

# Supporting Information:

## Understanding the impact of correlation on bond length alternation in polyenes

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### Abstract:

This article analyzes the electronic factors governing bond length alternation (BLA) in linear polyenes. The impact of the various effects is illustrated on small all-trans polyenes, namely butadiene, hexatriene and octatetraene prototype molecules. It is well-known that the geometry optimized using a self-consistent-field single determinant exhibits an overestimated bond-length alternation and the paper aims to identify physical effects of correlation which correct this defect. The question is addressed using an orthogonal valence-bond type formalism in which the full- $\pi$  complete active space self-consistent-field wave function is expressed in terms of strongly localized bonding and antibonding molecular orbitals. This paper shows that dynamic polarization effects of  $\pi$  orbitals accounted for in the full- $\pi$  complete active space wave-function significantly reduce bond alternation. These effects are brought by single excitations applied on the inter-bond charge transfer determinants. The dynamic polarization of  $\sigma$  bonds, of either CC or CH character, is analyzed afterwards by either enlarging the active space or by adding the 1hole-1particle excitations. It is shown that these effects also decrease the BLA and increase the coefficients of the charge transfer determinants. Moreover, the relation with dynamic polarization of ligand to metal and metal to ligand charge transfer (LMCT and MLCT respectively) components in magnetic transition metal compounds is discussed.

Table S1 : Butadiene: ground state energy +154 a.u for the reference  $\Phi_0$  and ground state energy +155 a.u. for  $\Phi_0$ +Doubles, for the SCF and the CAS(4,4)SCF, CAS(4,4)+S, CAS(4,4)+SD and CAS((10,10) (Full-Valence  $\sigma_{CC}$  and  $\pi_{CC}$ ) solutions as functions of the BLA (in Å).

BLA (Å)	$\Phi_0$	$\Phi_0 + D_\pi$	$\Phi_0 + SD_\pi$	$\Phi_0'$ (SCF)	$\Phi_0'$ +SD
0.20	-0.993996	-0.046772	-0.074863	-0.028645	-0.544225
0.16	-0.992501	-0.047434	-0.077898	-0.030596	-0.545933
0.14	-0.990799	-0.046714	-0.078446	-0.030670	-0.547036
0.12	-0.988444	-0.045360	-0.078407	-0.030171	-0.547557
0.10	-0.985454	-0.043388	-0.077799	-0.029121	-0.547518
0.08	-0.981840	-0.040811	-0.076638	-0.027537	-0.546939
Optimal BLA (energy)	0.20 (-0.993996)	0.171 (-0.047527)	0.133 (-0.078481)	0.147 (-0.030711)	0.131 (-0.547608)
BLA (Å)	CAS(4,4)	CAS(4,4)+S	CAS(4,4)+SD	CAS(10,10)	CAS(10,10)+S
0.20	-0.079564	-0.162451	-0.569597	-0.155035	
0.16	-0.083271	-0.166930	-0.573521	-0.159599	-0.276069
0.14	-0.084254	-0.168292	-0.574622	-0.161008	-0.277812
0.12	-0.084689	-0.169100	-0.575181	-0.161866	-0.279007
0.10	-0.084599	-0.169375	-0.575219	-0.162195	-0.279675
0.08	-0.084005	-0.169136	-0.574778	-0.162015	-0.279835
0.06					-0.279507
Optimal BLA (energy)	0.114 (-0.084717)	0.099 (-0.169375)	0.109 (-0.575264)	0.097 (-0.162200)	0.084 (-0.279843)

Table S2: butadiene: coefficients of the most important determinants obtained either with all MOs or freezing the core and  $\sigma_{\text{CH}}$  MOs. Calculations have been performed for BLA 0.099 Å.

	Core and $\sigma_{\text{CH}}$ frozen			All MOs		
	CAS(4,4)	CAS(4,4)+S	CAS(4,4)+SD	CAS(4,4)	CAS(4,4)+S	CAS(4,4)+SD
Energy (a.u.)	-155.084429	-155.131025	-155.246565	-155.084542	-155.169371	-155.575181
$C_0$	0.9083	0.8967	0.8847	0.9081	0.8879	0.8494
$C_{\text{CT}}/C_0$ $\pi_1 \rightarrow \pi_2^*$	0.1522	0.1666	0.1629	0.1522	0.1742	0.1624
$C_{\text{INTRA}}/C_0$ $\pi_1 \bar{\pi}_1 \rightarrow \pi_1^* \bar{\pi}_1^*$	0.2179	0.1935	0.1901	0.2185	0.1774	0.1859
$C_{\text{INTER}}/C_0$ $\pi_1 \bar{\pi}_2 \rightarrow \pi_1^* \bar{\pi}_2^*$	0.0186	0.0184	0.0169	0.0187	0.0176	0.0149
$C_{\text{INTER}}/C_0$ $\pi_1 \pi_2 \rightarrow \pi_1^* \pi_2^*$	0.0479	0.0511	0.0492	0.0480	0.0501	0.0463
$C_{\text{INTER}}/C_0$ $\pi_1 \bar{\pi}_2 \rightarrow \pi_2^* \bar{\pi}_1^*$	0.0665	0.0695	0.0668	0.0666	0.0678	0.0629

Table S3: hexatriene : ground state energy +231.0 a.u for different BLA at the SCF, CAS(6,6)SCF and CAS(6,6)+S levels of calculations.

BLA (Å)	SCF	CAS(6,6)SCF	CAS(6,6)+S
0.16	-0.970510	-1.048713	-1.176104
0.14	-0.970917	-1.050429	-1.178468
0.12	-0.970438	-1.051298	-1.179976
0.10	-0.969103	-1.051356	-1.180658
0.08	-0.966939	-1.050637	-1.180544
0.06	-0.963971	-1.049176	-1.179662
Optimal BLA Energy	0.1405 -0.970918	0.1078 -1.051431	0.0926 -1.180706

Table S4: octatetraene ground state energy +308.0 a.u for different BLA at the SCF, CAS(8,8)SCF and CAS(8,8)+S levels of calculations.

BLA (Å)	SCF	CAS(8,8)SCF	CAS(8,8)+S
0.16	-0.910529	-1.014242	-1.183580
0.14	-0.911300	-1.016712	-1.186954
0.12	-0.910879	-1.018043	-1.189176
0.10	-0.909304	-1.018283	-1.190288
0.08	-0.906614	-1.017483	-1.190334
0.06	-0.902844	-1.015695	-1.189355
Optimal BLA Energy	0.1372 -0.911312	0.1047 -1.018322	0.0889 -1.190443