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Reversing the Bond Length Alternation Order in Conjugated Polyenes by Substituent Effects

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Abstract: We have synthesised several push-pull substituted conjugated polyenes and determined their accurate C–C bond lengths and charge-density distribution by utilising quantum crystallographic techniques. In a series of alkene, diene, and triene bearing two (trifluoromethyl)sulfonyl (triflyl) groups on the terminal carbon atom, unique reversal of the bond-length alternation (BLA) order has been observed. This is a pronounced aberration from the molecular structure predicted by the Lewis structure-based neutral resonance structure. Such reversal of BLA order has not been observed in push-pull compounds bearing conventional electron-withdrawing groups such as carbonyl and cyano groups instead of triflyl groups. Bonding behaviour of both normal and reversed bond length alternating systems has been revealed by complementary bonding analysis using several bond descriptors based on the experimentally fitted wavefunctions.

Introduction

Chemical bonds in molecules are electronically and sterically perturbed by surrounding substituents. Most often, observable structural parameters such as bond lengths and angles have been widely utilised as an evidence of substituent effects. For example, the 'C–N' bond in common amides is about 15 pm shorter than that in typical aliphatic amines (132 pm vs. 147 pm).^[1] This fact evidences delocalisation of a lone electron pair on the nitrogen atom into the carbonyl group, which increases the double bond character of the 'C–N' bond and decreases that of the 'C=O' bond. In twisted amides, in which delocalisation of the lone electron pair is prohibited owing to distortion around the C–N bond axis (ideally, ~90°), the 'C–N' bond length is elongated to 145 pm.^[2,3] Such molecular geometric impact by the resonance (mesomeric) effect allows to estimate a contribution ratio of particular resonance structures; Pauling calculated a contribution ratio of neutral (I) and charge-separated (II) resonance structures in the 'O=C–N' system of acetamide as 60:40 on the basis of experimentally determined interatomic distances (Figure 1A).^[4] According to a later study

using Natural Resonance Theory (NRT),^[5] which is a quantum chemical theory closely linked to the Lewis structure concept, the contribution ratio between resonance structures I/II is 70:30.^[6]

Buta-1,3-diene is another textbook example for the impact of resonance on the molecular geometry (Figure 1B). In this molecule, the nominal double bonds C1–C2 and C3–C4 are slightly longer than an ideal carbon–carbon double bond in

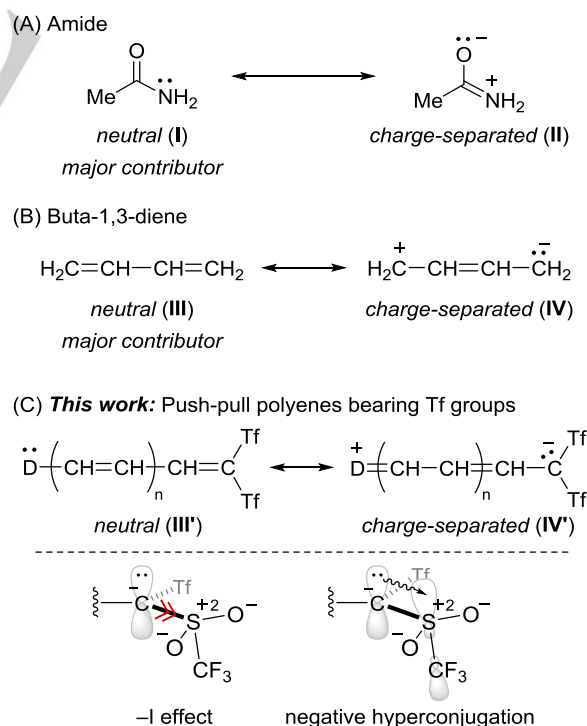


Figure 1. Resonance structures of (A) acetamide, (B) buta-1,3-diene, and (C) push-pull polyenes. The triflyl group is drawn in its most relevant charge-separated resonance structure.^[10]

ethylene (133.76 pm vs 133.05 pm).^[7] At the same time, its nominal single bond C2–C3 is shorter than usual C(sp³)–C(sp³) bonds (153 pm). Minor contribution of charge-separated resonance structure **IV** through delocalisation of π -electrons provides a good explanation for such geometric features. However, note that the nominal double bonds are still significantly shorter than the nominal single bond. In other words, each carbon–carbon bond length in buta-1,3-diene does not deviate from what the neutral resonance structure **III** suggests. Such bond-length alternation (BLA) is widely found in acyclic π -conjugated polyenes. Although the difference between short and long bonds decreases by elongation of the π -conjugation, reversal of the BLA order has not been reported so far.^[8]

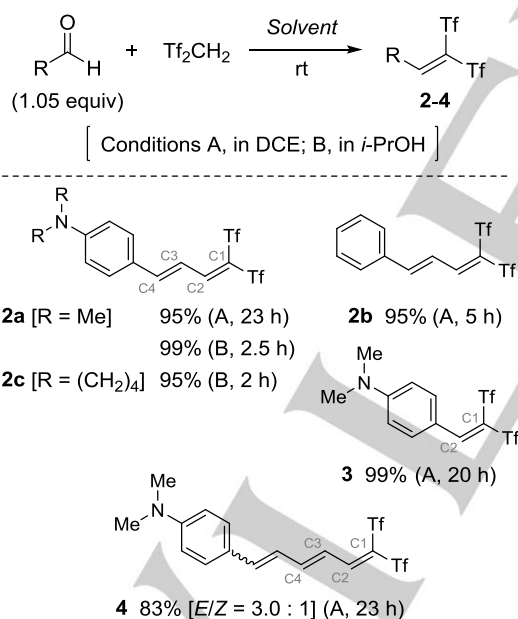
Recently, we reported synthesis and quantum crystallographic bonding analysis of electron-deficient push-pull ethylenes depicted as Tf₂C=C(NHR)₂ (Tf = CF₃SO₂).^[9] Among these, the 'C=C' bond in Tf₂C=C(NH*p*-Tol)₂ **1a**, which has a nearly planar ethylene geometry, showed an intermedium character between charge-separated and π -bonding resonance structures, which means a relatively heavy contribution of the former, in the chemical bonding analysis by several bond descriptors. Moreover, Tf₂C=C(NH*i*-Pr)₂ **1b**, which is a twisted ethylene bearing a large distortion around the central 'C=C' bond, exhibited a pronounced charge-separated nature. Surprisingly, despite such huge difference in the distortion, the 'C=C' bond lengths of both push-pull ethylenes are similar. This finding

motivated us to study the impact of the 'push-pull' effect on the molecular geometries of bond alternating polyene systems (Figure 1C). The triflyl group is known to be one of the strongest electron-withdrawing groups (EWGs) and it can stabilise α -carbanions through an electron-withdrawing inductive (–I) effect and negative hyperconjugation.^[10,11] In this article, we describe a clear relationship between the C–C bond lengths in push-pull polyene systems and the ability of the EWGs. Despite expanding applications of polymethine dyes and π -conjugated polymers, any quantitative relationships between the strength of push/pull abilities of the substituents and the BLA have not been examined.^[12,13] During this study, we have also found that the triflyl group successfully reverses the order of alternating short/long bonds.

Results and Discussion

Polyenes employed in this project were prepared by dehydrative condensation reaction between Tf₂CH₂ and substituted cinnamaldehydes (Figure 2A).^[14] Although less electrophilic 4-(dimethylamino)cinnamaldehyde required prolonged reaction time until complete consumption of starting materials under the standard conditions with 1,2-dichloroethane (DCE) as the solvent (conditions A), notable rate acceleration was achieved

(A) Synthesis of 1,1-bis(triflyl)alkene and polyenes

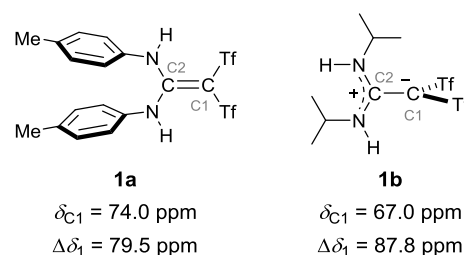


(B) ¹³C NMR chemical shift δ

[100 MHz, 0.20 mol L⁻¹ solutions, rt, in ppm]

	C1	C2	C3	C4	$\Delta\delta_1$
2a	99.3	161.8	115.8	167.2	62.5
2b	118.7	171.3	121.7	166.9	52.6
2c	97.8	160.5	115.5	166.7	62.7
3	103.4	160.3	–	–	56.9
4^[b]	97.7	158.8	121.1	168.0	61.1

^[a] For *E* isomer.



(C) Synthesized dienes bearing different EWGs

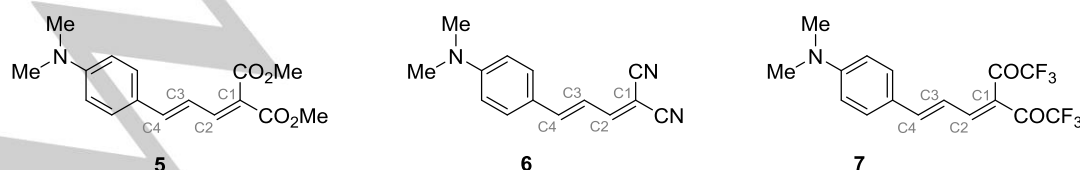
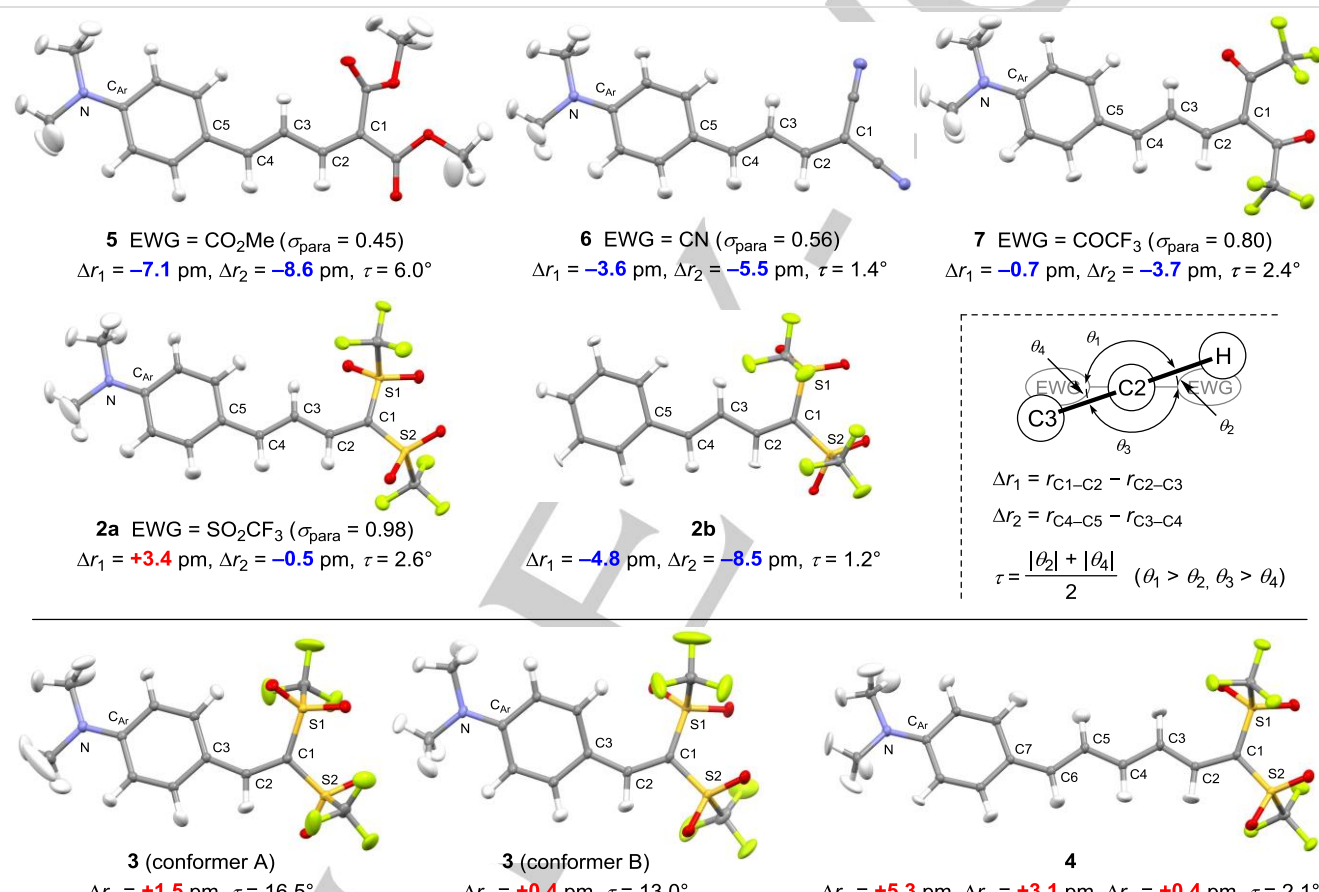


Figure 2. (A) Polyene synthesis through self-promoting condensation reaction, (B) ¹³C NMR data of *gem*-bis(triflyl)alkenes **1-4**, (C) Structures of other push-pull dienes **5-7**.

by using propan-2-ol (conditions B) instead of DCE to give **2a** in excellent yield.^[15] By applying these conditions, non-push-pull diene **2b**, push-pull diene **2c**, alkene **3**, and triene **4** were also prepared in good to excellent yields. In addition, known push-pull dienes **6-7** bearing other EWGs including methoxycarbonyl (**5**), cyano (**6**), and trifluoroacetyl (**7**) groups were prepared (Figure 2C and the Supporting Information). All synthesised compounds are stable under air atmosphere. ¹³C NMR data of *gem*-bis(triflyl)ated products in CD₃CN are summarised in Figure 2B. The C1 and C2 atoms of diene **2a** bearing the 4-(dimethylamino)phenyl group as the 'push' moiety and two triflyl groups as the 'pull' moiety were observed at 99.3 ppm and 161.8 ppm, respectively. The chemical shift difference $\Delta\delta_i$

between C2 and C1 atoms can be used as an indicator to evaluate the magnitude of the C1–C2 bond polarisation.^[16] Compared with the $\Delta\delta_i$ value of the reference compound **2b** (52.6 ppm), that of push-pull derivative **2a** is much larger (62.5 ppm). A remarkable up-field shift of atom C1 in **2a** (99.3 ppm) supports higher anionic character. Indeed, the 4-(dimethylamino)phenyl group in **2a** serves as an effective 'push' moiety. From a comparison of $\Delta\delta_i$ values, the C1–C2 polarisation of push-pull diene **2a** can be regarded to be weaker than those of **1** (**1a**, 79.5 ppm; **1b**, 87.5 ppm), but stronger than non-push-pull derivative **2b**. As shown in ¹³C NMR data of **2c**, structural modification around the amino functionality does not

Table 1. HAR-derived X-ray crystallographic structures and selected interatomic distances r (pm) of **2-7**. BLA parameters Δr_1 and Δr_2 are also shown.



5 EWG = CO₂Me ($\sigma_{para} = 0.45$)
 $\Delta r_1 = -7.1$ pm, $\Delta r_2 = -8.6$ pm, $\tau = 6.0^\circ$

6 EWG = CN ($\sigma_{para} = 0.56$)
 $\Delta r_1 = -3.6$ pm, $\Delta r_2 = -5.5$ pm, $\tau = 1.4^\circ$

7 EWG = COCF₃ ($\sigma_{para} = 0.80$)
 $\Delta r_1 = -0.7$ pm, $\Delta r_2 = -3.7$ pm, $\tau = 2.4^\circ$

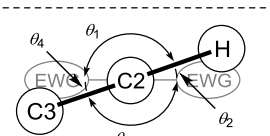
2a EWG = SO₂CF₃ ($\sigma_{para} = 0.98$)
 $\Delta r_1 = +3.4$ pm, $\Delta r_2 = -0.5$ pm, $\tau = 2.6^\circ$

2b
 $\Delta r_1 = -4.8$ pm, $\Delta r_2 = -8.5$ pm, $\tau = 1.2^\circ$

3 (conformer A)
 $\Delta r_1 = +1.5$ pm, $\tau = 16.5^\circ$

3 (conformer B)
 $\Delta r_1 = +0.4$ pm, $\tau = 13.0^\circ$

4
 $\Delta r_1 = +5.3$ pm, $\Delta r_2 = +3.1$ pm, $\Delta r_3 = +0.4$ pm, $\tau = 2.1^\circ$



$$\Delta r_1 = r_{C1-C2} - r_{C2-C3}$$

$$\Delta r_2 = r_{C4-C5} - r_{C3-C4}$$

$$\tau = \frac{|\theta_2| + |\theta_4|}{2} \quad (\theta_1 > \theta_2, \theta_3 > \theta_4)$$

	C1–C2	C2–C3	C3–C4	C4–C5	C5–C6	C6–C7	CAr–N
5	136.11 (6)	143.25 (5)	135.98 (7)	144.57 (5)	--	--	136.36 (4)
6	138.05 (4)	141.64 (4)	137.70 (4)	143.21 (4)	--	--	136.00 (4)
7	139.76 (8)	140.46 (8)	138.46 (9)	142.11 (9)	--	--	135.48 (8)
2a	141.60 (4)	138.23 (4)	139.91 (5)	140.42 (4)	--	--	134.01 (4)
2b	137.47 (5)	142.23 (5)	136.38 (5)	144.90 (5)	--	--	--
3-A	141.26 (7)	139.80 (8)	--	--	--	--	133.38 (7)
3-B	140.79 (6)	140.38 (8)	--	--	--	--	133.73 (7)
4	143.2 (1)	137.9 (1)	141.8 (1)	138.7 (1)	140.8 (1)	140.4 (1)	134.32 (9)

affect the $\Delta\delta_i$ values significantly. Although the $\Delta\delta_i$ value of alkene **3** is slightly smaller than that of **2a**, ^{13}C NMR data of push-pull triene **4** (61.1 ppm) also imply that its polarisation is comparable to **2a**.

Next, we conducted single-crystal X-ray structure analyses of the polyenes. Coordinates and anisotropic displacement parameters (ADPs) of all atoms including hydrogen atoms^[17] were refined by the Hirshfeld Atom Refinement (HAR) technique (Table 1).^[18] The crystallographic molecular geometry of **5** is fully consistent with the major contribution coming from the neutral resonance structure **V** in the light of bond lengths [C1–C2, 136.11(6); C2–C3, 143.25(5); C3–C4, 135.98(7); C4–C5, 144.57(5); C_{Ar}–N, 136.36(4)] (Figure 3).

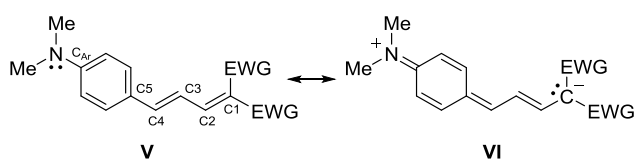


Figure 3. Resonance in (4-(dimethylamino)phenyl)butadienes.

A similar situation was found in the cases of push-pull dienes **6** and **7**. These results suggest that the *normal* BLA order -- that the nominal double bonds in **VI** are shorter than the nominal single bonds -- is not reversed by mere push-pull substitution. However, we did find that the bond lengths in the push-pull diene framework are sensitive to the electron-withdrawing ability of the terminal EWGs. Indeed, the bond length difference Δr_1 between C1–C2 and C2–C3 bonds notably allayed in order of diester **5** (–7.1 pm), dinitrile **6** (–3.6 pm), and diketone **7** (–0.7 pm) (Table 1). The same trend is also confirmed by the Δr_2 value for the C3–C4–C5 system. In this context, a HAR-derived X-ray crystallographic structure of disulfone **2a** was quite unique. It exhibited a pronounced reversing of the BLA order in the C1–C2–C3 system; compared with the C2–C3 bond, a 2.5% longer C1–C2 bond brought about a positive Δr_1 value (+3.4 pm). A similar reversal of the BLA order was not found in non-push-pull diene **2b**. As shown in Figure 4A, a linear relationship of Δr_1 (and Δr_2) with the Hammett substituent constant σ_{para} ,^[19] which is an

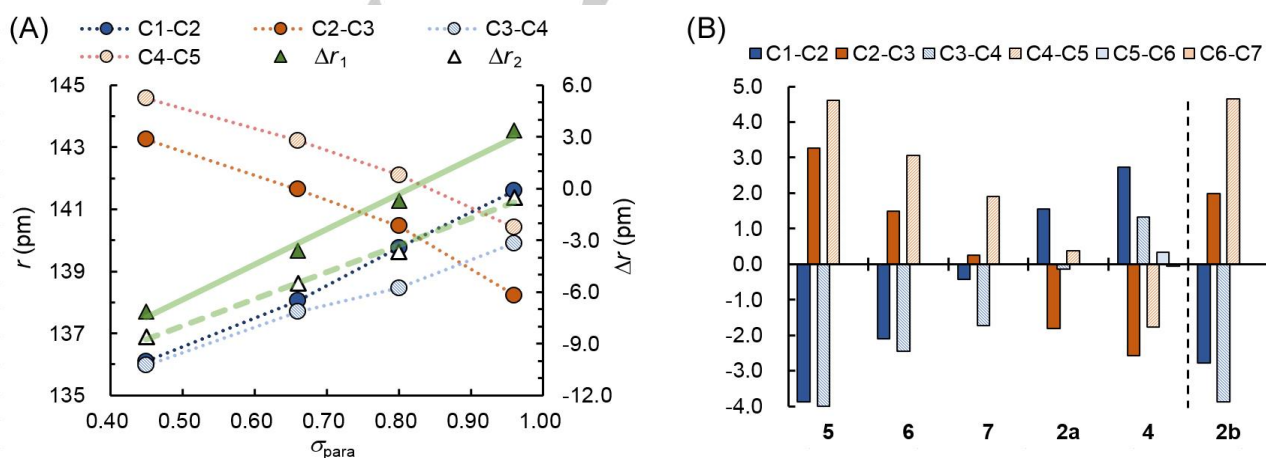


Figure 4. Summary of bond lengths. (A) Correlations of bond lengths with σ_{para} in push-pull dienes **2a**, **5-7**. Linear relationships of Δr_1 (green solid triangles, $y = 20.5x - 16.4$, $R^2 = 0.990$) and of Δr_2 (green empty triangles, $y = 15.6x - 15.8$, $R^2 = 0.993$) with σ_{para} are shown in green lines. (B) Deviations of each bond length from the averaged one in each push-pull polyene **2a**, **4-7** and non-push-pull diene **2b**.

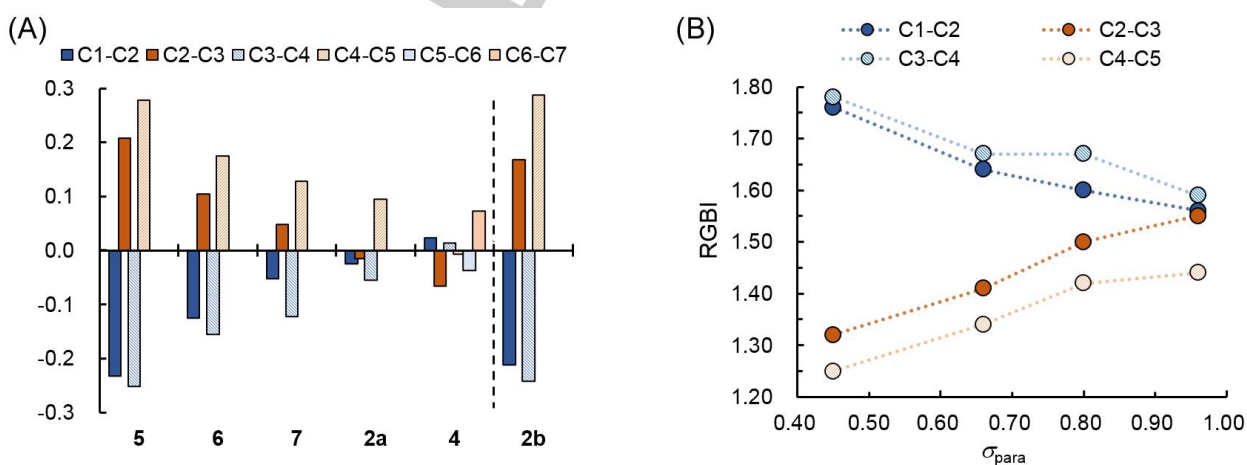
Table 2. Bond indices of push-pull polyenes **6**, **2a**, and **4**, for abbreviations see text

		C1–C2	C2–C3	C3–C4	C4–C5	C5–C6	C6–C7	C _A –N
Diene 6 (EWG = CN)								
RGBI		1.64	1.41	1.67	1.34	–	–	1.39
DI		1.47	1.24	1.53	1.18	–	–	1.02
NLMO/NPA BO		1.52	1.18	1.67	1.13	–	–	1.04
NBO BO	<i>Total</i>	1.64	1.36	1.68	1.29	–	–	1.30
	<i>Cov. / lon.</i>	1.41 / 0.23	1.26 / 0.10	1.58 / 0.10	1.18 / 0.11	–	–	0.87 / 0.43
Diene 2a (EWG = Tf)								
RGBI		1.56	1.55	1.59	1.44	–	–	1.44
DI		1.34	1.35	1.41	1.27	–	–	1.04
NLMO/NPA BO		1.34	1.31	1.54	1.20	–	–	1.07
NBO BO	<i>Total</i>	1.69	1.31	1.60	1.23	–	–	1.60
	<i>Cov. / lon.</i>	1.32 / 0.36	1.23 / 0.08	1.48 / 0.12	1.15 / 0.08	–	–	1.02 / 0.57
Triene 4 (EWG = Tf)								
RGBI		1.51	1.60	1.52	1.54	1.57	1.46	1.46
DI		1.29	1.42	1.33	1.37	1.40	1.29	1.09
NLMO/NPA BO		1.16	1.56	1.28	1.52	1.32	1.39	1.09
NBO BO	<i>Total</i>	1.14	1.66	1.18	1.63	1.24	1.53	1.32
	<i>Cov. / lon.</i>	1.02 / 0.12	1.54 / 0.12	1.15 / 0.03	1.52 / 0.11	1.19 / 0.05	1.36 / 0.17	0.91 / 0.41

Information). The RGBI values for C1–C2 decrease in order of **5**, **6**, and **7**, a trend which is fully consistent with the geometric observation. Figure 5B shows that the RGBIs of triflylated push-pull diene **2a** correlate with σ_{para} if put in line with the values for **5-7**. However, an unambiguous BOA relationship was not observed because deviations between RGBIs for each bond compared to averaged ones are very small. On the other hand, both C1–C2–C3 and C3–C4–C5 moieties in triene **4** exhibit a pronounced *reversed* BOA nature, which is also supported by other bond indices. Note that the C₃ subunits starting from a

carbon atom constructing the benzene ring such as C3–C4–C5 in dienes **2**, **5-7** and C5–C6–C7 in triene **4** are exceptional because they are strongly affected by aromaticity of the ring.

The NBO bond order, which allows to evaluate both covalent and ionic bond contributions, provides a deeper understanding of the bonding system in triene **4**. In the picture of NPA charges (Supporting Information), we can regard the C1 atoms in both **4** and **2a** as anionic centres (**4**, –0.88 e; **2a**, –0.80 e) and the sulfur atoms as doubly charged cationic centres (**4**, +2.07 and +2.06 e; **2a**, +2.05 and +2.08 e), in agreement with our previous

**Figure 5.** (A) Deviations of RGBIs in push-pull polyenes **2a**, **4-7** and non-push-pull diene **2b**. (B) Correlations of RGBI with σ_{para} in push-pull dienes **2a**, **5-7**.

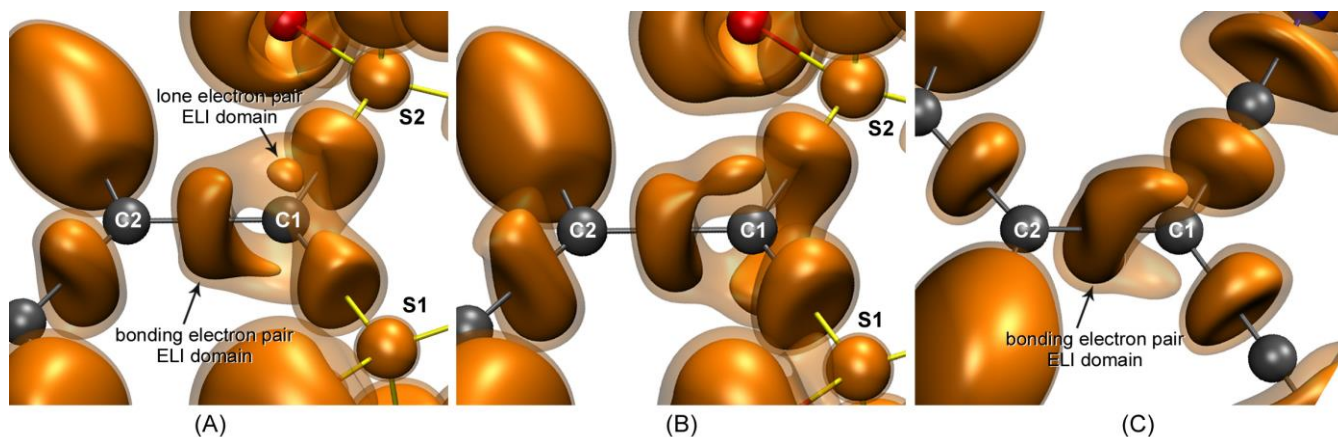


Figure 6. Isosurfaces of XWR-derived ELI for (A) **2a**, (B) **4**, and (C) **6**. Isovalue = 1.30 (transparent), 1.50 (solid).

observation.^[10] Lowering the ionic bond contribution in the C1–C2 bond of **4** (0.12 vs **2a**, 0.36) and higher total and covalent NBO bond orders of the C2–C3 bond in **4** imply an effective delocalisation of a counter positive charge in the more extended π -system of **4** relative to **2a** (Table 2).

The ELI analysis successfully visualises such unique bonding behaviour of push-pull triene **4** as well as diene **2a** (Figures 6A/B). In the C1–C2 bond of **2a**, not only a bonding electron pair ELI domain with a population of 2.866 e for the corresponding bond basin (N_{ELI}) but also a lone electron pair ELI domain with a population of 0.658 e for the corresponding valence basin were computed.^[28] Similar lone electron pair ELI domains were obtained in C1 (1.425 e) and C3 (0.240 e) atoms of **4**. The RJI of **4** shows that the electron density of the lone pair stems to more than 95% from the QTAIM basins of the parent atoms C1 and C3. This confirms the existence of carbon lone pairs that are part of a delocalised system. A much lower N_{ELI} value (2.287 e) for the C1–C2 bonding basin in **4** compared to **2a** (2.866 e) again supports the most pronounced anionic character of the C1 atom in **4**.^[29,30] In contrast, ELI analysis of push-pull dienes bearing other EWGs did not give any lone electron pair ELI basins (Figure 6C). Much larger N_{ELI} values for bonding electron pair ELI basins of the C1–C2 bond in diester **5** (3.533 e), dinitrile **6** (3.440 e), and diketone **7** (2.929 e) fully agree with a prevailing double bond characters.

Conclusion

In this paper, we demonstrated two structural features of push-pull conjugated polyenes. First, we discovered a linear relationship between the electron-withdrawing ability of the substituents and the bond-length alternation. Such clear correlations in bond-length alternating systems have not been reported before. Second, as an extension of this finding, we found that the triflyl group, which shows the strongest electron-withdrawing ability, causes a reversion of the BLA order. Among a series of push-pull polyenes that we investigated, triflyl-based push-pull diene **2a** and triene **4** exhibited a pronounced *reversed* BLA. These examples are clear deviations from the textbook case of bond lengths predicted from neutral Lewis structures. Considering that the degree of BLA in **4** has been diminished in

order of Δr_1 , Δr_2 , and Δr_3 , the significant polarisation in the C1–C2 bond is propagated into the surrounding carbon–carbon bonds in a distance-dependent fashion. Therefore, the present outcome can mostly be attributed to the outstandingly strong electron-withdrawing ability of the end triflyl groups. To the best of our knowledge, such substituent-based reversal of the BLA order has not been reported previously either. In addition, a complementary chemical bonding analysis using X-ray refined wavefunctions provided a reliable view of the carbon–carbon bonds in the present push-pull polyenes. Pronounced anionic characters of C1 atoms in **2a** and **4** are fully consistent with their *reversed* BLA and BOA order. Highly polarised π -conjugated compounds are attractive chemicals as dyes, fluorescence materials, and nonlinear optical materials.^[31] Our results on the substituent-based reversals of BLA and BOA orders would bring about opportunities for a new design of conjugated polyene materials.

Experimental Section

(E)-4-(4,4-Bis((trifluoromethyl)sulfonyl)buta-1,3-dien-1-yl)-N,N-dimethylaniline (2a). To a solution of Tf_2CH_2 (69.1 mg, 0.247 mmol) in *i*-PrOH (1.0 mL), 4-(dimethylamino)cinnamaldehyde (45.3 mg, 0.259 mmol) was added. After being stirred for 2.5 h at room temperature, the resulting mixture was directly evaporated. Thus obtained residue was purified by column chromatography on neutral silica gel (hexane/EtOAc = 2 : 1 to 1 : 2) to give this compound in 99% yield (106.9 mg, 0.244 mmol). The molecular structure was also confirmed by HAR-derived X-ray structure analysis. Dark blue crystals (from EtOAc/hexane); Mp. 198–199 °C; IR (ATR) ν 2920, 2851, 1617, 1523, 1369, 1185, 1119, 819, 729, 677, 609, 579 cm^{-1} ; ^1H NMR (400 MHz, CD_3CN) δ 3.24 (6H, s), 6.88 (2H, d, $J = 8.8$ Hz), 7.50 (1H, t, $J = 13.6$ Hz), 7.51–7.90 (1H, brs), 7.87 (1H, d, $J = 13.6$ Hz), 8.11 (1H, d, $J = 13.6$ Hz); ^{13}C NMR (100 MHz, CD_3CN) δ 41.2, 99.3, 114.4 (br), 114.7, 115.8, 121.1 (q, $J_{\text{CF}} = 326$ Hz), 124.1, 158.3, 161.8, 167.2; ^{19}F NMR (376 Hz, CD_3CN) δ –15.8 (6F, brs); HRMS (ESI-TOF) m/z calcd for $\text{C}_{14}\text{H}_{13}\text{F}_6\text{NNaO}_4\text{S}_2$ [$\text{M}+\text{Na}$] $^+$, 460.0088; found, 460.0081; Anal. Calcd for $\text{C}_{14}\text{H}_{13}\text{F}_6\text{NO}_4\text{S}_2$: C, 38.45; H, 3.00; N, 3.20. Found: C, 38.53; H, 3.13; N, 3.18.

The synthesis and characterisation of all other compounds is described in the Supporting Information.

Complementary bonding analysis. All bonding descriptors for compounds **2a**, **3–7** used in this study were derived from the XWR

wavefunctions at the XC-HF/def2-TZVPP level of theory. Pertinent details are given in the Supporting Information.

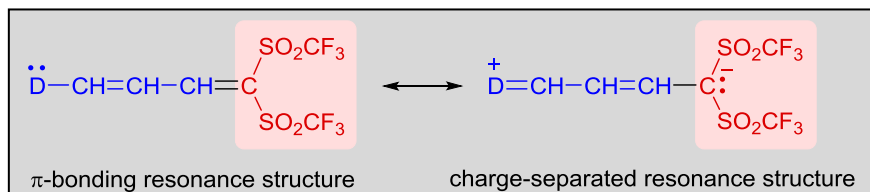
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Keywords: bond alternations • bond lengths • complementary bonding analysis • polyenes • quantum crystallography

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- [27] Here, the total RGBI is used because in each bond, the ionic bond contribution is negligibly small and the total values are close to the covalent RGBI. Full details of RGBI analysis are shown in the Supporting Information.
- [28] In a case of non-push-pull diene **2b**, lone electron pair ELI domain on C1 atom is not obtained and N_{ELI} of C1–C2 bonding basin was notably large (3.553 e). See, Ref. 10.
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Entry for the Table of Contents



Bond lengths are widely utilised as observable structure parameters to estimate the contributions of particular resonance structures. Herein, we demonstrate that outstandingly strong electron-withdrawing groups can reverse the textbook bond-length alternation order in polyene systems. This is a pronounced aberration from the molecular structure predicted by the neutral Lewis resonance form.

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