Proacetylenicity

Push–Pull Buta-1,2,3-trienes: Exceptionally Low Rotational Barriers of Cumulenic C=C Bonds and Proacetylenic Reactivity

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Abstract: A variety of asymmetrically donor–acceptor-substituted [3]cumulenes (buta-1,2,3-trienes) were synthesized by developed procedures. The activation barriers to rotation ΔG^{\neq} were measured by variable temperature NMR spectroscopy and found to be as low as 11.8 kcal mol⁻¹, in the range of the barriers for rotation around sterically hindered single bonds. The central C=C bond of the push–pull-substituted [3]cumulene moiety is shortened down to 1.22 Å as measured by X-ray crystallography, leading to a substantial bond

Introduction

The barrier for rotation ΔG^{\neq} about the cumulenic axis in [*n*]cumulenes decreases with increasing *n*, starting with $\Delta G^{\neq} =$ 65 kcal mol⁻¹ for 1,2-dideuterioethene (n=1),^[1] decreasing to $\Delta G^{\neq} =$ 46.2 kcal mol⁻¹ for 1,3-dimethylallene (n = 2)^[2] and ΔG^{\neq} = 31.8 kcal mol⁻¹ for 1,4-dimethylbutatriene (n=3),^[3] and reaching approximately 20 kcalmol⁻¹ for 1,6-di(*tert*-butyl)-1,6diphenylhexapentaene (n=5).^[4] A large bond-length alternation (BLA)^[5] between the three C=C bonds in the cumulene moiety is strongly correlated to a decrease in the barrier to rotation. While the central C=C bond in non-polarized [3]cumulenes adopts values of about 1.25 Å^[6] the two peripheral C=C bonds are guite elongated compared to typical double bonds, reaching almost 1.40 Å^[7] in push-pull [3]cumulenes and about 1.35 Å^[8,9] in tetraaryl[3]cumulenes. We reported in the early 1990s the synthesis of 1,1,4,4-tetrakis(trialkylsilylethynyl)buta-1,2,3-trienes.^[10] Later, we found that these peralkynylated [3]cu-

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201406583. length alternation (BLA) of up to 0.17 Å. All the experimental results are supported by DFT calculations. Zwitterionic transition states (TS) of bond rotation confirm the postulated proacetylenic character of donor–acceptor [3]cumulenes. Additional support for the proacetylenic character of these chromophores is provided by their reaction with tetracyanoethene (TCNE) in a cycloaddition-retroelectrocyclization (CA– RE) cascade characteristic of donor-polarized acetylenes.

mulenes feature remarkably low barriers for rotation about the cumulene axis, with activation free enthalpies ΔG^{\neq} around 20 kcal mol⁻¹, in the range of the rotational barrier of a peptide amide bond.^[11] Extensive computational studies suggested a biradical transition state for *cis*-*trans* isomerization of asymmetrically substituted 1,1,4,4-tetraalkynyl[3]cumulenes.^[12]

Upon polarization of [3]cumulenes by donors and acceptors at the terminal C atoms, the BLA increases significantly, with the central C=C bond adopting nearly the length of an acetylenic bond, around 1.21 Å.^[7,13] In a preliminary communication,^[14] we showed that the central C=C bond in push-pullsubstituted [3]cumulene 1, with a length of 1.22 Å, indeed features characteristic acetylenic reactivity, in addition to olefinic reactivity.^[15] Similar to donor-polarized alkynes, 1 reacted at room temperature with tetracyanoethene (TCNE) in a formal [2+2] cycloaddition-retroelectrocyclization (CA-RE)^[16] reaction to give the stable zwitterionic tetracyanobuta-1,3-diene 2 as the exclusive product (Figure 1). More recently, we proposed the intermediacy of such zwitterions in the reaction of symmetrically substituted tetraaryl[3]cumulenes with TCNE at higher temperature (90-140°C) in dipolar-aprotic solvents, leading ultimately to 5,11-dihydrotetracenes.[8,17]

We coined the term "proacetylenic" to describe the acetylene-type structure and reactivity of the central C=C bond in [3]cumulenes,^[14] in analogy to the concept of proaromaticity of quinoid chromophores.^[18] According to Chauvin et al., but-3en-1-yne is significantly more "aromatic" than buta-1,2,3triene.^[19] Proacetylenic chromophores such as **1**, similar to their proaromatic counterparts, exhibit very low HOMO–LUMO gaps, as a result of the "aromaticity" gain in the charge-separated excited state.^[14,18] Such low-energy gap materials are of importance in molecular electronics.^[20]

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Figure 1. Cumulene 1 and its conversion with tetracyanoethene (TCNE) to zwitterion 2.^[14]

Here, we provide comprehensive support for the proacetylenic structure and reactivity of donor-acceptor-polarized [3]cumulenes. We report the new, asymmetrically substituted push-pull [3]cumulenes **3a-c** and **4a-d** (Figure 2) and their exceptionally low barriers to rotation about the cumulene axis. Based on theoretical calculations, we propose that the mechanism of rotation about the cumulenic axis involves a chargeseparated transition state (Figure 2). In addition, we demonstrate the proacetylenic reactivity of these donor-acceptorsubstituted [3]cumulenes by reacting them with TCNE in the CA-RE cascade to give new members of an unusual class of stable zwitterions. addition of electron-rich terminal olefins 5a,b to the electronpoor 1,1-dichloroethene derivatives 6a,b,^[22] followed by dehydrohalogenation in a one-pot reaction (Scheme 1). The symmetric olefin 5a was synthesized from Michler's ketone by reaction with methylmagnesium bromide.^[23] The second olefin 5b, with different amino groups, was obtained by addition of lithiated aryl bromide 7 to acetophenone 8 and subsequent elimination of water.

The synthesis of [3]cumulenes 4a-d required the preparation of the new electron-rich diaminoolefins 9a,b. Condensation of *N*-phenylacetamides 10a,b with *N*-methylaniline (11), followed by quenching with sodium perchlorate, afforded the amidinium salts 12a,b, respectively (Scheme 1). Deprotonation of 12a,b with NaOH (20% *w/w* aqueous solution) gave the corresponding 1,1-diaminoethenes 9a,b.^[24] A sequence of substitution and dehydrohalogenation reactions between 9a,band 6a,b yielded the [3]cumulenes 4a-d, respectively. In the preparation of the malononitrile derivatives 4a,c, a stepwise protocol was required since the reaction of 9a,b with 2-(dichloromethylene)malononitrile (6a), even after exhaustive reaction times, gave exclusively the buta-1,3-diene derivatives 13a,b. Dehydrohalogenation was subsequently performed with DABCO to provide [3]cumulenes 4a,c.

X-ray Crystal Structures and Bond-Length Alternation

The structures of [3]cumulenes **3a,b** and **4a–d** were confirmed by single-crystal X-ray diffraction. The crystal structures of **3a**

3a

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Figure 2. New push-pull-substituted [3]cumulenes investigated in this study (top) and postulated transition states for rotation about the cumulenic axis (bottom).

Results and Discussion

Synthesis of Push-Pull [3]Cumulenes

Compounds 3a-c were synthesized in good yields using the previously reported route to polarized [3]cumulenes,^[7, 13, 14, 21] by

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Figure 3. Crystal structures of **3 a** (top) and **4 b** (bottom), arbitrary numbering. *T* = 100 K. Thermal ellipsoids at 50% probability, hydrogen atoms omitted for clarity. White: C; light grey: O; dark grey: N. The lengths of the cumulenic bonds in **3 a** and **4 b** are shown as well as the short distance between the bridged phenyl rings in **4b**. Selected bond lengths [Å]: **3 a**: C4A–N4A 1.355(4), C4B–N4B 1.354(4); **4 b**: C1A–N1A 1.441(2), C1B–N1B 1.443(2). The quinoid character δ r of the anilino rings is calculated from the bond lengths using the following formula: $\delta r = [[(a + b)/2 - c] + [(a' + b')/2 - c']]/2$ (in benzene $\delta r = 0$ Å; in fully quinoid rings, δ r would be around 0.10–0.12 Å). For **3 a**: $\delta r_{A} = 0.041$ Å, $\delta r_{B} = 0.045$ Å, for **4 b**: $\delta r_{A} = -0.004$ Å, $\delta r_{B} = -0.002$ Å.

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Scheme 1. Synthesis of push-pull [3]cumulenes 3a-c and 4a-d. DABCO = 1,4-diazabicyclo[2.2.2]octane, Ts = 4-tol-uenesulfonyl.

stacking geometry (Figure 3). The shortest distance between the two bridged aromatic C atoms is approximately 2.88 Å, which is around 0.6 Å less than reqular π -stacking the distance.[26] For comparison, the two bridged C(sp²) atoms in strained [2.2]paracyclophane are at a distance of 2.751 Å^[27] and in [3.3]paracyclophane of 3.137 Å.^[28] Similar behavior has been reported for N,N'-dimethyl-N,N'-diaryl ureas,^[29] which even form stacked oligomeric chains.^[30] In the case of 4a-d, the syn alignment of the two phenyl rings is probably adopted to assure best possible pushpull conjugation between the amine donors and the nitrile acceptors along the [3]cumulene scaffold. The N atoms indeed are nearly in plane with the cumulene scaffold and the acceptor groups, ensuring efficient linear donor-acceptor π -conjugation. In the anti conformation, the N atoms would be in conjugation with the phenyl rings, which would obviously weaken pushpull conjugation across the cumulene scaffold.

and **4b** are depicted in Figure 3; all other crystal structures are included in Section S3 in the Supporting Information.

The influence of substituents on bond length alternation (BLA)^[5] of the buta-1,2,3-triene moiety is substantial and well documented. The two extremes are symmetric, electronically neutral cumulenes (average BLA = 0.10 Å)^[6] and polarized ones (highest reported BLA = 0.18 Å).^[13] All new [3]cumulenes reported here display significant BLA. Likewise, the strength of electron donor and acceptor have an impact on the BLA of the [3]cumulene inserted between them. Concerning 3a and 3b, anilines are weaker donors than amines, thus the BLA is in general lower than in 4a-d, where the amino donors are installed directly onto the cumulene (Table 1). Surprisingly, there is little difference between the compounds possessing two cyano groups (3b and 4a,c), or one cyano and one methyl ester group (3 a and 4 b,d), the latter of which is a weaker electron acceptor.^[25] The structural data confirm the proacetylenic character of push-pull cumulenes and the significant contribution of the charge-separated mesomeric structure in the ground state.

Unexpectedly, the phenyl rings in cumulenes 4a-d align themselves parallel to the cumulene axis, adopting a close π -

Variable-Temperature NMR and Rotational Barriers

The reduced symmetry of compounds 3a-c and 4b,d enables us to obtain kinetic parameters for [3]cumulene rotation by means of VT ¹H and ¹³C NMR spectroscopy (Table 2). Two moieties were investigated: the *N*-methylamino signal was fol-

Table 1. Bond lengths and bond length alternation (BLA) for cumulenes 3 a,b and 4 a-d . D = electron-donating group; A = electron-accepting group. BLA = $(C1=C2+C3=C4)/2-C2=C3$. Libration effects were tested, and the changes in bond lengths are negligible (see Section S3 in the				
Supporting information). $D_{C1=C2=C3=C4,A}$				
		D	A	
	C1=C2 [Å]	C2=C3 [Å]	C3=C4 [Å]	BLA [Å]
3a	1.375	1.226	1.364	0.144
3 b ^[a]	1.367	1.227	1.364	0.138
4a	1.394	1.216	1.378	0.170
4b	1.392	1.214	1.375	0.170
4c	1.391	1.213	1.379	0.172
4d	1.392	1.217	1.378	0.168
[a] Average values of two symmetry-unrelated molecules.				

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lowed by ¹H NMR (for 3a,c and 4b,d), while the nitrile signal was monitored by ¹³C NMR spectroscopy (for 3b). All studied compounds are in fast equiat 25°C, librium showing a single peak for both rotamers. The coalescence points for all compounds except 4c were met while cooling samples down, and splitting the initial singlet into two singlets of nearly equal intensity could be observed at lower temperatures (Figure 4 and Section S6 in the Supporting Information). For 4c, we did not observe signal splitting, even at -100 °C, possibly due to the time scale and resolution limits of the NMR method.

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Figure 4. VT ¹H NMR spectra (500 MHz) of 3 a in CD_2CI_2 . Peak intensities are normalized for clarity. * NCH₃ peak, evaluated for the determination of the kinetic parameters.

Unlike BLA, the barrier of rotation can be easily compared to other systems, such as ethene,^[1]

allene,^[2] or different cumulenes.^[3,4,9,11] Even though we predicted low rotational barriers for these systems, the values as low as $\Delta G^{\neq} = 11.8 \text{ kcal mol}^{-1}$ for **4b** exceed our expectations. This low activation free enthalpy, which is in the range of the barrier for rotation of a sterically hindered single bond,^[31] shows clearly the extent of the acetylenic character of push-pull substituted [3]cumulenes. Significant charge separation within the molecule results in the lengthening and weakening of the peripheral [3]cumulene bonds up to the length of the aromatic C=C bond in benzene^[32] (Table 1), thereby facilitating the rotation.

We note that the entropic contributions to the activation free enthalpy are very small in the case of 4b,d while they are much larger for 3a-c. Apparently, the stacking geometry of the phenyl groups on the amidine donors in 4b,d remains very much fixed in the transition state, while the two anilino donors in 3a-c undergo much stronger reorganization.

In general, the measured barriers of rotation correlate well with the crystallographic data. The barrier of rotation in **4b**,**d** is significantly smaller (approx. 3 kcalmol⁻¹) than in **3a**,**b**. At the same time, the BLA in **4b**,**d** is significantly enhanced (Table 1). These differences are a result of the insertion of the

Table 2. Kinetic parameters for rotation about the cumulenic axis in[3]cumulenes 3 a-c and 4 b,d.				
	$\Delta H^{ eq}$ [kcal mol $^{-1}$]	$\Delta S^{ eq}$ [cal K ⁻¹ mol ⁻¹]	$\Delta {\sf G}^{ eq}_{_{298\ {\sf K}}}$ [kcal mol $^{-1}$]	
3a	9.6±0.1	-19.8±0.1	15.5±0.1	
3b	4.4 ± 0.2	-35.2 ± 1.0	14.9 ± 0.4	
3c	8.1 ± 0.1	-24.8 ± 0.2	15.4 ± 0.1	
4b	13.3 ± 0.1	5.2±0.2	11.8 ± 0.1	
4d	11.3 ± 0.1	-4.5 ± 0.2	12.6±0.1	

additional benzene rings between the amine donors and the [3]cumulene scaffold in **3 a,b**. The force to maintain the aromatic character of these anilino rings diminishes the charge transfer in **3 a,b**, which in return leads to a higher barrier of rotation.

Electrochemistry and Electronic Absorption Spectroscopy

Electrochemical measurements were carried out in CH_2CI_2 containing 0.1 \bowtie Bu₄NPF₆ in a classical three-electrode cell by cyclic voltammetry (CV) and rotating-disk voltammetry (RDV) (Table 3, for more details see Section S7 in the Supporting Information).

Cumulenes 3a-c give two reduction steps as well as two oxidations. For 3b and 3c, the first reduction is a reversible oneelectron transfer whereas the second step is irreversible at any scan rate. The behavior of 3a differs from the others, as only irreversible electron transfers could be observed. Such behavior may occur due to adsorption phenomena at the electrode. We had previously observed that N,N-diisopropylanilino moieties, present in 3b and 3c, are more stable against irreversible oxidation than N,N-dimethylanilino (DMA) ones, which are the only electron donors in 3a.[33] Cumulenes 4a-d behave in a similar way. The reduction shows a first reversible one-electron step, followed by a second irreversible electron transfer, whereas the one oxidation step occurs irreversibly. In 4a and 4c, the presence of two strongly electron-withdrawing cyano substituents shifts the observed reduction potentials anodically, compared to 4b and 4d, which bear only one cyano group per molecule.

The electron-donating character of the amino groups in 4a-c is clearly stronger than that of the anilino substituents in 3a-c (Table 3). The first reduction potentials of 4a-c are more negative by about 500 mV than those of 3a-c. Likewise, the first

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Table 3. Electrochemical data of cumulenes **3a-c** and **4a-d** observed by cyclic voltammetry (CV) and rotating disk voltammetry (RDV) in CH_2CI_2+ 0.1 $\times nBu_4NPF_6$. All potentials are given versus ferrocene, used as internal standard.

	<i>E</i> ः[а] [V]	${ m CV} \Delta E_{ m p}^{ m [b]}$ [mV]	<i>E</i> _p ^[c] [V]	E _{1/2} [V]	RDV Slope ^(d) [mV]
3a			+0.72 +0.65 -1.38 -1.76 ^[e] -1.93 ^[e]	+0.72 (1 e ⁻) +0.60 (1 e ⁻) -1.37	60 60 100
3 b	+ 0.75	75		(1 e) +0.75	60
	-1.31	75	+0.55 -1.95	(1 e ⁻) +0.55 (1 e ⁻) -1.32	60 100
3c	+ 0.74	60	+0.48	-1.96 +0.76 $(1 e^{-})$	60
	-1.36	70	+0.48 -1.99	(1 e ⁻) +0.46 (1 e ⁻)	70 110
				- 1.38 (1 e ⁻) - 1.99 (1 e ⁻)	
4a	-1.76	145	+0.85	+0.82 (1 e ⁻)	70 100
			-2.21	– 1.76 (1 e [−]) –2.17 (1 e [−])	175
4b	-1.86	90	+0.71	+0.75 (1 e ⁻)	70 75
			-2.31	−1.89 (1 e ⁻) −2.27 (1 e ⁻)	90
4c	-1.90	200	+0.90	+0.85	60 60
4d	-1.96	80	-2.12 +0.76	-2.30 +0.80 (1 e ⁻)	240 70 100
			-2.37	-2.03 (1 e ⁻) -2.30 (1 e ⁻)	120
[a] $E^{\circ} = (E_{pc} + E_{pa})/2$, where E_{pc} and E_{pa} correspond to the cathodic and anodic neak notentials, respectively (b) $\Delta E = E_{pc}$ [c] E_{pc} irrepresentation					

anodic peak potentials, respectively. [b] $\Delta E_p = E_{pa} - E_{pc}$. [c] $E_p =$ irreversible peak potential. [d] Logarithmic analysis of the wave obtained by plotting *E* versus log[*I*/(*I*_{lim}-*I*)]. [e] Small amplitude signals.

oxidation potentials of 4a-d are more positive by about 200 mV compared with 3a-c. Accordingly, 3a-c are both better electron acceptors and better electron donors than 4a-d. The larger HOMO-LUMO gap of 4a-d is a consequence of the more pronounced interaction between the amino group and the acceptor moieties, compared to the interaction of the anilino groups and acceptor moieties in 3a-c. The UV/Vis spectra of the corresponding compounds are in very good agreement with the electrochemical data; the lowest-energy absorption of 3a-c are around 590 nm, whereas the corresponding absorptions for 4a-d appear at distinctly higher energies (ca.

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390 nm, see below). Another remarkable observation are the unusually high $\Delta E_{\rm p}$ values between 80 and 200 mV found for **4a-d**, pointing to a substantial rearrangement of the molecular geometry upon electron transfer (Table 3).

The deep-purple solutions (CH_2CI_2) of **3a**-c show two strong absorption bands in the Vis region and one much weaker one in the UV region. The lowest-energy absorption varies from λ_{max} = 584 nm (2.12 eV) for **3a** to λ_{max} = 594 nm (2.09 eV) for 3b. Cumulenes 4a-d show one high-intensity band in the Vis region at λ_{max} around 390 nm (3.19 eV), along with a weaker one in the UV region. Spectra of 3a and 4b are included as representative examples in Figure 5; all spectra are shown in Section S5 in the Supporting Information. The hypsochromic shift of the longest-wavelength absorption bands of 4a-d relative to **3a-c** is in line with the larger HOMO-LUMO gaps established by cyclic voltammetry. Upon introduction of the benzene spacers between amino donors and the cumulene scaffold in 3a-c, push-pull conjugation is reduced and the energies of HOMO and LUMO resemble more closely those of the individual donor and acceptor moieties. Such π -spacer effects on the HOMO-LUMO gap in push-pull chromophores had previously been fully established.[34]

The charge-transfer (CT) character of the lowest-wavelength absorption for all cumulenes was proven by protonation-reneutralization experiments (Section S5 in the Supporting Information). In acidified solution, the CT band disappeared in all cases, but after re-neutralization recovery of the original spectra took place only for **3b** and **3c**. The high initial strain energy of cumulenes is probably the reason behind the nonreversible protonation reactivity.

Computational Studies

The huge decrease in the rotational barrier from 1,4-dimethylbutatriene ($\Delta G^{\neq} = 31.8 \text{ kcal mol}^{-1}$)^[3] to **4b** ($\Delta G^{\neq} = 11.8 \text{ kcal mol}^{-1}$) clearly demonstrates the pronounced effect of molecular polarization through push–pull conjugation. Computational results at the B3LYP/6-31G(d) level of theory (Gaussian 09)^[35] show that the rotation of push–pull [3]cumulenes occurs, as expected, via perpendicular zwitterionic transition states (Figure 6 and Section S8 in the Supporting Information).

Barriers of rotation for the new [3]cumulenes were computed. Transition- and ground-state Gibbs free energies were obtained by adding the zero-point energy and thermal correction to the calculated electronic energies at 298 K. The calculated values are in good agreement with the experimental ones (Table 4).

The changes in geometry between the calculated ground state (GS) and the transition state (TS) are due to an increase in polarization of the molecule while the rotation occurs. Bond length changes in the cumulene moiety are slightly smaller than the ones obtained for the 1,1,4,4-tetraalkynylbuta-1,2,3-trienes.^[11] Because of the already strong BLA in the ground state, less change is needed to reach the geometry required for rotation. The central bond shrinks by approximately 0.014 Å for series **3a–c** and approximately 0.010 Å for series **4a–d**. The peripheral bonds stretch by approximately 0.042 Å





Figure 5. UV/Vis/NIR absorption spectra of compounds 3 a, 4b, 14 a, and 15 b in CH_2Cl_2 at 298 K, $c = 2 \times 10^{-5}$ m.



Figure 6. Top: Gibbs free energy reaction profile for rotation around the cumulene axis of 3 a. Bottom: electron density from total SCF density of 3 a (isovalue = 0.0004; mapped with electrostatic potential (ESP)). GS = ground state; TS = transition state.

Table 4. Calculated parameters for the rotation of cumulenes 3a-c and			
4 a–d: rotational barriers (ΔG^{\neq}), BLA change (ΔBLA_{GS-TS}), and dipole			
moment change (ΔP_{GS-TS}). GS = ground state; TS = transition state. The			
free enthalpies of activation are given at 298.15 K.			

	ΔG^{\neq} [kcal mol ⁻¹]	ΔBLA_{GS-TS} [Å]	$\Delta P_{\rm GS-TS}$ [D]	
3a	15.6	0.058	9.23	
3b	15.2	0.055	8.64	
3 c ^[a]	15.7	0.056	9.28	
4a	11.4	0.039	5.15	
4b	10.7	0.040	5.15	
4c	10.7	0.038	4.76	
4 d ^[a]	10.6	0.039	5.18	
[a] Average values for <i>E</i> and <i>Z</i> isomers.				

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for series **3a–c** and approximately 0.030 Å for series **4a–d**, with negligible difference between the two different bonds in the molecule (Section S8).

Increase in charge separation during the rotation can be conveniently monitored by both the change in dipole moment and the electrostatic potential along the molecule (shown for 3a in Figure 6; for all other cumulenes, see Section S8). A strong increase in the dipole moment is calculated for all studied [3]cumulenes (Table 4). Such a massive change confirms our hypothesis of a zwitterionic transition state (Figure 2) for the rotation around the cumulene axis. The

electrostatic potential map at the isosurface also supports this. Clear charge accumulation can be seen at both ends of molecule **3a**: positive at the amino groups and negative at the cyano groups (Figure 6).

The electronic transitions for the optimized molecular structures of cumulenes 3a-c and 4a-d were calculated by timedependent density functional theory (TD-DFT; for more details on the computational methods, see Section S8). The lowestenergy transition was underestimated for all cumulenes, compared to the experimental results (in the range of 0.5-0.6 eV), which is a known issue for TD-DFT methods applied to chargetransfer systems.^[36] Nevertheless, particular transitions are well resolved. Two low-energy transitions in cumulene series 3ac are strong HOMO-to-LUMO and (HOMO-1)-to-LUMO transitions, respectively. These can be described as intramolecular charge-transfer (ICT) bands, with electron density displacement from the anilino electron donors to the cyano electron acceptors. The origin of the lowest-energy transition in the cumulene series 4a-d is not as clear. Frontier molecular orbitals show strong displacement along the cumulene, but the tendency is not so apparent as in series 3a-c (see Section S8 in the Supporting Information).

Proacetylenic Reactivity of Push–Pull [3]Cumulenes and Properties of Formed Zwitterionic Species

The above sections have shown that cumulenes 3a-c and 4a-d have remarkable proacetylenic character making them ideal candidates for cycloaddition reactions with electron-poor olefins, such as TCNE.^[14, 16] Here, we describe the observed reactivity and shed some light on the properties of the produced push-pull-type zwitterionic products.

The CA-RE reaction of all [3]cumulenes **3a-c** and **4a-d** with TCNE was immediate, and the zwitterionic species **14a-c** and **15a-d** were isolated in good yields (Scheme 2). In all cases, the products had paramagnetic character, which hindered spectral characterization.^[37] Using EPR spectroscopy to follow

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Scheme 2. Synthesis of zwitterions 14a-c and 15a-d. * Yields are including paramagnetic contaminations.

As previously described,^[14] we observed complexation between the tetraphosphonate cavitand 16 (Figure 8)^[42] and the zwitterions of series 14ac by ¹H and ³¹P NMR in CDCl₃. The formed 1:1 complexes are stabilized by the strong iondipole interaction of the four convergent P=O dipoles with one of the terminal N,N-dimethyliminium ions. This binding mode had been previously confirmed by X-ray analysis for the complex formed by zwitterion 2.^[14] Complexation is indicated by a strong color change, origi-

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the concentration of the paramagnetic species during the reaction and investigate the temperature dependence of the EPR spectra, we found that rather persistent paramagnetic species are formed during the reaction but the zwitterions themselves are not paramagnetic (see Section S9 in the Supporting Information). Consequently, obtaining NMR spectra of zwitterions **14a-c** required several recrystallizations, and in the case of **15a-d**, the paramagnetic species were not separable from the parent compounds, thus X-ray crystallography was the method of choice for structure confirmation (Section S3 in the Supporting Information).

The structures of zwitterions 14a and 15a-c, confirmed by X-ray crystallography, are similar (Figure 7; for all structures, see Section S3). The same mechanism for charge separation holds as has been reported previously for 2.^[14] The charges are permanently separated by the central cross-conjugated dicyanoethenylidene moiety, with large torsion angles between the various chromophoric sub-moieties also contributing to the isolation of charges. The positive charge is located on the amino donor substituents. In 14a, there is high bond length alternation in the aniline rings which exhibit high guinoid character δr , as defined in the caption to Figure 7.^[38] The positive charge is mostly located on the terminal amino centers which possess high iminium ion character as evidenced by the short $N_{sp2}\text{-}C_{sp2}$ bond length of about 1.34 Å. $^{[39]}$ In series 15a-c, the charge is centered on the two nitrogens in an amidinium-type system. Again, such amidinium cation character is supported by the short C_{sp2} -N_{sp2} bond lengths varying between 1.33 and 1.35 Å.^[40] The negative charge in both series is stabilized in form of a flat tris- or tetracyanoallyl anion possessing almost equal C-C bonds of approximately 1.40 Å length within the allyl anion moiety.^[41] All these bonds lengths are in excellent agreement with those found in the CSD for similarly charged species (Section S4 in the Supporting Information). In 15a and 15 b, the aniline rings are no longer aligned as they are in 4ad and one of the rings is parallel with the polycyanated allyl anion. The bulkiness of the isopropyl group in 15c, however, forces the aniline rings to stay π -stacked together as in the parent cumulene 4c (Section S3).

nating from a hypsochromic shift of the ICT band, up to 50 nm. The association strength was determined by titration experiments (see Section S11). ¹H and ³¹P NMR titrations in



Figure 7. Crystal structures of **14a** (top) and **15b** (bottom), arbitrary numbering. *T* = 100 K. Thermal ellipsoids at 50% probability, hydrogen atoms omitted for clarity. White: C; light grey: O; dark grey: N. Selected bond lengths [Å], angles [°], and torsional angles [°]: **14a** C4A–N4A 1.342(2), C4B–N4B 1.340(2), C3–C4 1.395(3), C3–C3D 1.401(3); C4-C3-C3D 126.0(2), C1-C2-C3-C4 – 120.2(2); **15b**: C1A–N1A 1.440(1), C1B–N1B 1.450(1), C3–C4 1.408(2), C3–C3D 1.405(2); C4-C3-C3D 121.1(1), C1-C2-C3-C4 – 35.9(1). The quinoid character δ r of the anilino rings is calculated from the bond lengths in aniline moieties using the following formula: $\delta r = \{[(a + b)/2 - c] + [(a' + b')/2 - c']\}/2$ (in benzene, $\delta r = 0$; in fully quinoid rings, $\delta r = 0.001$ Å, $\delta r_{\rm B} = -0.001$ Å.

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Figure 8. Tetraphosphonate cavitand 16.

CDCl₃ yielded K_a values for the formed 1:1 complexes between 10000 and 40000 m⁻¹ whereas isothermal titration calorimetry (ITC) in nitrobenzene afforded K_a values between 2600 and 6300 m⁻¹ (for details, see Section S11). In contrast, zwitterions **15 a-d** do not bind to the tetraphosphonate cavitand because their amidinium groups do not fit into the cavity.

Electrochemical studies on the zwitterions were performed by CV and RDV in $CH_2Cl_2+0.1 \ M Bu_4NPF_6$ using ferrocene as internal standard (Table S7). Zwitterions 14a-c give two reversible one-electron reduction steps and an irreversible two-electron oxidation step associated on the reverse scan to a small amplitude peak at $+0.55 \ V$ for 14b and $+0.41 \ V$ for 14c(Table S7). During the oxidation of 14a, a deposit was formed on the electrode surface, giving rise, on the reverse scan, to a redissolution peak at $+0.40 \ V$ (Figure S62). Similarly to cumulene 3a, the deposit is probably caused by the DMA substituents which lead to poor solubility compared to the *N,N*-diisopropylanilino derivatives. Two reversible one-electron reductions and only one irreversible oxidation step were observed for zwitterions 15a-d. Oxidation of 15c occurs close to electrolyte discharge and could not be resolved.

Zwitterions **14a–c** are brown in CH_2Cl_2 and feature three broad absorption bands starting in near infrared (λ_{max} approx. 830 nm, 1.49 eV) and extending through the visible region (λ_{max} approx. 460 nm, 2.69 eV) into the UV (320 nm, 3.87 eV; see the spectrum of **14a** in Figure 5). The strong HOMO– LUMO bands arise from ICT, as already reported for **2** (Section S5).^[14] Removal of the phenyl rings from the conjugated π -system in zwitterions **15a–d** leads to a large intensity decrease and hypsochromic shift of the ICT band as compared to **14a–c** (see the spectrum of **15b** in Figure 5). While the intense high-energy band at λ_{max} approximately 380 nm (3.26 eV) stays relatively constant within the series **15a–d**, the HOMO–LUMO gap varies. The most sterically hindered zwitterion **15d** absorbs at λ_{max} =709 nm (1.75 eV) and the less crowded **15a** at λ_{max} =799 nm (1.55 eV, Figure S38).

Zwitterionic Chromophores Followed by EPR and Spectroelectrochemistry

The changes of the electronic structure of the donor-acceptor (D–A) compounds during redox reactions can be conveniently followed by UV/Vis spectroscopy and the corresponding paramagnetic ions characterized by EPR. A detailed in situ EPR/UV/ Vis spectroelectrochemical study of zwitterions **14a** and **15ad** was thus performed to get more insight into their redox chemistry. Compound **14a** was investigated in a more polar solvent, CH₃CN, to avoid the formation of the deposit at the electrode surface during oxidation. One-electron reduction produced paramagnetic **14a**⁻ giving an unresolved singlet in the EPR spectrum with ΔB_{pp} =0.65 mT at g=2.0027(1) (Figure 9a bottom). Changes in the intensity of the EPR signal during the voltammetric scan correlate well with the rise and decay of optical bands at 591 nm, 400 nm, and 270 nm (Figure 9a), particularly well separated from the bands of the parent compound. Additionally, the strong bleaching of the band at 469 nm indicates an almost complete conversion of the zwitterion **14a** during the experiment, and allows us to assign also the overlapping absorptions at 830 nm and 307 nm to the corresponding radical anion **14a**⁻⁻. The intensity of the EPR signal decreases during the potential scan in the region of the second electron transfer, and the EPR silent dianion shows absorptions at 550 nm and 319 nm (Figure 9a). Moreover, formation of dianion **14a**²⁻ results in the complete bleaching of the strong ICT absorption at 830 nm.

No new EPR signals were detected during the anodic oxidation of **14a**. Additionally, the four isosbestic points (at 283, 303, 326, and 371 nm) found in the simultaneously detected UV/Vis spectra confirm a clean conversion of the neutral compound to the diamagnetic dication, and its recovery after the reduction in the CV back scan (Figure 9b). No indication for the formation of other products was found. The electrochemically irreversible oxidation that proceeds as a simultaneous two-electron transfer, followed by a slow heterogeneous electron transfer, is likely responsible for the 0.3 V positive shift of the corresponding reduction peak in the CV back scan. The absorption bands of the dication appear at 452 nm and 275 nm (shoulder at 327 nm), respectively. Similar to the dianion, formation of the dication results in the complete bleaching of the ICT absorption.

The EPR spectra of the paramagnetic monoanions 15⁻⁻ show similar features with a single line at g = 2.0027(1), $\Delta B_{pp} =$ 0.9 mT, and the lineshape indicating an unresolved hyperfine structure (see Sections S9 and S10 in the Supporting Information). The signal characteristics are typical for delocalized organic radicals, but the low resolution of the spectra does not allow a clear-cut description of the one-electron reduced species. The simultaneously detected optical transitions appear around 520 and 300 nm, and in comparison with parent 15, the band positions for 15⁻⁻ seem to be less influenced by substituent effects or steric factors. The same holds for the diamagnetic dianions 15²⁻, showing the most intense absorption around 320 nm. The spectroelectrochemical investigations also show that the irreversible character of the oxidation of 15 can be traced back to chemical follow-up reactions. However, more investigations are needed to clarify details of this reaction.

Conclusions

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We conducted an extensive experimental and theoretical study which confirms the postulated proacetylenic character of the central C=C bond in [3]cumulenes.^[14] Small HOMO–LUMO gaps and high bond length alternation (BLA) are in agreement with theoretical predictions of a strong contribution of charge-separated resonance structures in the ground state. Additionally, we observed exceptionally low rotational barriers around the [3]cumulene axis. The lowest measured value of $\Delta G^{\neq} = 11.8 \text{ kcal mol}^{-1}$ is in the range of the barrier for rotation around a sterically crowded C–C single bond, and 20 kcal mol}^{-1} lower

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Figure 9. a) Top: UV/Vis spectra recorded during the reduction of **14a** on a Pt electrode in CH₃CN+0.1 M Bu₄NClO₄. The thick green, red, and blue lines correspond to spectra of **14a**, **14a**⁻, and **14a**², respectively. The inset shows the corresponding CV (scan rate = 3 mV s⁻¹). Bottom left: EPR spectrum of **14a**⁺ recorded at E = -0.5 V vs. Fc⁺/Fc, ($\Delta B_{pp} = 0.65$ mT, g = 2.0027(1)). Bottom right: dependence of the intensity of the EPR signal of **14a**⁻ (I_{EPR}), ΔA of selected bands ($\Delta A = A - A_{initial}$), and the transferred charge (|q| = | f|dt|) on the potential during the CV (scan direction indicated by arrows). b) Top: UV/Vis spectra recorded during the oxidation of **14a** on a Pt electrode in CH₃CN+0.1 M Bu₄NClO₄. The thick green and magenta lines correspond to the spectra of **14a** and **14a**²⁺, respectively. The inset shows the corresponding CV (scan rate = 3 mV s⁻¹). Bottom: dependence of ΔA on selected bands and the transferred charge (|q| = | f|dt) on the potential during the potential during the CV (scan direction indicated by arrows).

than the barrier measured for 1,4-dimethylbutatriene.^[3] Such rapidly rotating systems could have potential use in molecular motor construction.^[43,44] This facile rotation proceeds most probably through zwitterionic transition states, stabilized by the strong molecular polarization. Comprehensive DFT calculations confirm our experimental findings. In addition, reacting the cumulenes with TCNE in the CA–RE transformation, which is characteristic for donor-polarized acetylenes, corroborates the proacetylenic reactivity. The formed zwitterions were characterized by X-ray analysis and by an in-situ EPR/UV/Vis spectroelectrochemical study. They are truly unusual structures which we also postulated as intermediates in our recently reported new two-step synthesis of tetracenes with a rubrene-like substitution pattern, starting from tetraarylated [3]cumulenes.^[8]

Experimental Section

In the following, the experimental details for synthesis and characterization of zwitterions **14a–c** and **15a–d** are given. IUPAC names of zwitterions are given for structures with charge position defined on a single atom. All other synthetic details and experimental data, X-ray, UV/Vis, ¹H and ¹³C NMR data, electrochemistry, EPR spectroscopy, spectroelectrochemistry, binding studies, and theoretical calculations are given in the Supporting Information.

(2E/Z)-1,1-Dicyano-2-(1-cyano-2-methoxy-2-oxoethylidene)-3-(dicyanomethylidene)-4,4-bis[4-(dimethylamino)phenyl]but-4-

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ylium-1-ide (14a): A solution of 3a (56 mg, 0.15 mmol) and tetracyanoethene (19 mg, 0.15 mmol) in acetonitrile (10 mL) was stirred at 25 °C for 15 min. Evaporation of solvent, flash chromatography (FC) (CH₂Cl₂/MeOH 98:2), and recrystallization (EtOAc/CH₂Cl₂/hexanes 2:1:7) gave 14a (58 mg, 76%) as dark brown crystals with a copper luster. $R_f = 0.18$ (SiO₂; CH₂Cl₂/EtOAc 1:1); m.p. 262 °C (decomp.); ¹H NMR (400 MHz, $C_2D_2CI_4$, 25 °C) $\delta = 3.38$ (s, 12 H; 4 NCH₃), 3.78 (s, 3 H; OCH₃), 6.92 (d, J=9.4 Hz, 4H; 2 H-C(3",5")), 7.54 (d, J=9.4 Hz, 4H; 2 H-C(2",6")); ¹³C NMR (101 MHz, C₂D₂Cl₄, 25 °C) $\delta = 41.26$ (4 NCH₃), 47.22 (C(C=N)₂), 52.31 (OCH₃), 78.37 (C(1')), 111.6 (C(C≡N)(CO₂CH₃)), 112.24(C(C≡N)₂), 114.70 (2 C(3",5")), 120.17 (C≡N), 129.91 (2 C(1")), 140.58 (2 C(2",6")), 156.88 (2 C(4")), 161.49 ppm (C=O); 4 C hidden by the noise; IR (ATR): $\tilde{\nu}$ = 2919 (w), 2875 (w), 2203 (m), 2188 (m), 2171 (m), 1682 (s), 1617 (m), 1570 (s), 1523 (w), 1455 (s), 1349 (s), 1293 (m), 1264 (s), 1189 (m), 1155 (s), 1119 (br. S), 935 (s), 909 (s), 855 (w), 825 (m), 814 (w), 789 (w), 776 (s), 737 (w), 727 (m), 171 (m), 682 (s), 662 (w) 627 (w), 610 cm⁻¹ (w); UV/Vis (CH_2CI_2) : $\lambda_{\rm max}$ (ε) = 819 (26 500), 456 (21 200), 317 nm (26 500 m⁻¹ cm⁻¹); HR-ESI-MS: *m/z* (%): 502.1986 (100, [*M*+H]⁺, calcd for C₂₉H₂₄N₇O₂⁺: 502.1980).

1,1-Dicyano-2,3-bis(dicyanomethylidene)-4-[4-(dimethylamino)-phenyl]-4-{4-[di(propan-2-yl)amino]phenyl}but-4-ylium-1-ide

(14b): A solution of **3b** (32 mg, 0.08 mmol) and tetracyanoethene (10 mg, 0.08 mmol) in acetonitrile (5 mL) was stirred at 25 °C for 15 min. Evaporation of solvent, FC (CH₂Cl₂/MeOH 98:2), and recrystallization (EtOAc/CH₂Cl₂/hexanes 2:1:7) gave **14b** (35 mg, 83%) as dark brown crystals with a copper luster. R_f =0.39 (SiO₂; CH₂Cl₂/ EtOAc 1:1); m.p. 237 °C (decomp.); ¹H NMR (500 MHz, C₂D₂Cl₄, 25 °C) δ =1.51 (d, J=6.8 Hz, 12H; 4 CNCH₃), 3.38 (s, 6H; 2NCH₃), 4.33 (sept, J=6.8 Hz, 2H; 2 NCH), 6.95 (d, J=9.4 Hz, 2H; H-C(3',5')),

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7.13 (d, J=9.6 Hz, 2 H; H-C(3',5')), 7.44 and 7.46 ppm (2 d, J \approx 8.8 Hz, 4H; 2 H-C(3',6')); ¹³C NMR (101 MHz, C₂D₂Cl₄, 25 °C) δ = 20.88 (4 CHCH₃), 41.19 (2 NCH₃), 99.49 (2 C(C=N)₂), 110.73 (C(C=N)₂), 111.52 (C(C≡N)₂), 114.67 (C(3',5'), 114.81 (2 C≡N), 117.64 (2 C(2',6')), 117.82 (2 C=N), 120.17 (C(1')), 139.39 (2 C(2',6')), 156.48 (C(4')), 157.97, 158.21 (C(4')), 165.42 (C=O); 4 C hidden by the noise; IR (ATR): $\tilde{v} = 2969$ (w), 2934 (w), 2187 (s), 1615 (m), 1573 (s), 1530 (m), 1473 (s), 1432 (m), 1372 (s), 1333 (s), 1306 (S), 1196 (s), 1153 (s), 1111 (S), 1010 (w), 934 (m), 913 (s), 825 (m), 795 (w), 778 (w), 748 (w), 736 (m), 702 (w), 681 (s), 653 (w), 629 (w), 610 cm⁻¹ (w); UV/Vis $\lambda_{\rm max}$ (ε) = 835 (30 000), 460 (23800), (CH_2CI_2) : 319 nm (30700 μ⁻¹ cm⁻¹); HR-MALDI-MS: *m/z* (%): 547.2329 (49, [*M*+Na]⁺, calcd for $C_{32}H_{28}N_8Na^+$: 547.2329), 525.2509 (47, $[M+H]^+$, calcd for $C_{32}H_{29}N_8^+$: 525.2510), 524.2431 (100, $[M]^+$, calcd for $C_{32}H_{28}N_8^+$: 524.2431).

(2*E/Z*)-1,1-Dicyano-2-(1-cyano-2-methoxy-2-oxoethylidene)-3-(dicyanomethylidene)-4-[4-(dimethylamino)phenyl]-4-[4-[di(pro-

pan-2-yl)amino]phenyl}but-4-ylium-1-ide (14c): A solution of 3c (86 mg, 0.2 mmol) and tetracyanoethene (26 mg, 0.2 mmol) in acetonitrile (20 mL) was stirred at 25 °C for 15 min. Evaporation of solvent, FC (CH₂Cl₂/MeOH 98:2), and recrystallization (EtOAc/CH₂Cl₂/ hexanes 2:1:7) gave 14c (88 mg, 78%) as dark brown crystals with a copper luster. $R_f = 0.37$ (SiO₂; CH₂Cl₂/EtOAc 1:1); m.p. 268 °C (decomp.); ¹H NMR (500 MHz, $C_2D_2CI_4$, 25 °C) $\delta = 1.49$ (d, J = 6.9 Hz, 12H; 4 CHCH₃), 3.35 (s, 6H; 2 NCH₃), 3.78 (s, 3H; OCH₃), 4.31 (sept, J=6.9 Hz, 2H; 2 NCH), 6.90 (d, J=9.3 Hz, 2H; H-C(3",5")), 7.06 (d, J=9.5 Hz, 2H; H-C(3",5")), 7.61-7.42 ppm (m, 4H; 2 H-C(2",6")); ^{13}C NMR (101 MHz, C_2D_2Cl_4, 25 °C; 1:1 mixture of stereoisomers) $\delta\!=$ 20.81 (2 CHCH₃), 41.03 (2 NCH₃), 50.84 (OCH₃), 52.29 (2 NCH), 78.30 (C(1')), 111.61 (2 C≡N), 112.33 (2 C≡N), 114.22 (C(3",5")), 115.95 (2 C≡N), 117.28 (C(3",5")), 117.72 and 118.27 (C(1")), 129.44 and 130.18, 140.16 (2 C(2",6")), 156.35 (2 C(4")), 158.69 and 160.26, 166.05 and 166.77 ppm (C=O); 3 C hidden by the noise; IR (ATR): $\tilde{v} = 2974$ (w), 2206 (m), 2191 (s), 1678 (s), 1614 (m), 1577 (s), 1524 (m), 1456 (s), 1433 (s), 1382 (s), 1336 (S), 1308 (m), 1272 (s), 1198 (s), 1159 (m), 1114 (s), 1007 (w), 938 (m), 912 (s), 859 (w), 831 (s), 814 (m), 791 (w), 780 (w), 764 (w), 741 (w), 682 (s), 653 (w), 627 (w), 613 cm⁻¹ (w); UV/Vis (CH₂Cl₂): λ_{max} (ε) = 828 (29500), 457 (22700), 317 nm (28400 μ⁻¹ cm⁻¹); HR-MALDI-MS: *m/z* (%): 580.2431 (38, $[M\!+\!Na]^+\!,$ calcd for $C_{33}H_{31}N_7NaO_2^{+}\!\!:$ 580.2431), 558.2612 (100, $[M\!+\!$ H]⁺, calcd for C₃₃H₃₂N₇O₂⁺: 558.2612), 557.2533 (97, [*M*]⁺, calcd for $C_{33}H_{31}N_7O_2^+$: 557.2534).

1,1-Dicyano-2,3-bis(dicyanomethylidene)-4,4-bis[methyl(phenyl)amino]but-4-ylium-1-ide (15a): A solution of 4a (156 mg, 0.5 mmol) and tetracyanoethene (70 mg, 0.55 mmol) in acetonitrile (20 mL) was stirred at 25 °C for 15 min. Evaporation of solvent, FC (CH₂Cl₂/MeOH 98:2), and recrystallization (EtOAc/CH₂Cl₂/hexanes 2:1:7) gave **15a** (198 mg, 90%) as a black solid. $R_f = 0.23$ (SiO₂; cyclohexane/EtOAc 1:1); m.p. 235 °C (decomp.); IR (ATR): $\tilde{\nu} = 3065$ (w), 2988 (w), 2216 (w), 2193 (s), 1594 (m), 1558 (m), 1541 (s), 1471 (s), 1452 (s), 1432 (m), 1406 (m), 1336 (w), 1276 (w), 1239 (w), 1214 (w), 1159 (w), 1147 (w), 1107 (m), 1081 (m), 1057 (m), 1044 (w), 1022 (w), 1000 (m), 968 (w), 914 (w), 820 (w), 788 (w), 767 (s), 756 (s), 714 (w), 693 (s), 667 (w), 652 (w), 631 cm⁻¹ (w); UV/Vis (CH₂Cl₂): λ_{max} (ϵ) = 799 (580), 385 nm (14700 m⁻¹ cm⁻¹); HR-MALDI-MS: m/z(%): 463.1390 (56, $[M + Na]^+$, calcd for $C_{26}H_{16}N_8Na^+$: 463.1390), 441.1571 (62, $[M+H]^+$, calcd for $C_{26}H_{17}N_8^+$: 441.1570), 440.1492 $(100, [M]^+, \text{ calcd for } C_{27}H_{16}N_8^+: 440.1492).$

(2E/Z)-1,1-Dicyano-2-(1-cyano-2-methoxy-2-oxoethylidene)-3-(dicyanomethylidene)-4,4-bis[methyl(phenyl)amino]but-4-ylium-1ide (15b): A solution of 4b (173 mg, 0.5 mmol) and tetracyanoethene (70 mg, 0.55 mmol) in acetonitrile (20 mL) was stirred at 25 °C for 15 min. Evaporation of solvent, FC (CH₂Cl₂/MeOH 98:2), and recrystallization (EtOAc/CH₂Cl₂/hexanes 2:1:7) gave **15b** (221 mg, 93%) as a black solid. R_f =0.34 (SiO₂; cyclohexane/EtOAc 1:1); m.p. 228°C (decomp.); IR (ATR): $\dot{\nu}$ =3071 (w), 2953 (w), 2200 (m), 2185 (s), 1666 (s), 1598 (m), 1590 (m), 1556 (s), 1538 (m), 1490 (m), 1446 (s), 1435 (s), 1405 (s), 1336 (w), 1291 (s), 1249 (w), 1291 (s), 1249 (w), 1213 (w), 1189 (m), 1156 (w), 1126 (s), 1104 (m), 1084 (w), 1058 (w), 1021 (w), 1000 (w), 989 (m), 926 (w), 851 (w), 822 (w), 794 (w), 765 (s), 756 (s), 708 (w), 694 (s), 665 (m), 654 (w), 627 cm⁻¹ (m); UV/Vis (CH₂Cl₂): λ_{max} (ε)=790 (850), 395 nm (2000 m⁻¹ cm⁻¹); HR-ESI-MS: *m/z* (%): 506.1928 (100, [*M*+MeOH+H]⁺, calcd for C₂₈H₂₄N₇O₃⁺: 506.1935), 474.1676 (12, [*M*+H]⁺, calcd for C₂₇H₂₀N₇O₂⁺: 474.1673).

1,1-Dicyano-2,3-bis(dicyanomethylidene)-4-[methyl(phenyl)amino]-4-[phenyl(propan-2-yl)amino]but-4-ylium-1-ide (15c): A solution of 4c (136 mg, 0.4 mmol) and tetracyanoethene (56 mg, 0.44 mmol) in acetonitrile (10 mL) was stirred at 25 °C for 15 min. Evaporation of solvent, FC (CH₂Cl₂/MeOH 98:2), and recrystallization (EtOAc/CH₂Cl₂/hexanes 2:1:7) gave **15c** (180 mg, 96%) as a black solid. $R_f = 0.34$ (SiO₂; cyclohexane/EtOAc 1:1); m.p. 127 °C (decomp.); IR (ATR): $\tilde{\nu} = 2981$ (w), 2193 (s), 1596 (m), 1553 (s), 1465 (s), 1393 (w), 1372 (w), 1291 (w), 1227 (w), 1194 (w), 1174 (w), 1099 (m), 1081 (w), 1025 (w), 1003 (w), 970 (w), 942 (w), 884 (w), 814 (w), 790 (w) 767 (m), 759 (m), 693 (s), 666 (w), 648 (w), 631 cm⁻¹ (w); UV/Vis (CH₂Cl₂): λ_{max} (ε) = 729 (1460), 385 nm (18 200 m⁻¹ cm⁻¹); HR-ESI-MS: m/z (%): 501.2143 (63, $[M + MeOH + H]^+$, calcd for $C_{29}H_{25}N_8O^+$: 501.2145), 474.2033 (100, $[M-CN^- + MeOH]^+$, calcd for $C_{28}H_{24}N_7O^+$: 474.2037), 469.1882 (2, $[M+H]^+$, calcd for $C_{28}H_{21}N_8^+$: 469.1884).

(2E/Z)-1,1-Dicyano-2-(1-cyano-2-methoxy-2-oxoethylidene)-3-(dicyanomethylidene)-4-[methyl(phenyl)amino]-4-[phenyl(propan-2-yl)amino]but-4-ylium-1-ide (15d): A solution of 4d (187 mg, 0.5 mmol) and tetracyanoethene (70 mg, 0.55 mmol) in acetonitrile (20 mL) was stirred at 25 °C for 15 min. Evaporation of solvent, FC (CH₂Cl₂/MeOH 98:2), and recrystallization (EtOAc/CH₂Cl₂/hexanes 2:1:7) gave 15d (223 mg, 89%) as a black solid. $R_f = 0.29$ (SiO₂; cyclohexane/EtOAc 1:1); m.p. 129 °C (decomp.); IR (ATR): $\tilde{\nu} = 2952$ (w), 2190 (s), 1759 (w), 1673 (s), 1595 (m), 1525 (s), 1490 (m), 1525 (s), 1490 (m), 1452 (s), 1436 (s), 1391 (w), 1372 (w), 1301 (m), 1269 (s), 1238 (w), 1192 (m), 1131 (s), 1099 (s), 1081 (w), 1026 (w), 1003 (W), 972 (w), 925 (w), 883 (w), 848 (w), 820 (w), 792 (w), 764 (s), 694 (s), 647 (w), 632 (w), 618 cm $^{-1}$ (w); UV/Vis (CH_2Cl_2): $\lambda_{\rm max}$ ($\varepsilon)\!=\!709$ (1610), 370 nm (16500 m^{-1} cm⁻¹); HR-ESI-MS: *m*/*z* (%): 534.2236 $(100, [M + MeOH + H]^+, calcd for C_{30}H_{28}N_7O_3^+: 534.2248), 502.1979$ $(12, [M+H]^+, calcd for C_{29}H_{24}N_7O_2^+: 502.1986).$

Acknowledgements

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Keywords: [3]cumulenes • bond length alternation • proacetylenic • push-pull chromophores • rotational barrier • zwitterions

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FULL PAPER



A series of push-pull-substituted [3]cumulenes was synthesized. Extensive UV/ Vis, X-ray, VT NMR, and computational studies confirmed their proacetylenic character. The measured rotational barriers of the new cumulenes are in the range of those of sterically crowded single bonds and reach values down to



reactivity of the central C=C double bond was proven by the facile, highyielding cycloaddition-retroelectrocyclization reaction with tetracyanoethene at room temperature yielding stable zwitterions.

Proacetylenicity

P. Gawel, Y.-L. Wu, A. D. Finke, N. Trapp, M. Zalibera, C. Boudon, J.-P. Gisselbrecht, W. B. Schweizer, G. Gescheidt,* F. Diederich*



Push-Pull Buta-1,2,3-trienes: **Exceptionally Low Rotational Barriers** of Cumulenic C=C Bonds and **Proacetylenic Reactivity**