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such as the reaction of basic contaminants in the air with the surface of the resist film (vide infra) that consume acid without leading to removal of a *t*-BOC group. The fact that an unexpected drop in catalytic chain length and lithographic sensitivity has been observed (vide infra) while increasing the acidity of the photoreleased arylsulfonic acids (by increasing the electron-withdrawing ability of substituents) would tend to support this hypothesis as these stronger acids would be more reactive toward basic contaminants. Another possible factor that may be important are the changes of hydrophobicity induced by the introduction of different photogenerators of acid into the resist film. This may govern how quickly impurities from the air can penetrate into the film to react with photogenerated acid.

Conclusion

A Hammett plot of T_{min} versus the σ constants of various groups substituted onto the benzenesulfonate moiety of 2-nitrobenzyl sulfonate esters has shown that the thermal stability of 2-nitrobenzyl esters decreases as the inductive power of substituent groups increases. Thus, increasing the strength of the photochemically released acid decreases the thermal stability of 2-nitrobenzyl sulfonate photogenerators of acid. However, this effect can be countered by the introduction of bulky or inductively electron withdrawing substituents at the 6-position of the 2-nitrobenzyl chromophore. The CF_3 group, which is both strongly electron withdrawing and bulky, is particularly effective at stabilization and can enhance the thermal stability of 2-nitrobenzyl ester derivatives by 150 °C over the unsubstituted ester and by 50 °C over the ester with a 2-nitro substituent. This type of approach with even bulkier and more powerful electron-withdrawing groups positioned at the 6-position of 2-nitrobenzyl chromophore could permit the preparation of thermally stable photogenerators of acid incorporating such powerful acids as triflic acid.

Bis(*p*-chlorocinnamate) Ester of 2,4-Hexadiyne-1,6-diol: Crystallographic and Spectroscopic Studies of an Unreactive Crystal†

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While the molecular structure of the bis(*p*-chlorocinnamate) ester of 2,4-hexadiyne-1,6-diol (**2**) contains two groups known to be reactive in the solid state, namely, the chlorocinnamoyl and conjugated diyne moieties, the crystal of **2** obtained from chlorobenzene solution is unreactive to γ-radiation, X-rays, ultraviolet light, and heat at temperatures below its melting point. The crystal of **2** is monoclinic, space group $C2/c$, a = 45.724 (9) Å, b = 8.142 (2) Å, c = 11.336 (3) Å, β = 91.66 (3)°, V = 4218.5 (30) Å^3, and Z = 8. From the geometry of the unit cell, it is apparent that this phase of **2** is unreactive for structural reasons, as both the chlorocinnamoyl and diyne moieties do not have the preferred intermolecular orientation for solid-state reactivity. Generally similar room-temperature emission spectra were observed for **2** and the reactive *p*-chlorocinnamic acid (**3**). The emission spectra appear to be due to excimers, and the relative energies of the emission spectra correlate with ground-state overlap. A convenient procedure for the photodimerization of **3** to the corresponding truxinic acid (**4**) is reported. Refluxing of **4** with thionyl chloride results in the formation of the cyclic anhydride **5**.

Introduction

Polydiacetylenes (PDA, **1**) are a class of polymers with conjugated backbones available in the form of macroscopic single crystals.[1] In recent years, we have been interested in the study of chemical,[2,3] thermal,[4,5] photochemical,[6] and magnetic processes[7] whose origin may be traced to specific substituents in the PDA side group and that affect the electronic structure, spectroscopy, and reactivity associated with the conjugated chain.

The reports[8,9] that the photoconductivity action spectrum of the PDA from 1,6-di-*N*-carbazolyl-2,4-hexadiyne (DCH, **1a**) exhibits features that correspond to the maximum of the S_0–S_1 absorption of the carbazole group and the interpretation[9] that photoconductivity in poly-DCH is associated with charge transfer from the excited carbazole to the conjugated chain raise the following possi-

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[†] This paper is dedicated to Professor Michael Hanack, Universität Tübingen, on the occasion of his sixtieth birthday.

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bility. If a side-chain excited state can lead to photophysical phenomena, such an excited state can also lead to photochemical phenomena. Unsuccessful attempts to convert a diphenylamine group in both monomeric and polymeric 1,1,6,6-tetraphenylhexadiynediamine (THD) to a carbazole have been reported.[6] In our further pursuit of a light-induced reaction that would either precede or follow a diacetylene polymerization,[6] a series of *p*-(chlorocinnamate) esters of diacetylenediols was synthesized and characterized.[10] Our choice of *p*-chlorocinnamates was motivated by both the known solid-state photodimerization reaction of cinnamic acid derivaties[11] and also the tendency of chloro substituents to "engineer" 4-Å short-axis structures.[12] We have not observed the desired cinnamate photodimerization in any of the monomers or polymers studied to date.[10] One of the compounds synthesized, the bis(*p*-chlorocinnamate) ester of 2,4-hexadiyne-1,6-diol (**2**), was isolated in a form unreactive to heat below its melting point, ultraviolet light, and ^{60}Co γ-radiation. Since a given organic solid may be unreactive for either structural or mechanistic (photophysical)[13] reasons, we carried out both a structural determination and an emission spectroscopic study of the unreactive phase of **2**. For purposes of comparison, emission spectra were also recorded for *p*-chlorocinnamic acid (**3**), a phase that undergoes photodimerization. The results of these studies are presented in this paper.

In earlier related work, biscinnamates of 2,4-hexadiyne-1,6-diol[14] and 10,12-docosadiyne-1,22-diol[15] were prepared. The former was described[14] as not polymerizable, while the latter was reported to occur in two crystalline forms, one of which was not observed to polymerize while the other was polymerizable.[15] Neither monomers nor polymers were studied by single-crystal X-ray crystallography, and no mention of reactivity at the cinnamate esters was found.[14,15]

Experimental Section

General Techniques. Melting points are uncorrected. Elemental analysis was performed by Schwarzkopf Microanalytical Laboratory, Woodside, NY. Solution electronic absorption spectra were recorded on a Cary 17D spectrophotometer using 1-cm cells, and solid-state spectra were recorded on the same instrument by using the diffuse reflectance accessory with samples 1% by weight dispersed in sodium chloride. Emission spectra were recorded on the SLM 8000 spectrometer at 20 °C. Solid samples were mounted on two-sided sticky tape that gave no significant emission in the wavelength regions of interest. Infrared spectra were recorded on a Perkin-Elmer 299B spectrophotometer. Proton NMR spectra were recorded on a Varian 90-MHz spectrometer.

Preparation of the Bis(*p*-chlorocinnamate) Ester of 2,4-Hexadiyne-1,6-diol (2). *p*-Chlorocinnamoyl chloride was prepared from **3** and thionyl chloride refluxed for 3 h. Excess $SOCl_2$ was removed under reduced pressure, and this was followed by vacuum sublimation to give a solid, mp 76.5–78 °C. To a solution of this acid chloride (14.2 g, 0.071 mol) in tetrahydrofuran (THF, 80 mL) stirred mechanically under argon was added 2,4-hexadiyne-1,6-diol (Farchan, thrice recrystallized from toluene, 3.85 g, 0.035 mol). To this mixture was added dropwise a solution of pyridine (7.5 mL) in THF (35 mL), and the mixture was refluxed for 6 h. The mixture was poured into cold water, and the precipitated solid was filtered and washed with cold water. The solid was dissolved in chloroform (300 mL), and this solution was washed with three 100-mL portions of saturated sodium bicarbonate followed by 100 mL of water. The solution was dried over $MgSO_4$, filtered, evaporated, and vacuum dried to give **2** (13.83 g, 90% yield). The product was crystallized from 1:1 chloroform–hexane to give a white solid, mp 122–123 °C. The IR spectrum (Nujol) exhibited the following absorptions (cm^{-1}): 1715, 1640, 1590, 1490, 1405, 1320, 1275, 1250, 1185, 1170, 1150, 1085, 1030, 1010, 985, 955, 915, 870, 825, 720. Anal. Calcd for $C_{24}H_{16}O_4Cl_2$: C, 65.61; H, 3.68; Cl, 16.14. Found: C, 66.10; H, 3.63; Cl, 15.83.

As crystallized above or preferably from chlorobenzene with slow evaporation under argon, the unreactive phase of **2** is isolated, mp 125 °C. This phase is thermally unreactive below its melting point and turns orange on heating to 130 °C. In acetonitrile solution, the ultraviolet spectrum of **2** exhibited the following λ_{max} (nm) (log ϵ), sh = shoulder: 302 sh (4.50), 292 sh (4.69), 283 (4.76), 224 (4.41), 217.5 (4.50), 206 (4.48). No low intensity transitions are detected out to 400 nm. Diffuse reflectance of **2** revealed a shoulder near 312 nm and broad maxima at 287 and 228 nm.

Preparation of 4,4′-Dichloro-β-truxinic Acid (4). *p*-Chlorocinnamic acid (Aldrich, recrystallized from ethanol or glacial acetic acid) (9 g, 0.054 mol, finely ground powder) was irradiated at 370 nm for 28 h with a GTE Sylvania 2051 lamp. Unreacted **3** was extracted with toluene, and the residue was recrystallized from glacial acetic acid to give **4**, 8.11 g (90% yield), mp 186–191 °C (lit.[16] mp 190 °C).

Synthesis of 4,4′-Dichloro-β-truxinic Anhydride (5). A mixture of **4** (6.9 g, 0.02 mol) and thionyl chloride (3.5 mL, 5.85 g, 0.049 mol) was heated at reflux for 3 h. The excess $SOCl_2$ was removed under reduced pressure, and the residue crystallized from benzene to give **5**, 5.43 g (78% yield), mp 125 °C. The IR spectrum (Nujol) exhibited the following absorptions (cm^{-1}): 3030, 1855, 1780, 1595, 1490, 1410, 1240, 1205, 1090, 1060, 1015, 890, 850, 830, 820, 770, 735, 720, 670. The proton NMR spectrum (in DMSO-d_6) exhibited the following resonances: δ 6.8–7.3 (multiplet, 8 H), 4.4 (doublet, 2 H, J = 3 Hz), 4.1 (doublet, 2 H, J = 3 Hz). The mass spectrum of the compound exhibited the expected isotopic cluster with major peaks at m/e 346, 348. Anal. Calcd for $C_{18}H_{12}O_3Cl_2$: C, 62.27; H, 3.48; Cl, 20.42. Found: C, 61.60; H, 3.36; Cl, 20.12.

Ultraviolet and Raman Spectra of *p*-Chlorocinnamic Acid (3). In acetonitrile solution, the UV spectrum of **3** exhibited the following: λ_{max} (nm) (log ϵ): 301 sh (4.12), 292 sh (4.26), 274 (4.43), 222.5 (4.11), 216 (4.21), 205 (4.16). The diffuse reflectance spectrum of **3** exhibits shoulders near 335 and 315 nm with broad maxima at 275 and 226 nm. With 514.5-nm excitation, the Raman spectrum of polycrystalline **3** revealed shifts at 1644, 1591, 1446, 1404, 1290, 1258, 1210, 1173, 1090, 706, and 641 cm^{-1}.

Structure Determination of 2. Single crystals were grown from chlorobenzene solution. Laue photographs and a preliminary X-ray photographic study indicated the crystal to be of excellent quality. The crystal was then transferred to a Supper No. 455 goniometer and optically centered on a Syntex $P2_1$ diffractometer. Operations were performed as described previously.[17] The analytical scattering factors of Cromer and Waber were used; real and imaginary components of anomalous scattering were included in the calculations.[18] The structure was solved by using MULTAN;[19] all other computational work was carried out on a VAX 8650 computer using the Enraf-Nonius SDP software package.[20] Details of the structure analysis, in outline form, are presented

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Table I. Data for the X-ray Diffraction Study of $C_{24}H_{16}O_4Cl_2$

(A) Crystal Data at 21 (1) °C

cryst syst: monoclinic
space group: $C2/c$ [C_{2h}, No. 15]
a = 45.724 (9) Å
b = 8.142 (2) Å
c = 11.336 (3) Å
β = 91.66 (3)°
V = 4218.5 (30) Å^3
Z = 8
cryst size: 0.30 × 0.40 × 0.50 mm
formula wt: 439.30
ρ_{calc} = 1.383 g cm^{-3}
ρ_{obs} = 1.38 (1)^a g cm^{-3}
μ = 3.34 cm^{-1} (Mo Kα)
cell const determination: 12 pairs of $\pm(hkl)$ and refined 2θ, ω, χ values in the range $25 \leq |2\theta| \leq 27°$ (λ(Mo K$\bar{\alpha}$) = 0.71073 Å)

(B) Measurement of Intensity Data

radiation: Mo K$\bar{\alpha}$, graphite monochromator
reflns measd: $\pm h$, $+k$, $+l$ ($3 \leq 2\theta \leq 53°$)
scan type, speed: θ–2θ, vble, 2.93–5.33°/min
scan range: sym $[1.6 + \Delta(\alpha_2 - \alpha_1)]°$
no. of reflns measd: 4648; 4403 in unique set
standard reflns, period: 70; 020; 24,0,0; 008 reflns; variation $\leq \pm 3\sigma(I)$ for each
abs correction: empirical, normalized transmission factors 0.904–1.000; 114, 406, 0 2 11 reflns
data reduction: as before^b
statistical information: R_w = 0.024 ($hk0$ reflns)

(C) Refinement

refinement,^{c} with 3349 data for which $I > 1.96\sigma(I)$
weighting of reflns: as before,^{c} p = 0.04
solution: direct-methods (MULTAN)
refinement:^{d} full-matrix least-squares, with
  anisotropic temperature factors for Cl, O, and C atoms
  isotropic temp factors for H atoms
  secondary extinction param, 1.55 (4) × 10^6:
  R = 0.0401; R_w = 0.0480; SDU = 160
  R = (struct factor calcn with all 4403 reflections) = 0.066
final difference map: random peaks ≤0.22 e$^-$/Å^3

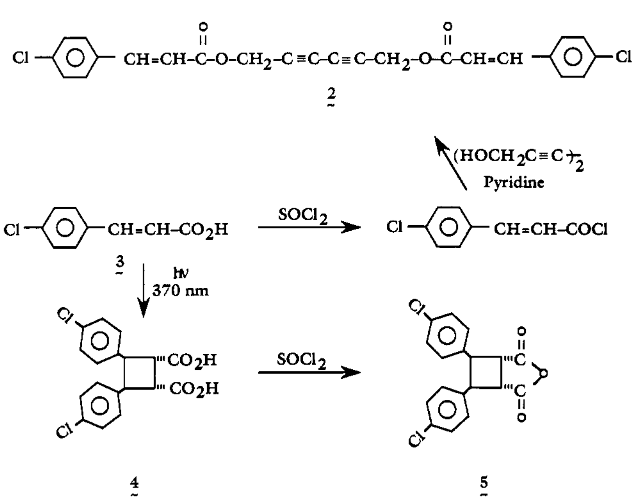
[a] Measured by neutral buoyancy in bromobenzene–chloroform. [b] Foxman, B. M.; Goldberg, P. L.; Mazurek, H. *Inorg. Chem.* 1981, *20*, 4381. All computations in the present work were carried out using the ENRAF-NONIUS Structure Determination Package. [c] Corfield, P. W. R.; Doedens, R. J.; Ibers, J. A. *Inorg. Chem.* 1967, *6*, 197. [d] $R_{av} = \sum|I - I_{av}|\sum I$; $R = \sum||F_o| - |F_c||/\sum|F_c|$; $R_w = \{\sum w[|F_o| - |F_c|]^2/\sum w|F_o|^2\}^{1/2}$. SDU = $\{\sum w[|F_o| - |F_c|]^2/(m - n)\}^{1/2}$, where m (=3349) is the number of observations and n (=336) is the number of parameters.

Table II. Atomic Coordinates for $C_{24}H_{16}O_4Cl_2$[a,b]

atom	x	y	z	B, Å^2
C11	0.47390 (1)	0.12991 (7)	0.58489 (5)	5.44 (1)
C12	0.92062 (1)	0.57188 (8)	1.28969 (5)	5.78 (1)
O1	0.64120 (3)	0.7066 (2)	0.4631 (1)	4.14 (3)
O2	0.62039 (3)	0.6814 (2)	0.2836 (1)	5.34 (3)
O3	0.76192 (3)	1.0498 (2)	0.9206 (1)	3.89 (3)
O4	0.79141 (3)	0.9726 (2)	0.7758 (1)	4.36 (3)
C1	0.50342 (4)	0.2390 (2)	0.5321 (2)	3.96 (4)
C2	0.50141 (4)	0.3038 (3)	0.4208 (2)	4.54 (4)
C3	0.52476 (4)	0.3909 (3)	0.3793 (2)	4.36 (4)
C4	0.55026 (4)	0.4142 (2)	0.4462 (2)	3.68 (4)
C5	0.55166 (4)	0.3439 (3)	0.5589 (2)	4.36 (4)
C6	0.52844 (4)	0.2571 (3)	0.6014 (2)	4.39 (4)
C7	0.57411 (4)	0.5072 (3)	0.3960 (2)	4.07 (4)
C8	0.59767 (4)	0.5634 (3)	0.4512 (2)	4.11 (4)
C9	0.62002 (4)	0.6549 (2)	0.3873 (2)	3.74 (4)
C10	0.66481 (4)	0.7965 (3)	0.4118 (2)	4.03 (4)
C11	0.68217 (4)	0.8657 (3)	0.5099 (2)	4.01 (4)
C12	0.69605 (4)	0.9260 (2)	0.5888 (2)	3.94 (4)
C13	0.71221 (4)	0.9996 (3)	0.6788 (2)	3.93 (4)
C14	0.72725 (4)	1.0618 (2)	0.7536 (2)	3.78 (4)
C15	0.74596 (4)	1.1528 (2)	0.8374 (2)	4.09 (4)
C16	0.78574 (4)	0.9727 (2)	0.8788 (1)	3.34 (3)
C17	0.80303 (4)	0.8975 (2)	0.9757 (2)	3.59 (4)
C18	0.82821 (4)	0.8250 (2)	0.9540 (1)	3.51 (4)
C19	0.84932 (4)	0.7550 (2)	1.0394 (1)	3.23 (3)
C20	0.87318 (4)	0.6681 (2)	0.9985 (1)	3.58 (4)
C21	0.89456 (4)	0.6072 (2)	1.0745 (2)	3.72 (4)
C22	0.89246 (4)	0.6360 (3)	1.1936 (2)	3.69 (4)
C23	0.86882 (4)	0.7178 (3)	1.2383 (2)	4.08 (4)
C24	0.84724 (4)	0.7763 (3)	1.1613 (2)	3.74 (4)

[a] Atoms refined by using anisotropic temperature factors are given in the frm of the isotropic equivalent displacement parameter defined as $1.33[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab\cos\gamma\, B_{12} + ac\cos\beta\, B_{13} + bc\cos\alpha\, B_{23}]$. [b] Numbers in parentheses in this and following tables are estimated standard deviations in the least significant digit.

Scheme I



in Table I. Atomic coordinates for all non-hydrogen atoms appear in Table II; selected bond distances and angles are in Table III; anisotropic displacement parameters are in Table S-I; H atom positions and thermal parameters are in Table S-II; all bond lengths and angles are in Table S-III; observed and calculated structure amplitudes are in Table S-IV (supplementary material; see the paragraph at the end of the paper).

Results and Discussion

Synthesis. Esterification of *p*-chlorocinnamoyl chloride with 2,4-hexadiyne-1,6-diol in the presence of pyridine straightforwardly led to 2 in 90% yield, as described in the Experimental Section. Crystallization from chlorobenzene gave the relevant crystalline phase of 2.

In the course of this work we found that the photodimer of 3 was conveniently prepared by irradiation of 3 with a lamp whose maximum output was at 370 nm. This truxinic acid was converted to its anhydride by refluxing with thionyl chloride. The chemistry is detailed in the Experimental Section and summarized in Scheme I.

Attempts To Observe Solid-State Reactivity of 2. Irradiation of 2 with UV light, using either a 370- or 253-nm lamp under conditions where 3 is readily photodimerized (see Experimental Section) led only to recovered 2. Exposure of 2 to ^{60}Co γ-radiation (>50 Mrad over 40 days, conditions that completely polymerize 1,6-di-*N*-carbazolyl-2,4-hexadiyne[8] and other reactive diacetylene monomers) resulted in no detectable change in 2.

As noted in the Introduction, a given compound may be unreactive in the solid state for either structural or mechanistic reasons. In the next section, our crystallographic study of this unreactive polymorph of 2 reveals for this phase that the relevant groups of this structure are not oriented for either chlorocinnamate photodimerization or for diacetylene polymerization. With a knowledge of the crystal structure of 2 and 3, we report and compare emission spectra of the reactive 3 and the unreactive 2.

Table III. Selected Bond Lengths (Å) and Angles (deg) for $C_{24}H_{16}O_4Cl_2$

at. 1	at. 2	dist	at. 1	at. 2	dist
C11	C1	1.737 (2)	C8	C9	1.472 (3)
C12	C22	1.742 (2)	C10	C11	1.460 (3)
O1	C9	1.344 (2)	C11	C12	1.188 (3)
O1	C10	1.441 (2)	C12	C13	1.379 (3)
O2	C9	1.196 (2)	C13	C14	1.189 (3)
O3	C15	1.444 (2)	C14	C15	1.461 (3)
O3	C16	1.354 (2)	C16	C17	1.468 (2)
O4	C16	1.203 (2)	C17	C18	1.323 (3)
C1	C2	1.368 (3)	C18	C19	1.463 (2)
C1	C6	1.377 (3)	C19	C20	1.391 (2)
C2	C3	1.376 (3)	C19	C24	1.398 (2)
C3	C4	1.385 (3)	C20	C21	1.377 (3)
C4	C5	1.400 (3)	C21	C22	1.376 (3)
C4	C7	1.457 (3)	C22	C23	1.379 (3)
C5	C6	1.374 (3)	C23	C24	1.383 (3)
C7	C8	1.312 (3)			

at. 1	at. 2	at. 3	angle	at. 1	at. 2	at. 3	angle
C9	O1	C10	115.8 (1)	C11	C12	C13	178.5 (2)
C15	O3	C16	115.9 (1)	C12	C13	C14	177.1 (2)
C11	C1	C2	118.9 (1)	C13	C14	C15	174.1 (2)
C11	C1	C6	120.0 (1)	O3	C15	C14	113.9 (2)
C2	C1	C6	121.2 (2)	O3	C16	O4	122.5 (2)
C1	C2	C3	118.8 (2)	O3	C16	C17	110.7 (1)
C2	C3	C4	122.2 (2)	O4	C16	C17	126.8 (2)
C3	C4	C5	117.3 (2)	C16	C17	C18	120.0 (2)
C3	C4	C7	119.0 (2)	C17	C18	C19	127.7 (2)
C5	C4	C7	123.6 (2)	C18	C19	C20	119.1 (1)
C4	C5	C6	121.0 (2)	C18	C19	C24	122.9 (2)
C1	C6	C5	119.5 (2)	C20	C19	C24	118.0 (2)
C4	C7	C8	127.5 (2)	C19	C20	C21	121.6 (2)
C7	C8	C9	121.0 (2)	C20	C21	C22	118.9 (2)
O1	C9	O2	122.8 (2)	C12	C22	C21	119.4 (1)
O1	C9	C8	110.0 (1)	C12	C22	C23	119.2 (1)
O2	C9	C8	127.2 (2)	C21	C22	C23	121.4 (2)
O1	C10	C11	106.6 (1)	C22	C23	C24	119.1 (2)
C10	C11	C12	178.2 (2)	C19	C24	C23	120.9 (2)

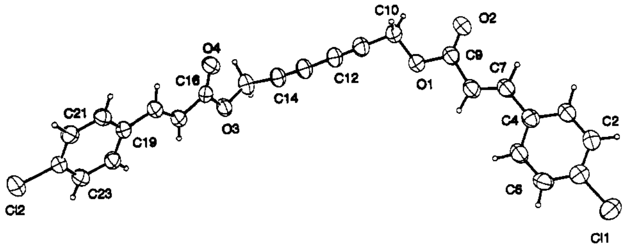


Figure 1. Molecular structure of 2, showing atom labels and 50% probability ellipsoids for atoms refined using anisotropic temperature factors. H atoms have been reduced in size for clarity.

Crystal and Molecular Structure of 2. Figure 1 shows the molecular structure of the title compound. This diacetylene clearly crystallizes in an unsymmetrical conformation. For example, the C9–O1–C10–C11 and C16–O3–C15–C14 torsion angles are 169.9 (2) and 77.5 (2)°, respectively. The angle between the planes of the two cinnamoyl moieties is 120.6 (1)°, similar to the interplanar angles in 2,4-hexadiyne-1,6-bis(*p*-*n*-hexyloxy) benzoate.[21] Bond distances and angles (Table III) lie within normal ranges. Examination of the pertinent intermolecular contacts for this unreactive phase indicates that the present packing arrangement does not satisfy topochemical criteria for either diacetylene polymerization[22,23] or photodimerization[24] of the cinnamoyl moieties. In particular, we show below that the molecules do not stack with the conventional ≈5-Å axis and that molecules with short intermolecular contacts are not related by translation. Figures 2 and 3 illustrate the most important interactions in terms of contacts between unsaturated C atoms; a conventional stereoview of the unit cell is available as supplementary material. Figure 2 shows three molecules that define the repetition pattern of short acetylene–acetylene contacts in the structure. The first and third molecules in the series are related to the center molecule by the *c* glide operation (x, $2 - y$, $\pm^1/_2 + z$). Note that the diacetylene moieties are skewed at an angle of 49.7°. Only an α(C11) and a δ′(C14) carbon atom approach one another at distances <4.1 Å. Other short interactions in the structure are depicted in Figure 3. Again, three molecules are shown that define the repetition patterns of ···C=C···C≡C··· and ···C=C···C=C··· contacts in the structure. The first and third molecules in the series are related to the center molecule by the 2 axis ($^3/_2 - x$, $\pm^1/_2 + y$, $^3/_2 - z$). The most significant interaction here is that between an α(C8) and a β′(C18) carbon atom of adjacent cinnamoyl groups. While pairs of cinnamoyl groups are nearly parallel [interplanar angle 165.4 (1)°], the distance between the α′(C17) and β(C7) carbon atoms is very long (5.83 Å). Finally, C12 (a β-diacetylene carbon atom) and C18 (a β-cinnamoyl carbon atom) approach one another at the short distance of 3.46 Å, but this contact apparently does not lead to solid-state reactivity.

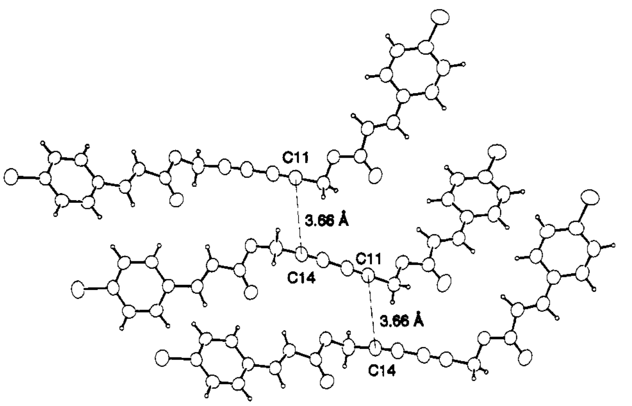


Figure 2. View of the structure of 2 emphasizing short intermolecular contacts between diyne moieties.

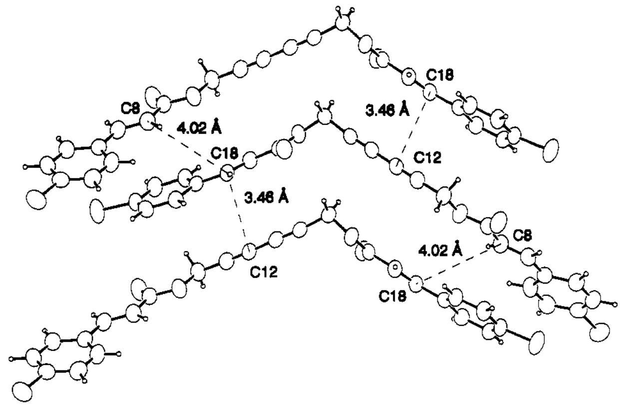


Figure 3. View of the structure of 2 emphasizing intermolecular contacts between double bonds of *p*-chlorocinnamates, and between —C=C— and —C≡C— moieties.

Solid-State Emission Spectra of 2 and 3. We initially recorded the emission spectrum of solid 2 before the solution of the crystal structure on the possbility that an

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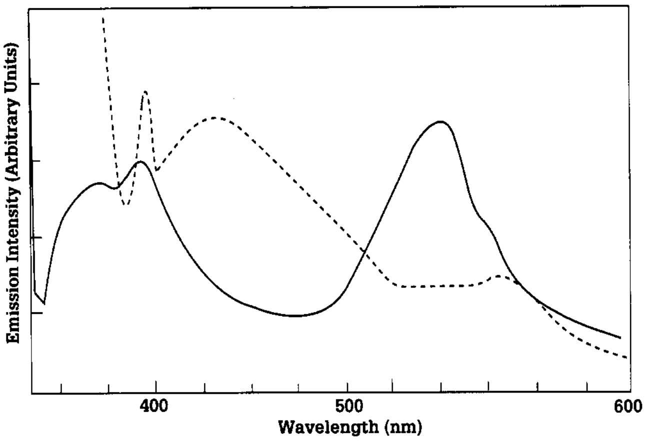

Figure 4. Emission spectra for polycrystalline samples of 2 (—, 340-nm excitation) and 3 (- - -, 370-nm excitation).

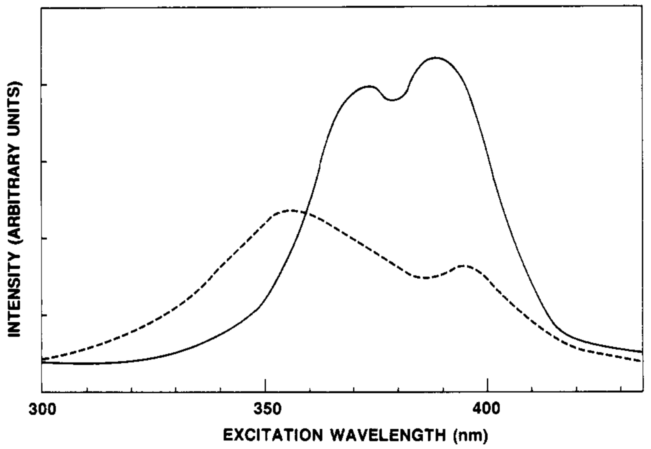

Figure 5. Excitation spectra for the emissions of Figure 4: (—) emission of 3 at 425 nm; (- - -) emission of 2 at 520 nm.

efficient luminescence could account for the lack of solid-state reaction. In view of the observed luminescence from the crystals of 2, which are unreactive for structural reasons, we felt it appropriate to compare the luminescence of 2 with that of a reactive chlorocinnamate, namely 3.[16]

For solid 2, the maximum emission intensity was observed with 340-nm excitation, and the spectrum, exhibited in Figure 4, is broad with maxima near 370, 395, and 520 nm. The spectrum in Figure 4 is different from that observed for 2 in acetonitrile solution, where a broad maximum of 350 nm clearly related to the solution absorption spectrum is noted. The excitation spectrum for the long-wavelength portion of the spectrum in Figure 4 is given in Figure 5, dashed line; a similar excitation spectrum is observed for the shorter wavelength emissions in Figure 4.

For the reactive 3, the strongest emission intensity was observed with 370-nm excitation. Figure 4, dashed line, displays the broad emission spectrum with maxima noted near 425 and 540 nm. The peak at 395 nm for 3 in Figure 4 is due to a Raman-shifted line. The excitation spectrum for the 425-nm emission is shown in Figure 5; the same features found in 3 in Figure 5 were noted in the excitation spectrum for the longer wavelength feature of this emission.

While this manuscript was in preparation, a publication[25] that reported the solid-state absorption, fluorescence, and Raman spectrum of 3 appeared. While the reported[25] absorption and Raman spectra are in good agreement with those given in the Experimental Section, the fluorescence spectrum[25] revealed a maximum at 392 nm. While the excitation wavelength used to obtain the spectrum with fluorescence maximum at 392 nm was not specified,[25] we observed emission spectra with a maximum near 395 nm using wavelengths of excitation in the 325–350-nm range. As displayed in Figure 4, we observed stronger emission using 370 nm as wavelength of excitation.

From data in the Experimental Section, in both solution and the solid state, the absorption maximum for 2 is at slightly longer wavelengths than that of 3. Yet, as shown in Figure 4, the solid-state emission spectrum for 3 is found at wavelengths longer than those for 2. Since the excitation spectra (Figure 5) do not show a close relationship to the monomeric absorption spectra, it is likely that the observed emission in the solid state is due to excimers.[26]

Excimers are established as reactive intermediates in solid-state molecular photodimerizations,[26-28] and excimeric emissions have also been observed in solid-state polymerizations involving photocycloadditions.[29-31] In the present work, similar excimeric emissions are observed in the reactive 3 and the unreactive 2. Hence, an excimeric emission may be found even in crystals unreactive to ultraviolet radiation. Solution studies of excimer formation in anthracenes where there is steric hindrance to photodimerization have been reviewed.[32]

Both components of the emission of the reactive 3 are found at longer wavelengths than those of the unreactive 2. On the assumption that the geometry of possible excimeric species parallels the relationships found in the ground state structures of 3[33] and 2, the overlap in 3, with an intermolecular distance of 3.89 Å between reactive carbon atoms in the ground state,[33] may be near optimal. It should also be recalled that excimeric energy is mobile.[27] Hence, the hydrogen-bonded 3 may have more delocalization possiblities than the unreactive 2. From the crystal structure of 2, the shortest ground-state distance between potentially reactive chlorocinnamate carbon atoms is an α–β' contact of 4.02 Å, significantly greater than the two relevant contact distances in 3.[33] Hence, there is poorer overlap in 2 relative to 3. We note further that an "in-plane" displacement[27] in excimeric 2, possibly near a defect, cannot be ruled out.

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Supplementary Material Available: Tables S-I–S-III, listing atomic displacement parameters, atomic coordinates for hydrogen atoms, and all bond lengths and angles; Figure S-I, stereo view of the unit cell (25 pages); Table S-IV, observed and calculated structure factor (16 pages). Ordering information is given on any current masthead page.

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