Length and Substituent-Scrambling Energies of Parent and Halogen-Substituted Conjugated Polyynes[†]

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Conjugated polyynes are a class of species of diverse and increasing interest. Length-scrambling and substituent scrambling reaction energies were examined using ab initio quantum chemistry calculations to investigate issues concerning the energetic effects of the molecular ends (substituent communication). Computations were performed for the parent, monohalogenated, and dihalogenated (F, Cl, Br, I) polyynes of up to 60 carbon atoms. A study of resonance effects using natural resonance theory and bond lengths demonstrates lone-pair-donating effects that increase in the series F < Cl < Br < I, but run counter to the halogen inductive effects which decrease in this series and dominate energetic effects.

Introduction

Conjugated polyynes, defined as species with alternating carbon−carbon triple and single bonds, are a class of species of diverse and increasing interest.[1−11] Among their recently investigated features is the question of their conjugation-derived stabilization. In disagreeing quantum chemical studies, Rogers and co-workers[12,13] suggest negligible stabilization while Houk, Schleyer, and their co-workers[14] suggest a value slightly larger than that of conjugated polyenes. Controversy has arisen and been acknowledged, especially since the same numbers have been used by the two sets of authors with divergent interpretations.[15] While Diederich was quoted for saying "there is so much overwhelming experimental evidence for stabilization arising from conjugation,"[16] Borden noted that the problem is in trying to define a conjugation stabilization energy, respectively saying "It's not an experimental question; it's a question of interpretation,"[17] and Carpenter commented that "One would be hard-pressed to defend a claim that either side is right or wrong."[18]

This and other polyyne properties have been difficult to assess because of the absence of enthalpy of formation data for these polyyne species, as noted earlier for diynes.[12,13] The sole experimentally measured thermochemical datum for triynes and beyond is but an indirectly determined (spectroscopic threshold) upper bound for the parent hexatriyne.[19] Surprisingly, the comparative lack of numbers is in fact shared by conjugated polyenes in that there are no data beyond that of hexatriene[20] except for an old measurement[21,22] for the solid "infinite case" material erstwhile known as cuprene and now recognized as "polyacetylene." (In fact, the analogous solid "infinite" case of a polyyne has been called "carbyne", and we note a thermochemical/electrochemical/synthetic study of this material with some key references.[23] We note, however, that the term "carbyne" has also been used for univalent carbon species CX, by analogy to the divalent one-carbon species, carbenes CX_2.)

Computational chemistry is needed to answer the call for data. In the current study, we do not directly address conjugative stabilization, but instead investigate some related thermodynamic properties in hopes of laying a broader data foundation for future research into the stability of polyynes. Here we ask, how much "communication" is there between the two ends of the polyyne and how does that communication depend on its length? By communication, we mean stabilization or destabilization depending on the substitution pattern. As such, we include the effects of both π donation and σ withdrawal by halogen substituents, as well as conjugation of triple bonds.

Two types of reactions are investigated. The first addresses the thermoneutrality of the isodesmic "length-scrambling" reaction

$$2XC_nY \rightarrow XC_{n'}Y + XC_{n''}Y, \quad \text{where } 2n = n' + n'' \quad (1)$$

The second addresses the thermoneutrality of the likewise isodesmic substituent-scrambling reaction

$$XC_nX + YC_nY \rightarrow 2XC_nY \quad (2)$$

For both questions, the X and Y substituent will be chosen among {H,F,Cl,Br,I} using MP2 electron-correlation calculations for polyynes up to $n = 6$ carbons. For polyynes of up to 60 carbons, X and Y will be restricted to H and I, the substituents of greater interest to the experimental[2] and theoretical[7] communities. (It is clear that the reactions with $n = 0$ need not be studied. They are not unequivocally thermoneutral— indeed, it is the nonthermoneutrality for such reactions from which the concept of electronegativity arises.) In addition, we provide data on bond lengths and resonance structure contributions for selected polyynes.

Methods

The Gaussian03 software program[24] was used to compute optimized geometries and vibrational harmonic frequencies of normal modes. The frequencies were used for zero-point

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TABLE 1: HF Molecular Energies (au) of a Variety of Parent Polyynes and Their Mono and Diiodo Derivatives

	$n = 2$	$n = 4$	$n = 6$	$n = 8$	$n = 14$	$n = 20$	$n = 40$	$n = 60$
HC_nH	−76.826043	−152.509807	−228.194699	−303.879710	−530.934694	−757.989542	−1514.838836	−2271.688063
IC_nH	−87.398290	−163.082831	−238.767785	−314.452862	−541.507882	−768.562749	−1525.412063	−2282.261292
IC_nI	−97.970466	−173.655823	−249.340864	−325.026002	−552.081066	−779.135956	−1535.985301	−2292.834534

TABLE 2: MP2 Molecular Energies (au) of Mono- and Dihalogen Substituted Polyynes

	$n = 2$	$n = 4$	$n = 6$	$n = 2$ + ZPVE	$n = 4$ + ZPVE	$n = 6$ + ZPVE
HC_nH	−77.082680	−153.009167	−228.939343	−77.056302	−152.972904	−228.893609
FC_nF	−275.093120	−351.026415	−426.956583	−275.080067	−351.003279	−426.924148
ClC_nCl	−995.164751	−1071.096269	−1147.027680	−995.154104	−1071.075664	−1146.997552
BrC_nBr	−5220.920789	−5296.851907	−5372.783575	−5220.911246	−5296.832486	−5372.754597
IC_nI	−98.429397	−174.361255	−250.293289	−98.420666	−174.342406	−250.264911
HC_nF	−176.093251	−252.017885	−327.947994	−176.073236	−251.988243	−327.908842
HC_nCl	−536.124546	−612.052704	−687.983481	−536.105860	−612.024139	−687.945504
HC_nBr	−2649.001714	−2724.930409	−2800.861390	−2648.983515	−2724.902436	−2800.823976
HC_nI	−87.755105	−163.684928	−239.616191	−87.737264	−163.657215	−239.579060
FC_nCl	−635.130017	−711.061125	−786.992075	−635.117971	−711.039321	−786.960756
FC_nBr	−2748.008487	−2823.938854	−2899.869978	−2747.996912	−2823.917675	−2899.839236
FC_nI	−186.763559	−262.693359	−338.624756	−186.752322	−262.672482	−338.594306
ClC_nBr	−3108.042818	−3183.974078	−3259.905621	−3108.032708	−3183.954064	−3259.876070
ClC_nI	−546.797314	−622.728704	−698.660455	−546.787591	−622.708996	−698.631206
BrC_nI	−2659.675207	−2735.606564	−2811.538425	−2659.666060	−2735.587433	−2811.509746

TABLE 3: ΔE(MP2, kJ mol^{-1}) for Reactions (1a,1b)

X	reacn 1a no ZPVE	reacn 1a with ZPVE	reacn 1b no ZPVE	reacn 1b with ZPVE
F	−14.38	−14.68	8.21	6.15
Cl	−6.87	−8.10	0.28	−0.86
Br	−6.00	−6.88	−1.44	−2.29
I	−3.78	−4.97	−0.46	−2.01
H	−9.68	−10.77	−9.68	−10.77

TABLE 4: ΔE(HF, No ZPVE, kJ mol^{-1}) for Reactions 1a and 1b for Longer Polyynes

	{n/n′,n″}			
	{4/2,6}	{6/4,8}	{14/8,20}	{40/20,60}
HC_nH	−2.96	−0.31	0.36	0.18
IC_nH	−1.08	−0.33	0.40	0.22
IC_nI	0.83	−0.26	0.46	0.29

vibrational energy (ZPVE) corrections in the usual manner, although computed ΔE results containing ZPVE corrections are generally not presented because the effects of the corrections are minor, and we did not wish to mask the purely electronic effects which are of the greatest importance. Molecular energy and its first and second derivatives were computed analytically using the Hartree−Fock self-consistent field (HF) and Møller−Plesset second-order perturbation theory (MP2) methods.[25] The basis set used for atomic orbital generation was of double-ζ plus polarization (DZP) quality; it was cc-pVDZ[26] for all atoms except I, for which the LANL2DZ basis set[27] was appended with a single set of d functions with exponent taken from Radom and co-workers.[28] We had difficulties converging the SCF to the default 10^{-7} in the density for polyynes having more than 20 carbons; for these we reduced the SCF convergence criteria to 10^{-5} in the density, with no apparent effect on energies to the microhartree. All the computed molecular energies appear in Table 1 (HF) and Table 2 (MP2).

Results and Discussion

Length-Scrambling Energies of Polyynes. Table 3 presents the computed MP2 reaction energies for two specific subsets of reaction 1:

$$2HC_4X \rightarrow HC_2X + HC_6X \qquad (1a)$$

$$2XC_4X \rightarrow XC_2X + XC_6X \qquad (1b)$$

(Mathematically, the enthalpy of reaction 1a is the same as the difference of the difference of the total energies, or enthalpies of formation, of a monohalogenated ethyne and butadiyne, and that of the corresponding hexatriyne and butadiyne. Reaction 1b is likewise the difference of the difference for the corre-

sponding dihalogenated species.) For the parent polyyne, this length-scrambling reaction is exothermic (−10 kJ mol^{-1} before ZPVE correction). Replacing one H atom with one halogen atom (first two columns) makes it less exothermic, except for the F substitution which makes it more exothermic. Replacing both H atoms with two halogen atoms (last two columns) enhances the effect, making the reactions almost thermoneutral, except for the double-F substitution which dramatically reverses the effect of single-F substitution and makes the reaction endothermic. This result is unique, and perhaps indicates an unusually weak stability of the FCCF product molecule. The electronegativity trend from I to F is monotonic for HC_4X species, but not quite monotonic for XC_nX species.

Table 4 presents the computed HF reaction energies for the same subsets, but involving the longer parent, monoiodinated, and diiodinated polyynes with only I. These length-scrambling energies are effectively thermoneutral, sometimes endothermic and sometimes exothermic, but being almost always less than RT (ca. 2.5 kJ mol^{-1}). The results suggest that the conjugation energy of polyynes, however defined, is linear with the number of triple bonds—this parallels the situation in the better, or at least longer, understood case of polyenes.[29]

We also deduce from Table 3 that the effect of zero-point energies on the reaction energies is rather negligible, suggesting that the observed trends are entirely due to electronic effects.

We further considered a more general length-scrambling of three polyynes,

$$XC_iY + XC_jY + XC_kY \rightarrow XC_{i'}Y + XC_{j'}Y + XC_{k'}Y \quad (1c)$$

for four examples, and Table 5 presents the results. The trends are the same as for the length-scrambling of two molecules; i.e., results involving the two-carbon ethyne are more extreme, and ΔE values become somewhat more positive with the

TABLE 5: ΔE(HF, No ZPVE, kJ mol^{-1}) for Three-Molecule Length-Scrambling Reactions (Reaction 1c)

	{8,8,8/2,2,20}	{8,8,8/4,6,14}	{8,8,14/4,6,20}	{14,14,20/4,4,40}
HC$_n$H	−6.56	−0.18	0.17	1.26
IC$_n$H	−1.95	0.23	0.63	2.07
IC$_n$I	2.94	0.67	1.12	2.99

TABLE 6: MP2 Substituent-Scrambling Energies (kJ mol^{-1}) for XC$_6$X + YC$_6$Y → 2XC$_6$Y

	X = F	X = Cl	X = Br	X = I	X = H
Y = F	0.00	0.30	0.53	0.94	−0.16
Y = Cl	0.30	0.00	0.03	0.15	0.16
Y = Br	0.53	0.03	0.00	0.03	0.36
Y = I	0.94	0.15	0.03	0.00	0.66
Y = H	−0.16	0.16	0.36	0.66	0.00

TABLE 7: MP2 Substituent-Scrambling Energies (kJ mol^{-1}) for XC$_4$X + YC$_4$Y → 2XC$_4$Y

	X = F	X = Cl	X = Br	X = I	X = H
Y = F	0.00	1.14	1.61	2.50	−0.49
Y = Cl	1.14	0.00	0.05	0.30	0.07
Y = Br	1.61	0.05	0.00	0.09	0.67
Y = I	2.50	0.30	0.09	0.00	1.48
Y = H	−0.49	0.07	0.67	1.48	0.00

TABLE 8: MP2 Substituent-Scrambling Energies (kJ mol^{-1}) for XC$_2$X + YC$_2$Y → 2XC$_2$Y

	X = F	X = Cl	X = Br	X = I	X = H
Y= F	0.00	−5.68	−8.05	−12.08	−28.10
Y= Cl	−5.68	0.00	−0.25	−1.26	−4.36
Y= Br	−8.05	−0.25	0.00	−0.60	0.11
Y= I	−12.08	−1.26	−0.60	0.00	4.90
Y= H	−28.10	−4.36	0.11	4.90	0.00

TABLE 9: Resonance Contributions (Percent) for Ethynes in the Natural Resonance Theory (B3LYP/cc-pVDZ)

resonance form	H,H	F,F	Cl,F	Cl,Cl
$\ddot{X}-C{\equiv}C-\ddot{Y}$	99.0	83.9	82.7	81.0
$X{=}C{=}\ddot{C}-\ddot{Y}$	0	7.8	8.1	9.0
$\ddot{X}-\ddot{C}{=}C{=}Y$	0	7.8	8.6	9.0

TABLE 10: Resonance Contributions (Percent) for Butadiynes in the Natural Resonance Theory (B3LYP/cc-pVDZ)

resonance form	H,H	F,F	Cl,F	Cl,Cl
$\ddot{X}-C{\equiv}C-C{\equiv}C-\ddot{Y}$	83.6	67.8	65.6	63.1
$X{=}C{=}\ddot{C}-C{\equiv}C-\ddot{Y}$	0	9.2	10.1	10.2
$\ddot{X}-C{\equiv}C-\ddot{C}{=}C{=}Y$	0	9.2	9.3	10.2
$\ddot{X}-C{=}C{=}C{=}\ddot{C}-\ddot{Y}$	6.7	5.7	6.0	6.6
$\ddot{X}-\ddot{C}{=}C{=}C{=}C-\ddot{Y}$	6.7	5.7	6.3	6.6

addition of iodine substituents. This near equality likewise relates to the above enunciated polyene results.

Substituent-Scrambling Energies of Polyynes. Table 6 gives the calculated reaction energies, without zero-point corrections, for reaction 2 for the six-carbon ($n = 6$) case, where the substituent scrambling energies should be close to zero. Tables 7 and 8 give the same data but for the $n = 4$ and $n = 2$ cases, where increasing deviations from thermoneutrality might be expected.

First we consider Tables 6 and 7 for the mono and disubstituted hexatriyne and butadiynes, respectively. The substituent-scrambling reaction is weakly endothermic in all such cases, and the reaction gets more endothermic as the difference in electronegativity between substituents increases. This we will consider to be the "normal" trend. Furthermore, in going from Table 6 to Table 7, the polyyne lengths are decreased, and the reaction energies approximately triple in magnitude as their separation is reduced from six carbon atoms to four.

In Table 8, however, when only two carbon atoms separate the substituents, the scrambling energies become exothermic (again we are ignoring the H-terminated results), and the ones involving FCCF are substantially exothermic. The exothermic reactions involving FCCF as reactant are likely just indicating the unusually weak stability of FCCF, just as the length-scrambling results did. However, even for the other pairs of substituents, it now appears that the sign reversal is general, i.e., that mixed-halogens polyynes are enthalpically favored for $n = 2$ but symmetrically substituted polyynes are favored for longer lengths. Furthermore, this anomalous exothermicity for $n = 2$ is enhanced as the electronegativity difference between substituents increases (ignoring the results involving monosubstituted polyynes).

To demonstrate the general validity of our other numbers in the current paper and thereby add confidence to qualitative interpretations of our results, we compare our calculated 0 K results with the calculated 298 K from a recent high-level computational study[30] that included the three small cases of FC≡CF, ClC≡CCl, and FC≡CCl. Let us assume the two sets of results are at the same temperature (298 K) by applying a constant rotational and translational correction independent of the molecule. For these three species, we calculated substituent-scrambling destabilization energies relative to ethyne and its monohalo derivatives of 20.3, 5.3, and 9.9 kJ mol^{-1}, in comforting agreement with the 23.3, 4.3, and 12.4 kJ mol^{-1} derivable from that latter source. Beyond this comparison, however, we are hesitant to quantify the above interpretation any more strictly, because reliable experimental data on any of our halogenated polyynes are nonexistent. As noted above, there are no reliable experimentally measured values for the enthalpies of formation of any of our halogenated polyynes. Unfortunately, there are likewise few for any corresponding halogenated monoenes (CH$_2$=CHX, X = F, Cl, Br data available; (*Z*)- and (*E*)-XCH=CHX, X = Cl, I) and none for so substituted polyenes or mixed halogenated polyenes. And should one wish to be brazen and consider halogenated benzenes, and compare the mono- and, most plausibly, the para-disubstituted derivatives, again there is incomplete experimental data (C$_6$H$_5$X, all data available; *p*-C$_6$H$_4$X$_2$, X = F, Cl available in gas phase, X = Br, I, only for the solids).[31] There are no relevant thermochemical data for mixed halogenated benzenes, either. Nonetheless, the few results available are interesting. For example, the gas-phase benzenoid reaction 3

$$2C_6H_5X \rightarrow C_6H_6 + \text{*p*-}C_6H_4X_2 \qquad (3)$$
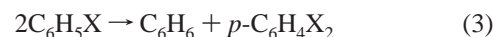
is endothermic by some 10 kJ mol^{-1} for X = F while it is essentially thermoneutral for X = Cl.

Resonance Analysis. We briefly report the results of calculations on some relevant resonance contributions, as done using natural resonance theory[32] with the B3LYP/cc-pVDZ level of theory. In Tables 9 and 10, resonance structures and their contributions are given for difluoro, dichloro, the mixed chlorofluoro, and the parent ethyne and butadiyne. In all cases, in the longer chain species, the contribution of the classical structure X−(C≡C)$_2$−Y is significantly less than the corresponding shorter chain contribution X−C≡C−Y. Likewise, in all cases, there is considerable contribution of donation of a halogen p orbital into an empty π^* orbital of the π electron carbon backbone ($n_{\text{Halogen}} \rightarrow \pi^*_{\text{CC}}$) as documented by contributors with a formally doubly bonded halogen. Interestingly, the contributions are roughly the same for F and Cl substitution.

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TABLE 11: Resonance Contributions (Percent) for an Octatetryne in the Natural Resonance Theory (B3LYP/cc-pVDZ)

resonance form	F,F
$\ddot{X}-C{\equiv}C-C{\equiv}C-C{\equiv}C-C{\equiv}C-\ddot{X}$	28.8
$X{=}C{=}\ddot{C}-C{\equiv}C-C{\equiv}C-C{\equiv}C-\ddot{X}$	9.6×2
$\ddot{X}-C{=}C{=}C{=}\ddot{C}-C{\equiv}C-C{\equiv}C-\ddot{X}$	8.4×2
$\ddot{X}-C{\equiv}C-\ddot{C}{=}C{=}C{=}C-C{\equiv}C-\ddot{X}$	8.4×2
$\ddot{X}-\ddot{C}{=}C{=}C{=}C-C{\equiv}C-C{\equiv}C-\ddot{X}$	6.4×2

TABLE 12: Optimized Bond Lengths (Ångstroms) for the Parent and Symmetrically Dihalogen Substituted (X = Y) Ethynes, Butadiynes, and Hexatriynes (MP2/cc-pVDZ)

	$n = 2$ $C{\equiv}C$	$n = 4$ $C{\equiv}C$	$n = 4$ $C{-}C$	$n = 6$ $C_1{\equiv}C_2$	$n = 6$ $C_2{-}C_3$	$n = 6$ $C_3{\equiv}C_4$
HC_nH	1.2296	1.2371	1.3840	1.2398	1.3743	1.2472
FC_nF	1.2108	1.2275	1.3838	1.2308	1.3754	1.2451
ClC_nCl	1.2282	1.2380	1.3753	1.2408	1.3682	1.2502
BrC_nBr	1.2326	1.2409	1.3735	1.2434	1.3666	1.2515
IC_nI	1.2389	1.2447	1.3716	1.2471	1.3647	1.2533

In addition, as the length of the polyyne chain grows, the number of nonclassical resonance contributors increase as well as does their total contribution. For example for the difluoro species, for $n = 2$, 4, and 8 (Also, see Table 11), the contribution from the classical $F{-}(C{\equiv}C)_{n/2}{-}F$ structure drops rather precipitously from 83.9 and 67.8 to 28.8%

Bond Lengths. Table 12 displays the MP2/cc-pVDZ-optimized CC triple bond and single bond lengths of the parent and symmetrically dihalogen (X = Y) substituted ethynes, butadiynes and hexatriynes investigated in this work.

Several general trends can be seen in these data. The first trend is that as the halogen substituent proceeds down the periodic table from F to I, the formal $C{\equiv}C$ bonds get longer and the formal $C{-}C$ bonds get shorter. This is consistent with increasing lone-pair π conjugation with the $C{\equiv}C$ bonds in the order F < Cl < Br < I, as demonstrated in the previous section. Despite electrostatic repulsion from the positive carbons, the $C{\equiv}C$ bonds in the fluorinated species are shorter than in the parent hydrocarbons. The second trend is that the $C{\equiv}C$ bonds get longer as one proceeds from ethyne to butadiyne to hexatriyne and the $C{-}C$ bonds get shorter as one proceeds from butadiyne to hexatriyne. This is consistent with conjugation of the π bonds in the polyynes, a conclusion consonant with the $C_3{\equiv}C_4$ bond being the longest "triple bond" as it has two other triple bonds to interact with, and the cumulenic resonance structures gain prominence with increasing numbers of carbons. These geometry results suggest that conjugation is important in both the parent and halogenated polyynes. However, this resonance analysis does not itself quantify particular energetic benefits to conjugation. This situation, this ambiguity, is hardly unique: conclusions from the geometric and energetics criteria for aromaticity, delocalization, and conjugation generally writ large, are distinct, and are often dissonant.[33]

None of our analysis should be construed as saying there is no interaction between the π orbitals in polyynes or between any affixed halogens thereto. Photoelectron spectroscopy documents this interaction for the diverse halogenated ethynes and butadiynes, much as it does for the dihalogens.[34] It is well established that summing orbital energies does not give total energies. Indeed, we must admit that a simple quantitative and unifying explanation for the various halogen substituent effects on polyynes evades us.

A New Consideration of Stabilization of Diynes. Let us take what may appear to be a diversion, from conjugated organic molecules to the homonuclear dihalogens, X_2. From the archival

literature, we find that the ionization energy of the four X_2 species are lower than that of either the corresponding HX or X. From the textbook literature, we find the highest occupied orbital (HOMO) for X_2 is an antibonding π^*, while that of HX and X are both atomic-based p orbitals. We also find the bond energies of the diatomics are rather low. Relatedly, single bonds between their neighbors O and S, and even N, are quite weak. This provides the basis of the textbook assertion that antibonding is more antibonding than bonding is bonding. That is, when two doubly occupied atomic orbitals φ_L and φ_R on neighboring atoms are mixed, there is net destabilization; the sum of the resulting orbital energies of $\varphi_L + \varphi_R$ and $\varphi_L - \varphi_R$ is greater than the sum of the original orbital energies of φ_L and φ_R.

Now consider the united-atom limit in which the two C atoms of an ethyne are fused together. The HOMOs, the occupied π orbitals, become lone-pair p-orbitals on the fused atom. Hence, one might actually expect the approach of two $-C{\equiv}C-$ (or $>C{=}C<$) groups to be a destabilizing interaction, from the argument of the preceding paragraph. Why, then, does the π-type interaction of these groups allow for stabilization while the π-type interaction of two halogen atoms result in destabilization? The answer is that we have neglected to consider what happens to the π^* orbitals in the united atom limit. They become d orbitals of the fused atom. Hence, the analogous "conjugative stabilization" in a dihalogen would be for an occupied atomic p-orbital to donate into an unoccupied d orbital on the neighboring atom. However, it appears that in the dihalogens these d's are seemingly inaccessible. That is, the sequence of the occupied molecular orbitals of the dihalogens closes with $\pi_p^4 \, \sigma_p^2 \, \pi_{p*}^4$ and not the alternative[35] $\pi_p^4 \, \sigma_p^2 \, \pi_d$.[4]

Summary

By the use of ab initio quantum chemical calculations we deduce there is minimal interaction between the substituents on conjugated polyynes. On a fine energetic scale, we have found some interesting trends: (i) symmetric XCCX species seem slightly *less stable* than asymmetric XCCY species; (ii) for conjugated polyynes, the symmetric XC_nX species are slightly *more stable* (enthalpically) than asymmetric XC_nY species; and (iii) FCCF seems particularly less stable than other XCCX species. Lone pair donation into the conjugated polyyne chain increases in the substituent series F < Cl < Br < I, but inductive effects decrease in this series and dominate the energetic effects. Structurally, (i) $C{\equiv}C$ bonds lengthen and $C{-}C$ bonds shorten with increasing number of carbons, and the $C{\equiv}C$ bonds lengthen as one proceeds from F to I, with those found in the fluorinated species shorter than in the unsubstituted polyynes themselves.

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