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Synthesis and Crystallographic Study of 1,6-bis-(*N*-phenothiazinyl)-2,4-hexadiyne

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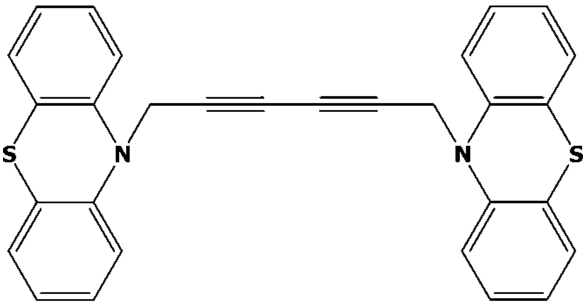
*1,6-bis-(N-phenothiazinyl)-2,4-hexadiyne (**I**) was synthesized in high yield by oxidative coupling of N-propargyl phenothiazine. Grown from methylene chloride-hexane solution, **I** is a monoclinic crystal, space group C2/c $\underline{a} = 14.9500(18)$ Å; $\underline{b} = 13.5512(15)$ Å; $\underline{c} = 12.0116(10)$ Å; $\beta = 102.628(9)^\circ$ Å; $V = 2374.6(4)$ Å^3. The intermolecular distances and arrangement of **I** in the unit cell preclude the usual diacetylene reactivity.*



I

*Nevertheless, heating of **I** at 145°C results in decomposition of **I** to phenothiazine and a dark brown solid. In addition, cation-radicals of **I** were prepared by oxidation with nitrosonium tetrafluoroborate and iodine to give stable ion-radical salts.*

Keywords polydiacetylene, diacetylene monomer, X-ray crystal structure, thermal reactivity

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Introduction

The initially synthesized polydiacetylene (PDA) single crystals did not exhibit electronic absorption at energies lower than the charge-transfer exciton (1). This situation changed with the report of electronic spectral features at energies lower than the exciton in the PDA of bis-*N*-ethyl-*p*-benzylidenemalononitrile of 2,4-hexadiyne (2). The new near infrared feature was associated with charge transfer from the electron-rich PDA backbone to the electron deficient cyano groups of the side chain (2). Such features were also observed in another PDA single crystal (3).

Interesting extensions of PDA crystals with a charge-transfer band would include PDA with a neutral-to-ionic transition (4). This might involve a material with an insulator-to-conductor transition leading to a single crystal specimen of a conducting polymer. Another approach to a single crystal conducting PDA would involve a monomer with a side group that would lead to a stable cation radical. Electron transfer from the electron-rich PDA backbone to an oxidized side group would result in a *p*-doped crystal. The list of potential side group precursors includes phenothiazines, dihydrophenazines, tetrathiafulvalenes, and *p*-phenylenediamines. In this paper we report the synthesis of **I**, the determination of its crystal and molecular structure, and an initial study of the solid-state reactivity of this monomer.

Experimental

Synthesis of 10-(prop-2-ynyl)-10H-phenothiazine (5)

In a flask with a reflux condenser, 5.0 g (25.0 mmol) of phenothiazine was dissolved in 50.0 mL anhydrous toluene under nitrogen. Sodium carbonate (3.98 g, 37.5 mmol) was added into the clear solution. After stirring for 1 h, 13.3 g (125.5 mmol) of propargyl bromide was added. The mixture was refluxed for 24 h and then mixed with 2M hydrochloric acid until the solution was acidic. The product was extracted with methylene chloride (100 mL × 2), and the organic layer was dried over anhydrous sodium sulfate. After purification by silica gel column chromatography with hexane as eluent, a pale yellow solid was obtained (4.4 g, 73% yield.), m.p. 91°C, IR (KBr, cm^{-1}) ν_{max}: 3320, 1600 cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$, TMS) δ (ppm): 7.1 (m, 8H, C_6H_4); 4.4 (d, 2H, CH_2); 2.3 (t, 1H, CH).

Synthesis of 1,6-bis-(N-phenothiazinyl)-2,4-hexadiyne (I, (6))

To a round-bottomed flask in a water bath at 28°C was added isopropanol (10.0 mL), copper (I) chloride (0.08 g, 0.8 mmol) and *N,N,N′,N′*-tetramethylethylenediamine (0.1 g 0.8 mmol).

Oxygen was bubbled into the solution as it was vigorously stirred. 2.0 g (8.4 mmol) of 10-(prop-2-ynyl)-10*H*-phenothiazine in isopropanol was added to the reaction mixture over a 15 min period in a dropwise manner. After the addition was complete, the reaction was continued for 5 h; then isopropanol was removed and 20 mL water containing 2 drops concentrated hydrochloric acid was added. The colorless solid was filtered, washed with a small amount of water, and dried under vacuum. A pale brown solid (3.2 g, 81%) that turned dark brown on heating at 200°C (decomposition) was obtained. IR (KBr, cm^{-1}) ν_{max}: 1600 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ (ppm): 7.2 (m, 8H, C_6H_4); 4.6 (s, 4H, CH_2). ^{13}C-NMR ($CDCl_3$, TMS) δ (ppm): 144.3 (C_6H_4); 128.0 (C_6H_4); 127.5 (C_6H_4); 123.8 (C_6H_4); 123.5 (C_6H_4); 115.1 (C_6H_4); 75.0 (CC), 70.5 (CC); 39.5 (CH_2).

Preparation of Tetrafluoroborate Salt of I

I (0.1 g, 0.2 mmol) was dissolved in methylene chloride; nitrosonium tetrafluoroborate (0.03 g, 0.2 mmol) was added at −40°C, and the reaction mixture was stirred for 1 h. After removal of NO gas, hexane was added. The precipitate of the cation radical was filtered, washed with cold hexane, and dried under vacuum. It gave a turbid white solid (0.08 g, 82% yield) that turned dark on heating at 155°C.

Preparation of Iodide Salt of I

To a stirred solution of 0.1 g (0.2 mmol) of **I** in methylene chloride (10.0 ml) was added a solution of iodine (0.08 g, 0.6 mmol) in methylene chloride by a dropping funnel. The reaction mixture was stirred at 0°C. After 1 h, the solution was poured into aqueous sodium bicarbonate, the mixture was extracted with benzene, and the benzene was removed to give 0.08 g (80%) of **I** iodide salt as a pale red solid. The solid turned black on heating at 180°C.

X-Ray Structure Determination

Single crystals of **I** were obtained from a methylene chloride-hexane solution and mounted on a Pyrex fiber affixed to a brass pin. The crystal was optically centered and placed on an Enraf-Nonius CAD4-U diffractometer. X-ray data were collected using the Enraf-Nonius EXPRESS (7) program. The structure was solved by direct methods using SIR-92 (8) and refined using the Oxford CRYSTALS package (9,10). Non-hydrogen atoms were refined using anisotropic displacement parameters; hydrogen atoms were refined by using isotropic displacement parameters. Crystallographic data is presented in Table 1. CCDC 299079 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Results and Discussion

Synthesis

I was synthesized in high yield by oxidative coupling of *N*-propargyl phenothiazine according to Scheme 1.

The monomer became very dark after heating for 24 h at 145°C in a vacuum oven. After heating, phenothiazine itself was isolated as a colorless crystal and a dark brown solid as an unidentified product. Raman spectroscopy of the brown solid did not reveal the features expected for a PDA. From this result, it is indicated that **I** undergoes thermal decomposition at temperatures above 145°C. Note that bis-(3′, 6′-dibromo-*N*-carbazolyl)-2,4-hexadiyne undergoes thermal reaction with a loss of 3,6-dibromocabazole and PDA formation (11).

The formation of cation-radical salts of **I** was studied. Salts of **I** were prepared by oxidation with nitrosonium tetrafluoroborate and iodine, respectively, to give stable ion-radical salts (Scheme 2).

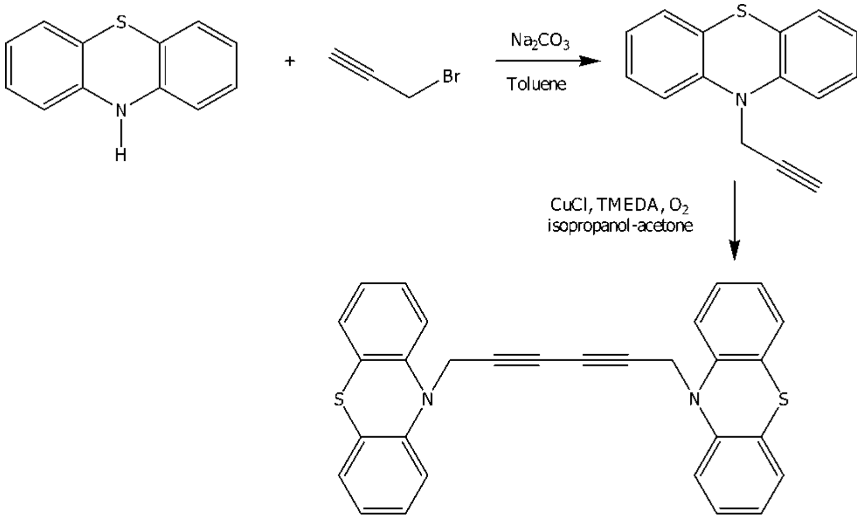
Thermogravimetric Analysis of I and Iodide Salt

TGA was carried out under nitrogen at a heating rate of 10°C/min. From Figure 1, **I** lost about 60% of its weight in the 225–500°C temperature range. Loss of one

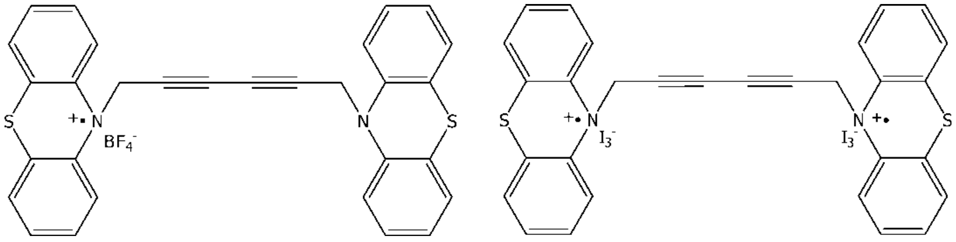
Table 1
Crystallographic data of **I**

Compound	**I**
Chemical formula	$C_{30}H_{20}N_2S_2$
a, Å	14.9500 (18)
b, Å	13.5512 (15)
c, Å	12.0116 (10)
β, deg.	102.628 (9)
V, Å^3	2374.6 (4)
Z, Z′	4, 0.5
Formula Wt. g/mol	472.62
Space group	$C2/c$
T, °C	21 (1)
λ, Å	1.54178
ρ_{calc}, g cm^{-3}	1.322
μ, mm^{-1}	2.189
Transmission factors	0.53 − 0.58
R_{av}	0.028
R^{a}	0.0354
R_w^{b}	0.0474
S^{c}	0.95
No. reflections	2353
No. parameters	195
Secondary extinction parameter	109 (6)

[a] $R = \sum\|F_o| - |F_c\|/\sum| F_o|$.
[b] $R_w = [\sum {}_w(| F_o| - | F_c|)^2/\sum {}_w| F_o|^2]^{1/2}$.
[c] $S = [\sum_w(|F_o| - |F_c|)^2/(n - m)^{1/2}$.



Scheme 1. The synthesis of **I**.



Scheme 2. The structure of **I** salts.

molecule of phenothiazine from **I** would involve a 42.2% wt loss. The iodide salt (Figure 2) seems to lose weight in three stages. In the narrow temperature range 130–155°C, it lost 7% of its weight. At about 400 °C, the material has lost about 40% of its weight. This might correspond to loss of 4 I atoms, but further work is needed to establish this suggestion.

Crystal and Molecular Structure of I

The molecular structure and numbering scheme for **I** is shown in Figure 3; bond lengths and angles lie in normal ranges. Compound **I** crystallizes in space group $C2/c$; **I** resides on a crystallographic C_2 axis. The phenothiazine side groups are arranged in a *syn*-fashion, with a pseudo-torsion angle, N1-C3 … C3′-N1′ of 30.7°.

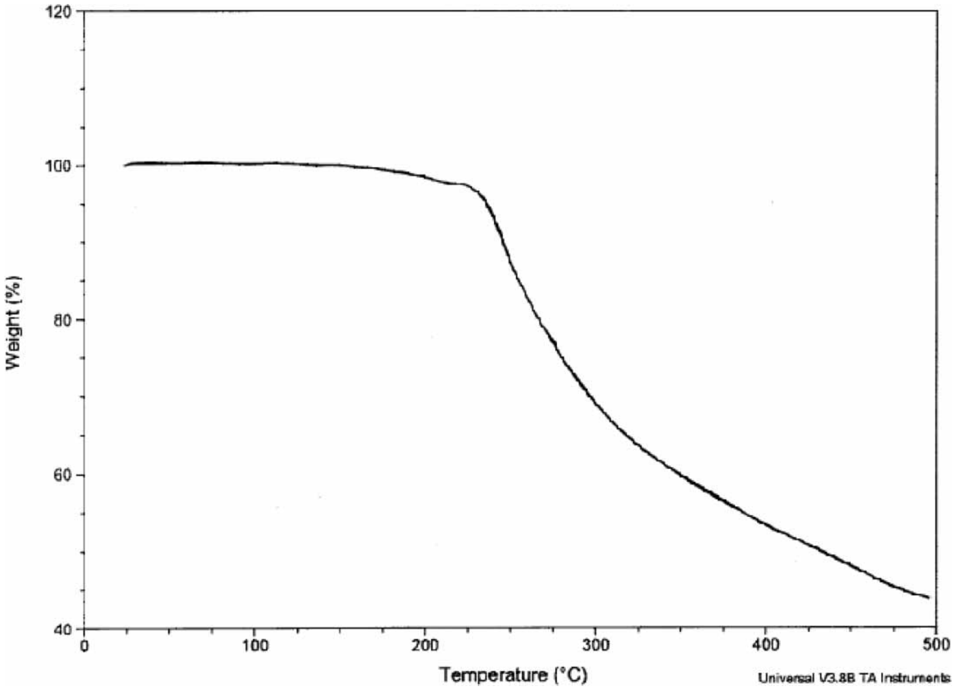


Figure 1. Thermogravimetric analysis of **I**.

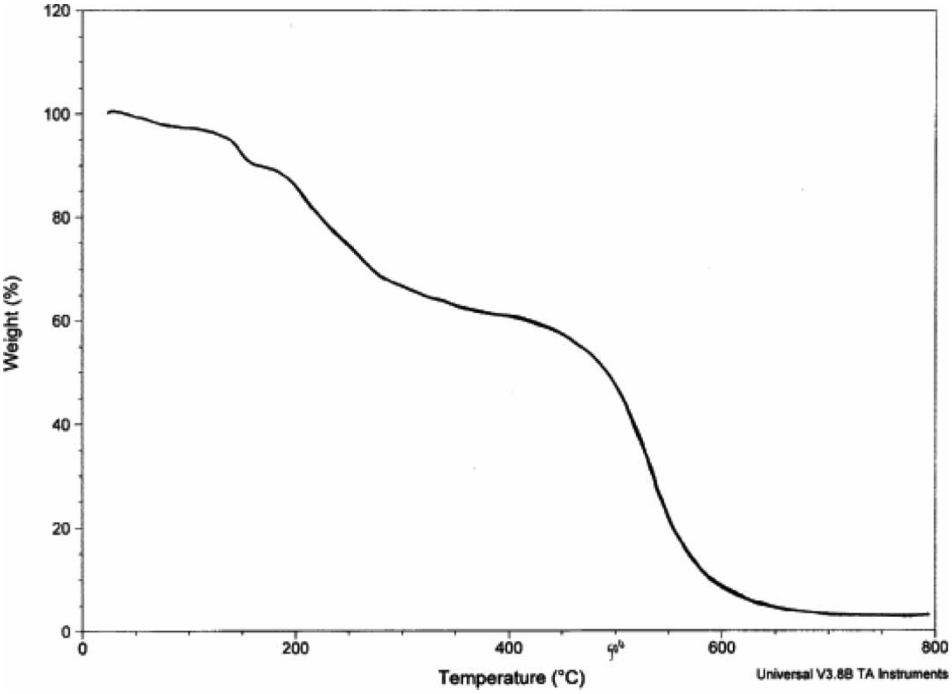


Figure 2. Thermogravimetric analysis of **I** iodide.

As shown in Figure 4, the molecular conformation influences the packing such that the often-encountered short —C≡C—C≡C— contacts observed for diacetylenes that are reactive in the solid state are not present in this structure (12). The shortest intermolecular contact between acetylenic carbon atoms is C1—C2 ($1 - x$, $1 - y$, $-z$); the 7.35 Å distance observed for this contact precludes the usual diacetylene solid-state reactivity (12).

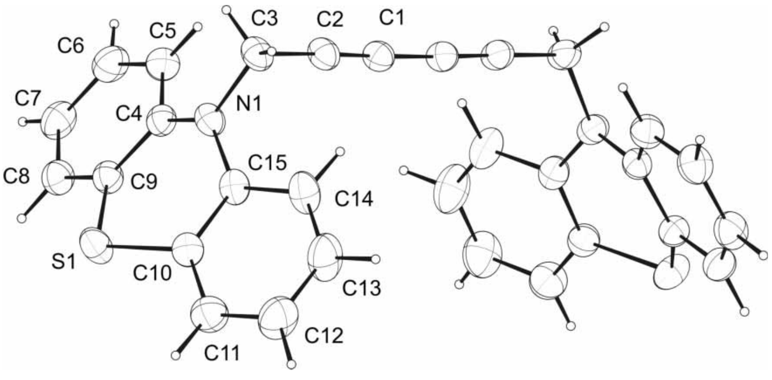


Figure 3. Molecular structure of **I**, showing 40% probability ellipsoids for atoms refined by using anisotropic displacement parameters; only the asymmetric unit is labeled.

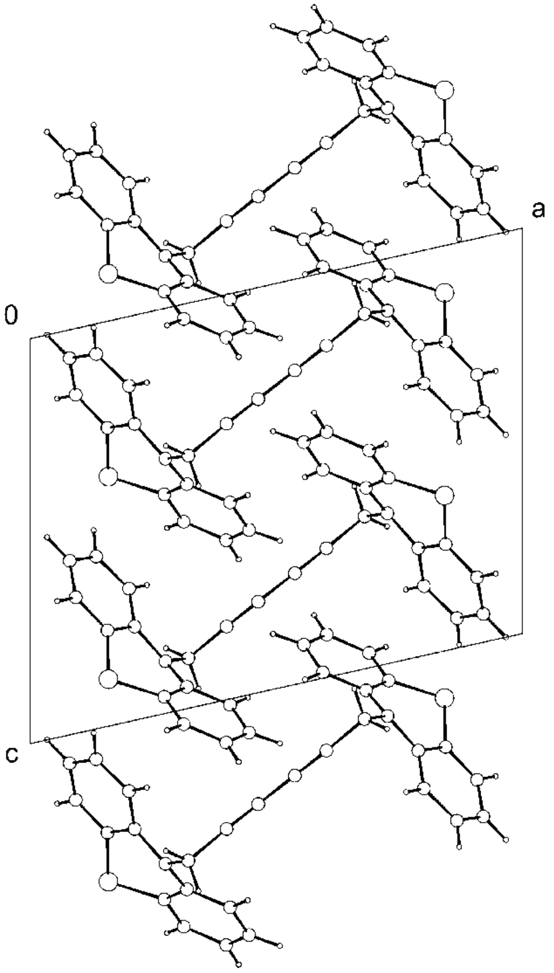


Figure 4. Packing of molecules viewed in projection down the b-axis.

Conclusions

Diacetylene monomer **I** was synthesized by oxidative coupling of propargyl phenothiazine. The crystal structure of **I** precludes the usual 1,4-addition polymerization of the diacetylene. Nevertheless, **I** decomposes on heating to phenothiazine and an undefined solid.

Acknowledgements

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