

New Cyanofluorene Derivatives as Electron Acceptors in Semiconducting Complexes

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9,9'-Bifluorenylidene-3,3',6,6'-tetracarbonitrile (TCBF) and (3,6-dicyano-9*H*-fluoren-9-ylidene)propanedinitrile (TCPF) have been synthesized starting from 9-oxo-9*H*-fluorene-3,6-dicarbonitrile. A 2:1 charge transfer complex of TCPF with *NNN'*-tetramethyl-*p*-phenylenediamine has been obtained, and the electrical and spectral properties investigated. Conductivity measurements performed on polycrystalline samples gave a value of the order of $0.02 \Omega^{-1} \text{ cm}^{-1}$. These results support the ability of this new acceptor in forming charge-transfer complexes with semiconducting properties.

The electrical conductivity of organic materials is generally very low. However, a new class of organic solids which exhibit high conductivity has been discovered and form the basis of the field of organic semiconductors.^{1,2} Strong molecular donors and acceptors react to form ion radical salts and charge-transfer compounds, whose optical, magnetic, and structural properties are directly related to the electronic interaction between molecules.³

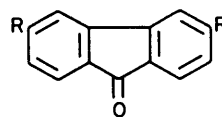
Tetracyanoquinodimethane (TCNQ) is the best molecular acceptor discovered to date; it forms organic semiconductors with a large number of cations.^{4,5}

Recently we devoted our attention to the study of the electronic and vibrational properties of 9,9'-bifluorenylidene,^{6,7} a highly symmetric molecule. In view of the chemical and physical properties of this material, we decided to synthesize new compounds by choosing fluorene and 9,9'-bifluorenylidene as starting compounds on which to construct functionalised electron acceptors. In this paper we report the synthesis and the study of 9,9'-bifluorenylidene-3,3',6,6'-tetracarbonitrile (TCBF) and (3,6-dicyano-9*H*-fluoren-9-ylidene)propanedinitrile (TCPF) which are important for the preparation of semiconducting salts. They allow for high structural symmetry and comparable dimensions of both acceptors and donors, high affinity of acceptors, and electron availability of donors. *NNN'*-Tetramethyl-*p*-phenylenediamine (TMPD) was chosen as the donor for use in the synthesis of complexes. With TCPF it formed a charge-transfer complex showing the characteristic features of semiconducting material.

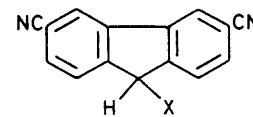
Results and Discussion

Synthesis.—Dimethylfluorenone (1) was prepared according to the procedure reported in refs. 8 and 9. The oxidation of (1) to yield acid (2) was accomplished with sodium dichromate in a shaking autoclave at 250° for 12 h, following the method of Friedman *et al.*¹⁰ Conversion of (2) into the chloride (3) was attempted by several methods. Success was achieved only under severe conditions using phenylphosphonic dichloride at 160–170 °C for 9 h. The diester (4) and the diamide (5) were prepared by the usual methods. The conversion of the diamide (5) into the corresponding dinitrile (6) was performed with phenylphosphonic dichloride under severe conditions of temperature (200 °C) and time of heating (20 h).

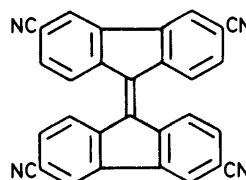
In order to obtain TCBF (9) the oxo-group of (6) was first reduced to the hydroxy-derivative (7), which was then brominated to yield (8). The latter was converted into TCBF (9) by heating at 60 °C with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in the dark and under nitrogen. Compound (9) was



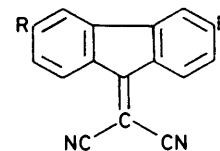
- (1) R = Me
- (2) R = CO₂H
- (3) R = COCl
- (4) R = CO₂Et
- (5) R = CONH₂
- (6) R = CN



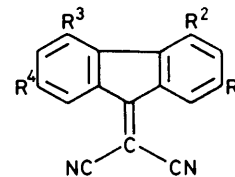
- (7) X = OH
- (8) X = Br



(9)



- (10) R = Me
- (11) R = CO₂Et
- (12) R = CN



- (13a) R¹ = R² = R³ = NO₂, R⁴ = CO₂Me
- (13b) R¹ = R² = R⁴ = NO₂, R³ = CO₂Me
- (13c) R¹ = R² = R⁴ = NO₂, R³ = H

found to be very sensitive to light and oxygen. Thus it underwent a photodecomposition process resulting in the formation of 3,6-dicyanofluorenone (6), as previously observed in the case of unsubstituted 9,9'-bifluorenylidene.¹¹ It crystallized as shining red microcrystals with m.p. > 320 °C. Sublimation of (9) under vacuum was unsuccessful. Due to its very low solubility in most organic solvents (only very slightly soluble in DMF, DMSO, and MeCN), we were not able fully to

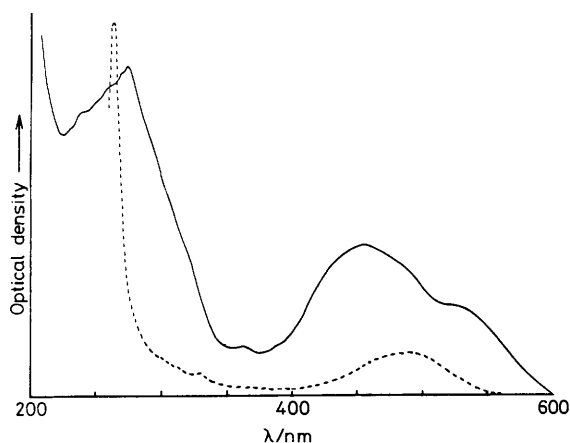


Figure 1. Electronic spectra of TCBF in dimethylformamide solution (dotted line) and in Nujol mull (full line)

investigate its chemical and spectroscopic properties. Only u.v. spectrum in DMF was measured, showing a maximum (490 nm) due to the π - π^* transition shifted toward longer wavelengths compared with that of 9,9'-bifluorenylidene (450 nm) (Figure 1). Figure 1 also reports the u.v. spectrum of (9) in a Nujol mull. The i.r. spectrum of the solid in a KBr pellet was also measured.

Conversion of the fluorene-9-ones (1), (4), and (6) into the corresponding derivatives (10)–(12), respectively, was carried out by reaction with propanedinitrile in dimethyl sulphoxide at 110 °C for 6 h.

Charge-transfer Complexes.—It is well known that the peculiar properties of the best acceptors are connected with structural characteristics such as planarity, high symmetry of the molecules, and the presence of electron-withdrawing groups. Thus, in the synthesis of new electron acceptors we choose to prepare fluorene derivatives with electron-withdrawing groups at the 3 and 6 positions which seemed best suited to affect the charge distribution on the whole system. The presence of four cyano groups at the 3,3',6, and 6' positions was expected to impoverish the electron density in the core of the molecule. In addition substituents at these positions ensured the desired high symmetry and planarity of the system. We were able to reach our goal by preparing TCBF (9). Several attempts were made to prepare charge-transfer complexes by using different types of donors. However our efforts to favour interaction with the counterpart were unsuccessful owing to the lack of sufficient solubility of TCBF under any experimental conditions.

In order to overcome this difficulty and to maintain the most relevant electronic and structural properties of TCBF, we prepared the propanedinitrile derivatives (10)–(12) and we checked their ability to form charge-transfer complexes by using TMPD as donor.

Complexes between TMPD and the fluorene derivatives (13a–c) have been reported¹² and studied by u.v. spectroscopy. Since they have not been isolated, no information exists about their stoichiometric ratio and their chemical and physical properties.

In our case the tetracyano-derivative (12) reacted with TMPD to give a charge-transfer complex as violet-black, shining needles in a 2 : 1 ratio (TCPF : TMPD) which decompose at 190–210 °C to regenerate the components. The complex was prepared by mixing warm solutions of the reagents in acetonitrile. After 30 min the complex precipitated from the mixture. Temperature, time of heating, and different ratios of the reagents did not affect the stoichiometry of the compound.

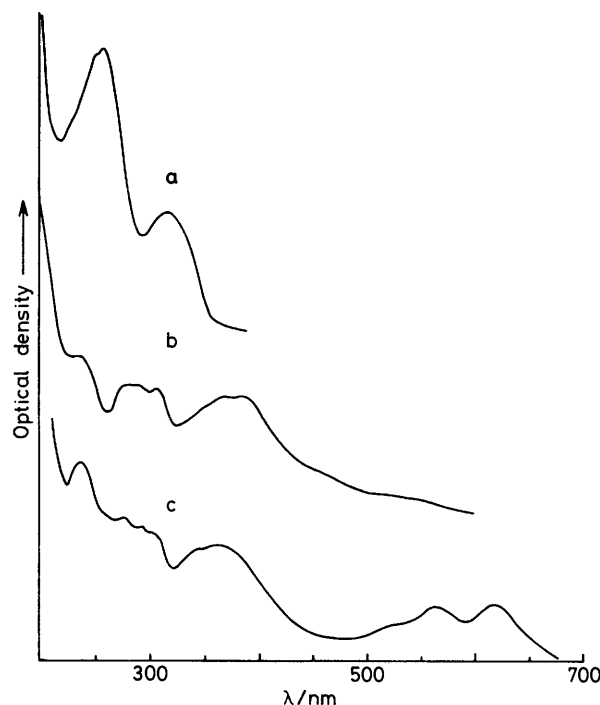


Figure 2. Electronic spectra in Nujol mull of a, TMPD; b, TCPF; and c, (TCPF)₂TMPD complex

The same procedure was followed with compounds (10) and (11) in order to obtain the corresponding complexes. Although different reaction conditions were used, only the starting products were isolated. In addition no evidence for the formation of 1 : 1 complexes between TMPD and compounds (10)–(12) was found when following the method reported in ref. 12. This behaviour is possibly caused by the influence of different functional groups and/or different positions on the fluorene framework.

Physical and Spectroscopic Properties of (TCPF)₂TMPD Semiconducting Complex.—Complexes with a 2 : 1 TCNQ : donor stoichiometric ratio are known to have the lowest resistivity at room temperature. X-Ray studies established crystal structures characterized by parallel columns of anions and cations. Due to the large overlap of the π orbitals of TCNQ molecules, the electrons move along the axis of the column causing unidirectional conductivity in the crystals.

These compounds show peculiar morphologic and spectroscopic properties which are directly related to their electrical conductivity. Generally they appear as black-blue needles with a metallic shine. The absorption spectrum is characterized by a large vibronic band which extends from the u.v. to the far-i.r. region.

TCPF is a new acceptor which is able to give semiconducting complexes. The conductivity of the (TCPF)₂TMPD compound was found to be ca. 0.02 $\Omega^{-1} \text{cm}^{-1}$ at room temperature. This value, similar to that for (TCNQ)₂TMPD complex,¹³ suggests that TCPF has promise as an acceptor in the synthesis of semiconducting materials.

The u.v.–visible spectra for the solid state of TMPD, TCPF, and 2 : 1 complex are shown in Figure 2. In the higher frequency region spectra b and c are quite similar showing broad absorptions with several peaks. Maxima are detected in spectrum b at 238, 280, 292, 307, 370, and 384 nm. Few changes in frequencies are observed for most peaks in spectrum c. Three additional bands are present in spectrum c at 530, 565, and 620 nm. The last two maxima are due to the

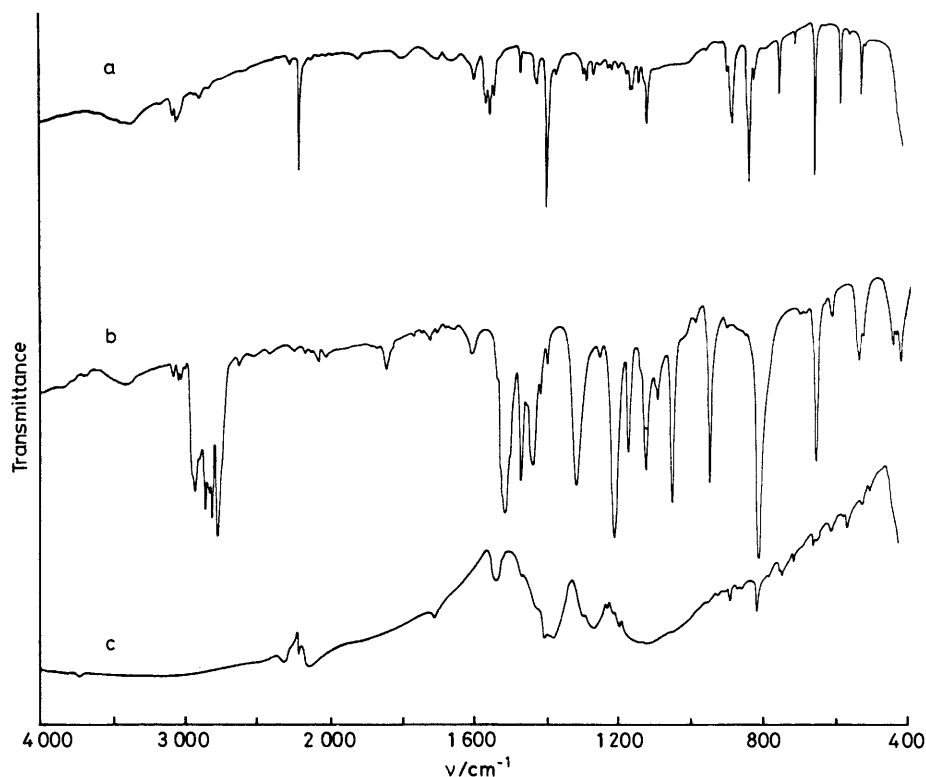


Figure 3. I.r. spectra in KBr pellet of a, TCPF; b, TMPD; and c, (TCPF)₂TMPD complex

TMPD radical ion and are generally observed at about the same frequency in all the charge-transfer complexes.¹⁴ In solution the 2:1 complex is largely dissociated and the corresponding spectrum (c 0.046 g l⁻¹, l 0.1 cm) exhibits the characteristic maxima of the components. Two weak bands at 565 and 614 nm are still observed in a spectrum taken for a 5 cm pathlength cell, suggesting the presence in solution of a small amount of TMPD radical ion.

The i.r. spectra in the solid state of the complex and of the components are reported in Figure 3. Spectrum c shows the peculiar spectroscopic features of the 2:1 semiconducting complexes.^{14,15} The broad absorption bands which extend over the whole i.r. region originate from the vibronic transitions due to the large coupling between the vibrational motions and the electronic transitions responsible for the conductivity. In the spectrum, only few peaks are observed which correspond to bands of the components. These peaks probably derive from vibrational transitions not involved in the conduction process.

Conclusions.—The results indicate that fluorene and 9,9'-bifluorenylidene are suitable frameworks which can be functionalized to construct strong electron acceptors. The preliminary data observed for the (TCPF)₂TMPD complex by electrical measurements and spectroscopic methods confirm the ability of TCPF molecule in forming semiconducting materials with properties analogous to those of the TCNQ compounds. Further studies are in progress on the structural and physical properties of this complex.

Experimental

I.r. spectra were measured with a Perkin-Elmer model 225 spectrometer for dispersions in potassium bromide. U.v. spectra were recorded with a Cary 14 recording spectro-

photometer in solution and in the solid state. ¹H N.m.r. spectra were recorded with a Perkin-Elmer R32 instrument; chemical shifts are reported relative to internal tetramethylsilane. Resistivity measurements were performed on powder compacted under a pressure of 2 tons cm⁻². Four gold probes were included in the pellet and connected with a picoammeter (external probes) and a nanovoltmeter (internal probes) in order to measure the current intensity and the voltage difference, respectively. In order to avoid polarization effects, the current intensity was maintained below 5 × 10⁻⁵ A.

9-Oxo-9H-fluorene-3,6-dicarboxylic Acid (2).—3,6-Dimethyl-9H-fluoren-9-one (1)⁹ (20 g, 0.096 mol) and a solution of Na₂Cr₂O₇·2H₂O (89.74 g, 0.30 mol) in water (145 ml) were heated in a shaking autoclave (500 ml) for 12 h at 250 °C and 500–600 lb in⁻² (35–42 atm). The reactor was emptied at 60 °C and the content was filtered to remove chromic oxide. The filtered residue was washed several times with warm water. The aqueous solution was acidified with 6N-HCl. After the mixture had cooled overnight, the yellow precipitate which formed was filtered, washed well with water, and air dried. Yellow 9-oxo-9H-fluorene-3,6-dicarboxylic acid (2) (22.70 g, 88%) was obtained, m.p. >350 °C (Found: C, 67.45; H, 3.15. C₁₅H₈O₅ requires C, 67.15; H, 3.0%); ν_{max} 3300–2700 (OH), 1720 (CO), and 1690 (COOH) cm⁻¹; λ_{max} (DMF) 304, 316, and 330 nm (log ε 3.63, 3.62, and 3.58); δ (DMSO) 7.74 (1 H, d, J 8 Hz), 8.0 (1 H dd, J 8 and 2 Hz), and 8.40 (1 H, d, J 2 Hz).

9-Oxo-9H-fluorene-3,6-dicarbonyl Dichloride (3).—A mixture of the acid (2) (12.29 g) and an excess of phenylphosphonic dichloride was heated at 160–170 °C for 9 h. Filtration of the cooled mixture gave the dichloride (3), as yellow microcrystals which was thoroughly washed with benzene, m.p. 240–241 °C (from benzene) (12.83 g, 91.7%) (Found:

C, 59.45; H, 2.05. $C_{15}H_6Cl_2O_3$ requires C, 59.0; H, 1.95%; ν_{\max} , 1 750 (COCl) and 1 710 (CO) cm^{-1} .

Diethyl 9-Oxo-9H-fluorene-3,6-dicarboxylate (4).—Compound (3) (12 g) was refluxed with ethanol in excess for a few minutes. Filtration of the cooled mixture gave the *fluorene-dicarboxylate* (4), as yellow microcrystals, m.p. 144–145 °C (from ethanol) (7.54 g, 62%) (Found: C, 70.3; H, 5.05. $C_{19}H_{16}O_5$ requires C, 70.35; H, 4.95%; ν_{\max} , 1 720 (CO), 1 710 (CO), and 1 278 (C–O–C) cm^{-1} ; λ_{\max} (MeOH) 207, 253, 261, 302, 312, and 326 nm (log ϵ 4.55, 4.85, 4.97, 3.72, 3.69, and 3.71).

9-Oxo-9H-fluorene-3,6-dicarboxamide (5).—A mixture of the dichloride (3) (12.5 g) and an excess of ammonium hydroxide was refluxed for 2 h. Filtration of the cooled mixture gave the yellow *diamide* (5), which was washed with water, ethanol, and ether, m.p. >310 °C (from ethanol) (8.9 g, 81.6%) (Found: C, 67.0; H, 3.85; N, 10.2. $C_{15}H_{10}N_2O_3$ requires C, 67.65; H, 3.75; N, 10.55%; ν_{\max} , 3 400 and 3 200 (NH₂), 1 712 (CO), 1 675 (CONH), and 1 667 (CONH) cm^{-1} ; λ_{\max} (DMSO) 264, 305, 319, and 334 nm (log ϵ 4.84, 3.69, 3.68, and 3.60).

9-Oxo-9H-fluorene-3,6-dicarbonitrile (6).—A mixture of compound (5) (7.5 g) and an excess of phenylphosphonic dichloride was heated at 200 °C for 20 h. The cooled mixture was filtered, washed with benzene, and ethanol, and crystallized from DMSO to give the *dicarbonitrile* (6), as light yellow powder (5.8 g, 89%), m.p. >305 °C (Found: C, 78.45; H, 2.85; N, 12.25. $C_{15}H_6N_2O$ requires C, 78.25; H, 2.6; N, 12.15%; ν_{\max} , 2 224 (CN) and 1 710 (CO) cm^{-1} ; λ_{\max} (DMSO) 225, 264, 302, 315, and 326 nm (log ϵ 4.73, 4.89, 3.64, 3.62, and 3.54).

9-Hydroxy-9H-fluorene-3,6-dicarbonitrile (7).—To a boiling solution of compound (6) (1.5 g) in glacial acetic acid (230 ml) was added portionwise zinc powder (1.8 g) with stirring. After the reaction was complete, the boiling mixture was filtered. To the cooled filtrate was added water to precipitate *compound* (7) (1.11 g, 74%), m.p. >300 °C (after sublimation at 120 °C and 0.03 mmHg) (Found: C, 77.15; H, 3.75; N, 12.35. $C_{15}H_8N_2O$ requires C, 77.6; H, 3.45; N, 12.05%; ν_{\max} , 3 480 (OH) and 2 222 (CN) cm^{-1}).

9-Bromo-9H-fluorene-3,6-dicarbonitrile (8).—A mixture of compound (7) (1.26 g) and an excess of PBr_3 were heated at 150 °C for 1 h. The cooled mixture was filtered, washed with ethanol till pH 7, and then with ether to give the *bromo-derivative* (8) (0.8 g, 50%), m.p. 250 °C (decomp.) (from MeCN) (Found: C, 60.7; H, 2.5; N, 9.6. $C_{15}H_7BrN_2$ requires C, 61.0; H, 2.35; N, 9.55%; ν_{\max} , 2 228 (CN) cm^{-1}).

9,9'-Bifluorenylidene-3,3',6,6'-tetracarboxynitrile (9).—To a suspension of compound (8) (0.2 g) in acetonitrile (50 ml) was added 1,5-diazabicyclo[5.4.0]undec-5-ene (0.12 ml) under nitrogen and in the dark at 60 °C. After 2 h the mixture was filtered and washed with warm acetonitrile to give *compound* (9) as orange microcrystals, m.p. >320 °C (Found: C, 83.85; H, 2.95; N, 13.1. $C_{30}H_{12}N_4$ requires C, 84.1; H, 2.8; N, 13.1%; ν_{\max} , 3 070, 2 226 (CN), 1 462, 1 400, 1 324, 890, 824, and 612 cm^{-1} ; u.v. see Figure 1).

(9H-Fluoren-9-ylidene)propanedinitrile (10)—(12).—A mixture of the appropriate fluoren-9-one (1.0 mmol) and propanedinitrile (freshly sublimed) (1.1 mmol) in DMSO (5 ml) was heated at 110 °C for 5 h. The solution was cooled, the

solid was filtered, and washed with ether to give the corresponding propanedinitrile.

(3,6-Dimethyl-9H-fluoren-9-ylidene)propanedinitrile (10) gave orange needles (89%), m.p. 295–296 °C (from DMSO) (Found: C, 83.8; H, 4.8; N, 11.35. $C_{18}H_{12}N_2$ requires C, 84.35; H, 4.7; N, 10.95%; ν_{\max} , 2 230 (CN) and 1 570 (C=C) cm^{-1} ; λ_{\max} (MeCN) 222, 229, 242, 265, 274, 285, 297, 335, and 365 sh nm (log ϵ 4.31, 4.31, 3.94, 4.57, 4.83, 4.01, 4.09, 4.39, and 4.34).

(3,6-Bisethoxycarbonyl-9H-fluoren-9-ylidene)propanedinitrile (11) gave orange plates (62%), m.p. 254–256 °C (from DMSO) (Found: C, 70.3; H, 4.45; N, 7.5. $C_{22}H_{16}N_2O_4$ requires C, 70.95; H, 4.3; N, 7.55%; ν_{\max} , 2 222 (CN), 1 715 (CO), 1 568 (C=C), and 1 263 (C–O–C) cm^{-1} ; λ_{\max} (MeCN) 231, 238, 252, 271, 283, 300, 349, and 360 sh nm (log ϵ 4.66, 4.70, 4.52, 4.69, 4.32, 4.38, 4.38, and 4.35).

(3,6-Dicyano-9H-fluoren-9-ylidene)propanedinitrile (12) gave orange microcrystals (76%), m.p. >300 °C (from MeCN) (Found: C, 76.95; H, 2.4; N, 19.85. $C_{18}H_6N_4$ requires C, 77.7; H, 2.15; N, 20.15%; ν_{\max} , 2 230 (CN) and 1 570 (C=C) cm^{-1} ; λ_{\max} (MeCN) 230, 238, 262, 272, 287, 299, 340, and 355 nm (log ϵ 4.64, 4.71, 4.49, 4.69, 4.31, 4.39, 4.34, and 4.31).

Complex between TCPF (12) and Tetramethyl-p-phenylene-diamine.—TMPD was obtained from the hydrochloride (Aldrich) neutralized with sodium hydroxide and sublimed.

To a warm solution of compound (12) (0.3 g) in MeCN (150 ml) was added a solution of TMPD (0.18 g) in MeCN (2 ml). The stirred solution was heated at 50° for 30 min. The solution was cooled and the solid filtered and washed with ethanol to give the *complex*, as violet needles (0.3 g, 37%) (Found: C, 76.8; H, 3.6; N, 19.75. $C_{46}H_{28}N_{10}$ requires C, 76.65; H, 3.9; N, 19.45%; u.v. and i.r. spectra are shown in Figures 2 and 3, respectively.

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