

Peralkynylated Buta-1,2,3-Trienes: Exceptionally Low Rotational Barriers of Cumulenenic C=C Bonds in the Range of Those of Peptide C–N Bonds

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Dedicated to Prof. Julius Rebek, Jr. on the occasion of his 60th birthday

Abstract: A variety of 1,1,4,4-tetraalkynylbutatrienes and 1,4-dialkynylbutatrienes was synthesized by dimerization of the corresponding gem-dibromoolefins. Both ¹H and ¹³C NMR spectroscopy indicated that the di- and tetraalkynylated butatrienes are formed as a mixture of *cis* and *trans* isomers. Variable temperature NMR studies evidenced a facile *cis–trans* isomerization, thus preventing the separation of these isomers by gravity or high-performance liquid chromatography (HPLC). For

1,1,4,4-tetraalkynylbutatrienes, the activation barrier $\Delta G^\ddagger$ was measured by magnetization transfer to be around 20 kcal mol^{−1}, in the range of the barrier for internal rotation about a peptide bond. Unlike the tetraalkynylated [3]cumulenes, 1,4-dialkynylbutatrienes are more difficult to isomerize and

could, in one case, be obtained isomerically pure. Based on experimental data, the rotational barrier $\Delta G^\ddagger$ for 1,4-dialkynylbutatrienes is estimated to be around 25 kcal mol^{−1}. The hypothesis of a stabilizing effect of the four alkynyl substituents on the proposed but-2-yne-1,4-diyl singlet diradical transition state of this *cis–trans* isomerization is further supported by a computational study.

Keywords: alkynes • cumulenes • density functional calculations • isomerization • magnetization transfer

Introduction

The activation energy for the thermal *cis–trans* isomerization of 1,2-dideuteroethene has been determined as 65 kcal mol^{−1}.^[1] Doering et al. showed that the rotational barrier is considerably lowered in conjugated polyenes. Thus, the activation enthalpy ($\Delta H^\ddagger$ [kcal mol^{−1}]) for thermal *cis–trans* isomerization across the central double bond in a series of semirigid conjugated all-*trans* polyenes decreases from hexa-1,3,5-triene (38.9), to deca-1,3,5,7,9-pentaene (31.9), to tetradeca-1,3,5,7,9,11,13-heptaene (27.8), and to octadeca-1,3,5,7,9,11,13,15,17-nonaene (24.5).^[2,3] This was

rationalized in terms of an increasing conjugative stabilization of the proposed 90°-twisted, singlet diradical-like transition state. Extrapolation to an infinite number of conjugated double bonds gave an activation enthalpy of 18 kcal mol^{−1}.^[3c] Concerning cumulenes,^[4] the rotational barriers ($\Delta G^\ddagger$ [kcal mol^{−1}]) for 1,3-dimethylallene (46.2),^[5] 1,4-dimethylbutatriene (31.8),^[6] and 1,6-di(*tert*-butyl)-1,6-diphenylhexapentaene (20.0)^[7a] have been measured, revealing strongly facilitated bond rotation with increasing cumulenenic length.^[7b] Focusing on butatrienes, the large bond length alteration evidenced by X-ray analysis, represents another remarkable structural parameter. With a length of 1.22–1.25 Å, the central double bond, is much shorter than the terminal ones, measuring around 1.35 Å.^[8,9] An interesting property resulting from this structural peculiarity is the facile, thermally induced, 1,4-free-radical polymerization of butatrienes.^[10]

In our efforts to develop new versatile building blocks for acetylenic scaffolding in one, two, or three dimensions,^[11] we became interested in polyalkynylated [*n*]cumulenes. While several 1,3-alkynylallenes have recently been prepared,^[12] symmetrically substituted 1,1,4,4-tetrakis[(trialkylsilyl)ethynyl]butatrienes are the only known polyalkynylated [3]cumulenes.^[8b] Here, we report the synthesis of a series of variously functionalized 1,1,4,4-tetraethynylbutatrienes and give a preliminary account of their interesting optoelectronic prop-

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erties. In particular, we demonstrate their surprisingly facile thermal *cis-trans* isomerization, featuring rotational barriers $\Delta G^\ddagger$ in the range of those observed for the internal rotation about C–N bonds in amides^[13] and peptides.^[14] Our theoretical study suggests that the exceptionally low rotational barrier results in part from the large stabilization imparted to a but-2-yne-1,4-diyl singlet diradical transition state by the four alkynyl substituents. Stabilization of the ground state by the alkynyl groups also plays a role in the observed geometry and the magnitude of the observed barrier.

Results and Discussion

Synthesis: The preparation^[15] of the 1,1,4,4-tetraalkynylbutatrienes **1a–d** and the 1,4-dialkynylbutatrienes **2a–d** was accomplished by dimerization of the corresponding gem-dibromoolefins **3a–d** and **4a–d**, respectively (Scheme 1).^[8b] The gem-dibromoolefins were obtained in 20–58% yield by addition of the appropriate lithium acetylide to either (*i*Pr)₃Si-protected propynal ($\rightarrow$ **3a–d**) or paraformaldehyde ($\rightarrow$ **4a–d**), oxidation of the resulting propargyl alcohols with MnO₂, and dibromoolefination.^[16] The dimerization to the butatrienes was first attempted by metallation with Zn, followed by addition of a catalytic amount of CuBr. This method, which proved successful for the preparation of fluorinated butatrienes,^[17] gave no product in the present case. Alternatively, treatment of the dibromoolefins with one equivalent of *n*BuLi in Et₂O at –110°C followed by one equivalent of [CuI·PBu₃] at –85°C afforded the alkynylated butatrienes in modest to excel-

lent yields.^[18] The intensely colored aryl- and ferrocenyl-substituted tetraethynylbutatrienes **1a–d** are remarkably stable and can be stored for months in the solid state at –30°C. On the other hand, 1,4-dialkynylbutatrienes, in particular (*i*Pr)₃Si-protected **2d**, exhibit only limited stability; this may actually have prevented the isolation of product from the dimerization of **4a** and **4c**.

Both ¹H and ¹³C NMR spectra clearly showed that the di- and tetraalkynylated butatrienes were formed as mixtures of *cis* and *trans* isomers (in a ratio close to 1:1.5, without configurational assignment).

Electronic absorption spectroscopy: First investigations of the optical properties of these mixtures yielded promising results. The UV-visible spectrum (CH₂Cl₂) of the purple donor-substituted **1b** (Figure 1) is dominated by a strong, broad, longest wavelength absorption band at $\lambda_{\text{max}} = 573$ nm ($\epsilon = 40\,500$ L mol^{–1} cm^{–1}) and features an end-absorption around 650 nm (1.84 eV). Upon acidification with *p*-toluene-sulfonic acid, the purple solution turns yellow, while the intense absorption at 573 nm disappears, the most intense ab-

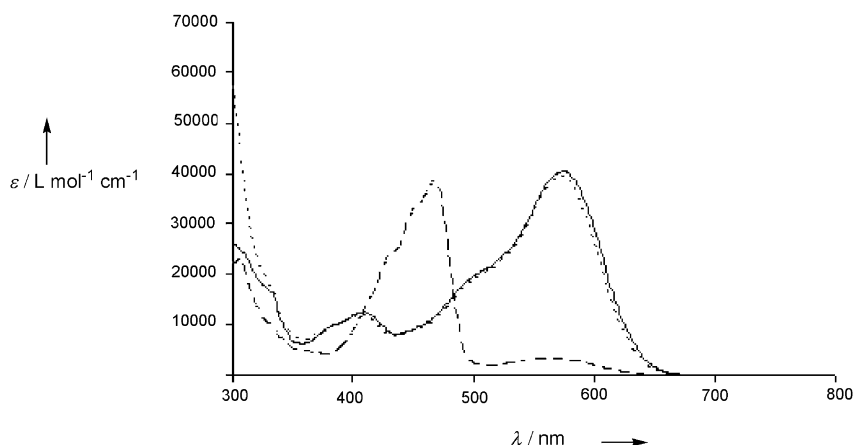
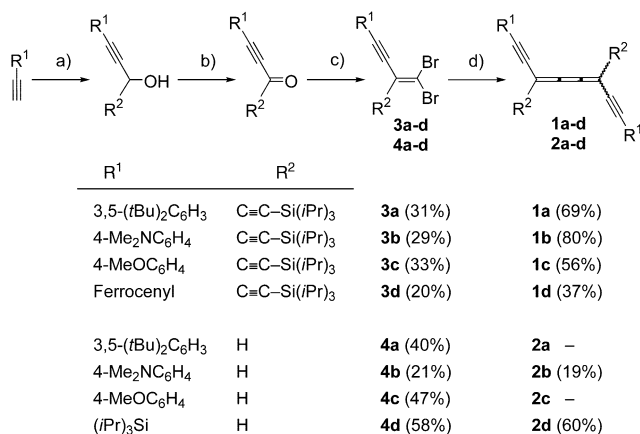


Figure 1. Electronic absorption spectra of **1b** in pure CH₂Cl₂ (—), after addition of *p*-toluene-4-sulfonic acid (---), and after neutralization with Et₃N (----).



Scheme 1. Synthesis of tetra- and dialkynylated butatrienes **1a–d** and **2a–d**. a) *n*-BuLi, THF, –20°C, then (*i*Pr)₃SiC≡C–CHO or paraformaldehyde; b) MnO₂, Et₂O, 20°C; c) CBr₄, PPh₃, Zn (except for **3a** and **3b**), CH₂Cl₂ or benzene (for **3a** and **3b**), 20°C; yields over three steps; d) *n*BuLi, Et₂O, –110°C, then [CuI·PBu₃], –85→20°C.

sorption band being shifted to 468 nm (2.56 eV). Neutralization with triethylamine regenerates the original spectrum. Such a behavior allows us to assign the strong longest wavelength absorption band at $\lambda_{\text{max}} = 573$ nm as a charge-transfer band, resulting from efficient intramolecular charge-transfer interactions between the electron-donating anilino groups and the electron-accepting all-carbon core. A comparison with the similarly substituted tetraethynylethene ($\lambda_{\text{max}} = 459$ nm; $\Delta\lambda_{\text{max}} = 114$ nm, $\Delta E = 0.53$ eV) demonstrates that the two additional C(sp) atoms strongly increase the electron-acceptor strength of the [3]cumulene core.

The *cis-trans* isomerization: Based on the available data for butatrienes,^[6,15] we expected barriers to rotation high enough to allow isolation and characterization of the pure isomers at ambient temperature. However, exhaustive attempts to separate the *cis* and *trans* isomers of 1,1,4,4-tetraalkynylbutatrienes **1a–d** by gravity or high-performance

liquid chromatography (HPLC) all failed. Therefore, we eventually had to consider the possibility that *cis*–*trans* isomerization would occur rapidly under ambient conditions, thereby preventing the isolation of isomerically pure products. Variable-temperature (VT) ^1H NMR studies (between 25 °C and 100 °C) were undertaken as shown in Figure 2 for the bisferrocenyl derivative **1d**.

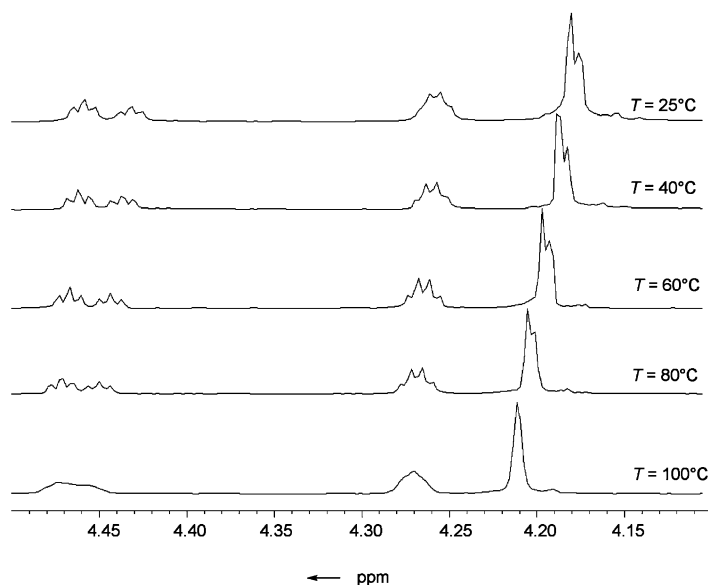


Figure 2. VT ^1H NMR spectra of **1d** in $(\text{CDCl}_2)_2$.

The ^1H NMR spectrum in $(\text{CDCl}_2)_2$ at 25 °C features two triplets at 4.46 and 4.43 ppm, one for each isomer and assignable to two protons of the $\eta^5\text{-C}_5\text{H}_4$ rings, one broad signal at 4.25 ppm corresponding to the other protons of the $\eta^5\text{-C}_5\text{H}_4$ rings of both isomers, and two singlets at 4.18 and 4.17 ppm, each for the five $\eta^5\text{-C}_5\text{H}_5$ protons of one isomer. Upon heating, all resonances move downfield, while, more interestingly, the characteristic signals of the two isomers broadened and partially merged at 100 °C. Similar VT NMR spectral behavior was observed for the other tetraalkynyl derivatives **1a**–**c**. Since coalescence would require heating to temperatures well above 120 °C at which the compounds start to decompose, the determination of the activation parameters for the thermal *cis*–*trans* isomerization by line shape analysis was not further pursued. Rather, these data were obtained by magnetization transfer^[19] after selective inversion of the signal of one isomer (for a depiction of the spectral evolution, see the Supporting Information). The temperature range investigated is the maximum window as determined by the need to have significant transfer within the delay time and on the other hand not too much longitudinal relaxation of the signal. The results are gathered in Table 1 and evidence a surprisingly low rotational barrier $\Delta G^\ddagger$ of 20.3 and 20.1 kcal mol^{−1} at 298 K for the tetraalkynyl derivatives **1a** and **1d**, respectively (for the Eyring plots, see Supporting Information). These values for rotation around a C=C double bond are in the range of those for rotation about peptide bonds! Magnetization transfer experiments

Table 1. Activation parameters for the *cis*–*trans* isomerization of tetraalkynylbutatrienes **1a** and **1d**.

1a ^[a]		1d ^[b]	
<i>T</i> [K]	<i>k</i> ₁ [s ^{−1}]	<i>T</i> [K]	<i>k</i> ₁ [s ^{−1}]
323.3	0.0798 ± 0.0035	323.7	0.104 ± 0.021
333.5	0.203 ± 0.005	333.3	0.282 ± 0.016
350.9	0.823 ± 0.01	343.8	0.525 ± 0.090
361.9	1.624 ± 0.1	351.4	0.924 ± 0.13
<i>K</i>	0.87 ± 0.05		0.68 ± 0.0044
$\Delta H^\ddagger$ [c]	17.5 ± 0.5		16.6 ± 0.8
$\Delta S^\ddagger$ [d]	−9.4 ± 2		−11.7 ± 3
$\Delta G^\ddagger$ (298 K) [e]	20.3 ± 0.8		20.1 ± 1.2

[a] R = 3,5-*(t*Bu)₂C₆H₃, [b] R = (C₅H₅)Fe(C₅H₄). [c] In kcal mol^{−1}. [d] In cal K^{−1} mol^{−1}. [e] In kcal mol^{−1}.

for **1b** and **1c** could not be performed, since it was impossible to selectively excite a “doublet” (*J* = 9 Hz) for the aromatic protons of one isomer without affecting the other one.

Unlike the tetraethynylated [3]cumulenes, 1,4-dialkynylbutatrienes are more difficult to isomerize. Indeed, VT ^1H NMR (CDCl_2)₂ did not show any broadening for compound **2b** up to 100 °C (Supporting Information). Moreover for compound **2d** isomer separation by chromatography (SiO₂, hexane) was successful and *trans*-**2d** was isolated in pure form in 13 % yield.^[20] However, prolonged heating of pure *trans*-**2d** in toluene restored the mixture of *cis* and *trans* isomers (Supporting Information). We conclude that the rotational barrier $\Delta G^\ddagger$ for 1,4-dialkynylbutatrienes such as **2d** is around 25 kcal mol^{−1}. A complete kinetic study to accurately determine the activation parameters was not possible, because of the chemical instability of the two isomers.

Computational study: The comparison between the rotational barriers $\Delta G^\ddagger$ for 1,4-dimethylbutatriene (31.8 kcal mol^{−1}),^[6] 1,4-dialkynylbutatriene **2d** ($\approx$ 25 kcal mol^{−1}), and **1a/1d** ($\approx$ 20.2 kcal mol^{−1}) clearly demonstrates the dramatic stabilizing effect of the alkynyl substituents on the transition state of the isomerization process. Computational results at the unrestricted B3LYP/6-31G(d) level of theory calculated with Gaussian 98,^[21] show that the rotation of ethynyl-, methyl-, and ethenyl-substituted butatriene, as well as the parent butatriene,^[10c] proceeds via perpendicular singlet diradical transition states (Scheme 2).

The barrier to rotation and the ground state geometry are both influenced by introduction of radical stabilizing groups. The effect of substitution can be clearly illustrated by geometric analysis of the ground and transition states (Figure 3).

The ground-state α bond lengths (Scheme 2) of the derivatives are shortened relative to butatriene, while the β bond length is elongated. This effect is a function of the radical stabilizing ability of the substituent on the ground-state diradicaloid resonance form. The ground-state γ bond length

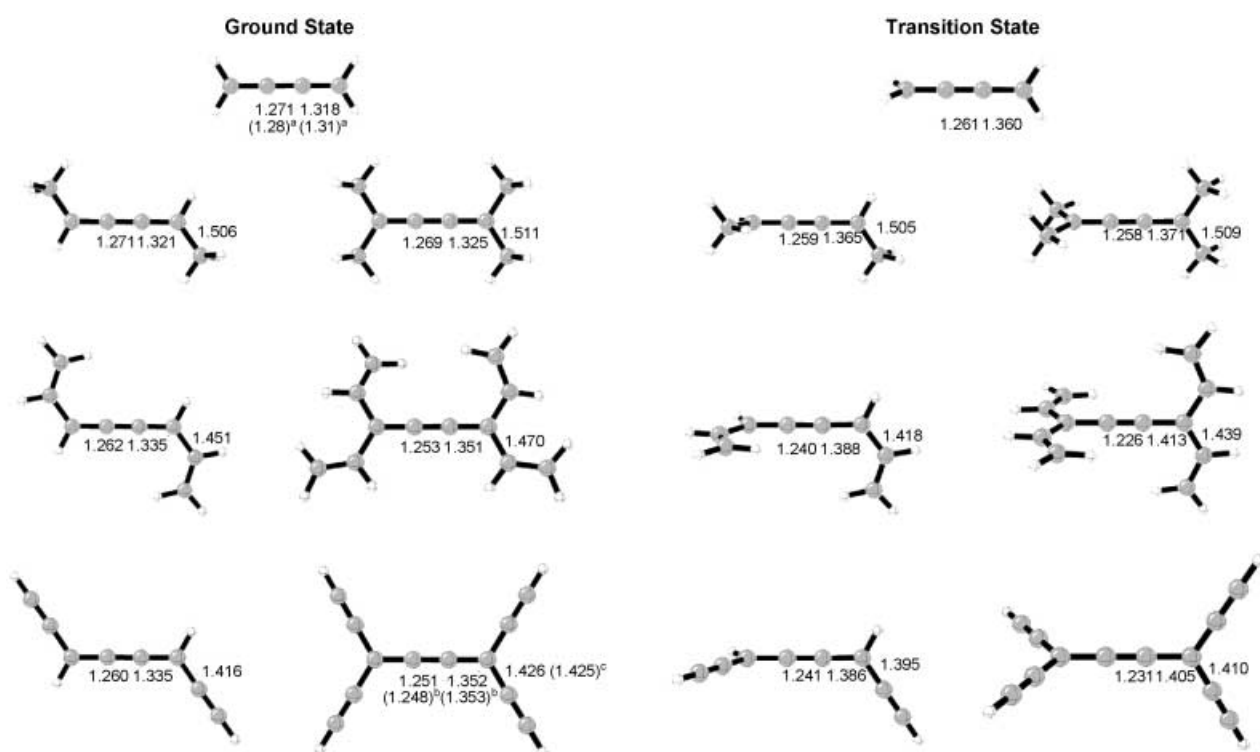
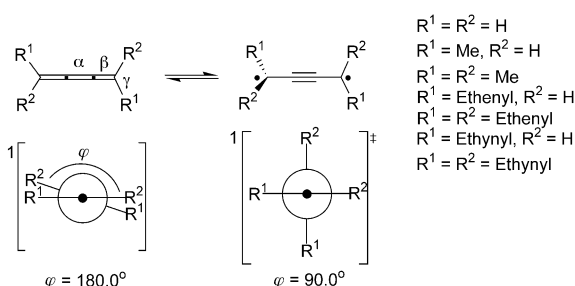


Figure 3. Ground- (left) and transition-state (right) geometries for butatriene, *trans*-1,4-dimethylbutatriene, tetramethylbutatriene, *trans*-1,4-diethynylbutatriene, tetraethynylbutatriene, and tetraethynylbutatriene. Unrestricted B3LYP6-31G(d) computed bond lengths α , β , and γ are given along with experimental values in parentheses. a) See reference [22] for details. b) From the crystal structure analysis of the $(\text{Me}_3\text{Si})_4$ derivative in reference [8b]. c) Averaged bond lengths, see reference [8b].



Scheme 2. Bond assignments, α , β , and γ , and singlet diradical transition-state torsional geometries for unsubstituted and methyl-, ethenyl-, and ethynyl-substituted butatriene derivatives.

tends to decrease in length as this ability increases. The predicted order of radical stabilizing ability is ethenyl > ethynyl > methyl. The ethenyl and ethynyl groups are comparably stabilizing, although both are considerably more stabilizing than methyl.^[23] With tetramethylbutatriene, methyl substitution has a minimal geometric effect on the α bond (1.271 to 1.269 Å), but a more pronounced effect on the β bond (1.318 to 1.325 Å). Both ethynyl and ethenylation result in large geometrical changes. The α bond in tetraethynylbutatriene is shorter than this bond length in butatriene by 0.02 Å, and the β bond length is longer by 0.034 Å. The tetraethenyl derivative experiences a nearly identical effect on the geometry of the butatriene moiety as that of tetraethynyl derivative. In all cases the 1,4-disubstituted butatriene experiences smaller changes upon substitution than the corre-

sponding tetrasubstituted derivative. The γ bonds for the tetra-substituted derivatives tend to be longer than in the corresponding disubstituted butatriene. In the transition state a formal, doubly propargylic, diradical exists; these geometric effects are expected to be enhanced. For example, butatriene experiences a decrease in the α bond length of 0.01 Å and an increase in the β bond length of 0.043 Å, while tetraethynylbutatriene has double the affect in the α bond (0.02 Å) and an increase in β of 0.053 Å, a full 0.01 Å more than the increase in butatriene. In the transition state, the α bond in tetraethynylbutatriene is shortened by 0.027 Å, and the β bond length is elongated by 0.062 Å. This represents the largest geometric change in going from the ground to transition state as expected from the larger radical stabilizing ability of this substituent.

Barriers to rotation for butatriene, *trans*-1,4-dimethylbutatriene, tetramethylbutatriene, *trans*-1,4-diethynylbutatriene, tetraethynylbutatriene, *trans*-1,4-diethynylbutatriene, and tetraethynylbutatriene were computed. Transition-state free energies and enthalpies were calculated by adding the zero-point energy and thermal correction to the calculated electronic energies (Table 2).

Comparison of the calculated barrier for tetraethynylbutatriene to the experimental for **1a** shows good agreement for the enthalpy of activation (16.0 vs 17.3 kcal mol⁻¹). The calculated enthalpy of activation for dimethylbutatriene is also in good agreement with experiment (29.0 vs 31.2 kcal mol⁻¹).^[6] The free energy of activation, in both cases, deviates to a greater degree. The 25 kcal mol⁻¹ estimate for the

Table 2. Unrestricted B3LYP6-31G(D) calculated rotational-energy barriers [kcal mol⁻¹] for butatriene derivatives. The enthalpies and free energies of activation are given at 298 K. Singlet–triplet vertical transition energy gaps [$\Delta H_{\text{ST}}^{\text{VERT}}$] are given for both the singlet ground and transition state geometries.

Compound	Calculated $\Delta H^{\ddagger}(\Delta G^{\ddagger})$	$\Delta H_{\text{ST}}^{\text{VERT}}$
butatriene	0.0	64.2
butatriene TS	28.5(28.1)	2.2
butatriene TS	29.3(28.9) ^[a]	
<i>trans</i> -1,4-dimethylbutatriene	0.0	62.8
<i>trans</i> -1,4-dimethylbutatriene TS	29.0(28.3)	2.1
tetramethylbutatriene	0.0	61.2
tetramethylbutatriene TS	29.4(28.7)	1.9
<i>trans</i> -1,4-diethynylbutatriene	0.0	42.7
<i>trans</i> -1,4-diethynylbutatriene TS	21.2(21.2)	1.4
<i>trans</i> -1,4-diethenylbutatriene	0.0	41.0
<i>trans</i> -1,4-diethenylbutatriene TS	20.1(20.8)	1.3
tetraethenylbutatriene	0.0	28.9
tetraethenylbutatriene TS	9.4(11.4)	0.5
tetraethynylbutatriene	0.0	31.0
tetraethynylbutatriene TS	16.0(16.8)	0.8

[a] B3LYP6-311+G(2df,p).

free energy of activation of 1,4-diethynylbutatriene is supported by the computed value of 21.2 kcal mol⁻¹. Interestingly, tetramethylation increases the barrier to rotation by about 1 kcal mol⁻¹, although methyl groups should stabilize the diradical transition state, thereby lowering the barrier to rotation. This effect can be explained by the corresponding ground-state stabilization of the cumulenic center imparted by these same methyl groups. Ethynyl substituents also stabilize the ground state, but the stabilization of the diradical transition state is much larger resulting in a net decrease of the transition state energy. The same argument can be made for the ethenyl derivatives, which were found to have significantly stabilized transition-state energies relative to their ethynyl 1,4-disubstituted and tetrasubstituted counterparts. The tetraethenyl derivative, with a low barrier of only $\Delta H^{\ddagger}=9.4$ kcal mol⁻¹, and the 1,4-disubstituted compound ($\Delta H^{\ddagger}=20.1$ kcal mol⁻¹) are predicted to undergo rapid isomerization and/or rotation at ambient temperatures. Interestingly, the conformation of the ground state for the tetraethenyl derivative is in the C_{2v} point group, whereas the transition state geometry (D_{2d} point group) corresponds to the rotation of a C_{2h} symmetric conformer.

Vertical triplet–singlet energy gaps were also calculated (Table 2). A pure diradical, in which the spatial overlap of the SOMOs is zero, orthogonal in the present case, will have a triplet–singlet gap of zero. The energy of the triplet in the ground-state geometry is dramatically lowered by both ethenyl and ethynyl substituents; however, in all cases the energy gap is nonetheless large. In the transition-state geometry the triplet–singlet gap is small, with the singlet state also of lower energy, and approaches zero as the radical stabilization increases.

Conclusion

In summary, we have observed an unexpectedly facile *cis*–*trans* isomerization of novel di- and tetraalkynylbutatrienes, proceeding most probably through singlet diradical transition states that benefit from a dramatic stabilization by the alkynyl substituents. With four alkynyl substituents, the barrier for *cis*–*trans* isomerization in [3]cumulenes is lowered to $\Delta G^{\ddagger}$ around 20 kcal mol⁻¹, thereby resembling the rotational barrier for the peptide bond.

Experimental Section^[16]

General: All reactions were carried out under an inert atmosphere (of argon or nitrogen) by applying a positive pressure. Chemicals were purchased from commercial suppliers and used as received.

Thin-layer chromatography (TLC) was conducted on alumina sheets pre-coated with 0.25 mm Macherey-Nagel silica gel, with fluorescent indicator. Column chromatography was carried out with SiO₂ 60 (particle size 0.04–0.063 mm, 230–400 mesh) from Fluka and distilled technical solvents.

Melting points (m.p) were measured in open capillaries with a Büchi 540 apparatus and are uncorrected.

Infrared-red (IR) spectra were recorded on a Perkin–Elmer FT16000 spectrometer. Selected absorption bands are reported in wavenumbers (cm⁻¹) and their relative intensity described as vs (very strong), s (strong), m (medium), w (weak) or vw (very weak).

300 MHz ¹H and 75 MHz ¹³C NMR spectra were recorded on Varian Gemini 300 spectrometer. Chemical shifts are indicated in ppm downfield from tetramethylsilane using the solvent's peak as internal reference ($\delta_{\text{H}}=7.25$ ppm, $\delta_{\text{C}}=77.2$ ppm).

Elemental analyses were performed by the Mikroelementaranalytisches Laboratorium at ETH Höggerberg.

General procedure for butatriene synthesis

Synthesis of 1,8-bis(3,5-di-*tert*-butylphenyl)-3,6-bis[(triisopropylsilyl)ethynyl]octa-3,4,5-ene-1,7-diyne (1a): A solution of *n*BuLi in hexane (0.8 mmol, 0.53 mL) was added to a solution of **3a** (0.461 g, 0.8 mmol) in Et₂O (7 mL) at –110°C. After stirring for 1 h at –100°C, a solution of [CuI·PBu₃] (0.314 g, 0.8 mol) in Et₂O (7 mL) was added, and the resulting red solution was stirred for 1 h at –85°C. After warming to 20°C within 5 h, stirring was continued for 14 h. The mixture was filtered through SiO₂, and the solvent was removed under reduced pressure affording an orange solid, which was purified by chromatography (SiO₂; hexane/CH₂Cl₂ 9:1) to provide **1a** (235 mg, 69%) as a mixture of *cis* and *trans* conformers in a 39:61 ratio (¹H NMR, without configurational assignment). *R*_f=0.16 (hexane); m.p. 122°C (decomp); ¹H NMR (300 MHz, CDCl₃) for the major isomer: δ =1.15 (m, 42H; SiCH(CH₃)₃), 1.33 (s, 18H; CH₃), 7.38 (d, *J*=2 Hz, 4H; CHAr), 7.43 ppm (t, *J*=2 Hz, 2H; CHAr); for the minor isomer: δ =1.16 (m, 42H; SiCH(CH₃)₃), 1.33 (s, 18H; CH₃), 7.34 (d, *J*=2 Hz, 4H; CHAr), 7.43 ppm (t, *J*=2 Hz, 2H; CHAr); ¹³C NMR (75 MHz, CDCl₃): δ =151.2 and 151.0 (CAr), 149.1 and 149.0 (C=C=C), 126.5 and 126.4 (CHAr), 124.0 (CHAr), 121.6 and 121.5 (CAr), 104.8 and 104.7 (C≡), 100.4 and 100.0 (C≡), 98.4 and 98.2 (C≡), 88.0 (≡C), 87.6 (≡C), 35.0 (C(CH₃)₃), 31.5 (CH₃), 18.8 and 18.7 (CH₃), 11.7 and 11.6 ppm (CH); IR (CCl₄): $\tilde{\nu}$ =2964 (vs), 2866 (s), 2187 (m), 1866 (s), 1589 (m), 1539 (w), 1463 (m), 1427 (w), 1394 (w), 1364 (m), 1248 (w), 1184 (w), 1158 (w), 1072 (vw), 904 (w), 878 (m), 833 (w), 812 cm⁻¹ (vs); UV/Vis (CH₂Cl₂): λ (ϵ)=481 (41 500), 456 (35 500), 443 nm (30 600 L mol⁻¹ cm⁻¹); MALDI-MS (matrix DCTB): *m/z*: 837 [*M*⁺], 794 [*M*⁺–iPr]; HR-MALDI: *m/z* calcd for C₃₈H₈₄Si₂ [*M*⁺]: 836.6112; found: 836.6117 (100) [*M*⁺].

Magnetization transfer measurements: The exchange rates were determined by the selective inversion variant of the Forsén–Hoffman technique^[19a] by using the pulse sequence of PFGSE-NOE^[19b–c] and iSNOB^[19d] selective inversion pulses.

Temperatures (± 0.1 K) were measured with an internal Pt-100 resistance thermometer inserted into the probehead instead of the NMR tube before and after each measurement.

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