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Palladium-Catalyzed Dimerization of Conjugated Diynes: Synthesis of (*E*)-1,2-Divinyldiethynylethenes Having Donor and Acceptor Chromophores at the Terminus of Alkyne

Nirmal K. Pahadi, Draxel H. Camacho, Itaru Nakamura, and Yoshinori Yamamoto*

Department of Chemistry, Graduate School of Science, Tohoku University, Sendai 980-8578, Japan

yoshi@mail.tains.tohoku.ac.jp

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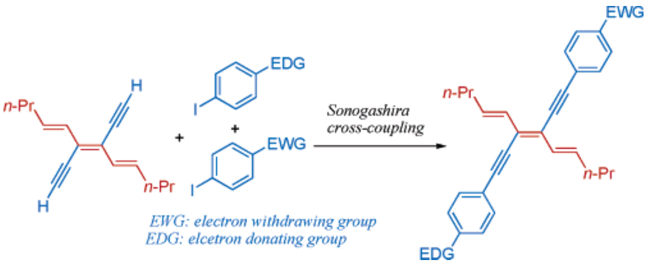

(*E*)-1,2-Divinyldiethynylethenes (DVDEEs) having donor and acceptor chromophores at the terminals of alkyne unit **7′** were synthesized by the palladium/HOAc-catalyzed dimerization of the conjugated diynes **8** bearing an Si group at the terminus of alkyne (R^1 position), followed by desilylation and subsequent Sonogashira reaction of the resulting terminal alkyne **10** with aryl iodides.

Introduction

The synthesis of novel chromophores, which may be useful for quadratic nonlinear optical (NLO) materials, has received much attention due to their further application in optoelectronics and all-optical data processing technology. Therefore, considerable effort has been devoted by synthetic chemists since past decades to synthesize thienylene,[1a] phenylene,[2] and other arylene oligomers in a selective and efficient manner.[1d,2] In acetylenic scaffolding,[3] derivatives of tetraethynylethene (**1**, TEE, 3,4-diethynylhex-3-ene-1,5-diyne) and (*E*)-1,2-diethynylethene (**2**, DEE, (*E*)-hex-3-ene-1,5-diyne) containing the repeated unit of a cross-conjugated framework have provided a unique class of π-conjugated building blocks (Scheme 1).[4] Their planarity, one- and two-dimensionally conjugated frameworks, inherent synthetic flexibility, potential ease of processing, and the possibility of tailoring characteristic properties to accomplish a desired function make them promising candidates for manifold applications in materials sciences.[5] In this area, a number of organic compounds have been studied as possible NLO materials[6] because of their large hyperpolarizability and inherent advantage over conventional inorganic crystals in some respects.[7] It is well-known that organic compounds having donor (D) and acceptor (A) moieties at both ends which are connected via a π-conju-

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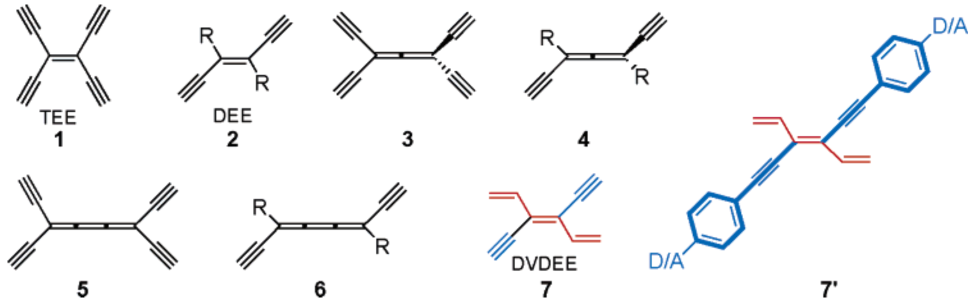
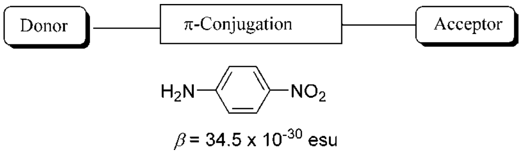
10.1021/jo052262v CCC: $33.50

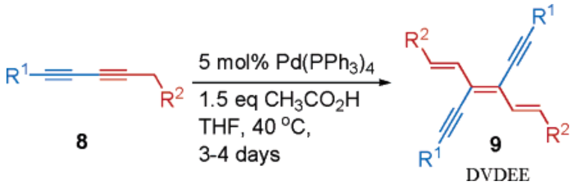
SCHEME 1. Carbon-Rich Building Blocks for Acetylenic Scaffolding



SCHEME 2



gated linker exhibit high hyperpolarizability in general.[7] Until now, most efforts to obtain better hyperpolarizabilities have been directed toward finding both the right combination of D and A and the right length of the conjugated bridge between the donor (D) and acceptor (A) (for example, 4-nitroaniline; Scheme 2).[7] Nowadays, the progress in acetylenic-based molecular construction is greatly urged by the advent of powerful novel metal-catalyzed acetylenic homo- and cross-coupling protocols and has caused an increasing interest from both academic and industrial research laboratories. Owing to those methodologies, the expansion of the central olefinic fragment of TEE and DEE leading to the allenes **3** and **4**[8] and butatrienes **5** and **6**[9] (Scheme 1) has also been explored. However, to the best of our knowledge, there have been no synthetic reports and structural studies of a potentially viable module, containing a *trans*-divinyldiethynyl moiety around the central olefinic fragment, for acetylenic scaffolding. During the studies on the transition-metal-catalyzed C−C bond formation reactions, we previously found a new method for the one-pot synthesis of the compounds containing the core module of (*E*)-1,2-divinyldiethynylethene **7** (Scheme 1), which we defined as DVDEE.[10] The conjugated diynes **8** underwent facile dimerization to give **9** in moderate to good yields upon treatment with 5 mol % $Pd(PPh_3)_4$ and 1.5 equiv of acetic acid in THF at 40 °C for 3−4 days (eq 1). It was thought that, if appropriate donor and acceptor groups were attached at the R^1 or R^2 position of **9**, such π-electron systems might work as potentially useful candidates for NLO materials. This idea was further supported by the crystal structure of the DVDEE core module, which was flat and satisfied the planarity criteria for efficient conjugation in NLO materials. Herein, we report[10] the further extension of the palladium-catalyzed dimerization of diynes (eq 1) to the synthesis of various terminally functionalized donor (D) and acceptor (A) substituted chromophores and their β_0 values for evaluating them as NLO materials.



(1)

Results and Discussion

To install D and A groups at the terminus (R^1 position) of the alkyne unit, a silyl-protected diyne was dimerized first. Second, the silyl protection was removed, and third, the resulting terminal alkyne was treated with aryl iodides under the Sonogashira conditions.[11] The palladium/HOAc-catalyzed dimerization of R_3Si-substituted diynes **8** was carried out under the standard conditions, giving **9** in good to allowable yields (Scheme 3, Table 1). As reported previously,[10] the trimethylsilyl-substituted (TMS) diynes **8a** and **8b** underwent the dimerization with a longer reaction time to give **9a** and **9b**, respectively, in moderate yields (Table 1, entries 1 and 2). To improve the chemical yields, we carried out many attempts,[12] but we failed to increase the yield and decrease the reaction time. However, the diynes **8c** and **8d**, having triethylsilyl (TES) and triisopropylsilyl (TIPS) protecting groups at the alkyne terminus, underwent smooth dimerization to give the corresponding products **9c** and **9d**, respectively, in good yields (entries 3 and 4).

The silyl group of the DVDEE **9c** was cleanly removed by treating with KOH/MeOH systems[12] at 40 °C to give the deprotected DVDEE **10** in 71% yield (Scheme 3). However,

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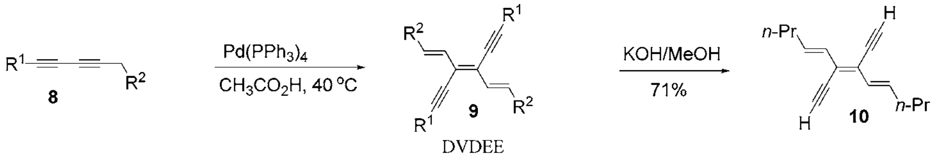
[11] For reviews, see: (a) Campbell, I. B. In *The Sonogashira Cu-Pd-Catalyzed Alkyne Coupling Reaction. Organocopper Reagents*; Taylor, R. J. K., Ed.; IRL Press: Oxford, U.K., 1994; pp 217−235. (b) Sonogashira, K.; Takahashi, S. *Yuki Gosei Kagaku Kyokaishi* **1993**, *51*, 1053. (c) Sonogashira, K. In *Comprehensive Organic Synthesis*; Trost, B. M., Ed.; Pergamon: Oxford, 1991; Vol. 3, pp 521−549.

[12] See the Supporting Information for details.

SCHEME 3



8a: R^1 = Me_3Si, R^2 = *n-Pr*
8b: R^1 = Me_3Si, R^2 = Cyclopentyl
8c: R^1 = Et_3Si, R^2 = *n-Pr*
8d: R^1 =$(i\text{-}Pr)_3Si$, R^2 = *n*-Pr

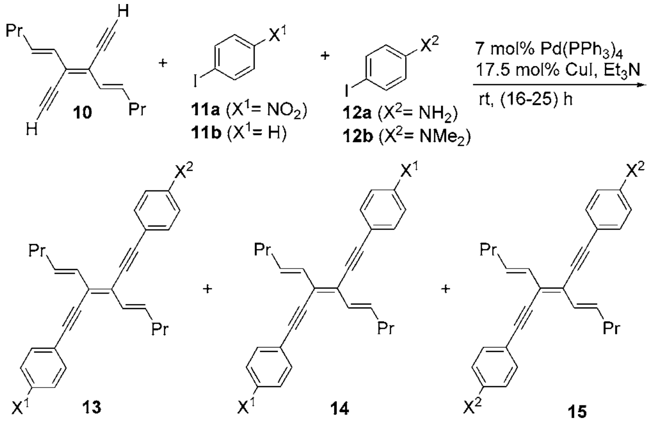
9a: R^1 = Me_3Si, R^2 = *n-Pr*
9b: R^1 = Me_3Si, R^2 = Cyclopentyl
9c: R^1 = Et_3Si, R^2 = *n-Pr*
9d: R^1 = $(i\text{-}Pr)_3Si$, R^2 = *n*-Pr

TABLE 1. Palladium-Catalyzed Dimerization of Conjugated Diynes 8[a]

entry	diynes 8	R^1	R^2	time/day	products 9	yields %[b]
1	**8a**	Me_3Si	*n*-Propyl	4	**9a**	40
2	**8b**	Me_3Si	cyclopentyl	4	**9b**	41
3	**8c**	Et_3Si	*n*-Propyl	2	**9c**	70
4	**8d**	$(i\text{-}Pr)_3Si$	*n*-Propyl	2	**9d**	75

[a] All reactions were carried out in a microreactor with **8** (1.0 mmol) in the presence of 5 mol % $Pd(PPh_3)_4$ and 1.5 equiv of acetic acid in THF at 40 °C for 2−4 days, unless otherwise indicated. The reaction was monitored by GC. [b] Isolated yields through column chromatography.

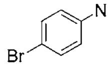
TABLE 2. Palladium-Catalyzed Cross-Coupling Reaction of the Diyne (10) with Aryl Iodides[a]



13a: X^1 = NO_2, X^2 = NH_2
13b: X^1 = NO_2, X^2 = NMe_2
13c: X^1 = H, X^2 = NH_2
13d: X^1 = NO_2, X^2 = H

14a: X^1 = NO_2

15a: X^2 = NH_2
15c: X^2 = NMe_2

Entry	11	12	Yields%[b] 13	14	15
1	**11a** (X^1= NO_2)	**12a** (X^2 = NH_2)	40 (**13a**)	25 (**14a**)	24 (**15a**)
2		**12a** (X^2 = NH_2)	45 (**13a**)	20 (**14a**)	24 (**15a**)
3	**11a** (X^1= NO_2)	**12b** (X^2 = NMe_2)	38 (**13b**)	40 (**14a**)	-
4	**11b** (X^1 = H)	**12a** (X^2 = NH_2)	60 (**13c**)	-	5 (**15a**)
5	**11a** (X^1= NO_2)	**11b**	40 (**13d**)	21 (**14a**)	-

[a] The reaction of **10** (0.5 mmol) with **11** (0.9 equiv) and **12** (3.0 equiv) was carried out in the presence of 7 mol % $Pd(PPh_3)_4$ and 17.5 mol % CuI in triethylamine at room temperature. [b] Isolated yields.

the other DVDEEs having trimethylsilyl (TMS) and triisopropylsilyl (TIPS) groups gave comparatively lower yields upon deprotection.[12] Finally, the Sonogashira reaction of the deprotected species **10** with iodobenzenes **11a** and **12**, bearing an electron-withdrawing (EWG) and an electron-donating (EDG) group at the para position, respectively, was carried out. The results are summarized in Table 2.

The reaction of **10** with *p*-iodonitrobenzene **11a** and *p*-iodoaniline **12a** gave a mixture of three different products, **13a**, **14a**, and **15a** (entry 1). The selective formation of the desired product **13a** was not achieved even after variation of the reaction parameters.[12] The use of *p*-bromonitrobenzene instead of **11a** (entry 2) gave a slightly better yield of the product **13a**. In any case, the formation of the side products **14a** and **15a** was unavoidable. This is quite in the nature of things. An interesting observation was that *p*-iodonitrobenzene **11a** exhibited higher reactivity than *p*-iodoaniline **12a** in the Sonogashira coupling. Accordingly, we used excess amounts of **12a**, in comparison with **10** and **11a**, to obtain a higher yield of **13a.** The reaction of **10** with *p*-iodonitrobenzene **11a** and *p*-iodo-*N*,*N*-dimethylaniline **12b** gave the desired product **13b** in a lower yield (entry 3) along with the undesired product **14a**. It is noteworthy that **15c** ($X^2 = NMe_2$) was not obtained at all. When we carried out the reaction with iodobenzene **11b** and *p*-iodoanilline **12a** (entry 4), **13c** was obtained with higher selectivity and only small amounts of **15a** were obtained as a byproduct. The reaction with *p*-iodonitrobenzene **11a** and iodobenzene **11b** gave a mixture of two different products, **13d** and **14a**, in moderate yields (entry 5).

Electronic Absorption Spectra and β_0 Values of DVDEEs Bearing Donor and Acceptor Groups. The UV−vis spectra of DVDEEs and their derivatives bearing donor and acceptor groups at the terminus of alkynes provide information about their electronic structures which is useful and important when we think about nonlinear optical (NLO) properties of conjugated π-systems.[15] Longest-wavelength absorption bands of DVDEEs and their functionalized derivatives were measured in $CHCl_3$ (Table 3). The longest-wavelength absorption bands (λ_{max} [nm], ϵ [M^{-1} cm^{-1}]) of the two different DVDEEs having silyl groups were as follows: **9a** (343, 6150) and **9c** (302, 7100). The λ_{max} of **9b** (λ_{max} = 347 nm)[13] appeared at the region similar to that of **9a**. It is clear that the substituent at the R^2 position of **9** (cyclopentyl vs *n*-propyl) does not exert a significant influence on the λ_{max} value of DVDEEs. However, it is noteworthy that the λ_{max} of the TES-substituted **9c** appeared at the region significantly shorter than that of the TMS-substituted **9a**. The most interesting electronic properties presumably arise from the extended one-dimensional conjugation present in the planar functionalized DVDEEs. To gain further insight into the influence of those novel chromophores on the electronic absorption wavelength and molar absorptivity, UV−vis spectra

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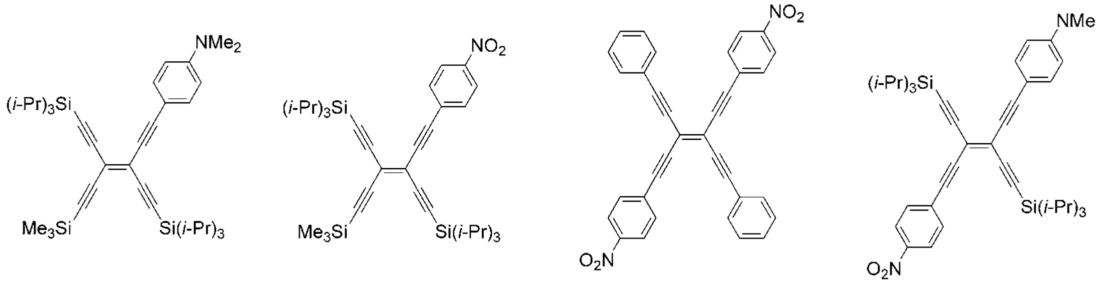
(13) Camacho, D. H. Ph.D. Dissertation book.

(14) The intrinsic hyperpolarizability value, β_0, was calculated using the MOPAC94 PM3 method.

(15) A similar kind of explanation was also made by another researcher. For an example, see: *Helv. Chim. Acta* **1996**, *79,* 2249 and references therein.

SCHEME 4



16
λ_{max} = 433, ε =29300,
β_0 = 86 x 10^{-30} esu

17
λ_{max} = 382, ε =26500,
β_0 = 36 x 10^{-30} esu

18
λ_{max} = 427, ε =29900,
β_0 = not known

19
λ_{max} = 468, ε =31200,
β_0 = 168 x 10^{-30} esu

TABLE 3. Maxima of the Longest-Wavelength Absorptions (λ_{max}, nm) and Molar Extinction Coefficients (ϵ, M^{-1} cm^{-1}) of the Functionalized DVDEE Derivatives[a]

entry	compound	λ_{max}/nm ($\epsilon/10^5$ M^{-1} cm^{-1})	β_0 ($\times 10^{-30}$ esu)[b]
1	**13a**	412 (19 872)	41
2	**13b**	420 (29 016)	47
3	**13c**	376 (19 033)	8.6
4	**13d**	386 (22 424)	21
5	**14a**	414 (22 538)	0.2
6	**15a**	377 (24 009)	2.8

[a] All absorption spectra were recorded in chloroform at ambient temperature. [b] The intrinsic hyperpolarizability value β_0 was calculated using the MOPAC94 PM3 method.[7,14]

of the functionalized DVDEEs were compared. In the absence of a significant contribution from cross conjugation, the major absorption of functionalized DVDEE derivatives may arise from the longest linear conjugated framework, the ene−yne segment[16] shown in bold in Scheme 1 (compound of type **7′**). Diederich et al. reported that incorporation of a donor group in the TEE system leads to a greater enhancement of the NLO activity, such as the β_0 value, than incorporation of an acceptor group (see Scheme 4, **16** vs **17**).[6b,17] Accordingly, we expected that the introduction of a donor group ($-NR_2$) at the alkyne terminus in our DVDEE system might increase the β_0 value. To our surprise, **13d**, having an NO_2 group (acceptor), exhibited a higher β_0 value than that of **13c**, bearing an NH_2 group (donor): **13d**, $\lambda_{max} = 386$ nm, $\epsilon = 22\,424$, and $\beta_0 = 21 \times 10^{-30}$ esu; and **13c**, $\lambda_{max} = 376$ nm, $\epsilon = 19\,033$, and $\beta_0 = 8.6 \times 10^{-30}$ esu. The longest-wavelength absorption band (λ_{max}) of **13d** was bathochromically shifted only by 10 nm, but there was a significant difference in the molar extinction (ϵ). On the other hand, **13a** and **13b**, in which the EWG group (NO_2) and the EDG group (NH_2 or NMe_2, respectively) were attached at the X^1 and X^2 positions, exhibited higher β_0 values and higher λ_{max} values: **13a**, $\beta_0 = 41 \times 10^{-30}$ esu, $\lambda_{max} = 412$ nm; and **13b**, $\beta_0 = 47 \times 10^{-30}$ esu, $\lambda_{max} = 420$ nm (Table 3, entries 1 and 2).[18] As expected, **14a**, in which the EWG was attached at both ends of the para position, and **15a**, in which the EDG was substituted at both ends of the para position, exhibited lower β_0 values (entries 5 and 6); it is interesting that their β_0 values are even lower than those of **13c** and **13d**.

It is interesting to compare the β_0 values of the DVDEE derivatives with those of similar types of arylated tetraethynylethenes (TEEs)[15] **16**−**19** (Scheme 4). The functionalized DVDEE derivatives **13a** and **13b** possess significantly lower β_0 values than **16** but have β_0 values a bit higher than **17**.

The compound **19** bearing the EWG and EDG groups at both ends of the para positions exhibited a very high β_0 value ($\beta_0 = 168 \times 10^{-30}$ esu). It is not clear at this stage whether the difference between the β_0 values of **13a,b** and the β_0 value of **19** is due to the presence of an $Si(i\text{-}Pr)_3$ group or due to the presence of the triple bond in the case of **19** (instead of the double bond of **13a,b**).

In conclusion, we synthesized the functionalized DVDEE derivatives via a Sonogashira cross-coupling reaction, measured the UV−vis spectra of some of those compounds, and obtained β_0 values for **13a**−**d**, **14a**, and **15a**. The β_0 values of the DVDEE derivatives were in general lower than those of TEEs. However, the λ_{max} values of DVDEEs are lower than those of TEEs, and this is an advantageous point of the newly synthesized DVDEEs because higher λ_{max} values approaching 532 nm are not desirable for NLO materials.[19]

Experimental Section

General Procedure for the Dimerization of Diynes. The preparation of **9a** is representative. To an argon flushed mixture of dry THF and $Pd(PPh_3)_4$ (0.05 mmol, 57.8 mg) was added the diyne **8a** (1.0 mmol, 19.0 mg) and acetic acid (1.5 equiv) in a microreactor, and the mixture was stirred at 40 °C for 3−4 days. The reaction is not sensitive to air, and opening the reaction vessel to allow air actually increases the reaction rate. The start of the reaction is indicated by a darkening of the reaction mixture from a previously clear yellow solution. After the completion of the reaction, which was monitored by GC, the mixture was then filtered through a short silica column using ethyl acetate as an eluent. Separation by silica column chromatography (hexane as an eluent) afforded the dimerized product **9a** in 40% yield (0.4 mmol, 142.4 mg).

Supporting Information Available: Experimental details, the synthetic method for the starting materials, characterization data, and ^{1}H NMR spectra of newly synthesized compounds. This material is available free of charge via the Internet at http://pubs.acs.org

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[16] R. R. Tykwinski et al. have mentioned that the major absorption of the periphenylated *iso*-polydiacetylene (*iso*-PDA) compound arises from the ene−yne−ene segments. For example, see: Zhao, Y.; Slepkov, A. D.; Akoto, C. O.; McDonald, R.; Hegmann, F. A.; Tykwinski, R. R. *Chem.*−*Eur. J.* **2005**, *11*, 321−329.

[17] Diederich, F.; Luca, G. *Top. Curr. Chem.* **1999**, *201*, 43.

[18] It is well-known that the elongation of the alkyl chains in *N,N*-dialkylanilines can enhance their electron-donating ability. For example, see: *Helv. Chim. Acta* **2004**, *87*, 1132 and reference therein.

[19] If the UV−vis absorptions of NLO materials overlap with (or are extended to the region of) the double frequency value, 532 nm (2 ω), of the wavelength of an irradiated laser (1064 nm, 1 ω), it means that the materials will be decomposed by the newly generated short-wavelength laser.