

The Synthesis, Photophysical Characterization, and X-Ray Structure Analysis of Two Polymorphs of 4,4'-Diacetylstilbene

by Cameron Pye^a), Frank R. Fronczek^b), and Ralph Isovitsch^{*a})

^a) Department of Chemistry, Whittier College, Whittier CA 90608, USA
(phone: +1-562-907-4200 ext. 4499; e-mail: risovits@whittier.edu)

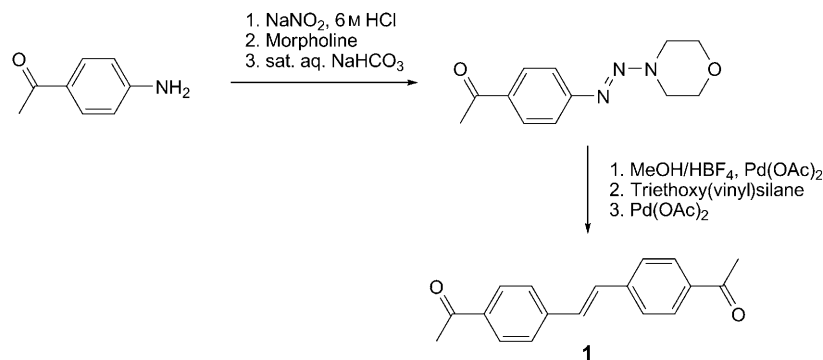
^b) Department of Chemistry, Louisiana State University, Baton Rouge LA 70803, USA

A palladium(II) acetate-catalyzed synthesis of **1** that utilizes the novel triazene 1-{4-[(*E*)-morpholin-4-yl-diazenyl]phenyl}ethanone as a synthon is described. The room temperature absorption spectra of **1** in various solvents exhibited a $\pi \rightarrow \pi^*$ transition in the range of 330–350 nm. Compound **1** was observed to be luminescent, with room-temperature solution and solid-state emission spectra that exhibited maxima in the range 400–500 nm. All room-temperature absorption and emission spectra exhibited some degree of vibrational structure. The emission spectrum of **1** at 77 K in propanenitrile glass was broad and featureless with a maximum at 447 nm. Compound **1** crystallized as a yellow and colorless polymorph. X-Ray structure analyses of both of these polymorphs and 1-{4-[(*E*)-morpholin-4-yl-diazenyl]phenyl}ethanone are presented.

Introduction. – For more than 45 years, numerous studies have been undertaken to characterize the unique excited-state properties of (*E*)-stilbene [1]. Towards the end of applying (*E*)-stilbene derivatives in a wide variety of research areas, this work has served as a catalyst for investigations into optimizing and tuning these excited-state properties by altering the functionality of (*E*)-stilbene [2][3]. Of particular interest is the preparation of materials that contain an (*E*)-stilbene moiety. Such materials exhibit novel photophysical, redox, and electroluminescent properties that have potential applicability to the construction of light-emitting diodes and liquid-crystal displays [4].

Our research involves the synthesis of unique ligands whose metal-binding moieties are positioned for the formation of luminescent metal-organic materials. A logical starting material for our ligands is 4,4'-diacetylstilbene (**1**; *Scheme*), with its synthetically versatile Ac groups and inherent luminescent properties. Since its first synthesis in 1945, its photophysical properties have been incompletely characterized [5]. In this article, we present a complete photophysical characterization of **1**, which was found to absorb and emit light at longer wavelengths than (*E*)-stilbene. A new Pd-catalyzed synthesis of **1** is discussed and illustrated in the *Scheme*. The crystal structures of the yellow and colorless polymorphs of **1** are also presented.

Results and Discussion. – *Synthesis of 1.* Preparation of 4,4'-disubstituted (*E*)-stilbene derivatives according to known protocols often have drawbacks that include numerous steps that utilize protecting groups and purification procedures that often result in a low yield. The classic synthesis of **1** by Zimmerman and Stille is an illustration of these difficulties [6].

Scheme. The Synthesis of Compound **1** from 1-(4-Aminophenyl)ethanone

Recently published *Heck* reaction methodologies that are notable for their high yields and the use of Pd(OAc)₂ as a ‘ligand-less’ catalyst overcome the difficulties inherent in the literature procedure for the synthesis of **1** [7]. Our synthesis of **1** is an extension of the work of *Sengupta* and co-workers, and is shown in the *Scheme*. This route to 4,4'-disubstituted (*E*)-stilbene derivatives was attractive because it stereoselectively yields the (*E*)-stilbene isomer, and uses economical and readily available starting materials [8]. It also utilizes mild reaction conditions that pose no threat to reactive substituents, such as an Ac group.

The presented preparation of **1** began with the synthesis of the novel triazene 1-[4-[(*E*)-morpholin-4-ylidiazanyl]phenyl]ethanone, an easily prepared and handled equivalent for the *in situ* generation of a reactive diazonium ion. This compound was prepared in good yield (64%) and recrystallized from light petroleum ether.

The triazene exhibited the predicted spectroscopic characteristics, except for the ¹³C-NMR spectrum. It exhibited the expected resonances for the aromatic ring and the Ac group, as well as three broad *singlets* at 44.1, 51.7, and 66.0 ppm for the morpholine ring. The assignment of these *singlets* to the C-atoms of the morpholine ring is supported by the HMQC-NMR spectrum of the triazene, which showed a clear connection between the broad ¹³C resonances and the morpholine H-atoms. Three signals were observed instead of the expected two, because the rotational dynamics of the triazene moiety resulted in the nonequivalence of the morpholine C-atoms [9]. The identity of the triazene was corroborated by an elemental analysis that provided acceptable values, and a HR-ESI-MS that had an [*M* + H]⁺ peak at *m/z* 234.1233, which was *ca.* 2.0 ppm less than the calculated value.

Triethoxy(vinyl)silane and the triazene were used together in a Pd(OAc)₂-catalyzed coupling reaction to prepare compound **1** in moderate yield (48%). The spectra of **1** compared well with those found in the literature [7b]. An acceptable elemental analysis supported the identity and purity of **1**. The HR-ESI-MS of **1** exhibited an [*M* + H]⁺ peak at *m/z* 265.1215 that was *ca.* 3 ppm lower than the calculated value.

Photophysics of 1. Excitation of an (*E*)-stilbene molecule leads to the population of a singlet state, S₁. The main deactivation pathway of S₁ has been found to involve rotation about the central C,C-bond with eventual formation of a mixture of (*Z*)- and (*E*)-stilbene. The second deactivation pathway for S₁ is fluorescence [1b][10].

The experimental photophysical data for compound **1** and the literature photophysical data for (*E*)-stilbene are listed in Table 1 [10]. Electronic-absorption spectra for **1** in CHCl₃ and propanenitrile solution are presented in Figs. 1 and 2, respectively.

Table 1. Photophysical Data for Compound **1** and (*E*)-Stilbene^{a)}

	$\lambda_{\text{max,abs}}$ [nm] (ϵ) ^{b)}	$\lambda_{\text{max,em}}$ [nm] (λ_{exc} [nm])	Φ_{fl}
CHCl ₃ solution	343 (45,300)	429 (343)	0.0015
MeCH ₂ CN solution	339 (50,500), 354 (35,700)	397 (339), 427, 456	0.0088
MeCH ₂ CN glass at 77 K		447 (339)	
Solid state		424 (343), 452, 487, 511	
(<i>E</i>)-Stilbene	295 (28,500), 307 (24,600)	350 (295)	0.023
MeCN solution ^{c)}			

^{a)} Spectra were acquired at room temperature unless otherwise noted. ^{b)} Extinction coefficient units M⁻¹ cm⁻¹. ^{c)} See [10].

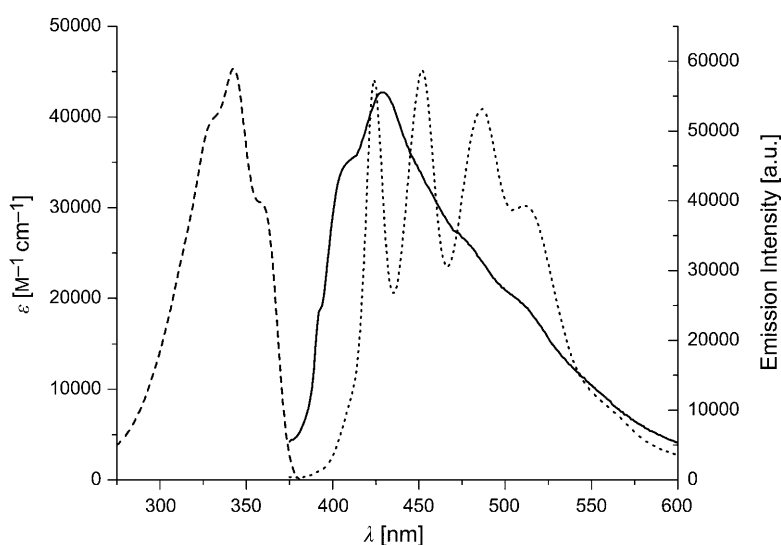


Fig. 1. Electronic-absorption and emission spectra of compound **1**. Absorption spectrum in CHCl₃ (---); room-temperature emission spectrum in CHCl₃ (λ_{exc} 343 nm) (—); room-temperature solid-state emission spectrum (λ_{exc} 343 nm) (···).

The room-temperature absorption spectra of **1** in CHCl₃ and propanenitrile were found to be similar. Each possessed an intense absorption assigned to a $\pi \rightarrow \pi^*$ transition that exhibited varying degrees of vibrational structure [11]. In dilute CHCl₃ solution, one maximum at 343 nm was noted, while two maxima at 339 and 354 nm were observed in dilute propanenitrile solution. Extinction coefficients for these maxima ranged from *ca.* 35,000 to 50,000 M⁻¹ cm⁻¹, which is not unusual for

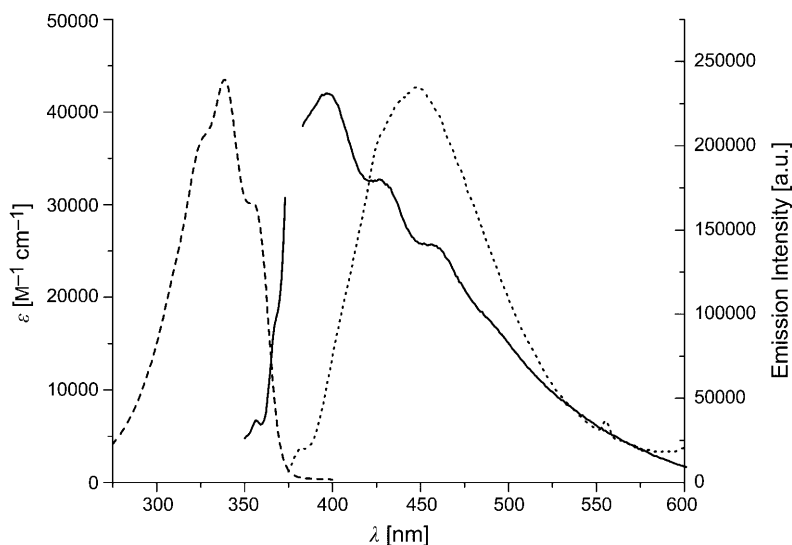


Fig. 2. Electronic-absorption and emission spectra of compound **1**. Absorption spectrum in propanenitrile (---); room-temperature emission spectrum in propanenitrile (λ_{exc} 339 nm) (—); emission spectrum in propanenitrile glass at 77 K (λ_{exc} 339 nm) (···).

disubstituted (*E*)-stilbene derivatives. The observed absorption spectral data for **1** in CHCl_3 and propanenitrile corresponded to the reported ones [6][11a].

The emission spectra of **1** in CHCl_3 and propanenitrile varied in their degree of vibrational-structure resolution. Excitation of a dilute (1.0×10^{-5} M) CHCl_3 solution of **1** at room temperature yielded an emission spectrum (Fig. 1) with a maximum at 429 nm and poorly resolved vibrational structure at wavelengths greater than 429 nm. The room-temperature emission spectrum of a 4.0×10^{-6} M propanenitrile solution of **1** (Fig. 2) resolved this vibrational structure as two maxima at 427 and 456 nm. A shorter wavelength maximum at 397 nm was also observed.

The room-temperature solid-state emission spectrum of **1** (Fig. 1) yielded the best resolution of the vibrational structure that was first observed in the solution-state spectra. The energy difference between the best-resolved maxima in Fig. 1 is 1461 cm^{-1} , and assigned to a vibrational mode of the phenyl ring of **1** [1a].

The excitation of a propanenitrile solution of **1** at 77 K yielded a featureless emission spectrum (Fig. 2) with a narrower band that had a maximum at 447 nm. The lack of vibrational structure in this spectrum is explained by the low temperature, which permitted relaxation of S_1 from a single preferred vibrational level.

The low fluorescence efficiency of **1** was illustrated by its small quantum yields in CHCl_3 and propanenitrile solution, 0.0015 and 0.0088, respectively. Other 4-substituted stilbenes with electron-withdrawing substituents have been shown to have similar quantum yields that result from the electron-withdrawing groups making fluorescence a less favored excited-state deactivation pathway [12]. The larger quantum yield observed for **1** in propanenitrile resulted from stabilization of the S_1 state *via*

interactions with the solvent, which caused the fluorescence deactivation pathway to be slightly more likely to occur.

X-Ray Analysis of **1 and Its Precursor.** Recrystallization of the triazene precursor to **1** from light petroleum ether yielded orange microplates that were suitable for X-ray analysis. Selected bond lengths for the triazene derivative are listed in Table 2, while its ORTEP representation is shown in Fig. 3. The N=N bond substituents adopted an (*E*)-configuration, with a N(3)–N(2)–N(1) bond angle of 114.08(7)°. The triazene moiety exhibited π -delocalization that was evidenced by N(1)–N(2) and N(2)–N(3) bond lengths of 1.3361(10) and 1.2766(10) Å, respectively. These values are between literature value of 1.222 Å for a N=N bond and 1.420 Å for a N(sp²)–N(sp³) single bond [13]. The morpholine ring adopted a conventional chair conformation. The structure of 1-[4-[(*E*)-morpholin-4-ylidiazanyl]phenyl]ethanone is similar to the structure of related triazenes [14].

Table 2. Selected Bond Lengths [Å] and Angles [°] for the Colorless Polymorph of **1** and Its Triazene Precursor

Triazene		1 ^{a)}	
O(1)–C(1)	1.4315(11)	O(1)–C(8)	1.229(2)
C(1)–C(2)	1.5186(12)	C(8)–C(9)	1.499(8)
N(1)–C(2)	1.4622(11)	C(5)–C(8)	1.489(3)
N(1)–N(2)	1.3361(10)	C(4)–C(5)	1.394(3)
N(2)–N(3)	1.2766(10)	C(1)–C(2)	1.467(3)
N(3)–C(5)	1.4206(11)	C(1)–C(1 ⁱ)	1.338(4)
C(5)–C(6)	1.3970(12)		
C(8)–C(11)	1.4905(12)		
O(2)–C(11)	1.2271(11)		
C(11)–C(12)	1.5076(12)		
C(1)–O(1)–C(4)	109.78(7)	C(1 ⁱ)–C(1)–C(2)	125.7(2)
O(1)–C(1)–C(2)	110.69(7)	C(5)–C(8)–C(9)	119.31(16)
N(3)–N(2)–N(1)	114.08(7)	O(1)–C(8)–C(9)	120.18(18)
N(2)–N(3)–C(5)	112.33(7)	C(3)–C(4)–C(5)	120.43(16)
C(6)–C(5)–C(10)	119.65(8)		
O(2)–C(11)–C(12)	121.01(8)		

^{a)} Symmetry code *i* is defined as $-x, 1-y, -z$.

A yellow and a colorless polymorph of compound **1** simultaneously formed when it was recrystallized from benzene. Polymorphs of different color have been observed in a variety of stilbene derivatives [15]. Selected bond lengths for the colorless polymorph of **1** are listed in Table 2, while its ORTEP representation is shown in Fig. 4.

Molecules of **1** in each polymorph were observed to have crystallographic inversion symmetry, and essentially identical bond lengths and angles. The colorless polymorph of **1** adopted (*E*)-geometry about the C=C bond, with a C(1ⁱ)–C(1)–C(2) bond angle of 125.7(2)° (symmetry code *i* for the colorless polymorph is defined as $-x, 1-y, -z$). The observed C=C bond length of 1.338(4) Å as well as other bond lengths and angles in **1** correlated with the values for a similar stilbene derivative [16]. The only difference

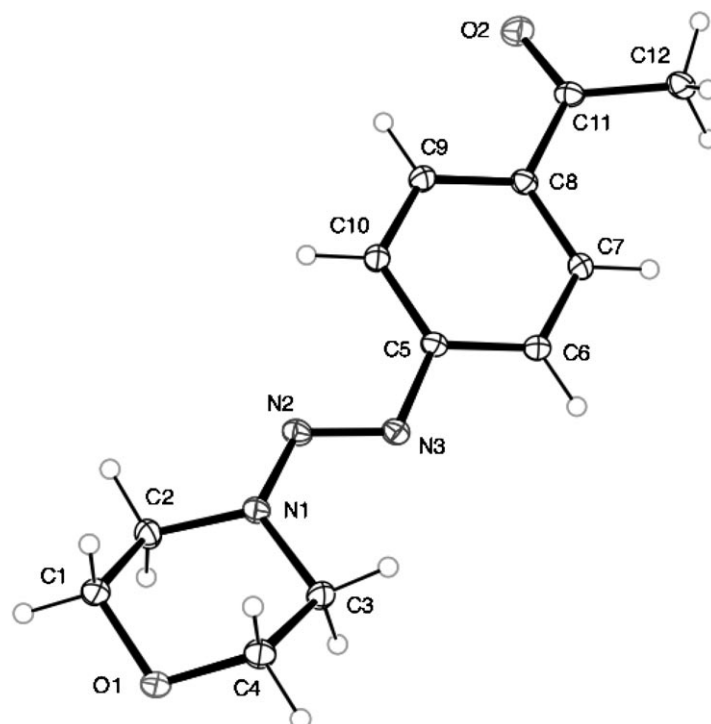


Fig. 3. ORTEP View of 1-[4-[(E)-morpholin-4-yl]diazenyl]phenyl]ethanone. Ellipsoids are represented at the 50% probability level.

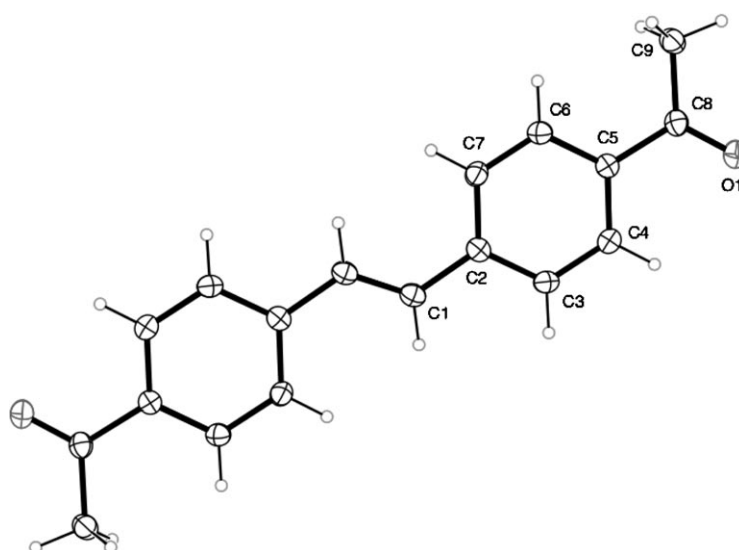


Fig. 4. ORTEP View of the colorless polymorph of **1**. Ellipsoids are represented at the 50% probability level.

between individual molecules of **1** was that the yellow polymorph deviated from planarity more than individual molecules of **1** in the colorless polymorph. The former had a C(1')–C(1)–C(2)–C(3) torsion angle of $175.55(16)^\circ$ (symmetry code i for the yellow polymorph is defined as $2 - x, 1 - y, 1 - z$), the corresponding angle of the latter was $165.3(2)^\circ$.

Each polymorph was found to have different unit-cell dimensions. Crystals of the colorless polymorph were found to have parallel stacks of **1** arranged at an angle of 62.1° to each other in a herringbone pattern. The distance between molecules of **1** in each stack was $3.5\text{--}3.6\text{ \AA}$. No overlap of the π -systems of the phenyl rings was observed. The yellow polymorph was found to consist of parallel planes of **1** separated by a distance of *ca.* $3.5\text{ \AA}$. The yellow color of this polymorph is attributed to the slight overlap of the π -systems of the phenyl rings, whose centroids were separated by *ca.* $4.2\text{ \AA}$. Similar variations in color and crystal packing have been observed in other stilbene derivatives [15d].

Conclusions. – A convenient Pd-catalyzed synthesis of compound **1** was presented. Room-temperature solution-state absorption spectra of **1** in CHCl_3 and propanenitrile were found to be similar, with each having an intense absorption that resulted from a $\pi \rightarrow \pi^*$ transition. Emission of **1** in differing media was observed from *ca.* 400 to 500 nm. Both the absorption and emission spectra of **1** exhibited vibrational structure. The quantum yields of **1** point to its low fluorescence efficiency, which is not unusual for (*E*)-stilbene derivatives that are substituted with electron-withdrawing groups. Recrystallization of **1** from benzene resulted in the formation of a yellow and colorless polymorph whose crystal structures were determined. The main difference between the two was in their crystal packing. The yellow polymorph exhibited overlap of its π -systems, while the colorless polymorph did not. Bond angles and lengths of individual molecules of **1** were essentially the same.

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Experimental Part

General. Synthetic procedures were carried out using standard techniques. Solvents and reagents were used as received. Anthracene used as a quantum-yield standard was of $>99\%$ purity. M.p.: in open capillaries; uncorrected. IR Spectra: as KBr disks on a *JASCO 460 FT-IR* spectrophotometer. ^1H - and ^{13}C -NMR spectra: *JEOL ECX 300* MHz spectrometer; TMS as the internal standard. MS: provided by the Washington University Mass Spectrometry Resource with support from the *NIH* National Center for Research Resources (Grant No. P41RR0954). Elemental analyses: performed by *M-H-W Laboratories* of Tucson, Arizona.

Photophysical Measurements. Emission and absorption spectra were recorded at r.t. in spectrophotometric-grade CHCl_3 and propanenitrile (99% purity) utilizing a *HoribaJobinYvon FluoroMax-4* fluorometer and a *Hewlett Packard 8453* diode array spectrometer. All solns. were deoxygenated with Ar prior to luminescence measurements. All emission spectra were corrected for detector response utilizing a correction curve supplied by the fluorometer manufacturer.

Fluorescence quantum yields were measured at r.t. in deoxygenated soln. of CHCl_3 and propanenitrile (λ_{ex} 343 and 339 nm, resp.) by comparison with anthracene ($\lambda_{\text{max,em}}$ 366–475 nm; $\Phi_{\text{fl}} = 0.27$ in

deoxygenated abs. EtOH at r.t.) [17]. The absorbances of the anthracene standard soln., and CHCl_3 and propanenitrile soln. of **1** were kept below 0.1 to avoid inner filter effects and matched to within 6 and 8%, resp. The fluorescence quantum yield values reported in Table 1 are averages of six trials.

Preparation of 1-[4-[(E)-Morpholin-4-ylidiazanyl]phenyl]ethanone. 1-(4-Aminophenyl)ethanone (1.50 g, 11.1 mmol) was added to 3.7 ml of 6M HCl and heated on a hot water bath to yield a clear orange soln., which was cooled to 0° to induce the formation of a light orange solid. This solid was maintained at 0°, and a soln. of 0.81 g (11.7 mmol) of NaNO_2 in 2.0 ml of H_2O was added dropwise under stirring over 10 min. A deep-orange-brown soln. resulted. To this stirred soln., 1.1 ml (1.06 g, 12.2 mmol) of morpholine were added dropwise over 10 min; a deep-orange solid formed. The mixture was allowed to reach r.t. and then brought to pH 8 with sat. aq. KHCO_3 . The orange solid was collected by suction filtration, washed well with H_2O , and dried in air. The crude product was recrystallized from light petroleum ether to give 1.66 g (64%) of 1-[4-[(E)-morpholin-4-ylidiazanyl]phenyl]ethanone orange crystalline microplates. M.p. 84.5–85.0°. IR (KBr): 3020, 2970, 1668, 1597, 1431. $^1\text{H-NMR}$ (300 MHz, (D_6) acetone): 2.54 (s, 3 H); 3.82 (s, 8 H); 7.50 (d, $^3J = 8.6$, 2 H); 7.95 (d, $^3J = 8.9$, 2 H). $^{13}\text{C-NMR}$ (75 MHz, (D_6) acetone): 25.7; 44.1; 51.7; 66.0; 120.3; 129.3; 134.7; 153.7; 196.3. HR-ESI-MS: 234.1233

Table 3. Crystal Data and Structure Refinement of the Polymorphs of **1** and Their Triazene Precursor.

	Triazene	1	
		colorless polymorph	yellow polymorph
Chemical Formula	$\text{C}_{12}\text{H}_{15}\text{N}_3\text{O}_2$	$\text{C}_{18}\text{H}_{16}\text{O}_2$	$\text{C}_{18}\text{H}_{16}\text{O}_2$
Formula weight	233.27	264.31	264.31
Crystal size [mm]	$0.27 \times 0.20 \times 0.19$	$0.33 \times 0.27 \times 0.02$	$0.27 \times 0.08 \times 0.07$
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$
Unit cell dimensions			
a [Å]	6.2107 (10)	8.595 (3)	5.6895 (15)
b [Å]	27.632 (5)	11.571 (4)	16.042 (4)
c [Å]	7.1969 (15)	7.269 (3)	7.421 (2)
β [°]	114.003 (7)	108.788 (18)	96.210 (14)
V [Å ³]	1128.3 (4)	684.4 (4)	673.3 (3)
Z	4	2	2
D_x [Mg/m ³]	1.373	1.283	1.304
μ [mm ⁻¹]	0.10	0.08	0.08
θ Range [°]	2.5–31.5	2.5–27.1	2.5–27.1
Index ranges	$-9 \leq h \leq 9$ $-35 \leq k \leq 40$ $-10 \leq l \leq 10$	$-11 \leq h \leq 11$ $-14 \leq k \leq 14$ $-9 \leq l \leq 9$	$-7 \leq h \leq 7$ $-20 \leq k \leq 20$ $-9 \leq l \leq 9$
Reflections collected	12393	5712	8371
Independent reflections	3553	1508	1493
Reflections with $I > 2\sigma(I)$	3068	936	1148
R (int)	0.023	0.043	0.023
Refinement method	Full-least squares matrix on F^2		
R_1/wR_2	0.039/0.108	0.049/0.121	0.041/0.106
Goodness-of-fit on F^2	1.04	1.02	1.05
Refined parameters	156	93	93
Extinction coefficient	0.021(5)	0.018(5)	0.010(3)
Residual density [eÅ ⁻³]	0.46, –0.24	0.22, –0.24	0.26, –0.19
CCDC deposition No.	739503	739504	739505

($[M+H]^+$; calc. 234.1243). Anal. calc. for $C_{12}H_{15}N_3O_2$ (233.27): C 61.79, H 6.48, N 18.01; found: C 62.00, H 6.36, N 17.96.

Preparation of 1,1'-[(E)-Ethene-1,2-diyl]dibenzene-4,1-diyl]diethanone (1). To a stirred suspension of 1-[4-[(E)-morpholin-4-ylidiazanyl]phenyl]ethanone (2.00 g, 8.6 mmol) in 20.0 ml of MeOH at 0°, 2.2 ml (17.2 mmol) of 40% HBF_4 were added dropwise over 10 min. This mixture was brought to r.t. and stirred for 15 min until a clear orange-red soln. formed. To this soln., 0.020 g (0.086 mmol) of $Pd(OAc)_2$ was added, which was followed by the dropwise addition of a soln. of 0.90 ml (4.29 mmol) triethoxy-(vinyl)silane in 3.0 ml of MeOH over 5 min. A second portion of 0.020 g (0.086 mmol) of $Pd(OAc)_2$ was added, and the mixture was stirred at r.t. for 30 min, then heated at 40° for 20 min, and heated to reflux for 15 min. The volume of the mixture was reduced by half, and then 20 ml of H_2O were added. The resulting olive-green solid was collected by suction filtration, washed with H_2O , and air-dried. The crude product was recrystallized twice from benzene to give 0.54 g (48%) of pure **1** as a mixture of yellow needles and colorless plates. M.p. 207–210°. IR (KBr): 3028, 1672, 1598. 1H -NMR (300 MHz, CD_2Cl_2): 2.57 (s, 6 H); 7.27 (s, 2 H); 7.62 (d, $^3J = 8.3$, 4 H); 7.93 (d, $^3J = 8.3$, 4 H). ^{13}C -NMR (75 MHz, CD_2Cl_2): 26.4; 126.6; 128.5; 129.8; 136.5; 141.3; 197.2. HR-ESI-MS: 265.1215 ($[M+H]^+$; calc. 265.1229). Anal. calc. for $C_{18}H_{16}O_2$ (264.32): C 81.79, H 6.10; found: C 81.75, H 6.03.

X-Ray Crystal-Structure Analyses of 1-[4-[(E)-Morpholin-4-ylidiazanyl]phenyl]ethanone and the Polymorphs of 1 (Table 3). X-Ray-quality crystals of 1-[4-[(E)-morpholin-4-ylidiazanyl]phenyl]ethanone and the colorless and yellow polymorphs of **1** were used for data collection at $T = 90$ K on a *Nonius KappaCCD* diffractometer equipped with an *Oxford Cryosystems Cryostream* chiller and graphite-monochromated MoK_α radiation ($\lambda = 0.71073$ Å). Structures were solved by direct methods, and structure refinement was carried out using SHELXL-97 [18]. All H-atoms were visible in difference maps, but were placed in idealized positions during refinement, with a torsional parameter refined for each Me group.

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