

5-Amino-3-imino-1,2,6,7-tetracyano-3*H*-pyrrolizine: synthesis of alkylimino derivatives. X-Ray crystal and molecular structures of the hex-5-enyl, and Langmuir–Blodgett film of the octyl and octadecyl derivatives

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The alkylimino-substituted derivatives of 5-amino-3-imino-1,2,6,7-tetracyano-3*H*-pyrrolizine, $\text{H}_2\text{N}-\text{C}_7\text{N}(\text{CN})_4=\text{NR}$, $\text{R} = \text{hex-5-enyl (1)}$, octyl (2), octadecyl (3), have been synthesized through a nucleophilic substitution reaction on the amino group of the anion 2-(5-amino-3,4-dicyano-2*H*-pyrrol-2-ylidene)-1,1,2-tricyanoethanide, $\text{C}_5\text{N}_3-\text{C}_4\text{N}(\text{CN})_2-\text{NH}_2^-$ (L'). A sigmatropic rearrangement *via* a [1,5]-H shift is involved in this synthesis and also in the deprotonation of **1**, leading to the anion $\text{C}_5\text{N}_3-\text{C}_4\text{N}(\text{CN})_2-\text{NH}(\text{CH}_2)_4\text{CH}=\text{CH}_2^-$ ($\text{1}'$) isolated as the tetraphenylarsonium salt, $\text{AsPh}_4\cdot\text{1}'$. All the new compounds have been characterized by elemental analysis and IR, UV–VIS and ^1H NMR spectroscopy. The X-ray crystal and molecular structure of **1** has been determined. Langmuir–Blodgett (LB) films from **2** and **3** have been deposited and characterized by polarised optical absorption spectroscopy.

Introduction

We have recently synthesized and characterized¹ a number of amino-derivatives of the anion 2-(5-amino-3,4-dicyano-2*H*-pyrrol-2-ylidene)-1,1,2-tricyanoethanide, $\text{C}_5\text{N}_3-\text{C}_4\text{N}(\text{CN})_2-\text{NH}_2^-$ (L'), with the aim of widening the prospective use of L' as a material for optical chemical sensors, able to detect species of environmental interest. The following specific properties of L' make it a suitable candidate for such a study: (i) L' is an intense dye, (ii) it isomerizes to the cyclized form **L** on coordination to transition metal cations **M** in ML pyrrolizinato complexes² with an easily detectable colour change, and (iii) it can be recovered unchanged from ML after substitution with a ligand stronger than **L**.

In addition, L' can add a proton affording the title pyrrolizine **HL**,³ which is also a molecule potentially useful for application in the construction of optochemical sensors, even more interesting than L' itself: **HL** is a fluorescent dye and coordinates to **M** more readily than L' . Furthermore, as a neutral molecule, **HL** can be sublimed to afford thickness-controlled thin films⁴ and, after appropriate modifications, it could be exploited for more advanced applications based on molecular monolayers covalently bound to the surface of crystalline silicon,⁵ or on ordered multilayer Langmuir–Blodgett (LB) films.⁶

In this context we have synthesized new derivatives of **HL**, taking advantage of the hydrogen substitution reaction of the $-\text{NH}_2$ group, previously carried out on L' as the tetraphenylarsonium salt, $\text{AsPh}_4\cdot\text{L}'$. In particular, we introduced an aliphatic chain (**R**) onto **HL**, suitable either for binding to a silicon surface after a hydrosilation reaction⁷ between the silane bond ($=\text{Si}-\text{H}$) on the activated silicon surface and the terminal carbon–carbon double bond in **R** ($\text{R} = \text{hex-5-enyl}$) or for building LB films ($\text{R} = \text{octyl}$, octadecyl). The full characterization of these new HLR derivatives revealed that they are alkylimino- rather than alkylamino-substituted. These results are presented

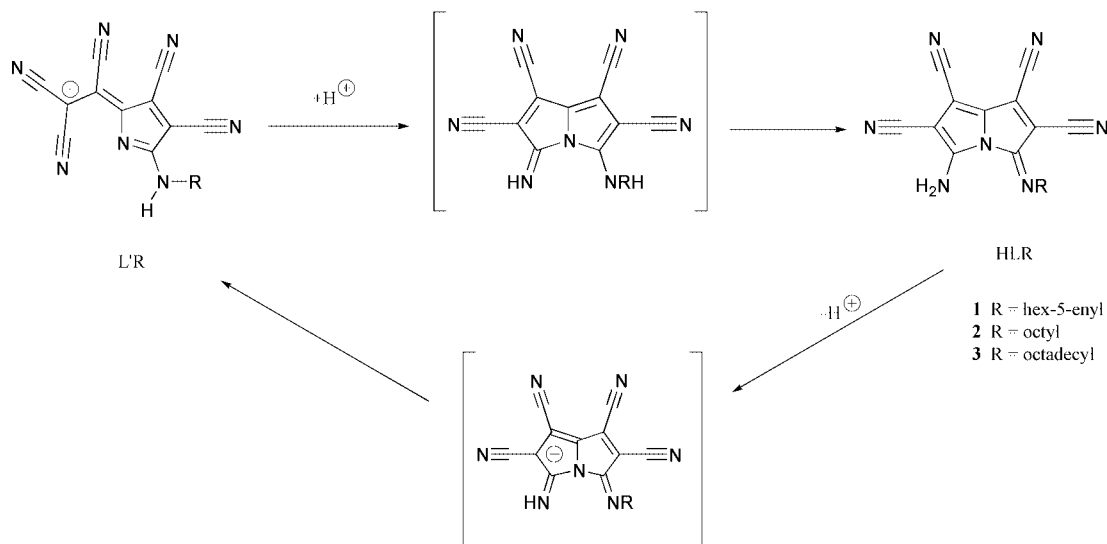
and discussed in this paper. The X-ray crystal and molecular structure of the hex-5-enyl-derivative (**1**) and LB films, built up from the analogous octyl- (**2**) and octadecyl-derivative (**3**), are also reported.

Results and discussion

Chemical substitution

The current molecules (**1**, **2**, **3**) were synthesized from **HL** by the reaction previously carried out on $\text{AsPh}_4\cdot\text{L}'$,¹ that is the nucleophilic substitution of one hydrogen atom of the $-\text{NH}_2$ group of L' with the appropriate aliphatic iodide **RI** in *N,N*-dimethylformamide (DMF), in the presence of the proton sponge *N,N,N',N'*-tetramethylnaphthalene-1,8-diamine (**PS**) taken in 6.5-fold molar excess. Actually, in the DMF–**PS** reaction mixture, **HL** is completely dissociated into L' and H^+ , as shown by the optical spectrum of this solution, which is superimposable on that of $\text{AsPh}_4\cdot\text{L}'$ under the same conditions. Therefore, the very first reaction product is the amino-substituted derivative of L' , even though the corresponding neutral conjugate acid, isolated after column chromatography (see the Experimental section), turned out to be **HLR**. This is consistent with the well known fact that proton addition to L' occurs on the nitrile nitrogen atom adjacent to the pyrrolic nitrogen with the formation of **HL**.³ Analogously, proton addition to $\text{L}'\text{R}$ should furnish an intermediate which immediately isomerizes to **HLR** (Scheme 1).

For compound **1**, whose X-ray structure has been solved, the reverse step, $\text{HLR} \rightarrow \text{L}'\text{R} + \text{H}^+$, has been also studied by reacting **HLR** with NaHCO_3 , which resulted in the clean and quantitative isolation of a stoichiometric amount of the tetraphenylarsonium salt of hex-5-enylamino- L' , $\text{AsPh}_4\cdot\text{1}'$. In conclusion, both proton addition and proton abstraction in these species, to $\text{L}'\text{R}$ and from **HLR** respectively, are always followed by sigmatropic rearrangement *via* a [1,5]-H shift,⁸ because the



Scheme 1

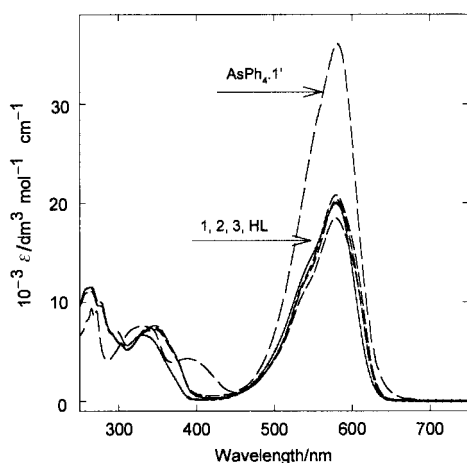


Fig. 1 Normalized solution optical spectra of the compounds **1**, **2**, **3**, AsPh₄·**1**' in CH₂Cl₂ (---) and of HL in THF (—).

corresponding intermediates are not stable. In accordance with this situation, the ¹H NMR nitrogen proton signal is a triplet in AsPh₄·**1**', while a singlet in **1**, **2** and **3**. Moreover, the IR spectra of **1**, **2** and **3**, in the N–H stretching region, are characterized by the absence of the imino signal, which, in contrast, dominates the spectrum of HL as a strong absorption at 3249 cm⁻¹. The optical spectra of these species, on the other hand, are not sensitive to the imino-hydrogen substitution, being almost superimposable on that of HL (Fig. 1). Also, the band intensity increase on going from **1** to AsPh₄·**1**' (ca. 50%) can be compared to that observed on going from HL to AsPh₄·**L**'.³

X-Ray structure of 5-amino-3-(hex-5-enylimino)-1,2,6,7-tetracyano-3H-pyrrolizine (**1**)

The molecular structure of **1** consists of a highly planar 5-amino-3-imino-1,2,6,7-tetracyanopyrrolizine moiety, in which the imino-hydrogen atom is replaced by a hex-5-enyl chain, whose carbon atoms lie (max. dev. 0.05 Å) on a plane almost orthogonal to the pyrrolizine plane (dihedral angle ca. 80°). A perspective view of two centrosymmetrical units, coupled through intermolecular –CN···HN– hydrogen bonds of 2.08 Å, is shown in Fig. 2.

On the basis of the structural results, significant localisation of the double bonds of the heterocyclic molecular system can be noted. Interatomic distances can be compared to the analogous ones found both in ML or ML₂ complexes,² and in the unsubstituted LH pyrrolizine.³ In the current case the imino

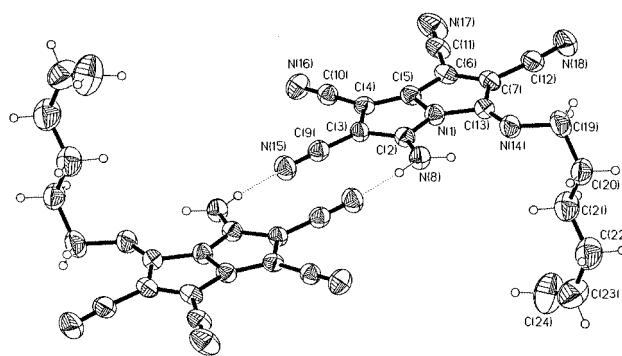


Fig. 2 Centrosymmetrical molecular units of compound **1**. Displacement ellipsoids are at 30% probability level. Hydrogen bonds are represented by dotted lines. Selected bond lengths (Å) and angles (°): N(1)–C(2) 1.355(6), C(2)–C(3) 1.420(6), C(2)–N(8) 1.321(6), C(3)–C(4) 1.429(7), C(4)–C(5) 1.372(8), C(5)–C(6) 1.415(7), C(6)–C(7) 1.383(7), C(7)–C(13) 1.485(8), C(13)–N(14) 1.262(7), N(14)–C(19) 1.443(7), C(19)–C(20) 1.507(9), C(20)–C(21) 1.515(9), C(21)–C(22) 1.50(1), C(22)–C(23) 1.52(1), C(23)–C(24) 1.15(1), H(81)···N(15') 2.08(1), H(82)···N(14) 2.34(1), C(13)–N(14)–C(19) 121.5(5), N(14)–C(19)–C(20) 110.3(5), C(19)–C(20)–C(21) 113.9(5), C(20)–C(21)–C(22) 113.4(6), C(21)–C(22)–C(23) 119.1(7), C(22)–C(23)–C(24) 129.9(8), N(8)–H(81)···N(15') 174(1), N(8)–H(82)···N(14) 125(1).

and amino character of N(14) and N(8) nitrogen atoms, respectively, is enhanced, as evidenced by the shortening of the C(13)–N(14) distance to 1.252 Å and the lengthening of C(2)–N(8) to 1.321 Å, in comparison with the corresponding values of 1.268 and 1.305 Å found in LH.

Moreover, the distances of 1.355, 1.420 and 1.429 Å found for N(1)–C(2), C(2)–C(3) and C(3)–C(4) bonds, respectively, strongly suggest a charge distribution, within the fused rings, compatible with a partial N(1)⁺···C(3)⁻ dipole in the solid state.

Finally, the very short C23–C24 double bond distance of 1.15 Å is due to a libration effect related to the exceptionally high thermal factors of the positionally disordered C24 carbon atom.

LB films

HL, like other similar aromatic heterocyclic molecules and their conjugate anions and complexes, shows suitable properties for application in the construction of optochemical sensors.^{9–17} For instance, an evaporated HL thin film undergoes specific spectral changes on interaction with ammonia and/or water in the gas phase.⁴ It is therefore likely that LB films of HLR might also be valuable for application in sensor devices. With this aim in mind

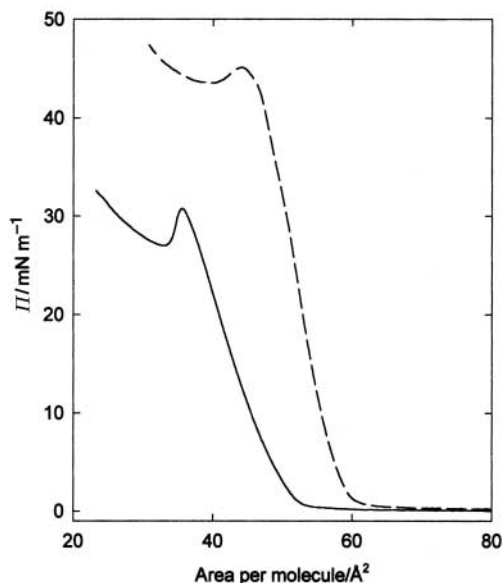


Fig. 3 Langmuir isotherms of compound 2 (—) and 3 (---).

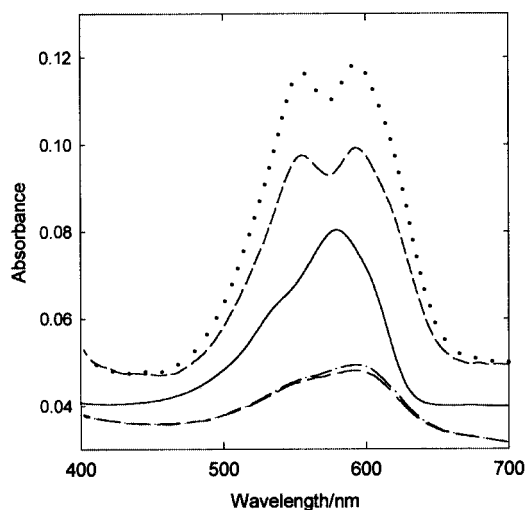


Fig. 4 Optical spectra of compound 3 in CH_2Cl_2 solution (—) and of LB films of compounds 2 and 3, both as 10 molecular layers deposited onto both sides of a glass slide: 3, $E_{\perp}d$ (.....); 3, $E_{\parallel}d$ (---); 2, $E_{\parallel}d$ (—); 2, $E_{\perp}d$ (—).

we started to study these films. In particular, LB films were deposited from both 2 and 3. The corresponding π - A isotherms are reported in Fig. 3. As expected, 3 exhibits better deposition properties than 2, the former being characterized by a steeper slope in the isotherm. Accordingly, the transfer ratio was higher for 3 (1.0 ± 0.1) than for 2 (0.7 ± 0.1). However, both isotherms show the absence of any two-dimensional liquid phase intermediate,¹⁸ showing just the formation of a close-packed monolayer with a minimal molecular area of 60 \AA^2 for 3 and 50 \AA^2 for 2, which is nearly the same area of the planar pyrrolizine chromophore as calculated from the X-ray data (*ca.* 56 \AA^2).³ The polarised optical spectra (Fig. 4) also show a better molecular ordering in the LB films for 3 than for 2: the extra band in the films at 556 nm, absent in solution, usually taken as an indication of the formation of a multilayer columnar structure,¹⁹ shows an enhanced intensity in 3 with respect to 2 and the dichroic ratio for the same film, R ($R = A_{E_{\perp}d} : A_{E_{\parallel}d}$), is almost equal to one in 2, while it is >1.2 for 3. Finally, it is to be noted that there is a large difference in the spectral intensity of the two films, despite the fact that they were built up with nominally the same number of molecular layers. However, it should be realized that the transfer ratio is markedly different in the two

cases, as stated above, so, consistently the true thickness of the two films will be also different.

Conclusions

The new compounds described are now being tested for the above outlined applications and are providing quite different results. Compound 1 undergoes hydrosilation on an activated silicon surface with difficulty, if at all, while compound 3 afforded good quality LB films. Moreover, two mixed monopyrrolizinato-metal complexes [$M(\text{II}) = \text{Ni}, \text{Cu}$] of 3 and acetylacetonato ligand have been synthesized, and these new complexes show suitable properties, such as stability and solubility as does 3 itself, for depositing LB films, the investigation of which is in progress. More importantly perhaps, it should be noted that these new derivatives still bear a reactive functional group ($-\text{NH}_2$) and thus they could be functionalized further. It is conceivable for instance that supramolecular chemistry might be observed, based on HL after introduction of another carbon-carbon double bond functionality onto the amino group of 1.

Experimental

Elemental analyses were carried out by Servizio Microanalisi of CNR, Area della Ricerca di Roma. Solution optical spectra were recorded in CH_2Cl_2 on a Cary 5 spectrometer; the wavelength band maximum (λ/nm), the corresponding extinction coefficient ($\epsilon/\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$) and half-height band width (hwh/nm) are given. IR measurements were recorded with a Perkin-Elmer 16F PC FT spectrometer on KBr pellets (0.75% w/w) and Nujol mulls; the stretching frequencies (ν/cm^{-1}) of the absorption maximum of the most significant bands are given. The ^1H NMR spectra were obtained in CD_2Cl_2 solution with a Bruker AMX-250 spectrometer. The chemical shifts [δ (ppm)] were referred to the residual CHDCl_2 proton (5.32 ppm, triplet) of CD_2Cl_2 . The J -values are given in Hz.

Materials

6-Bromohex-1-ene, 1-iodooctane, 1-iodooctadecane, N,N,N',N' -tetramethylnaphthalene-1,8-diamine (PS), N,N -dimethylformamide (DMF), tetrahydrofuran (THF), hexane, heptane, dichloromethane, acetone, NaHCO_3 , $\text{AsPh}_4\cdot\text{Cl}$ and NaI , were commercial analytical grade reagents from Fluka. DMF was carefully dried and freshly distilled before use, as given previously.¹ The acetone used for the metathesis reaction (*vide infra*) was first dried over Drierite, then shaken with Linde type 4 Å molecular sieves and finally distilled at atmospheric pressure under N_2 and stored under N_2 at low temperature ($-20 \text{ }^\circ\text{C}$). 6-Iodohept-1-ene was prepared by metathesis of 6-bromohex-1-ene with NaI and purified according to the literature.²⁰ HL was prepared following our method.³ The reaction products (1, 2, 3) were purified by column chromatography on silica gel (220–440 mesh) eluting with CH_2Cl_2 -acetone (95 : 5) and recrystallized by slow evaporation in air from the solvent mixture CH_2Cl_2 -heptane.

Synthesis of 5-amino-3-(hex-5-enylimino)-1,2,6,7-tetracyano-3H-pyrrolizine (1)

A solution of HL (400 mg, 1.72 mmol), 6-iodohex-1-ene (4.5 cm^3 , 30.0 mmol) and PS (2.4 g, 11.2 mmol) in DMF (30.0 cm^3) was heated under nitrogen at $90 \text{ }^\circ\text{C}$ for 4 h. The reaction was cooled to room temperature, after which DMF was removed under a stream of air. The residue was washed with hexane and purified by column chromatography. The eluted fraction, showing a band maximum at 580 nm, was collected and evaporated on a rotary evaporator. After crystallization, purple, needle-like crystals of 1 (98 mg, 18%) were obtained (Found: C, 64.26; H, 4.15; N, 30.83. $\text{C}_{17}\text{H}_{13}\text{N}_7$ requires C, 64.75; H, 4.16; N,

31.09%); λ_{\max} 580, ϵ_{\max} 20300, hhw 85; ν_{\max} 3330–3162 (m, N–H), 2979 (s, =C–H), 2946–2852 (m, C–H), 2224 (s, CN), 2212 (s, CN), 917 (s, out-of-plane=C–H); δ 7.58 (2H, s, br, NH₂), 5.82 (m, 1H), 5.00 (m, 2H), 3.99 (t, *J* 7.0, 2H), 2.12 (m, 2H), 1.79 (m, 2H), 1.53 (m, 2H).

Synthesis of 5-amino-3-octylimino-1,2,6,7-tetracyano-3H-pyrrolizine (2)

This was prepared following the above procedure adopted for the preparation of **1**, starting from the same amount of HL and by using the appropriate iodide (1-iodooctane, 5.5 cm³, 30.20 mmol). **2** was obtained as microcrystals (160 mg, 27%) (Found: C, 66.19; H, 5.35; N, 28.09. C₁₉H₁₉N₇ requires C, 66.07; H, 5.54; N, 28.39%); λ_{\max} 579, ϵ_{\max} 18500, hhw 85; ν_{\max} 3342–3158 (m, N–H), 2955–2853 (m, C–H), 2225 (s, CN), 2212 (s, CN); δ 7.62 (2H, s, br, NH₂), 3.97 (t, *J* 8.0, 2H), 1.79 (m, 2H), 1.30 (m, br, 6 × 2H), 0.89 (t, *J* 7, 3H).

Synthesis of 5-amino-3-octadecylimino-1,2,6,7-tetracyano-3H-pyrrolizine (3)

This was again prepared following the above procedure, but using 1-iodooctadecane (11.52 g, 30.30 mmol). It was necessary to purify it twice by column chromatography. **3** was obtained as microcrystals (124 mg, 15%) (Found: C, 71.32; H, 8.13; N, 19.92. C₂₉H₃₉N₇ requires C, 71.72; H, 8.09; N, 20.19%); λ_{\max} 579, ϵ_{\max} 20700, hhw 85; ν_{\max} 3333–3161 (m, N–H), 2955–2850 (m, C–H), 2227 (s, CN), 2210 (s, CN); δ 7.62 (2H, s, br, NH₂), 3.97 (t, *J* 7.0, 2H), 1.78 (m, 2H), 1.27 (m, br, 15 × 2H), 1.53 (t, *J* 7, 3H).

Synthesis of tetraphenylarsonium 2-[5-(hex-5-enylamino)-3,4-dicyano-2H-pyrrol-2-ylidene]-1,1,2-tricyanoethanide (AsPh₄·1')

Compound **1** (20 mg, 0.063 mmol) was dissolved in THF (20 cm³). NaHCO₃ (0.5 g) was added. The colour of the solution turned slowly from red-violet to dark violet. The suspension was stirred for several hours, until the optical spectrum maximum absorbance (λ_{\max} 583 nm) reached a steady value. The reaction mixture was filtered and evaporated to dryness in air, after which the residue was dissolved in water and AsPh₄·Cl (0.1 g) was added. On standing overnight, AsPh₄·1' separated as an oil, stuck on the walls of the reaction flask. The liquid was decanted off and the oil was washed with water, whereupon it became a tough analysable solid (Found: C, 69.75; H, 4.65; N, 14.02. C₃₃H₅₈AsN₇ requires C, 70.65; H, 4.77; N, 14.07%); λ_{\max} 583, ϵ_{\max} 36000, hhw 80; ν_{\max} 3335 (s, NH₂), 3090–2852 (m, C–H), 2198 (s, CN); δ 7.90–7.60 (20H, m, Ph), 5.79 (m, 1H), 4.95 (m, 2H), 4.00 (1H, t, *J* 7.0, NH), 3.47 (t, *J* 5.0, 2H), 2.08 (m, 2H), 1.62 (m, 2H), 1.48 (m, 2H).

LB film deposition and characterization

LB-monolayers were formed using a KSV 2000 trough apparatus with an automatic moving barrier in a clean room. The LB films were constructed as follows. The monolayer was spread from toluene solution (5 × 10⁻⁴ M, 300 μ l) onto a deionized water surface (resistivity greater than 18 m Ω cm⁻¹, pH = 6.5). Twenty minutes were allowed for evaporation of the solvent prior to monolayer compression. The isotherms were measured at 18 ± 2 °C with a constant compression rate of 5 mm min⁻¹. Glass slides were cleaned with detergent and pure water, then placed in pure acetone in an ultrasonic bath and finally exposed for 24 h to 1,1,1,3,3,3-hexamethyldisilazane vapour to obtain a hydrophobic substrate. All depositions were of Y-type and carried out at a surface pressure of 30 mN m⁻¹ for **3** and 25 mN m⁻¹ for **2** with the same dip rate of 5 mm min⁻¹ during the downstroke and upstroke. Optical absorption polarized spectra

were recorded with normal-to-substrate incident light with the plane of polarization parallel and perpendicular to the dipping direction (*d*). The dichroic ratio *R* is measured as: $R = A_{E\perp d} : A_{E\parallel d}$, where *A* is the absorbance at the band maximum wavelength (λ_{\max}), and *E* is the electric field vector of the light perpendicular (⊥) and parallel (∥) to the dipping direction.

X-Ray crystallography

General. Only platelet-like, low-diffracting crystals of compound **1** were available. X-Ray intensities were collected in the range 4° ≤ 2θ ≤ 124° on a Rigaku four-circle diffractometer equipped with a rotating anode (Cu-K α radiation) by the θ -2 θ scan method. Data were corrected for Lorentz and polarization effects and for absorption by the semiempirical ψ -scan method. The structure was solved by direct methods using the SIR97 package of crystallographic programs.²¹ 217 variables were segmented into two blocks and refined by full-matrix least-squares methods with the SHELXTL programs.²² Hydrogen atoms were included in calculated positions and refined in a riding mode.

Crystal data.† C₁₇H₁₃N₇, *M* = 315.3, crystallizes as bronze rectangular thin platelets; crystal dimensions 0.6 × 0.2 × 0.02 mm, monoclinic, *a* = 6.136(2), *b* = 30.470(4), *c* = 9.285(1) Å, β = 102.81(2)°, *U* = 1692.8(6) Å³, space group *P*₂₁/*n*, μ (Cu-K α) = 0.649 mm⁻¹, *T* = 293 K, *Z* = 4, ρ = 1.24 Mg m⁻³, final conventional *R* = 0.068 and *R*_w = 0.098 for 1492 unique reflections with *F*_o ≥ 6 σ (*F*_o). Goodness of fit = 2.20.

† CCDC reference number 163028. See <http://www.rsc.org/suppdata/p1/b1/b103423p/> for crystallographic files in .cif or other electronic format.

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