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

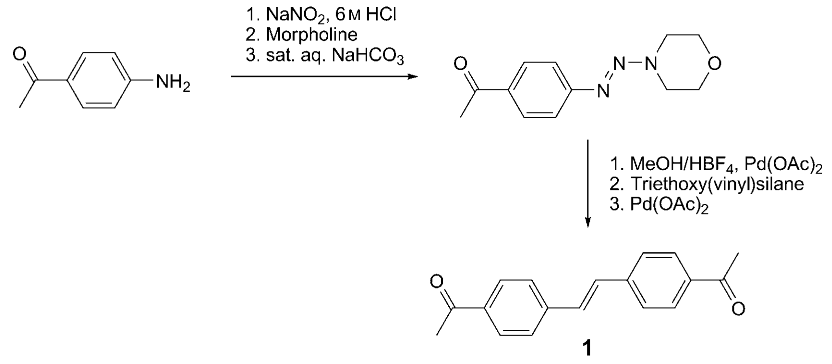
A palladium(II) acetate-catalyzed synthesis of **1** that utilizes the novel triazene 1-{4-[(*E*)-morpholin-4-yldiazenyl]phenyl}ethanone as a synthon is described. The room temperature absorption spectra of **1** in various solvents exhibited a $\pi \rightarrow \pi^*$ transition in the range of 330–350 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-yldiazenyl]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-yldiazenyl]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 ^{13}C-NMR spectrum. It exhibited the expected resonances for the aromatic ring and the Ac group, as well as three broad *singlet*s at 44.1, 51.7, and 66.0 ppm for the morpholine ring. The assignment of these *singlet*s 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 ^{13}C 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 $[M+\mathrm{H}]^+$ 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 $[M+\mathrm{H}]^+$ 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, S$_1$. The main deactivation pathway of S$_1$ 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 S$_1$ 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 $CHCl_3$ and propanenitrile solution are presented in *Figs. 1* and *2*, respectively.

Table 1. *Photophysical Data for Compound* **1** *and (*E*)-Stilbene*[a])

	$\lambda_{max,abs}$ [nm] (ε)[b])	$\lambda_{max,em}$ [nm] (λ_{exc} [nm])	Φ_{fl}
$CHCl_3$ solution	343 (45,300)	429 (343)	0.0015
$MeCH_2CN$ solution	339 (50,500), 354 (35,700)	397 (339), 427, 456	0.0088
$MeCH_2CN$ glass at 77 K		447 (339)	
Solid state		424 (343), 452, 487, 511	
(*E*)-Stilbene MeCN solution[c])	295 (28,500), 307 (24,600)	350 (295)	0.023

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

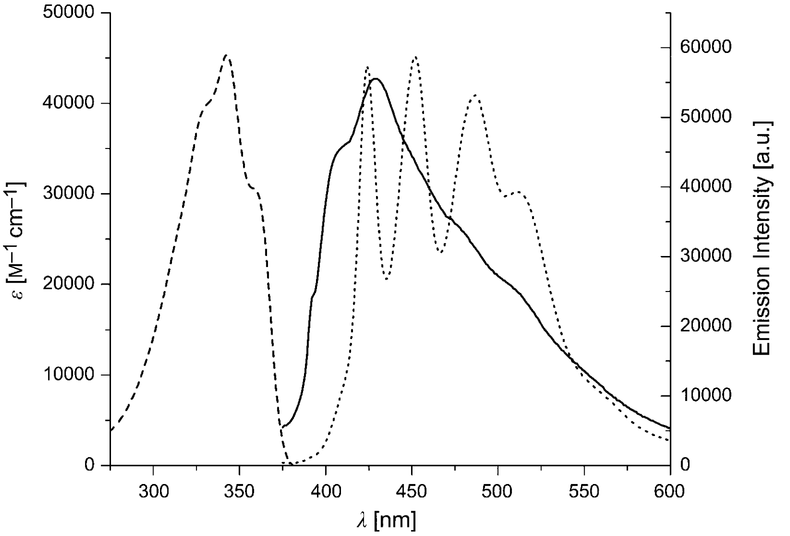


Fig. 1. *Electronic-absorption and emission spectra of compound* **1**. Absorption spectrum in $CHCl_3$ (---); room-temperature emission spectrum in $CHCl_3$ (λ_{exc} 343 nm) (—); room-temperature solid-state emission spectrum (λ_{exc} 343 nm) (···).

The room-temperature absorption spectra of **1** in $CHCl_3$ 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 $CHCl_3$ 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

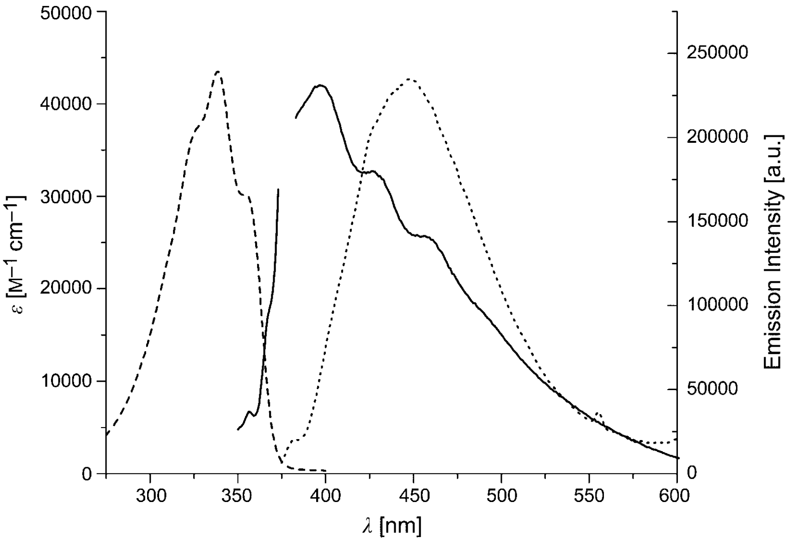


Fig. 2. *Electronic-absorption and emission spectra of compound* **1**. Absorption spectrum in propanenitrile (---); room-temperature emission spectrum in propanenitrile (λ_{exc} 339 nm) (—); emission spectrum in propanenitrile glass at 77 K (λ_{exc} 339 nm) (···).

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(sp^2)−N(sp^3) single bond [13]. The morpholine ring adopted a conventional chair conformation. The structure of 1-{4-[(*E*)-morpholin-4-yldiazenyl]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(30−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(1^i)−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

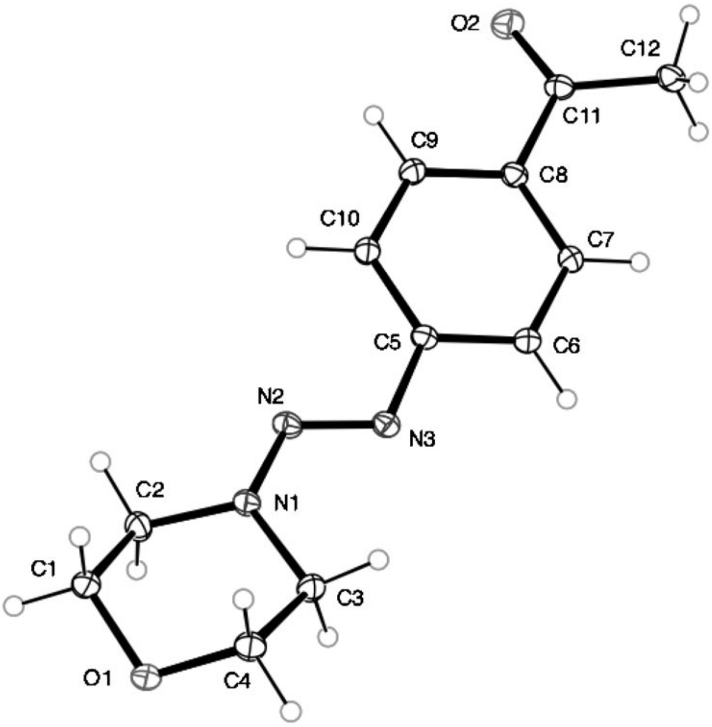


Fig. 3. *ORTEP View of 1-{4-[(*E*)-morpholin-4-yldiazenyl]phenyl}ethanone*. Ellipsoids are represented at the 50% probability level.

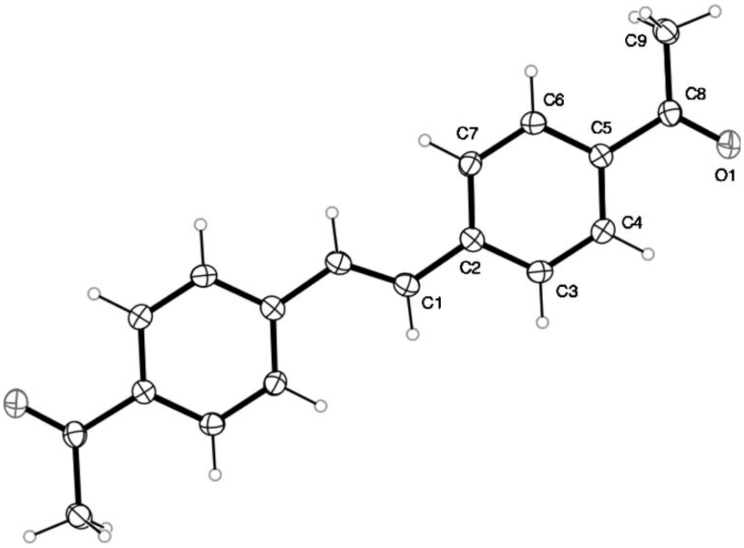


Fig. 4. *ORTEP View of the colorless polymorph of* **1**. Ellipsoids are represented at the 50% probability level.

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 $C(1^i)-C(1)-C(2)-C(3)$ torsion angle of 175.55(16)° (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)°.

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 3.5–3.6 Å. 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 Å. 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 Å. 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.

The authors would like to thank the *Fletcher Jones Foundation* for funds that allowed the purchase of the fluorometer. Whittier College is acknowledged for the funds that supported this research. Dr. *Andrew Maverick* is acknowledged for helpful discussion.

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 ($\lambda_{max,em}$ 366–475 nm; $\Phi_{fl} = 0.27$ 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-yldiazenyl]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-yldiazenyl]phenyl}ethanone orange crystalline microplates. M.p. 84.5–85.0°. IR (KBr): 3020, 2970, 1668, 1597, 1431. ^{1}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}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	$C_{12}H_{15}N_3O_2$	$C_{18}H_{16}O_2$	$C_{18}H_{16}O_2$
Formula weight	233.27	264.31	264.31
Crystal size [mm]	0.27 × 0.20 × 0.19	0.33 × 0.27 × 0.02	0.27 × 0.08 × 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	$-9 \leq h \leq 9$	$-11 \leq h \leq 11$	$-7 \leq h \leq 7$
	$-35 \leq k \leq 40$	$-14 \leq k \leq 14$	$-20 \leq k \leq 20$
	$-10 \leq l \leq 10$	$-9 \leq l \leq 9$	$-9 \leq l \leq 9$
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-diyldibenzene-4,1-diyl]diethanone* (**1**). To a stirred suspension of 1-{4-[(*E*)-morpholin-4-yldiazenyl]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. ^{1}H-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-yldiazenyl]phenyl}ethanone and the Polymorphs of* **1** (*Table 3*). X-Ray-quality crystals of 1-{4-[(*E*)-morpholin-4-yldiazenyl]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.

REFERENCES

[1] a) J. Saltiel, *J. Am. Chem. Soc.* **1967**, *89*, 1036; b) D. H. Waldeck, *Chem. Rev.* **1991**, *91*, 415; c) R. Improta, F. Santoro, *J. Phys. Chem. A* **2005**, *109*, 10058.

[2] J.-S. Yang, S.-Y. Chiou, K.-L. Liau, *J. Am. Chem. Soc.* **2002**, *124*, 2518.

[3] F. Tian, E. W. Debler, D. P. Millar, A. A. Deniz, I. A. Wilson, P. G. Schultz, *Angew. Chem., Int. Ed.* **2006**, *45*, 7763.

[4] C. J. Tonzola, M. M. Alam, S. A. Jenekhe, *Macromolecules* **2005**, *38*, 9539.

[5] W. C. J. Ross, *J. Chem. Soc.* **1945**, 536.

[6] E. K. Zimmerman, J. K. Stille, *Macromolecules* **1985**, *18*, 321.

[7] a) E. Alacid, C. Nájera, *J. Org. Chem.* **2009**, *74*, 2321; b) Á. Gordillo, E. de Jesús, C. López-Mardomingo, *Chem. Commun.* **2007**, 4056.

[8] S. Sengupta, S. Bhattacharyya, S. K. Sadhukhan, *J. Chem. Soc., Perkin Trans. 1* **1998**, 275.

[9] a) R. Tingley, M. B. Peori, R. Church, K. Vaughan, *Can. J. Chem.* **2005**, *83*, 1799; b) S. Moser, R. Church, M. B. Peori, K. Vaughan, *Can. J. Chem.* **2005**, *83*, 1071.

[10] J. C. Roberts, J. A. Pincock, *J. Org. Chem.* **2006**, *71*, 1480.

[11] a) T. Kubota, B. Uno, Y. Matsuhisa, H. Miyazaki, K. Kano, *Chem. Pharm. Bull.* **1983**, 373; b) F. D. Lewis, W. Weigel, X. Zuo, *J. Phys. Chem. A* **2001**, *105*, 4691.

[12] H. Görner, *Ber. Bunsen-Ges. Phys. Chem.* **1998**, *102*, 726.

[13] F. H. Allen, O. Kennard, D. G. Watson, L. Brammer, A. G. Orpen, R. Taylor, *J. Chem. Soc. Perkin Trans. 2* **1987**, S1.

[14] V. R. Little, H. Jenkins, K. Vaughan, *J. Chem. Crystallogr.* **2008**, *38*, 447.

[15] a) H. Hamazaki, S. Ohba, F. Toda, H. Takumi, *Acta. Crystallogr., Sect. C* **1997**, *53*, 620; b) C. R. Theocharis, W. Jones, C. N. R. Rao, *J. Chem. Soc., Chem. Commun.* **1984**, 1291; c) Y. Wang, W. Tam, S. H. Stevenson, R. A. Clement, J. Calabrese, *Chem. Phys. Lett.* **1988**, *148*, 136; d) A. Gleixner, J. Hiller, T. Debaerdemaeker, A. Lentz, L. Walz, *Z. Kristallogr.* **1998**, *213*, 411.

[16] B. Nohra, S. Graule, C. Lescop, R. Réau, *J. Am. Chem. Soc.* **2006**, *128*, 3520.

[17] a) A. K. Mohammed, R. A. Isovitsch, A. W. Maverick, *Inorg. Chem.* **1998**, *37*, 2779; b) M. Montalti, A. Credi, L. Prodi, M. T. Gandolfi, ' Handbook of Organic Photochemistry', CRC Taylor & Francis, Boca Raton, 2005; c) J. R. Lakowicz, 'Principles of Fluorescence Spectroscopy', Springer, New York, 2006.

[18] G. M. Sheldrick, *Acta Cryst., Sect. A* **2008**, *64*, 112.

Received September 25, 2009