the carbon 2s orbitals. What would happen if the two electrons which normally occupy this orbital were placed into a bonding MO instead? The possible $^1\Sigma_g^+$ state with $(2\sigma_g)^2 (\pi_u)^4 (3\sigma_g)^2$ occupation would lead to a quadruple bond!
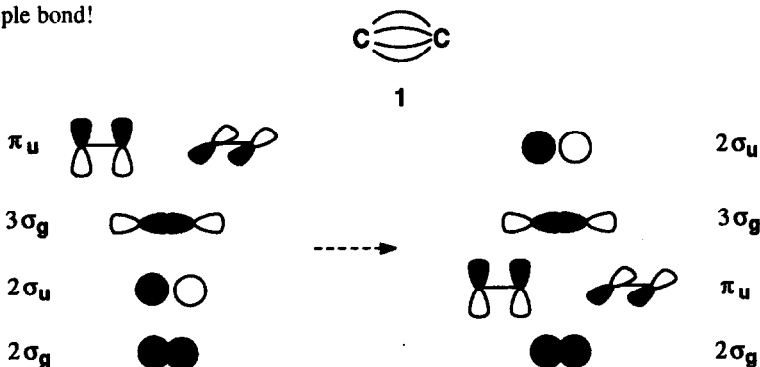

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Figure 1. Schematic representation of orbitals for homodiatomic species. The core orbitals are omitted. The excited state configuration is obtained by moving electrons from the $2\sigma_u$ orbital into a π_u orbital. As shown by computations, the resulting $3\sigma_g$ orbital is of higher energy than the π_u orbitals (apparently the interatomic separation is too short for the optimal overlap in this case).

This result can be achieved computationally quite easily by altering the orbitals to be occupied, eg., by employing the "guess=(huckel,alter)" keyword[3] in the Gaussian 92 ab initio program.[4] The orbitals to be switched, added as the last line of the input, are "4,7" for C_2 (or N_2^{2+}) and "12,15" for Si_2 and P_2^{2+}. The remarkable results are summarized in Table 1. Not only C_2, but also the isoelectronic first row (N_2^{2+}) and second row (Si_2, P_2^{2+}) species are indicated to possess quadruple bonds at all RHF (Restricted Hartree Fock)[5] levels investigated. For C≡C the basis sets ranged from the STO-3G to 6-311+G(3df)–the largest standard basis set in the Gaussian 92 program which includes a quadruple valence split as well as three sets of d and one set of f polarization functions. Intermediate basis sets gave similar results (Table 1). The bond length and the energy decreased with the increase of the basis set size.

Table 1. Bond Lengths and Bond Orders of C≡C and Related Species

| Species | HF-level | R_e (Å) | Bond Orders | | HF-Energy (H) |
			Wiberg	NPA/NLMO	
C≡C	STO-3G	1.1419	4.0000	4.0037	-74.13759
	3-21G	1.1441	4.0039	4.0064	-74.73425
	6-31G*	1.1402	4.0029	4.0063	-75.15012
	6-311+G*	1.1322	4.0037	4.0070	-75.18152
	6-311+G(3df)	1.1284	4.0038	4.0071	-75.18738
•C≡C•	6-311+G(3df)	1.2403	3.6919	3.5630	-75.39971
	MP2/6-311+G(3df)	1.2579	3.6627	3.5579	-75.75648[b]
	exp.[a]	1.2425			
H-C≡C-H	6-311+G(3df)	1.1794	2.9901	3.0126	
	exp.[a]	1.2024			
N≡N^{2+}	6-311+G*	1.0025	4.0020	4.0046	-107.02668
	6-311+G(3df)	0.9982	4.0021	4.0047	-107.03963
•N≡N•$^{2+}$	6-311+G(3df)	1.1176	3.5676	3.6475	-107.30764
	exp.[a]	1.1317			
N≡N	6-311+G(3df)	1.0665	3.0382	3.0192	
	exp.[a]	1.0977			
Si≡Si	6-311+G*	1.9224	4.0042	4.0085	
P≡P^{2+}	6-311+G*	1.7463	4.0026	4.0059	
	6-311+G(2df)	1.7472	4.0026	4.0059	

a) Experimental data are from ref 1 and 10. b) MP2 optimized geometry.

The 4.0 bond orders given in Table 1 are computed by means of natural population analysis[6] (an option in the Gaussian 92 program). These bond orders follow Wiberg's[7] and the NPA/NLMO[8] definitions. The computed length of the "quadruple bonds" in Table 1 all are remarkably short. For example, the C–C separation with the largest basis set, 1.1284 Å, is considerably shorter than the 1.1794 Å computed for acetylene at the same level. Table 1 also lists reference bond length for the other "quadruple bond" species. A "bond order-bond length" type analysis for C-C and N-N bonds is shown in Figure 2. The "quadruply bonded" C_2 and N_2^{2+} fit into these relations very well.
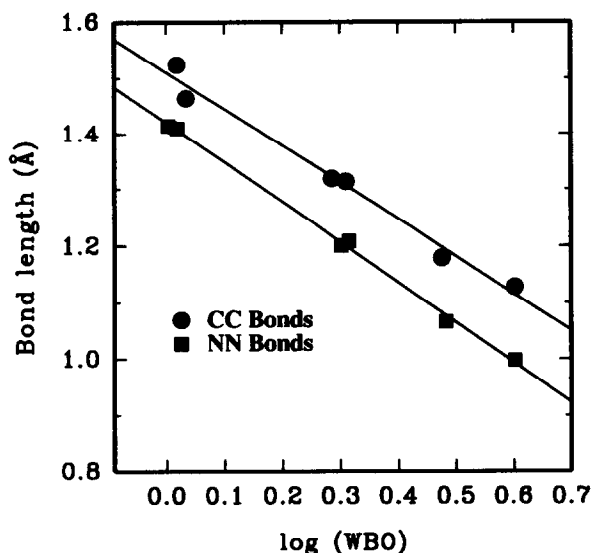

Figure 2. The bond length vs. Wiberg's bond order (WBO) relationship for C-C and N-N bonds computed at 6-311+G(3df) RHF level. The logarithmic formulations is analogous to that of Pauling.[9] At this level the bond lengths are underestimated as compared to those determined experimentally.[10,11] The points for C-C bonds include: CH_3CH_3, H_2CCH_2, HCCH, $H_2CCHCHCH_2$ (single and double bonds), and C_2 (quadruple bond). The correlation is $R_e(CC) = 1.510 - 0.66 \cdot \log(WBO)$. For N-N bonds the data include H_2NNH_2, HNNH, N_2, HNNNNH (single and double bonds), and N_2^{2+} (quadruple bond). The correlations is $R_e(NN) = 1.420 - 0.71 \cdot \log(WBO)$. The ground states of C_2 and N_2^{2+} do not fit these correlations.

Are these results real, or are they a computational artifact? The restricted Hartree Fock (RHF) theory used for the data in Table 1 enforces two electron occupancy of the individual molecular orbitals but does not provide the best wave function. A method capable of treating numerous states of the same symmetry, such as multireference CI, is required to accurately investigate such excited states.

We have obtained CI wavefunctions for C_2 in the range 1.05 - 1.45 Å for the three lowest states of $^1\Sigma_g^+$ symmetry that are in substantial agreement with the previous theoretical tratment[12] and experiments.[2,13] There is no evidence in these studies for a minimum energy structure corresponding to a quadruply bonded C_2 molecule. The "best" candidate is the $3^1\Sigma_g^+$ state (the "E" state[2]), which has an experimental bond length of 1.2529 Å. Our calculations,[14] which employed ground state CISD natural orbitals, show that

the $(2\sigma_g)^2$ $(\pi_u)^4$ $(3\sigma_g)^2$ configuration is the single largest contributor to the E state wavefunction, but its coefficient is only 0.59, representing mere 35% of the total wavefunction. Evidently, the steeply rising ground state potential enery surface at small distances, and the required orthogonality of the excited state, swamps out any minimum at quadruply bonded C–C distances.

This cautionary tale is instructive. Widely distributed quantum chemical programs now run effectively on inexpensive workstations and even personal computers. The exploration of unknown chemistry, eg. the possibility of "quadruple" bonding as suggested by oversimplified molecular orbital considerations, can be pursued easily. But surprising results need the control of more rigorous treatments. Some ideas will survive. "Quadruple C≡C bonding" does not.

Footnotes and References:

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11. There is a linear relation between the computed (6-311+G(3df)) and experimental (ref 2,9) bond lengths for the compounds in Fig. 2: $R_{CC}(exp) = 0.097 + 0.94 \cdot R_{CC}(calc)$ ($r^2 = 0.999$, n = 5), and $R_{NN}(exp) = 0.024 + 1.05 \cdot R_{NN}(calc)$ ($r^2 = 0.998$, n = 4).

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